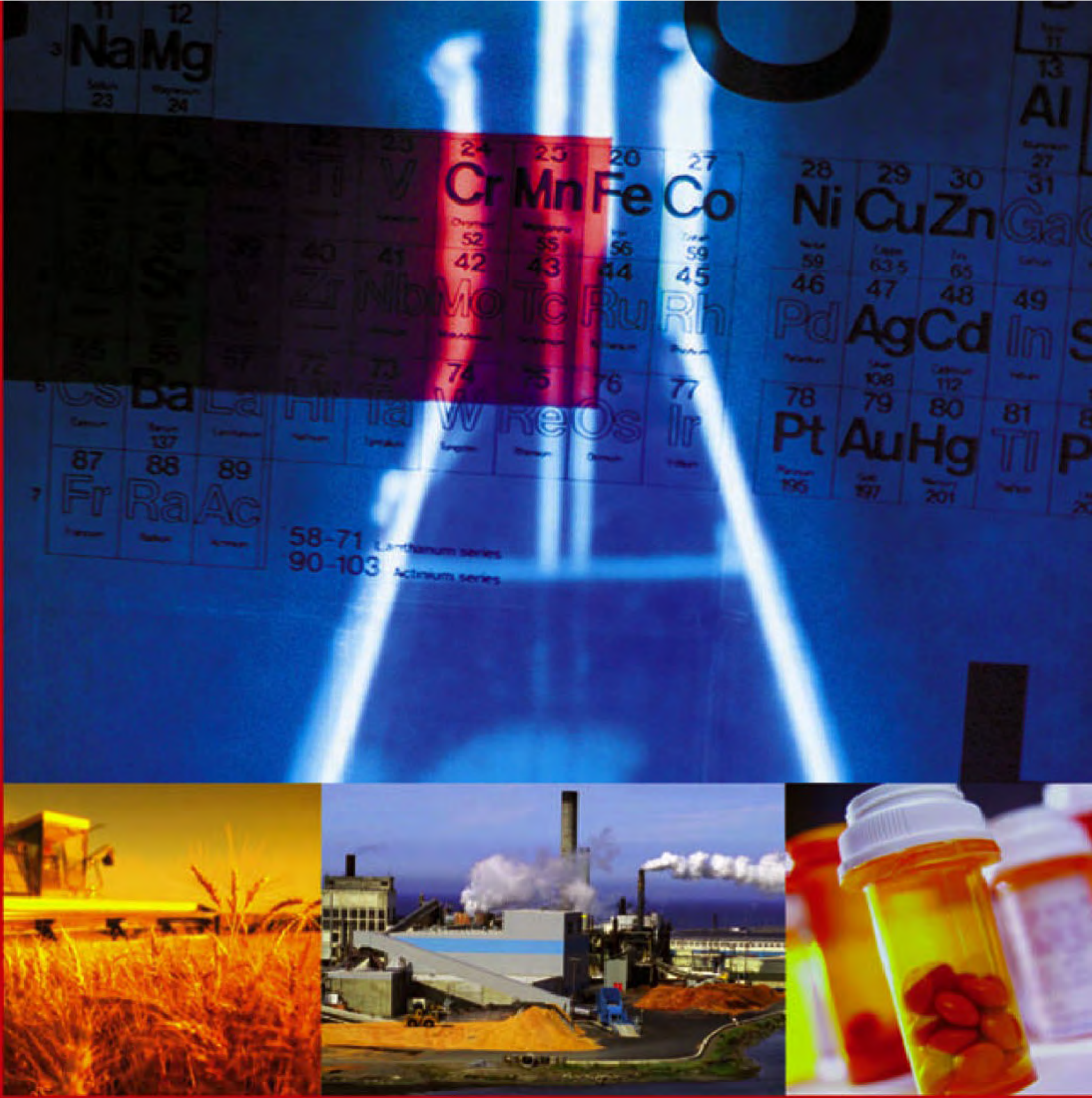

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Table of Contents

Volume 1

Volume 2

Volume 3

Volume 4

Preface

Chemistry. The word conjures up mystery—perhaps magic—smoke, fireworks, explosions, unpleasant odors. But it could evoke "smokeless burning," which would be invisible, fluorescent lights, "neon" signs, the quiet crumbling of rocks under the pressure of freezing water, the slow and quiet formation of caves in limestone, and the delightful scents of perfumes or fruit aromas. There is no magic, only knowledge and understanding. We offer this *Encyclopedia* as a contribution to help readers gain knowledge and understanding of chemistry.

Chemistry was manifested as an art at the beginnings of civilization. The early decorative chemical arts included the preparation of pigments such as the Egyptian blue applied to King Tutankhamen's golden death mask; the various bronze alloys that were used to make vases in the ancient world of the Middle East as well as in China; and the glass objects that have been found in Mesopotamia (now known as Iraq). Those chemical arts became a science in the eighteenth century when Antoine Laurent Lavoisier (1743–1794) led what has been called "the chemical revolution." Using accurate measurements of primarily mass, early chemists began to make order out of the myriad of substances that are found in the natural world. This order was eventually expressed in a number of chemical concepts that include the laws of chemical composition (constant composition, mass conservation, multiple proportions), periodicity, the nature of atoms, chemical bonding, and a variety of concepts involving chemical structures. The early symbiosis of chemistry with civilization remains. Chemistry is still a useful science in the advancement of civilization. Chemists have developed and refined the core concepts of chemistry to the point where they have become powerful tools to assist humankind in the acquisition of materials of practical use to extend and preserve civilization. Humans now have available a broader array of substances with a remarkable spectrum of properties than was available before chemistry became a science. Light emitting diodes (LEDs) produce more light than the individual torches, candles, and oil lamps of the distant past—indeed, than the incandescent light bulbs of the immediate past—more efficiently and with less pollution. Polymeric materials or composites can be produced with virtually any property desired—from stretching clingy Saran Wrap to Kevlar used in bullet proof vests; from nonstick Teflon to optical fibers; from rubber objects that are impervious to oil and gasoline to tires that can be used for 100,000 miles before needing replacement; from fibers that compete with (in some cases

surpass) natural materials to plastics that have more desirable optical properties than glass. In a word, chemistry is *everywhere*.

There is no magic, only knowledge and understanding.

These volumes are a contribution to assist readers in their understanding of chemistry and chemical ideas and concepts. The 509 articles have been carefully chosen to provide basic information on a broad range of topics. For those readers who desire to expand their knowledge of a topic, we have included bibliographic references to readily accessible sources.

The continual evolution of the discipline of chemistry is reflected in our treatment of the elements. The careful reader will note that we have included articles for the first 104 elements; the remainder of the elements are “recently” discovered or exist only as short-lived species and, accordingly, are not readily available for the usual chemical studies that reveal, for example, their bulk properties or reactivity and much of the “standard chemistry” that is of interest. Much of what little we know about the elements beyond 104 permits us to place these elements in their appropriate places in the periodic table, which nevertheless still turns out to be quite insightful from a chemical point of view.

Entries in the *Encyclopedia* are in alphabetic sequence. Cross-references appear in small capitals at the ends of the articles to help readers locate related discussions. Articles range from brief, but concise, definitions to extensive overviews that treat key concepts in larger contexts. A list of common abbreviations and symbols, and a list of the known elements, as well as a modern version of the periodic table are included in the For Your Reference section at the beginning of each volume. A glossary and a comprehensive index appear at the end of each volume. Contributors are listed alphabetically, together with their academic and professional affiliations, at the beginning of each volume.

Following this preface, we offer a topical arrangement of the articles in the *Encyclopedia*. This outline provides a general overview of the principal parts of the subject of chemistry and is arranged in alphabetical order.

Many individuals have contributed greatly and in many ways to this *Encyclopedia*. The associate editors—Alton J. Banks, Thomas Holme, Doris Kolb, and Herbert Silber—carried the major responsibility in shaping the intellectual content of the *Encyclopedia*. The authors of the articles executed that plan admirably and we thank them for that effort.

The staff at Macmillan Reference USA—Marie-Claire Antoine, Hélène Potter, Ray Abruzzi, Gloria Lam, and Christine Slovey—have been outstanding in their dedication and contributions to bring this *Encyclopedia* from its initial concept to the current reality. Without their considerable input, insightful guidance, and effort this *Encyclopedia* would never have seen the light of day. I take this opportunity to thank them personally and publicly. I am particularly grateful to Rita Wilkinson, my administrative assistant for her persistent and careful attention to details that kept the editorial office and my office connected for the smooth transmission of numerous critical details. I am especially grateful to Christine Slovey who, through her determined efforts and dedication, made a potentially difficult and tedious task far less onerous and, indeed, enjoyable.

J. J. Lagowski

Topical Outline

Analytical Chemistry Applications

Adhesives
Agricultural Chemistry
Analytical Chemistry
Bleaches
Ceramics
Chemical Engineering
Chemical Informatics
Coal
Cosmetics
Cryogenics
Detergents
Disposable Diapers
Dyes
Explosions
Fertilizer
Fibers
Food Preservatives
Forensic Chemistry
Formulation Chemistry
Freons
Gardening
Gasoline
Gemstones
Genetic Engineering
Glass
Hair Dyes and Hair Treatments
Herbicides
Industrial Chemistry, Inorganic
Industrial Chemistry, Organic
Insecticides
Irradiated Foods
Materials Science
Nanochemistry
Nylon
Pesticides
Pigments
Polymers, Synthetic
Recycling
Rocketry
Superconductors
Zeolites

Aqueous Chemistry

Acid-Base Chemistry
Bases
Bleaches
Chemical Reactions
Colloids
Corrosion
Equilibrium
Solution Chemistry
Water

Astrochemistry

Astrochemistry

Biochemistry

Acetylcholine
Active Site
Allosteric Enzymes
Amino Acid
Antibiotics
Artificial Sweeteners
Base Pairing
Bioluminescence
Caffeine
Carbohydrates
Cellulose
Chemiluminescence
Cholecalciferol
Cholesterol
Chromosome
Clones
Codon
Coenzyme
Cofactor
Collagen
Cortisone
Denaturation
Deoxyribonucleic Acid
Disaccharides
DNA Replication
Dopamine
Double Helix
Endorphins
Enzymes
Epinephrine
Estrogen
Fats and Fatty Acids
Fibrous Protein
Genes
Genetic Engineering
Genome
Globular Protein
Glycolysis
Glycoprotein
Hemoglobin
Hydrolase
Hydrolysis
Ion Channels
Kinase
Krebs Cycle
Lipid Bilayers
Lipids
Low Density Lipoprotein (LDL)
Membrane
Methylphenidate
Mutagen
Mutation
Neurochemistry
Neurotoxins
Neurotransmitters
Nicotinamide
Nicotinamide Adenine Dinucleotide (NAD)
Nicotine
Norepinephrine
Nucleic Acids
Nucleotide
Peptide Bond
Phospholipids

Photosynthesis
Polymerase Chain Reaction (PCR)
Polymers, Natural
Polysaccharides
Proteins
Primary Structure
Protein Solubility
Protein Synthesis
Protein Translation
Quaternary Structure
Residue
Restriction Enzymes
Retinol
Rhodium
Ribonucleic Acid
RNA Synthesis
Secondary Structure
Starch
Steroids
Stimulants
Storage Protein
Substrate
Taste Receptors
Teratogen
Tertiary Structure
Testosterone
Thiamin
Toxicity
Transmembrane Protein
Transport Protein
Triglycerides
Venom
Zwitterion

Biographies

Al Razi, Abu Bakr Muhammed ibn Zakariya
Anfinsen, Christian
Arrhenius, Svante
Avery, Oswald
Avogadro, Amedeo
Baekeland, Leo
Balmer, Johann Jakob
Bardeen, John
Becquerel, Antoine-Henri
Berg, Paul
Berthollet, Claude-Louis
Berzelius, Jöns Jakob
Black, Joseph
Bohr, Niels
Boltzmann, Ludwig
Boyle, Robert
Bragg, William Henry
Bragg, William Lawrence
Brønsted, Johannes Nicolaus
Bunsen, Robert
Caldwell, Mary
Calvin, Melvin
Cannizzaro, Stanislao
Carnot, Sadi
Carothers, Wallace
Carver, George Washington
Cavendish, Henry
Chadwick, James
Chappelle, Emmett
Chardonnet, Hilaire
Charles, Jacques
Chevreul, Michel
Cleve, Per Theodor
Cori, Carl and Gerty
Cottrell, Frederick
Coulomb, Charles
Curie, Marie Sklodowska
Dalton, John
Davy, Humphry
de Broglie, Louis
Dewar, James
du Pont, Éleuthère Irénée
Ehrlich, Paul
Einstein, Albert
Elion, Gertrude Belle
Fahrenheit, Gabriel
Faraday, Michael
Fermi, Enrico
Fischer, Emil Hermann
Fleming, Alexander
Franklin, Rosalind
Gadolin, Johan
Gay-Lussac, Joseph-Louis
Gibbs, Josiah Willard
Goodyear, Charles
Haber, Fritz
Hall, Charles
Heisenberg, Werner
Hess, Germain Henri
Heyrovsky, Jaroslav
Hodgkin, Dorothy
Julian, Percy
Kekulé, Friedrich August
Kelsey, Frances Kathleen Oldham
Khorana, Har Gobind
Krebs, Hans Adolf
Lavoisier, Antoine
Lawrence, Ernest
Le Bel, Joseph-Achille
Leblanc, Nicolas
LeChâtelier, Henri
Leclanché, Georges
Leloir, Luis
Lewis, Gilbert N.
Liebig, Justus von
Lister, Joseph
Lonsdale, Kathleen
Lucretius
Marsden, Ernest
Martin, Archer John Porter
Maxwell, James Clerk
Meitner, Lise
Mendeleev, Dimitri
Menten, Maud
Meyer, Lothar
Millikan, Robert
Morgan, Agnes Fay
Moseley, Henry
Nernst, Walther Hermann
Newton, Isaac
Nobel, Alfred Bernhard
Northrop, John
Oppenheimer, Robert
Ostwald, Friedrich Wilhelm
Paracelsus
Pasteur, Louis
Pauli, Wolfgang
Pauling, Linus
Perkin, William Henry
Planck, Max
Priestley, Joseph
Raman, Chandrasekhara
Ramsay, William
Remsen, Ira
Robinson, Robert
Röntgen, Wilhelm
Rutherford, Ernest
Rydberg, Johannes
Sanger, Frederick
Scheele, Carl
Schrödinger, Erwin
Seaborg, Glenn Theodore
Seibert, Florence
Soddy, Frederick
Stanley, Wendell
Staudinger, Hermann
Strutt, John (Lord Rayleigh)
Sumner, James
Svedberg, Theodor
Synge, Richard Laurence Millington
Szent-Györgyi, Albert
Thomson, Joseph John
Todd, Alexander
Travers, Morris
Urey, Harold
van der Waals, Johannes
Van Helmont, Johann Baptista
Van't Hoff, Jacobus Hendricus
Volta, Alessandro
Waksman, Selman
Watson, James Dewey
Weizmann, Chaim

Werner, Alfred
Willstätter, Richard
Wöhler, Friedrich
Woodward, Robert
Yalow, Rosalyn
Yukawa, Hideki
Zsigmondy, Richard

Chemical Substances

Coordination Compounds
Materials Science
Minerals
Nanochemistry
Nylon
Plastics
Rubber
Rydberg, Johannes
Silicone
Soap
Starch
Steel
Water

Computing

Chemical Informatics
Computational Chemistry
Digital X Ray
Molecular Modeling

Elements

Actinides
Actinium
Alkali Metals
Alkaline Earth Metals
Allotropes
Aluminum
Americium
Antimony
Argon
Arsenic
Astatine
Barium
Berkelium
Beryllium
Bismuth
Boron
Bromine
Cadmium
Calcium
Californium
Carbon
Cerium
Cesium
Chalcogens
Chlorine
Chromium
Cobalt
Copper
Curium
Dysprosium
Einsteinium
Erbium
Europium
Fermium
Fluorine
Francium
Fullerenes
Gadolinium
Germanium
Gold
Hafnium
Halogens
Helium
Holmium
Hydrogen
Indium
Iodine
Iridium
Iron
Lanthanides
Lanthanum
Lawrencium
Lead
Lithium
Lutetium
Magnesium
Manganese
Mendelevium
Mercury
Molybdenum
Neodymium
Neon
Neptunium
Nickel
Niobium
Nitrogen
Nobelium
Noble Gases
Osmium
Oxygen
Ozone
Palladium
Platinum
Plutonium
Polonium
Potassium
Praseodymium
Promethium
Protactinium
Radium
Radon
Rhenium
Rhodium
Rubidium
Ruthenium
Rutherfordium
Samarium
Scandium
Selenium
Silicon
Silver
Sodium
Sulfur
Tantalum
Technetium
Tellurium
Terbium
Thallium
Thorium
Thulium
Tin
Titanium
Transactinides
Tungsten
Uranium
Vanadium
Xenon
Ytterbium
Yttrium
Zinc
Zirconium

Energy

Chemistry and Energy
Energy
Energy Sources and Production
Explosions
Fire, Fuels, Power Plants
Fossil Fuels
Heat
Manhattan Project
New Battery Technology
Nuclear Fission
Nuclear Fusion
Petroleum
Solar Cells
Solid-State Devices
Storage Protein
Sustainable Energy Use
Temperature
Thermochemistry
Thermodynamics

Environmental Chemistry

Air Pollution
Atmospheric Chemistry
Environmental Pollution
Fertilizer

Freons
Global Warming
Green Chemistry
Herbicides
Insecticides
Pesticides
Recycling
Water Pollution
Water Quality

History

Alchemy

Inorganic Chemistry

Ceramics
Gemstones
Industrial Chemistry, Inorganic
Materials Science
Minerals
Nomenclature of Inorganic Chemistry

Medicine

Acetaminophen
Acetylsalicylic Acid
Acne Medication
Antibiotics
Ascorbic Acid
Carcinogen
Chemotherapy
CT Scans
Heavy Metal Toxins
Ibuprofen
Insulin
Interferon
Irradiated Foods
Neurotoxins
Neurotransmitters
Nuclear Medicine
Penicillin
Pharmaceutical Chemistry
Sulfa Drugs
Teratogen
Toxicity
Venom

Organic Chemistry

Aromaticity
Freons
Industrial Chemistry, Organic
Nylon
Organic Chemistry
Organic Halogen Compounds
Organometallic Compounds
Pesticides
Petroleum
Polyesters
Polymers, Synthetic
Rubber
Terpenes
Zwitterion

Physical Chemistry

Catalysis and Catalysts
Colloids
Concentration Gradient
Corrosion
Electrochemistry
International System of Units
Kinetics
Measurement
Nuclear Magnetic Resonance
Physical Chemistry
Quantum Chemistry
Spectroscopy
Surface Chemistry
Theoretical Chemistry

Radiation

Digital X Ray
Radiation
Radiation Exposure
Radioactivity

Reactions

Chemical Reactions
Combinatorial Chemistry
Equations, Chemical
Equilibrium
Inhibitors
Recombinant DNA
Synthesis, Chemical

States of Matter

Gases
Liquid Crystals
Liquids
Solid State

Structure

Chirality
Isomerism
Lewis Structures
Magnetism
Molecular Geometry
Molecular Modeling
Molecular Structure
Molecules
Periodic Table
Primary Structure
Quaternary Structure
Secondary Structure
Stoichiometry
Tertiary Structure

For Your Reference

TABLE 1. SELECTED METRIC CONVERSIONS

WHEN YOU KNOW	MULTIPLY BY	TO FIND
Temperature		
Celsius (˚C)	1.8 (˚C) +32	Fahrenheit (˚F)
Celsius (˚C)	˚C +273.15	Kelvin (K)
degree change (Celsius)	1.8	degree change (Fahrenheit)
Fahrenheit (˚F)	[(˚F) −32] / 1.8	Celsius (˚C)
Fahrenheit (˚F)	[(˚F −32) / 1.8] +273.15	Kelvin (K)
Kelvin (K)	K −273.15	Celsius (˚C)
Kelvin (K)	1.8(K −273.15) +32	Fahrenheit (˚F)

WHEN YOU KNOW	MULTIPLY BY	TO FIND
Distance/Length		
centimeters	0.3937	inches
kilometers	0.6214	miles
meters	3.281	feet
meters	39.37	inches
meters	0.0006214	miles
microns	0.000001	meters
millimeters	0.03937	inches

WHEN YOU KNOW	MULTIPLY BY	TO FIND
Capacity/Volume		
cubic kilometers	0.2399	cubic miles
cubic meters	35.31	cubic feet
cubic meters	1.308	cubic yards
cubic meters	8.107×10^{-4}	acre-feet
liters	0.2642	gallons
liters	33.81	fluid ounces

WHEN YOU KNOW	MULTIPLY BY	TO FIND
Area		
hectares (10,000 square meters)	2.471	acres
hectares (10,000 square meters)	107,600	square feet
square meters	10.76	square feet
square kilometers	247.1	acres
square kilometers	0.3861	square miles

WHEN YOU KNOW	MULTIPLY BY	TO FIND
Weight/Mass		
kilograms	2.205	pounds
metric tons	2205	pounds
micrograms (µg)	10^{-6}	grams
milligrams (mg)	10^{-3}	grams
nanograms (ng)	10^{-9}	grams

TABLE 2. ALPHABETIC TABLE OF THE ELEMENTS

Symbol	Element	Atomic Number	Atomic Mass*
Ac	Actinium	89	(227)
Al	Aluminum	13	26.982
Am	Americium	95	(243)
Sb	Antimony	51	121.75
Ar	Argon	18	39.948
As	Arsenic	33	74.922
At	Astatine	85	(210)
Ba	Barium	56	137.33
Bk	Berkelium	97	(247)
Be	Beryllium	4	9.012
Bi	Bismuth	83	208.980
Bh	Bohrium	107	(262)
B	Boron	5	10.811
Br	Bromine	35	79.904
Cd	Cadmium	48	112.411
Ca	Calcium	20	40.08
Cf	Californium	98	(251)
C	Carbon	6	12.011
Ce	Cerium	58	140.115
Cs	Cesium	55	132.90
Cl	Chlorine	17	35.453
Cr	Chromium	24	51.996
Co	Cobalt	27	58.933
Cu	Copper	29	63.546
Cm	Curium	96	(247)
Ds	Darmastadtium	110	(269)
Db	Dubnium	105	(262)
Dy	Dysprosium	66	162.50
Es	Einsteinium	99	(252)
Er	Erbium	68	167.26
Eu	Europium	63	151.965
Fm	Fermium	100	(257)
F	Fluorine	9	18.998
Fr	Francium	87	(223)
Gd	Gadolinium	64	157.25
Ga	Gallium	31	69.723
Ge	Germanium	32	72.61
Au	Gold	79	196.967
Hf	Hafnium	72	178.49
Hs	Hassium	108	(265)
He	Helium	2	4.003
Ho	Holmium	67	164.93
H	Hydrogen	1	1.008
In	Indium	49	114.82
I	Iodine	53	126.905
Ir	Iridium	77	192.22
Fe	Iron	26	55.847
Kr	Krypton	36	83.80
La	Lanthanum	57	138.906
Lr	Lawrencium	103	(260)
Pb	Lead	82	207.2
Li	Lithium	3	6.941
Lu	Lutetium	71	174.967
Mg	Magnesium	12	24.305
Mn	Manganese	25	54.938
Mt	Meitnerium	109	(266)
Md	Mendelevium	101	(258)
Hg	Mercury	80	200.59
Mo	Molybdenum	42	95.94
Nd	Neodymium	60	144.24
Ne	Neon	10	20.180
Np	Neptunium	93	237.048
Ni	Nickel	28	58.69
Nb	Niobium	41	92.908
N	Nitrogen	7	14.007
No	Nobelium	102	(259)
Os	Osmium	76	190.2
O	Oxygen	8	15.999
Pd	Palladium	46	106.42
P	Phosphorus	15	30.974
Pt	Platinum	78	195.08
Pu	Plutonium	94	(244)
Po	Polonium	84	(209)
K	Potassium	19	39.1
Pr	Praseodymium	59	140.908
Pm	Promethium	61	(145)
Pa	Protactinium	91	231.036
Ra	Radium	88	226.025
Rn	Radon	86	(222)
Re	Rhenium	75	186.207
Rh	Rhodium	45	102.906
Rb	Rubidium	37	85.47
Ru	Ruthenium	44	101.07
Rf	Rutherfordium	104	(261)
Sm	Samarium	62	150.36
Sc	Scandium	21	44.966
Sg	Seaborgium	106	(263)
Se	Selenium	34	78.96
Si	Silicon	14	28.086
Ag	Silver	47	107.868
Na	Sodium	11	22.990
Sr	Strontium	38	87.62
S	Sulfur	16	32.066
Ta	Tantalum	73	180.948
Tc	Technetium	43	(98)
Te	Tellurium	52	127.60
Tb	Terbium	65	158.925
Tl	Thallium	81	204.383
Th	Thorium	90	232.038
Tm	Thulium	69	168.934
Sn	Tin	50	118.71
Ti	Titanium	22	47.88
W	Tungsten	74	183.85
U	Uranium	92	238.029
V	Vanadium	23	50.942
Xe	Xenon	54	131.29
Yb	Ytterbium	70	173.04
Y	Yttrium	39	88.906
Zn	Zinc	30	65.38
Zr	Zirconium	40	91.224

*Atomic masses are based on the relative atomic mass of ^{12}C=12. These values apply to the elements as they exist in materials of terrestrial origin and to certain artificial elements. Values in parenthesis are the mass number of the isotope of the longest half-life.

TABLE 3. COMMON ABBREVIATIONS, SYMBOLS, AND ACRONYMS

’	minute (of arc); single prime
”	second (of arc); double prime
+	plus
$^+$	positive charge
−	minus
$^-$	negative charge
±	plus-or-minus
∓	minus-or-plus
×	multiplied by
·	multiplied by
÷	divided by
=	equals
≠	not equal to
∽	about, approximately
≅	congruent to; approximately equal to
≈	approximately equal to
≡	identical to; equivalent to
<	less than
≤	less than or equal to
>	greater than
≥	greater than or equal to
%	percent
°	degree (temperature; angle of arc)
@	at
—	single bond
═	double bond
: :	double bond
≡	triple bond
: : :	triple bond
∞	infinity
∝	variation
∂	partial derivative or differential
α	proportional to, alpha
√	square root
Δ	delta; increment of a variable
ϵ_0	dielectric constant; permittivity
θ	plane angle
λ	wavelength
μ	magnetic moment; micro
μA	microampere
μC	microcoulomb
μF	microfarad
μg	microgram
μg/ml	microgram per milliliter
μK	microkelvin
μm	micrometer (also called micron)
μmol;	micromole
μs, μsec	microsecond
ν	frequency
υ	velocity
π or pi	ratio of the circumference of a circle to its diameter; double as in double bond
σ	single as in single bond; Stefan-Boltzmann constant
Σ	summation
ϕ	null set
ψ	amplitude of a wave (as in *wave,* or *psi, function)*
→	reaction to right
←	reaction to left
↔	connecting resonance forms
⇆	equilibrium reaction beginning at right
⇄	equilibrium reaction beginning at left
⇌	reversible reaction beginning at left
⇋	reversible reaction beginning at right
↑	elimination
⇓	absorption
a	acceleration
A	area
a_o	Bohr Unit
AAS	atomic absorption spectroscopy
ABS	alkylbenzene sulfate
ACS	American Chemical Society
ADH	alcohol dehydrogenase
ADP	adenosine diphosphate
AEC	Atomic Energy Commission
AES	atomic emission spectroscopy
AFM	atomic force microscope; atomic force microscopy
AFS	atomic fluorescence spectroscopy
ALDH	aldehyde dehydronase
amp	ampere
AMS	accelerator mass spectrometry
AMU	atomic mass unit
atm.	standard atmosphere (unit of pressure)
ATP	adenosine triphosphate
β	beta
b.p.	boiling point
Btu	British thermal unit
c	centi-; speed of light
C	carbon; Celsius; centigrade; coulomb
C	heat capacity; electric capacitance

TABLE 3. COMMON ABBREVIATIONS, SYMBOLS, AND ACRONYMS [continued]

Ci	Curies
cm	centimeter
CT	computed tomography
d	d-orbital
D	dipole moment
DC	direct current
deg	degree
dr	diastereomer ratio
e	elementary charge
E	electric field strength; energy
E_a	activation energy
E_g	bandgap energy
EA	electron affinity
er	enantiomer ratio
eV	electron volts
f	f-orbital
F	Fahrenheit; Faraday's constant; fluorine
F	force
g	gram
g	g-orbital; gas
h	hour
h	Planck's constant
Hz	hertz
i	i-orbital
IUPAC	International Union of Pure and Applied Chemistry
J	joule
J	electric current density
k	k-orbital
K	degrees Kelvin; Kelvin; potassium
K_a	acidity constant for the dissociation of weak acid (the weaker the acid, the lower the K_a value
k_B	Boltzmann's constant
Kg	kilogram
kHz	kilohertz
kJ	kilojoule
kJ mol	kilojoule mole
km	kilometer
K_m	Michaelis constant
l	length; liquid
L	lambert; liter
L	length; Avogadro's constant
LD	lethal dose
L/mole	liters per mole
ln	natural logarithm
log	logarithm
m	meter; milli-; molal (concentration)
m	mass
M	molar (concentration)
m_e	electron mass
mA	milliamperes
mg	milligram
mg/L	milligrams per liter
MHz	megahertz
min	minute
ml	milliliter
MO	molecular orbital
p	p-orbital
ω	omega
ppb	parts per billion
ppm	parts per million
ppt	parts per trillion
psi	per square inch; English for ψ
q	quantity
REM	Roentgen Equivalent Man (radiation-dose unit of measure)
s	solid; s-orbital
S	entropy
sec	second; secant
SEM	scanning electron microscope
SI	Système Internationale (International System of Measurements)
SPM	scanning probe microscope
STM	scanning tunneling microscope
STP	standard temperature and pressue (˚C, 1 atm)
Sv	sievert unit (1 Sv = 100 REM; used to measure radiation dose)
t	time
T	moment of force, thermodynamic temperature (in degrees Kelvin); torque
T_c	critical temperature
TEM	transmission electron microscope
u	unified atomic mass unit
U	electric potential
V	electric potential; vanadium; volume
V	volt
vap.	vaporization
VB	valence bond
vel.	velocity
VSEPR	valence shell electron pair repulsion
Z	atomic number

PERIODIC TABLE OF THE ELEMENTS*†

	I	II
5	3 LITHIUM **Li** 6.941	4 BERYLLIUM **Be** 9.012
	11 SODIUM **Na** 22.990	12 MAGNESIUM **Mg** 24.305
	19 POTASSIUM **K** 39.1	20 CALCIUM **Ca** 40.08
	37 RUBIDIUM **Rb** 85.47	38 STRONTIUM **Sr** 87.62
	55 CESIUM **Cs** 132.90	56 BARIUM **Ba** 137.33
	87 FRANCIUM **Fr** (223)	88 RADIUM **Ra** 226.025

1 HYDROGEN **H** 1.008

d	21 SCANDIUM **Sc** 44.966	22 TITANIUM **Ti** 47.88	23 VANADIUM **V** 50.942	24 CHROMIUM **Cr** 51.996	25 MANGANESE **Mn** 54.938	26 IRON **Fe** 55.847	27 COBALT **Co** 58.933	28 NICKEL **Ni** 58.69	29 COPPER **Cu** 63.546	30 ZINC **Zn** 65.38
	39 YTTRIUM **Y** 88.906	40 ZIRCONIUM **Zr** 91.224	41 NIOBIUM **Nb** 92.908	42 MOLYBDENIUM **Mo** 95.94	43 TECHNETIUM **Tc** (98)	44 RUTHENIUM **Ru** 101.07	45 RHODIUM **Rh** 102.906	46 PALLADIUM **Pd** 106.42	47 SILVER **Ag** 107.868	48 CADMIUM **Cd** 112.411
	71 LUTETIUM **Lu** 174.967	72 HAFNIUM **Hf** 178.49	73 TANTALUM **Ta** 180.948	74 TUNGSTEN **W** 183.85	75 RHENIUM **Re** 186.207	76 OSMIUM **Os** 190.2	77 IRIDIUM **Ir** 192.22	78 PLATINUM **Pt** 195.08	79 GOLD **Au** 196.967	80 MERCURY **Hg** 200.59
	103 LAWRENCIUM **Lr** (260)	104 RUTHERFORDIUM **Rf** (261)	105 DUBNIUM **Db** (262)	106 SEABORGIUM **Sg** (263)	107 BOHRIUM **Bh** (262)	108 HASSIUM **Hs** (265)	109 MEITNERIUM **Mt** (266)	110 DARMASTADTIUM **Ds** (269)	111 UNUNUNIUM **Uuu** (272)	112 (?)

	III	IV	V	VI	VII	VIII
						2 HELIUM **He** 4.003
p	5 BORON **B** 10.811	6 CARBOM **C** 12.011	7 NITROGEN **N** 14.007	8 OXYGEN **O** 15.999	9 FLUORINE **F** 18.998	10 NEON **Ne** 20.180
	13 ALUMINUM **Al** 26.982	14 SILICON **Si** 28.086	15 PHOSPHORIUS **P** 30.974	16 SULFUR **S** 32.066	17 CHLORINE **Cl** 35.453	18 ARGON **Ar** 39.948
	31 GALLIUM **Ga** 69.73	32 GERMANIUM **Ge** 72.61	33 ARSENIC **As** 74.922	34 SELENIUM **Se** 78.96	35 BROMINE **Br** 79.904	36 KRYPTON **Kr** 83.80
	49 INDIUM **In** 114.82	50 TIN **Sn** 118.71	51 ANTIMONY **Sb** 121.75	52 TELLURIUM **Te** 127.60	53 IODINE **I** 126.905	54 XENON **Xe** 131.29
	81 THALLIUM **Tl** 204.383	82 LEAD **Pb** 207.2	83 BISMUTH **Bi** 208.980	84 POLONIUM **Po** (209)	85 ASTATINE **At** (210)	86 RADON **Rn** (222)

f	57 LANTHANUM **La** 138.906	58 CERIUM **Ce** 140.15	59 PRAESEODYMIUM **Pr** 140.908	60 NEODYMIUM **Nd** 144.24	61 NEODYMIUM **Pm** (145)	62 SAMARIUM **Sm** 150.36	63 EUROPIUM **Eu** 151.965	64 GADOLINIUM **Gd** 157.25	65 TERBIUM **Tb** 158.925	66 DYSPROSIUM **Dy** 162.50	67 HOLMIUM **Ho** 164.93	68 ERBIUM **Er** 167.26	69 THULIUM **Tm** 168.934	70 YTTERBIUM **Yb** 173.04
	89 ACTINIUM **Ac** 227.03	90 THORIUM **Th** 232.038	91 PROTACTINIUM **Pa** 231.036	92 URANIUM **U** 238.029	93 NEPTUNIUM **Np** 237.048	94 PLUTONIUM **Pu** (244)	95 AMERICIUM **Am** (243)	96 CURIUM **Cm** (247)	97 BERKELIUM **Bk** (247)	98 CALIFORNIUM **Cf** (251)	99 EINSTEINIUM **Es** (252)	100 FERMIUM **Fm** (257)	101 MENDELEVIUM **Md** (258)	102 NOBELIUM **No** (259)

*Each element in the table is listed with (from top to bottom) its atomic number, its name, its symbol, and its atomic mass. Atomic mass numbers in parentheses are the mass numbers of the longest-lived isotope. Other atomic mass numbers are the average mass number of the naturally occurring isotopes.

†The names and labels for elements beyond number 103 are controversial. IUPAC initially ruled in favor of Latin names based on atomic number, but in 1994 a set of specific names and symbols was suggested. After considerable debate, a revised final list of names for elements 104-109 was issued on August 30, 1997. Temporary names were also assigned for elements 110 and 111. Various groups have suggested alternatives names for some of these elements. Additional elements continue to be synthesized, though with increasing difficulty, with no definite upper atomic-number limit yet established.

Contributors

Catalina Achim
Carnegie Mellon University
Pittsburgh, Pennsylvania

David T. Allen
University of Texas at Austin
Austin, Texas

Carolyn J. Anderson
Washington University School of Medicine
St. Louis, Missouri

Ronald D. Archer
Professor Emeritus
University of Massachusetts, Amherst
Amherst, Massachusetts

D. Eric Aston
University of Idaho
Moscow, Idaho

Peter Atkins
University of Oxford
Oxford, United Kingdom

Cynthia Atterholt
Western Carolina University
Cullowhee, North Carolina

Michèle Auger
Laval University
Quebec, Quebec, Canada

Karl W. Böer
Professor Emeritus
University of Delaware
Newark, Delaware

Catherine H. Banks
Peace College
Raleigh, North Carolina

Joseph Bariyanga
University of Wisconsin
Milwaukee, Wisconsin

Nathan J. Barrows
University of Northern Colorado
Greeley, Colorado

David A. Bassett
Brockton, Massachusetts

James D. Batteas
CUNY - College of Staten Island
Staten Island, New York

Bruce Beaver
Duquesne University
Pittsburgh, Pennsylvania

C. Larry Bering
Clarion University
Clarion, Pennsylvania

Bill Bertoldi
Kingsford, Michigan

W. E. Billups
Rice University
Houston, Texas

Koen Binnemans
Catholic University of Leuven
Leuven, Belgium

James P. Birk
Arizona State University
Tempe, Arizona

Jeffrey R. Bloomquist
Virginia Polytechnic Institute and State University
Blacksburg, VA

John E. Bloor
University of Tennessee
Knoxville, Tennessee

George Bodner
Purdue University
West Lafayette, Indiana

Paul W. Bohn
University of Illinois
Urbana, Illinois

Valerie Borek
Boothwyn, Pennsylvania

Erwin Boschmann
Indiana University
Indianapolis, Indiana

Wayne B. Bosma
Bradley University
Peoria, Illinois

Ole Bostrup
The Danish Society of The History of Chemistry
Fredensborg, Denmark

F. Javier Botana
University of Cadiz
Cadiz, Spain

Lawrence H. Brannigan
Southwestern Illinois College
Bellville, Illinois

Ronald Brecher
GlobalTox International Consultants Inc.
Guelph, Ontario, Canada

Jeffrey C. Bryan
University of Wisconsin-La Crosse
La Crosse, Wisconsin

Robert A. Bulman
National Radiological Protection Board
Oxfordshire, England

Jean-Claude Bunzli
Swiss Federal Institute of Technology
Lausanne, Switzerland

Douglas Cameron
Montana Tech of the University of Montana
Butte, Montana

Michael C. Cann
University of Scranton
Scranton, Pennsylvania

Charles E. Carraher Jr.
Florida Atlantic University
Boca Raton, Florida

Henry A. Carter
Augustana University College
Camrose, Alberta, Canada

John Castro
Huntington Station, New York

Lyman R. Caswell
Texas Woman's University
Denton, Texas

Raymond Chang
Williams College
Williamstown, Massachusetts

Philip J. Chenier
University of Wisconsin
Eau Claire, Wisconsin

Peter E. Childs
University of Limerick
Limerick, Ireland

Gregory R. Choppin
Florida State University
Tallahassee, Florida

Abraham Clearfield
Texas A&M University
College Station, Texas

Brian P. Coppola
University of Michigan
Ann Arbor, Michigan

Eugene C. Cordero
San José State University
San José, California

Paul A. Craig
Rochester Institute of Technology
Rochester, New York

M. J. Crawford
Ludwig-Maximilians-Universtät-München
Munich, Germany

Mary R. S. Creese
University of Kansas
Lawrence, Kansas
(retired)

Bartow Culp
Purdue University
West Lafayette, Indiana

Carlos Eduardo da Silva Cortes
Universidade Federal Fluminense
Rio de Janeiro, Brazil

G. Brent Dawson
University of North Carolina at Greensboro
Greensboro, North Carolina

Stephanie E. Dew
Centre College
Danville, Kentucky

Anthony Diaz
Central Washington University
Ellensburg, Washington

Diego J. Diaz
University of Illinois at Urbana-Champaign
Urbana, Illinois

James S. Dickson
Iowa State University
Ames, Iowa

David A. Dobberpuhl
Creighton University
Omaha, Nebraska

Daryl J. Doyle
Kettering University
Flint, Michigan

Michael Eastman
Northern Arizona University
Flagstaff, Arizona

Andrew Ede
University of Alberta
Edmonton, Canada

Edward M. Eyring
University of Utah
Salt Lake City, Utah

Scott E. Feller
Wabash College
Crawfordsville, Indiana

Kurt W. Field
Bradley University
Peoria, Illinois

Matthew A. Fisher
St. Vincent College
Latrobe, Pennsylvania

George Fleck
Smith College
Northampton, Massachusetts

Michael J. Fosmire
Purdue University
West Lafayette, Indiana

Mark Freilich
The University of Memphis
Memphis, Tennessee

Ken Geremia
Copper Development Association, Inc.
New York, New York

Gregory S. Girolami
University of Illinois, Champaign-Urbana
Urbana, Illinois

Carmen Giunta
Le Moyne College
Syracuse, New York

Harold Goldwhite
California State University, Los Angeles
Los Angeles, California

Barbara E. Goodman
University of South Dakota
Vermillion, South Dakota

Gordon W. Gribble
Dartmouth College
Hanover, New Hampshire

Robert K. Griffith
West Virginia University
Morgantown, West Virginia

Neena Grover
Colorado College
Colorado Springs, Colorado

William G. Gutheil
University of Missouri-Kansas City
Kansas City, Missouri

David G. Haase
North Carolina State University
Raleigh, North Carolina

Arthur M. Halpern
Indiana State University
Terre Haute, Indiana

R. Adron Harris
The University of Texas at Austin
Austin, Texas

John Harwood
Tennessee Technological University
Cookeville, Tennessee

Ian S. Haworth
University of Southern California
Los Angeles, California

James M. Helt
CUNY- College of Staten Island
Staten Island, New York

J. Carver Hill
Cary, North Carolina

Darleane C. Hoffman
Lawrence Berkeley National Laboratory, University of California
Berkeley, California

Thomas A. Holme
University of Wisconsin-Milwaukee
Milwaukee, Wisconsin

Chaim T. Horovitz
Emeritus Professor
Rehovot , Israel

John D. Hostettler
San José State University
San José, California

Brian R. James
University of British Columbia
Vancouver, British Columbia, Canada

Frank A. J. L. James
The Royal Institution
London, England

Mark Jensen
Argonne National Laboratory
Argonne, Illinois

Melvin D. Joesten
Vanderbilt University
Nashville, Tennessee

W. L. Jolly
University of California, Berkeley
Berkeley, California

Loretta L. Jones
University of Northern Colorado
Greeley, Colorado

David A. Juckett
Michigan State University
Lansing, Michigan
Barros Research Institute
Holt, Michigan

Paul J. Karol
Carnegie Mellon University
Pittsburgh, Pennsylvania

Vladimir Karpenko
Charles University
Prague, Czech Republic

George B. Kauffman
California State University, Fresno
Fresno, California

W. Frank Kinard
College of Charleston
Charleston, SC

Thomas M. Klapotke
Ludwig-Maximillians-Universität München
Munich, Germany

Kyle Knight
University of Tennessee at Chattanooga
Chattanooga, Tennessee

Paul E. Koch
Penn State, Behrend College
Erie, Pennsylvania

Doris K. Kolb
Bradley University
Peoria, Illinois

Kenneth E. Kolb
Bradley University
Peoria, Illinois

Daniel P. Kramer
Kramer & Asscociates, Ltd.
Centerville, Ohio

Ágúst Kvaran
University of Iceland
Reykjavik, Iceland

J. J. Lagowski
The University of Texas
Austin, Texas

Michael Laing
Professor Emeritus
University of Natal
Durban, South Africa

Rattan Lal
The Ohio State University
Columbus, Ohio

Thomas H. Lane
Dow Corning Coporation
Midland, Michigan

Alan B. G. Lansdown
Imperial College School of Medicine
London, United Kingdom

Amanda Lawrence
University of Illinois, Champaign-Urbana
Urbana, Illinois

Peter B. Leavens
University of Delaware
Newark, Delaware

G. J. Leigh
University of Sussex
Brighton, United Kingdom

H. Eugene LeMay, Jr.
University of Nevada
Reno, Nevada

Kenneth B. Lipkowitz
North Dakota State University
Fargo, North Dakota

Ingrid A. Lobo
University of Texas at Austin
Austin, Texas

Walter Loveland
Oregon State University
Corvallis, Oregon

Phyllis A. Lyday
U.S. Geological Survey
Reston, Virginia

Paul A. Maggard Jr.
North Carolina State University
Raleigh, North Carolina

Michael E. Maguire
Case Western Reserve University
Cleveland, Ohio

Keith L. Manchester
University of the Witwatersrand, Johannesburg
South Africa

Dean F. Martin
University of South Florida
Tampa, Florida

Barbara B. Martin
University of South Florida
Tampa, Florida

James D. Martin
North Carolina State University
Raleigh, North Carolina

Anthony F. Masters
University of Sydney
New South Wales, Australia

Seymour Mauskopf
Duke University
Durham, North Carolina

Sean McMaughan
Texas A&M University
College Station, Texas

Paul F. McMillan
University College London, Christopher Ingold Laboratories
London, United Kingdom

Edward A. Meighen
McGill University
Montreal, Canada

Louis Messerle
University of Iowa
Iowa City, Iowa

Donald E. Moreland
Professor Emeritus
North Carolina State University
Raleigh, North Carolina

Matthew J. Morra
University of Idaho, Soil & Land Resources Division
Moscow, Idaho

Richard Mowat
North Carolina State University
Raleigh, North Carolina

Frank Mucciardi
McGill University
Montreal, Quebec, Canada

Kathleen L. Neeley
University of Kansas
Lawrence, Kansas

John Michael Nicovich
Georgia Institute of Technology
Atlanta, Georgia

Robert Noiva
University of South Dakota School of Medicine
Vermillion, South Dakota

Charles E. Ophardt
Elmhurst College
Elmhurst, Illinois

Richard Pagni
University of Tennessee
Knoxville, Tennessee

Gus J. Palenik
University of Florida
Gainsville, Florida

Robert P. Patterson
North Carolina State University, Crop Science Department
Raleigh, North Carolina

Harry E. Pence
State University of New York, College at Oneonta
Oneonta, New York

Mark A. Pichaj
Biola University
La Marada, California

John Pickering
San José State University
Nuclear Science Facility
San José, California

Tanja Pietraß
New Mexico Tech
Socorro, New Mexico

A. G. Pinkus
Baylor University
Waco, Texas

Jennifer L. Powers
Kennesaw State University
Kennesaw, Georgia

Suzanne T. Purrington
North Carolina State University
Raleigh, North Carolina

Ray Radebaugh
National Institute of Standards and Technology, Cryogenics Technologies Group
Boulder, Colorado

Thomas B. Rauchfuss
University of Illinois, Champaign-Urbana
Urbana, Illinois

Geoffrey W. Rayner-Canham
Sir Wilfred Grenfell College

Corner Brook, Newfoundland, Canada

Marelene Rayner-Canham
Sir Wilfred Grenfell College
Corner Brook, Newfoundland, Canada

Jeffrey C. Reid
North Carolina Geological Survey
Raleigh, North Carolina

Richard E. Rice
Florence, Montana

D. Paul Rillema
Wichita State University
Wichita, Kansas

Frank Rioux
St. John's University
College of St. Benedict
St. Joseph, Minnesota

Robert Rittenhouse
Walla Walla College
College Place, Washington

Elizabeth S. Roberts-Kirchhoff
University of Detroit Mercy
Detroit, Michigan

Brett Robinson
Horticultural and Food Research Institute of New Zealand
Palmerston North, New Zealand

Herbert W. Roesky
University of Göttingen
Göttingen, Germany

Hiranya S. Roychowdhury
New Mexico State University
Las Cruces, New Mexico

Gordon Rutter
Royal Botanic Garden Edinburgh
Edinburgh, United Kingdom

Martin D. Saltzman
Providence College
Providence, Rhode Island

Jerry L. Sarquis
Miami University
Oxford, Ohio

Nancy N. Sauer
Los Alamos National Laboratory
Los Alamos, New Mexico

Wolf-Dieter Schubert
Vienna University of Technology
Vienna, Austria

Joachim Schummer
University of South Carolina
Columbia, South Carolina

Alan Schwabacher
University of Wisconsin-Milwaukee
Milwaukee, Wisconsin

A. Truman Schwartz
Macalester College
Saint Paul, Minnesota

William M. Scovell
Bowling Green State University
Bowling Green, Ohio

Lydia S. Scratch
Ottawa, Ontario, Canada

Peter Rudolf Seidl
Universidade Federal do Rio de Janeiro
Rio de Janeiro, Brazil

N. M. Senozan
California State University
Long Beach, California

James F. Shackelford
University of California at Davis
Davis, California

Stephanie Dionne Sherk
Westland, Michigan

Ben Shoulders
The University of Texas at Austin
Austin, Texas

David B. Sicilia
University of Maryland
College Park, Maryland

Herbert B. Silber
San José State University
San José, California

Robert J. Silva
Lawrence Berkeley National Laboratory, University of California
Berkeley, California

Sharron W. Smith
Hood College
Frederick, Maryland

C. Graham Smith
Penicuik, United Kingdom

Mary L. Sohn
Florida Institute of Technology
Melbourne, Florida

David Speckhard
Loras College
Dubuque, Iowa

Jonathan N. Stack
North Dakota State University
Fargo, North Dakota

Conrad L. Stanitski
University of Central Arkansas
Conway, Arkansas

Donald H. Stedman
University of Denver
Denver, Colorado

Anthony N. Stranges
Texas A&M University
College Station, Texas

Dan M. Sullivan
University of Nebraska at Omaha
Omaha, Nebraska

Tammy P. Taylor
Los Alamos National Laboratory
Los Alamos, New Mexico

Ann T. S. Taylor
Wabash College
Crawfordsville, Indiana

Sidney Toby
Rutgers University
Piscataway, New Jersey

Reginald P. T. Tomkins
New Jersey Institute of Technology
Newark, New Jersey

Anthony S. Travis
The Hebrew University
Jerusalem, Israel

Donald G. Truhlar
University of Minnesota
Minneapolis, Minnesota

Georgios Tsaparlis
University of Ioannina
Ioannina, Greece

Dennis G. Tuck
University of Windsor
Windsor, Ontario, Canada
(deceased)

Geraldo Vicentini
Instituto de Quimíca, *University of São Paulo*
São Paulo, Brazil

Nanette M. Wachter
Hofstra University
Hempstead, New York

George H. Wahl Jr.
North Carolina State University
Raleigh, North Carolina

Helen R. Webb
Monash University
Clayton, Victoria, Australia

Laurence E. Welch
Knox College
Galesburg, Illinois

J. Reed Welker
University of Arkansas
Fayetteville, Arkansas
(retired)

Guang Wen
Tottori University
Tottori, Japan

Todd W. Whitcombe
University of Northern British Columbia
Prince George, British Columbia, Canada

Vivienne A. Whitworth
Ryerson University
Toronto, Ontario, Canada

David A. Williams
University College London
London, United Kingdom

Robert K. Wismer
Millersville University
Millersville, Pennsylvania

Ronni Wolf
Kaplan Medical Center
Rechovot, Israel

Adele J. Wolfson
Wellesley College
Wellesley, Massachusetts

Burghard Zeiler
Wolfram Bergbau und Hüttenges m.b.H.
Austria, Germany

Lea B. Zinner
Departamento de Química
São Paulo, Brazil

Cynthia G. Zoski
Georgia State University
Atlanta, Georgia

Thomas M. Zydowsky
FMC Corporation
Princeton, New York

A, Vitamin *See **Retinol**.*

a

Acetaminophen

The drug acetaminophen is a pain reliever (an **analgesic**) and a fever-**reducing agent** (an antipyretic). It is found in over-the-counter medicines such as Tylenol and Excedrin. It is widely used to treat both chronic and acute pain and is considered to have a pain-relieving potency similar to that of other over-the-counter analgesics, such as aspirin and ibuprofen. Its chemical name is 4-hydroxyacetanalide. Its chemical formula is $C_8H_9NO_2$ (see Figure 1).

analgesic: compound that relieves pain, e.g., aspirin

reducing agent: substance that causes reduction, a process during which electrons are lost (or hydrogen atoms gained)

Acetaminophen was used as a pain reliever as early as the late 1800s. It was approved for use by the U.S. Food and Drug Administration in 1950, shortly after it was discovered that the closely related drug paracetin was broken down in the body to acetaminophen, and that the beneficial effects of paracetin were actually the effects of acetaminophen.

Acetaminophen works by inhibiting the **synthesis** of chemical messengers called prostaglandins, which help to transmit pain signals and induce fever. The body produces prostaglandins in response to an injury or illness. Acetaminophen reduces the pain by helping to block this signaling. Acetaminophen stops some prostaglandin functions while not affecting others. Prostaglandins are known to promote inflammation and swelling of many body tissues. Unlike aspirin and ibuprofen, acetaminophen does not have anti-inflammatory action.

synthesis: combination of starting materials to form a unified product

The differences in the actions of these drugs involve their tissue specificities. Aspirin and ibuprofen act on a broad range of tissues. Acetaminophen inhibits prostaglandin synthesis more specifically in the cells of the nervous system and is a much less effective inhibitor of this in other tissues. This selectivity gives acetaminophen its analgesic and antipyretic effects without acetaminophen's acting as an anti-inflammatory drug.

platelet: smallest noncellular component of human blood

Acetaminophen is known to cause less stomach irritation than aspirin and ibuprofen, and it does not inhibit **platelet** aggregation and blood clotting (as does aspirin).

When given in its therapeutic dose (500 mg every 4–6 hours), acetaminophen is a safe and effective pain reliever. However, at higher doses it can be severely toxic to the liver, and even fatal.

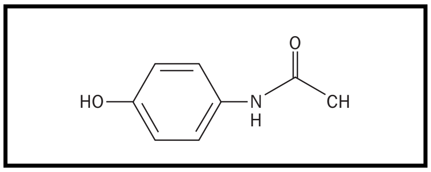

Figure 1. Structure of acetaminophen.

The drug itself is not toxic, but a toxic compound, N-acetyl-*p*-benzoquinonimine, is formed from it as it is broken down by enzymes in the liver. In small amounts this compound can be detoxified and **excreted**. But in large amounts it overwhelms the detoxification system and the compound begins killing liver tissue. Overdose can be treated by giving the patient activated charcoal, which absorbs the acetaminophen in the patient's stomach and intestines, and by administering *N*-acetylcystine, a compound that can deactivate the toxic product of **metabolism**. SEE ALSO ACETYLSALICYLIC ACID; IBUPROFEN.

excrete: to eliminate or discharge from a living entity

metabolism: the complete range of biochemical processes that take place within living organisms; comprises processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those which break down complex food molecules, thus liberating energy (catabolism)

Kyle Knight

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Acetylcholine

Acetylcholine is the neurotransmitter produced by neurons referred to as cholinergic neurons. In the peripheral nervous system acetylcholine plays a role in skeletal muscle movement, as well as in the regulation of smooth muscle and cardiac muscle. In the central nervous system acetylcholine is believed to be involved in learning, memory, and mood.

Acetylcholine is synthesized from choline and acetyl coenzyme A through the action of the enzyme choline acetyltransferase and becomes packaged into membrane-bound **vesicles**. After the arrival of a nerve signal at the termination of an axon, the vesicles fuse with the cell membrane, causing the release of acetylcholine into the **synaptic cleft**. For the nerve signal to continue, acetylcholine must diffuse to another nearby neuron or muscle cell, where it will bind and activate a **receptor** protein.

vesicle: small compartment in a cell that contains a minimum of one lipid bilayer

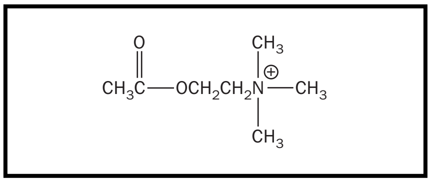
synaptic cleft: tiny space between the terminal button of one neuron and the dendrite or soma of another

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

There are two main types of cholinergic receptors, nicotinic and muscarinic. Nicotinic receptors are located at synapses between two neurons and at synapses between neurons and skeletal muscle cells. Upon activation a nicotinic receptor acts as a channel for the movement of ions into and out of the neuron, directly resulting in **depolarization** of the neuron. Muscarinic receptors, located at the synapses of nerves with smooth or cardiac muscle, trigger a chain of chemical events referred to as signal transduction.

depolarization: process of decreasing the separation of charge in nerve cells; the opposite of hyperpolarization

For a cholinergic neuron to receive another impulse, acetylcholine must be released from the receptor to which it has bound. This will only happen if the concentration of acetylcholine in the synaptic cleft is very low. Low synaptic concentrations of acetylcholine can be maintained via a hydrolysis reaction catalyzed by the enzyme acetylcholinesterase. This enzyme hydrolyzes acetylcholine into acetic acid and choline. If acetylcholinesterase activity is inhibited, the synaptic concentration of acetylcholine will remain higher than normal. If this inhibition is irreversible, as in the case of exposure to many nerve gases and some pesticides, sweating, bronchial constriction, convulsions, paralysis, and possibly death can occur. Although irreversible inhibition is dangerous, beneficial effects may be derived from transient (reversible) inhibition. Drugs that inhibit acetylcholinesterase in a



$$CH_3\overset{O}{\overset{\|}{C}}-OCH_2CH_2\overset{CH_3}{\underset{CH_3}{N^{\oplus}}}-CH_3$$

Figure 1. The structure of acetylcholine.

reversible manner have been shown to improve memory in some people with Alzheimer's disease. SEE ALSO Neurotransmitters.

Jennifer L. Powers

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Acetylsalicylic Acid

Aspirin (acetylsalicylic acid, see Figure 1) was introduced as an **analgesic** (pain-relieving agent) in the late nineteenth century by chemists at Bayer, a German pharmaceutical company. Acetylsalicylic acid is a **prodrug** and is transformed in the body to salicylate, the active form of the drug. Salicylates are also anti-inflammatory (i.e., prevent swelling and phenomena related to swelling associated with trauma or allergic response). Salicylates were initially isolated from white willow (*Salix alba*) bark, from which the name of the drug is derived. Indeed, ancient Greek physicians, notably **Hippocrates** and Dioscorides, suggested chewing on willow bark to relieve pain.

analgesic: compound that relieves pain, e.g., aspirin

prodrug: compound that is converted to its active form after being administered or ingested

Hippocrates: Greek physician of fifth century B.C.E. known as "Father of Medicine"

Although aspirin is chiefly extolled for its analgesic properties, it has other equally important therapeutic benefits. Aspirin is an antipyretic (fever-reducing) agent and is used to reduce elevated body temperature. Since the 1980s aspirin has been prescribed for the prevention of heart attack and stroke. Recent studies suggest that aspirin may guard against colon cancer.

Acetylsalicylic acid is a weak acid ($pK_a = 3.5$) that can be absorbed across the mucosal lining of the stomach. However, most of the drug is absorbed from the upper regions of the small intestine. Once the drug has entered the bloodstream it is hydrolyzed to acetic acid and salicylic acid (see Figure 2).

The most widely recognized mode of action of the salicylates is the inhibition of the formation of prostaglandins. Prostaglandins are 20-carbon molecules having side chains of varying degrees of saturation and **oxidation**, synthesized from polyunsaturated fatty acids in the body in response to tissue damage. The localized release of prostaglandins in response to injury or invasion by foreign agents (antigens) results in an increased blood flow to the affected area, and stimulation of the sensory nerve endings that **mediate** pain. Salicylates inhibit prostaglandin **synthesis** by binding to prostaglandin cyclooxygenases (the enzymes responsible for transforming fatty acids into prostaglandins), thereby inactivating the enzymes.

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

mediate: to act as an intermediary agent

synthesis: combination of starting materials to form a desired product

Aspirin is one of the most widely used drugs in modern society. It is most frequently used to treat mild to moderate pain or to reduce fever. Because of its anti-inflammatory action, aspirin is prescribed to individuals who suffer from joint inflammation conditions such as rheumatoid arthritis and osteoarthritis. In addition to its antipyretic, anti-inflammatory, and analgesic properties, aspirin is also prescribed to patients at high risk for heart attack

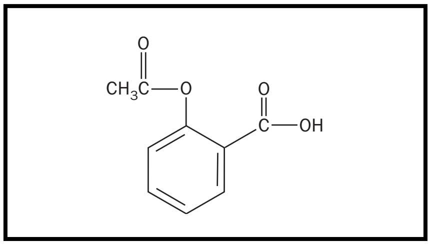

Figure 1. Structure of acetylsalicylic acid.

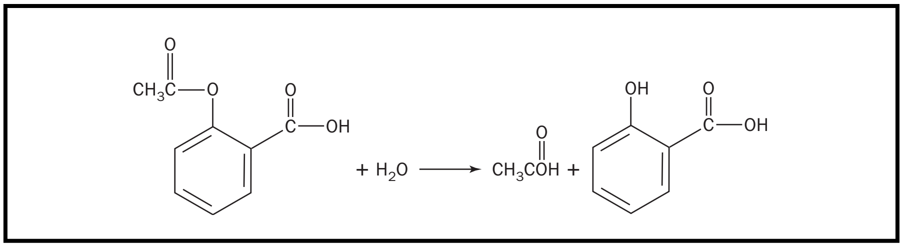

Figure 2. Hydrolysis of acetylsalicylic acid to acetic acid and salicylic acid.

retardation: to slow down a chemical reaction

platelet: smallest noncellular component of human blood

or stroke. Salicylates **retard** the clotting of blood by inhibiting **platelet** aggregation. When platelets aggregate, clotting is promoted and blood flow through vessels and valves is impeded. A stroke results when blood flow to regions of the brain is blocked. Aspirin inhibits enzymes in platelet membranes responsible for the formation of platelet aggregation factors, and thus reduces the risk of blood clots. Enzyme inhibition may also be responsible for aspirin's purported anticancer action. Recent findings suggest that regular doses of aspirin reduce the risks of some cancers (particularly colon cancer). Although scientists do not know how aspirin reduces the risk of cancer, they suspect it could be related to its anti-inflammatory effects and its ability to inhibit enzymes produced by some cancer cells.

Not all of aspirin's health effects are beneficial. Salicylate therapy is associated with many adverse side effects, generally pertaining to the gastrointestinal system. Gastric ulcers and gastric bleeding can occur in individuals on high doses of aspirin. More worrisome is the occurrence of Reye's syndrome in children with viral illnesses such as influenza or chicken pox who have been given aspirin. Reye's syndrome is a serious condition characterized by sudden vomiting, violent headaches, and, in 20 to 30 percent of cases, death. Because of the potential risk of Reye's syndrome in young people administered aspirin, many physicians and the Food and Drug Administration (FDA) warn against the use of salicylates in children under sixteen years of age. SEE ALSO ACETAMINOPHEN; ACID-BASE CHEMISTRY; HYDROLYSIS; IBUPROFEN.

Nanette M. Wachter

FRIEDRICH BAYER (1825–1880)

In 1863 Friedrich Bayer co-founded a dye manufacturing company in Germany. Eight years after his death, in 1888 the company opened a pharmaceutical division. A decade later, employee Felix Hoffman, concerned over his father's aches and pains, discovered a useful chemical in the waste of the dye process. Known as aspirin, it remains a popular painkiller over 100 years later.

—Valerie Borek

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Acid-Base Chemistry

vitamins: organic molecules needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

Acids and bases have been known by their properties since the early days of experimental chemistry. The word "acid" comes from the Latin *acidus*, meaning "sour" or "tart," since water solutions of acids have a sour or tart taste. Lemons, grapefruit, and limes taste sour because they contain citric acid and ascorbic acid (**vitamin** C). Another common acid is vinegar, which is the sour liquid produced when apple cider, grape juice, or other plant juices ferment beyond the formation of alcohol. Vinegar is a 5 percent water solution of acetic acid. Besides having a sour taste, acids react with active **metals** to give hydrogen, they change the colors of indicators (for example, litmus turns from blue to red), and they neutralize bases. Bases change the colors of indicators (litmus turns from red to blue) and they neutralize acids. Hence, bases are considered the chemical opposite of acids.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Most common acid-base reactions take place in water solutions (commonly referred to as **aqueous solutions**). One of the earliest definitions of acids, advanced by the Swedish physicist and chemist Svante Arrhenius in 1887, stated that acid ionizes in aqueous solution to produce hydrogen ions (which are protons), H^+, and **anions**; and a base ionizes in aqueous solution to produce hydroxide ions (OH^-) and cations. Later studies of aqueous solutions provided evidence of a small, positively charged hydrogen ion combining with a water molecule to form a hydrated proton, $H^+(H_2O)$ or H_3O^+, which is called the hydronium ion. Often, the hydronium ion or hydrated proton is represented as H^+ (*aq*). Hydrogen chloride (HCl), a gas, is an acid because it dissolves in water to yield hydrogen ions and chloride ions. This water solution of HCl is referred to as hydrochloric acid.

aqueous solution: solution in which water is the solvent (primary component)

anion: negatively charged chemical unit, like Cl^-, CO_{32}^-, or NO_3^-

$$\mathrm{HCl}\ (g) \xrightarrow{\mathrm{H_2O}} \mathrm{H^+}\ (aq) + \mathrm{Cl^-}\ (aq) \tag{1}$$

A typical base, according to the Arrhenius definition, is sodium hydroxide (NaOH). It dissolves in water to give sodium ions and hydroxide ions.

$$\mathrm{NaOH}\ (s) \xrightarrow{\mathrm{H_2O}} \mathrm{Na^+}\ (aq) + \mathrm{OH^-}\ (aq) \tag{2}$$

Neutralization

In the reaction of an acid with a base in aqueous solution, the hydrogen ions of the acid react with the hydroxide ions of the base to give water. The second product is a salt, which is composed of the positive metal ion from the base and the negative ion from the acid. For example,

$$\mathrm{HCl}\ (aq) + \mathrm{KOH}\ (aq) \rightarrow \mathrm{H_2O}\ (l) + \mathrm{KCl}\ (aq) \tag{3}$$

Since HCl (*aq*) and KOH (*aq*) are fully ionized in solution, the preceding equation can be written as

$$\begin{aligned}&\mathrm{H^+}\ (aq) + \mathrm{Cl^-}\ (aq) + \mathrm{K^+}\ (aq) + \mathrm{OH^-}\ (aq) \rightarrow \\ &\qquad\qquad \mathrm{H_2O}\ (l) + \mathrm{K^+}\ (aq) + \mathrm{Cl^-}\ (aq)\end{aligned} \tag{4}$$

Ions common to both sides can be canceled to yield

$$\mathrm{H^+}\ (aq) + \mathrm{OH^-}\ (aq) \rightarrow \mathrm{H_2O}\ (l) \tag{5}$$

This is referred to as the net ionic equation for the neutralization reaction. If H_3O^+ is substituted for H^+ (*aq*), the neutralization equation becomes

$$\mathrm{H_3O^+}\ (aq) + \mathrm{OH^-}\ (aq) \rightarrow 2\ \mathrm{H_2O}\ (l) \tag{6}$$

Strengths of Acids and Bases

The strength of an acid or base is determined by the extent of its **ionization** in aqueous solution. Strong acids, such as hydrochloric acid, are 100 percent ionized in aqueous solution, whereas weak acids, such as acetic acid, are less than 5 percent ionized. Experimentally, the extent of ionization is determined by measuring the electrical conductance of solutions. Strong acids and bases are strong electrolytes, and weak acids and bases are weak

ionization: dissociation of a molecule into ions carrying + or − charges

Table 1. Common acids and bases.

COMMON ACIDS AND BASES

Strong Acids		Strong Bases	
HCl	hydrochloric acid	NaOH	sodium hydroxide
HNO_3	nitric acid	KOH	potassium hydroxide
H_2SO_4	sulfuric acid	$Ba(OH)_2$	barium hydroxide
Weak Acids		**Weak Bases**	
CH_3COOH	acetic acid	NH_3	ammonia
H_2CO_3	carbonic acid	CH_2NH_2	methyl amine
H_3PO_4	phosphoric acid		

electrolytes. Table 1 lists some common acids and bases and indicates whether they are strong or weak.

For weak acids and bases, partial ionization is a dynamic **equilibrium** between unionized molecules and its ion, as indicated by the double arrow in equation (7). For example, acetic acid is only partially ionized in aqueous solution

equilibrium: condition in which two opposite reactions are occurring at the same speed, so that concentrations of products and reactants do not change

$$CH_3COOH\ (aq) \rightleftarrows H^+\ (aq) + CH_3COO^-\ (aq) \qquad (7)$$

In acetic acid, hydrogen ions and acetate ions recombine to form acetic acid molecules. The double arrow signifies that at any given instant, less than 5 percent of acetic acid molecules dissociate into hydrogen ions and acetate ions, while the hydrogen ions and acetate ions recombine to form acetic acid molecules.

Ammonia (NH_3) is a weak base, and although it does not have OH^- ions in its formula, it produces the ion on reaction with water.

$$NH_3\ (aq) + H_2O\ (l) \rightleftarrows NH_4^+\ (aq) + OH^-\ (aq) \qquad (8)$$

THOMAS M. LOWRY (1874–1936)

A meticulous experimenter, Thomas Lowry is best known for his conceptualization of acid–base chemistry. Studies of nitrogenous compounds led Lowry to question fundamental aspects of the role of hydrogen during acid–base reactions. Three months before Brønsted published his theory, Lowry released his own similar thoughts on proton acceptors and donors in print.

—Valerie Borek

Brønsted-Lowry Theory

A major problem with Arrhenius's acid-base theory is that some substances, like ammonia, produce basic solutions and react with acids, but do not contain hydroxide ions. In 1923 Johannes Brønsted, a Danish chemist, and Thomas Lowry, an English chemist, independently proposed a new way to define acids and bases. An acid donates hydrogen ions (also called a proton donor); a base accepts hydrogen ions (also called a proton acceptor). These definitions not only explain all the acids and bases covered by Arrhenius's theory, they also explain the basicity of ammonia and ions such as carbonate, CO_3^{2-}, and phosphate, PO_4^{3}.

The Brønsted-Lowry theory includes water as a reactant and considers its acidity or basicity in the reaction. In the partial ionization of acetic acid, water is a base because it accepts the hydrogen ion to form hydronium ion.

$$\underset{\text{acid}}{CH_3COOH\ (aq)} + \underset{\text{base}}{H_2O\ (l)} \rightleftarrows \underset{\text{conjugate acid}}{H_3O^+\ (aq)} + \underset{\text{conjugate base}}{CH_3COO^-\ (aq)} \qquad (9)$$

In the reaction, a new acid and a new base are formed, which are called the conjugate acid and conjugate base, respectively. The hydronium ion, H_3O^+, is the conjugate acid of the base, H_2O, and the acetate ion, CH_3COO^-, is

CONJUGATE ACID-BASE PAIRS

	Acid	Conjugate Base	
Strong acids	H_2SO_4	HSO_4^-	Weak bases
	HCl	Cl^-	
	H_3O^+	H_2O	
	HSO_4^-	$SO_4{}^-$	
	H_3PO_4	$H_2PO_4^-$	
	CH_3COOH	CH_3COO^-	
	H_2CO_3	HCO_3^-	
	$H_2PO_4^-$	HPO_4^{2-}	
	NH_4^+	NH_3	
	HCO_3^-	CO_3^{2-}	
	HPO_4^{2-}	PO_4^{3-}	
Weak acids	H_2O	OH^-	Strong bases

Table 2. Conjugate acid-base pairs.

the conjugate base of acetic acid, CH_3COOH. A pair of molecules or ions related to one another by the gain or loss of a single hydrogen ion is called a conjugate acid-base pair. In the reaction of ammonia, water is an acid because it donates a hydrogen ion to ammonia.

$$\underset{\text{base}}{NH_3\ (aq)} + \underset{\text{acid}}{H_2O\ (l)} \rightleftarrows \underset{\text{conjugate acid}}{NH_4^+\ (aq)} + \underset{\text{conjugate base}}{OH^-\ (aq)} \tag{10}$$

This ability of water to donate or accept hydrogen ions, depending on whether it reacts with a base or an acid, is referred to as "amphiprotic." The conjugate acid-base pairs in this reaction are NH_3/NH_4^+ and H_2O/OH^-.

The Brønsted-Lowry definitions also explain why carbonate salts such as sodium carbonate (washing soda) dissolve in water to give basic solutions. Carbonate ion removes a hydrogen ion from a water molecule, which leaves behind a hydroxide ion:

$$\underset{\text{base}}{CO_3^{2-}\ (aq)} + \underset{\text{acid}}{H_2O\ (l)} \rightleftarrows \underset{\text{conjugate acid}}{HCO_3^-\ (aq)} + \underset{\text{conjugate base}}{OH^-\ (aq)} \tag{11}$$

In the preceding reaction, water and hydroxide ion are a conjugate acid-base pair, whereas carbonate ion and bicarbonate ion are a conjugate base-acid pair. Every Brønsted-Lowry acid has a conjugate base, and every Brønsted-Lowry base has a conjugate acid. Familiarity with conjugate acid-base pairs is important to understanding the relative strengths of acids and bases. Table 2 lists some conjugate acid-base pairs and their relative strengths. Strong acids have weak conjugate bases, and weak acids have strong conjugate bases.

Polyprotic Acids

Several common acids have more than one ionizable hydrogen ion (Table 1). Each successive hydrogen ion in these polyprotic acids ionizes less readily. For example, sulfuric acid is a strong acid because of the complete ionization of the first hydrogen ion.

$$H_2SO_4\ (aq) + H_2O\ (l) \rightarrow H_3O^+\ (aq) + HSO_4^-\ (aq) \tag{12}$$

The HSO_4^- also acts as an acid, but it is not 100 percent ionized, so HSO_4^- is an acid of moderate strength. For example, sodium hydrogen sulfate is used to increase the acidity of swimming pools, whereas sodium carbonate is used to increase the basicity of swimming pools.

$$HSO_4^- (aq) + H_2O (l) \rightleftarrows H_3O^+ (aq) + SO_4^{2-} (aq) \qquad (13)$$

Phosphoric acid has three ionizable hydrogen ions. Each stepwise ionization of phosphoric acid occurs to a lesser extent than the one before it. Phosphoric acid is stronger than acetic acid because the first step ionizes to a greater extent than acetic acid.

$$H_3PO_4 (aq) + H_2O (l) \rightleftarrows H_3O^+ (aq) + H_2PO_4^- (aq) \qquad (14)$$

However, $H_2PO_4^-$ is a weaker acid than acetic acid because the second ionization is much smaller (by a factor of 10^5) than the first step.

$$H_2PO_4^- (aq) + H_2O (l) \rightleftarrows H_3O^+ (aq) + HPO_4^{2-} (aq) \qquad (15)$$

The third ionization is also much smaller than the second step (by a factor of 10^5).

$$HPO_4^{2-} (aq) + H_2O (l) \rightleftarrows H_3O^+ (aq) + PO_4^{3-} (aq) \qquad (16)$$

The anions of phosphoric acid can also accept hydrogen ions and act as bases with a strong acid like hydrochloric acid. For example,

$$PO_4^{3-} (aq) + H_3O^+ (aq) \rightleftarrows HPO_4^{2-} (aq) + H_2O (l) \qquad (17)$$

Ions such as $H_2PO_4^-$, HPO_4^{2-}, HCO_3^-, and HSO_4^- can act as an acid by donating a hydrogen ion or as a base by accepting a hydrogen ion. This ability to act as either an acid or a base is referred to as an amphoteric property.

The pH Scale

The Brønsted-Lowry acid-base definitions are based on the amphiprotic properties of water: Water is capable of acting as both a hydrogen ion donor and a hydrogen ion acceptor, depending on the acidic or basic properties of the dissolved substance (equations 9 and 10). Water can also act as a proton donor and proton acceptor towards itself. This is referred to as the autoionization of water.

$$H_2O (l) + H_2O (l) \rightleftarrows H_3O^+ (aq) + OH^- (aq) \qquad (18)$$

Pure water is neutral because it contains equal numbers of hydronium ions and hydroxide ions. However, pure water only slightly ionizes, about 1 in every 55,000,000 water molecules is ionized at any given time. The actual molar concentration of hydronium ions and hydroxide ions in pure water at 25°C is 1.0×10^{-7}. The product of the molarity of the hydronium ions and hydroxide ions of pure water is $(1.0 \times 10^{-7})\,(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$.

The value of 1.0×10^{-14} is important to the study of aqueous solutions of acids and bases because it is a constant that is always the product of the molar concentration of H_3O^+ and OH^-.

$$[H_3O^+]\,[OH^-] = 1.0 \times 10^{-14} \qquad (19)$$

If acid is added to pure water, the concentration of H_3O^+ will be greater than 1.0×10^{-7}, and then the concentration of OH^- will be less than 1.0×10^{-7}. However, the product of the two must equal 1.0×10^{-14}. This relationship is the basis for calculating the concentration of one of the two ions, hydronium or hydroxide, when the other one is known. For example, a 0.1 *M* solution of hydrochloric acid is 0.1 *M* in H_3O^+ since hydrochlo-

pH OF COMMON SUBSTANCES

pH	$[H_3O^+]$, M	Example
0	1.0	Battery acid, 1 M sulfuric acid
1	0.1	Stomach acid, 0.1 M hydrochloric acid
2	1×10^{-2}	Lemon juice
3	1×10^{-3}	Vinegar
4	1×10^{-4}	Soft drink
5	1×10^{-5}	Rain water
6	1×10^{-6}	Milk
7	1×10^{-7}	Pure water
8	1×10^{-8}	Baking soda, $NaHCO_3$
9	1×10^{-9}	Washing soda, Na_2CO_3
10	1×10^{-10}	Milk of magnesia, $Mg(OH)_2$
11	1×10^{-11}	Aqueous household ammonia, NH_3
12	1×10^{-12}	Limewater, $Ca(OH)_2$
13	1×10^{-13}	Drano, 0.1 M NaOH
14	1×10^{-14}	Drano, 1.0 M NaOH

Table 3. pH of common substances.

ric acid is fully ionized. From the equation, the molar concentration of OH^- is 10^{-13}. For a 0.1 *M* solution of NaOH, the OH^- is 0.1 *M*, but the hydrogen ion concentration is 10^{-13}. Hence, the value of the exponent for hydronium ion concentration goes from -1 in strong 0.1 *M* acid to -13 in strong 0.1 *M* base.

In 1909 the Danish biochemist S. P. L. Sørensen proposed that these exponents be used as a measure of acidity. He devised a scale that would be useful in testing the acidity of Danish beer. Sorensen's scale came to be known as the pH scale, from the French *pouvoir hydrogene*, which means hydrogen power. pH is defined as the negative logarithm (log) of the hydronium ion concentration.

$$\text{pH} = -\log[H_3O^+] \qquad (20)$$

The brackets around hydronium ion mean moles per liter of hydronium ions.

The pH scale includes values between 0 and 14. The pH of pure water is 7 because $[H_3O^+]$ is 1.0×10^{-7}. The pH of 0.1 *M* HCl is $1[-\log 10^{-1} = -(-1)]$. The pH of 0.1 *M* NaOH is $13(-\log 10^{-13}) = 13$. The pH scale does not apply to concentrations greater than 1.0 *M* for a strong acid (pH = 0) or 1.0 *M* for a strong base (pH = 14).

For solutions in which $[H_3O^+]$ is not an exact power of 10 (0.1, 0.01, . . .), a calculator can be used to determine the logarithm. For example, if the $[H_3O^+]$ is 1.5×10^{-3} *M*, the logarithm is $-3 + \log 1.5 = -3 + 0.18 = -2.82$, and the pH is $-(-2.82)$ or 2.82. Table 3 provides the pH values of some common solutions.

Acid-Base Indicators

Many natural substances are acid-base indicators. The most familiar one is litmus, an organic dye extracted from certain lichens. Litmus turns from blue to red in acidic solutions (< pH 7) and from red to blue in basic solutions (∼ pH 7). Some other natural indicators include red cabbage extract, blueberry juice, black tea, beet juice, rhubarb, and tomato leaves, and flowers such as the rose, daylily, blue iris, and purple dahlia. Red cabbage extract undergoes sharp changes of color at several pH values. The deep purple color of red cabbage leaves is caused by a mixture of water-soluble

Table 4. Common acid-base indicators.

COMMON INDICATORS

Indicator	pH Range	Color Change
Thymol blue	1.2 – 2.8	red → yellow
Methyl red	4.4 – 6.2	red → yellow
Litmus	5 – 8	red → blue
Bromothymol blue	6.2 – 7.6	yellow → blue
Phenolphthalein	8.0 – 10.0	colorless → pink

anthocyanins. Over the pH range of 2 to 12, these anthocyanins change from red (pH 2) to pink (pH 4) to purple (pH 6–7) to green (pH 10) to yellow (pH 12), which makes red cabbage extract a "universal indicator."

Acid-base indicators are weak acids and bases. A typical indicator will ionize in aqueous solution according to the equation

$$\mathrm{HIn}\ (aq) + \mathrm{H_2O}\ (l) \rightleftarrows \mathrm{H_3O^+}\ (aq) + \mathrm{In^-}\ (aq) \qquad (21)$$

The chemical species HIn and In^- are different colors. When the solution is acidic to the degree that the HIn species dominates, it will be the color of HIn. When the solution is more basic with In^- dominating, it will be the color of In^-. Some common indicators and the pH ranges for their color changes are listed in Table 4.

Buffer Solutions

Buffer solutions contain a base and an acid that can react with an added acid or base, respectively, and they maintain a pH very close to the original value. Buffers usually consist of approximately equal quantities of a weak acid and its conjugate base, or a weak base and its conjugate acid. For example, a buffer solution of acetic acid and its conjugate base, the acetate ion, can neutralize small amounts of a strong acid or strong base as follows:

$$\mathrm{CH_3COOH}\ (aq) + \mathrm{OH^-}\ (aq) \rightarrow \mathrm{CH_3COO^-}\ (aq) + \mathrm{H_2O}\ (l) \qquad (22)$$

$$\mathrm{CH_3COO^-}\ (aq) + \mathrm{H_3O^+}\ (aq) \rightarrow \mathrm{CH_3COOH}\ (aq) + \mathrm{H_2O}\ (l) \qquad (23)$$

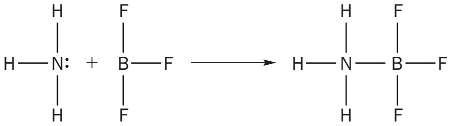
As illustrated in equations (22) and (23), the addition of either a strong base or a strong acid produces one of the components of the buffer mixture and so the pH does not change. Buffers are limited in their buffer capacity, that is, the amount of a strong acid or strong base that can be added before the pH changes by 1 pH unit.

Buffers are very important to many industrial and natural processes. For example, controlling the pH of blood is essential to human health. The pH of blood is normally 7.40 ± 0.05, and good health depends on the ability of buffers to maintain the pH of blood within this narrow range. If the pH falls below 7.35, a condition known as acidosis occurs; increasing pH above 7.45 leads to alkalosis. Both these conditions can be life threatening. Two buffer systems, H_2CO_3/HCO_3^- and $H_2PO_4^-/HPO_4^{2-}$, control the pH of the blood.

Lewis Acid-Base Theory

In the early 1930s Gilbert Lewis, an American chemist, proposed a more general acid-base theory that is based on sharing electron pairs rather than proton transfers. A Lewis acid is a substance that can accept a pair of electrons to form a new bond, and a Lewis base is a substance that can donate a pair of electrons to form a new bond. All Arrhenius and Brønsted-Lowry acids and bases are Lewis acids and bases. However, Lewis acid-base theory is more general because a Lewis base can donate an electron pair to something other than H^+. For example, the gas **phase** reaction of NH_3 with BF_3 is a Lewis acid-base reaction.

phase: homogeneous state of matter.



(24)

Solvent System Acid-Base Theory

Another acid-base theory that is useful for solvents other than water was postulated by American chemist Edward Franklin in 1905. It makes use of the autoionization of solvents, and defines an acid as a solute that produces the positively charged species of the solvent and a base as a solute that produces the negatively charged species of the solvent. In the case of the autoionization of water (equation 18) H_3O^+ is the acid and OH^- is the base. For the nonaqueous solvent, liquid ammonia, the autoionization gives

$$NH_3\ (l) + NH_3\ (l) \rightleftarrows NH_4^+ + NH_2^- \qquad (25)$$

so an acid in liquid ammonia is any solute that produces NH_4^+ and a base in liquid ammonia is any solute that produces NH_2^-. An example of an acid-base reaction in liquid ammonia is

$$\underset{\text{acid}}{NH_4Cl} + \underset{\text{base}}{NaNH_2} \rightarrow \underset{\text{salt}}{NaCl} + \underset{\text{ammonia}}{2\ NH_3} \qquad (26)$$

Note that liquid ammonia still falls within the Brønsted-Lowry definitions since NH_4^+ is a proton donor and NH_2^- is a proton acceptor.

Summary

The Brønsted-Lowry theory, which defines acids as proton donors and bases as proton acceptors, covers all acid-base reactions in aqueous solution. The strength of acids and bases is related to the percent of their ionization in water. Strong acids and bases are 100 percent ionized, whereas weak acids and bases are less than 5 percent ionized. There are a number of salts that have acidic or basic properties in solution. For example, baking soda, $NaHCO_3$, can be used as an antacid because the bicarbonate ion, HCO_3^-, is a strong enough conjugate base to combine with H_3O^+ to give carbonic acid.

$$HCO_3^-\ (aq) + H_3O^+\ (aq) \rightarrow H_2CO_3\ (aq) + H_2O\ (l) \qquad (27)$$

The pH scale is a convenient way to represent the acidity or basicity of dilute acid and base solutions. Pure water has a pH of 7; acidic solutions have pH values < 7 and basic solutions have pH values > 7. Each change of one unit of pH is a tenfold change in acidity. Acid-base indicators, such as litmus and phenolphthalein, can be used to measure whether a solution is acidic or basic. A natural "universal indicator," red cabbage extract, can be used to determine the pH within 2 pH units. A buffer contains equal amounts of either a weak acid and its conjugate base or a weak base and its conjugate acid.

SEE ALSO ARRHENIUS, SVANTE; BASES; BRØNSTED, JOHANNES NICOLAUS; CHEMICAL REACTIONS; LEWIS, GILBERT N.; SOLUTION CHEMISTRY.

Melvin D. Joesten

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Acid-Rain ***See Atmospheric Chemistry.***

Acne Medication

Acne is a skin condition in which pimples (comedones) appear on the skin, usually on the face, chest, or back. Adolescents and young adults are most often afflicted. Acne tends to be more severe in males; however, with females, acne may persist into adulthood.

Causes and Types of Acne

The skin has hair follicles that each contains a hair shaft and an oil gland. The oil glands continuously produce and secrete oil to lubricate and protect the skin. However, when dead skin cells and oil (sebum) build up inside the follicle and close off the follicle's pore, pimples appear, in the form of either blackheads or whiteheads. If the plugging material protrudes from the opening at the surface of the skin, this plug of oil and dead cells darkens, forming blackheads; if the plugging material does not protrude, whiteheads form. This type of acne is referred to as comedonal. When the accumulated material of a closed-off pimple causes the follicular wall to rupture, an internal inflammatory reaction occurs, causing oil, dead cells, and bacteria to spill onto the skin. The skin around the pore becomes red and inflamed, and the result is inflammatory acne. When white blood cells infiltrate the area to repair the inflammation, papules, nodules, and cysts may develop. Papules form near the surface of the skin, whereas nodules and cysts are caused by inflammation deeper in the skin.

In the past many persons attributed abnormally high oil secretion and the development of acne to the afflicted individual's diet and hygiene. However, current research suggests that oil secretion is under genetic control, primarily related to the ability of androgenic hormones to stimulate oil secretion. The bacterial species *Propionibacterium acnes* is believed to play a role in converting acne into an inflammatory condition. Stress and the use of certain cosmetics may also be contributing factors.

Treatment of Acne

There are many ways to treat acne. Gentle washing of the face is important because it helps to remove accumulated oil, bacteria, and dead cells on the skin's surface. Other treatments help to unclog pores, kill bacteria, or minimize oil. Products that help to open up pores include mild cleansers, scrubs, exfoliants, and masques. All of these are available without a prescription. Exfoliants remove the outer layer of skin, thus opening pores. These agents, as well as astringents and toners, help to wipe away excess oil. Antibacterial agents are used to kill bacteria. The most common mild antibacterial agent is benzoyl peroxide. It is available in the form of creams or lotions that are applied to affected areas, and may even be found in some cleansers. Other antibacterial agents available by prescription include topical antibiotics such as **erythromycin**, clindamycin, and sulfacetamide, and oral antibiotics such as tetracycline, doxycycline, minocycline, and sulfa drugs.

Benzoyl peroxide. Benzoyl peroxide encourages peeling of the outermost layer of the skin and, as mentioned previously, is a mild bactericidal agent. It kills bacteria by virtue of its oxidizing properties. It is often included in prescription acne medications, and in nonprescription acne products such as gels, lotions, and cleansers. It may be used alone or with other treatments. At even low concentrations (2.5–10%), benzoyl peroxide diminishes the population of *Propionibacterium acnes.* The most common adverse effects are dry skin and bleaching of the skin.

Retinoids. The term "retinoid" refers to retinol or other closely related derivatives, either natural or synthetic. Retinoids may or may not have retinol-like (**vitamin** A–like) activity. Retinoids affect epithelial cells by binding to **receptors** inside these cells, inducing alterations in the **transcription** of genes. Retinoids enhance the **synthesis** of some proteins, such as proteins that serve as receptors for certain hormones and growth factors, and reduce the synthesis of others. Some of the most commonly prescribed treatments for acne—tretinoin, isotretinoin, and adapalene—are retinoids. (See Table 1.)

Tretinoin became available as a topical treatment for acne in the United States in 1971. Tretinoin is also known by its chemical name, all-*trans*-retinoic acid. It increases the turnover of skin cells at the surface of the hair follicle. This leads to the extrusion of comedones. Side effects include local skin irritation and increased sun sensitivity. Newer preparations of tretinoin, designed to achieve slow absorption of the drug into epithelial cells, cause less skin irritation than forms available initially. Improvement in acne may not be noticeable until two to three weeks after treatment begins.

In 1982 the Food and Drug Administration (FDA) approved the oral use of isotretinoin (Accutane) for the treatment of severe nodulocystic acne that has not responded to antibiotics. This drug is not active topically. As the name suggests, isotretinoin is an **isomer** of tretinoin. The only structural difference between the two molecules lies in the spatial arrangement of the atoms around one carbon-carbon double bond. Isotretinoin has the chemical name 13-*cis*-retinoic acid. Through mechanisms not well understood, it decreases the size of the sebaceous glands and inhibits closure of the pore. These actions may diminish the ultimate formation of cysts. As is

A female with untreated acne on her face. Several prescription and nonprescription drugs are used to effectively treat acne.

erythromycin: antibiotic used to treat infections

vitamins: organic molecules needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

transcription: enzyme-catalyzed assembly of an RNA molecule complementary to a strand of DNA

synthesis: combination of starting materials to form a desired product

isomer: molecules with identical compositions but different structural formulas

Table 1. Generic and brand names of some commonly prescribed acne medications.

GENERIC AND BRAND NAMES OF SOME COMMONLY PRESCRIBED ACNE MEDICATIONS

Brand Name	Generic Name
Desquam-E, Benzac W, Benzagel, Clinac BPO, Triaz	benzoyl peroxide
Retin-A, Renova, Avita	tretinoin
Accutane	isotretinoin
Differin	adapalene

SOURCE: Data obtained from *http://www.healthsquare.com/drugmain.htm*

the case with other retinoids, arachidonic acid release from macrophages is inhibited. This may account for the anti-inflammatory effects of retinoids. Isotretinoin's anti-acne effects can last for months to years following a twenty week course. And, unlike antibiotic treatments, treatment with isotretinoin does not promote antibiotic-resistant bacteria.

Reservations toward the use of isotretinoin (Accutane) are related to its severe side effects. Any of the retinoids, including vitamin A, can have severe side effects. Some of the symptoms of hypervitaminosis A are the same as the major toxic effects associated with the therapeutic use of retinoids. When retinoids are applied to the skin, few systemic side effects occur. For isotretinoin, which is administered orally, side effects are much more common. Among those reported are skin blistering, skin fragility, hair loss, headache, nausea, vomiting, visual disturbances, and increased levels of triglycerides and decreased levels of high density lipoproteins in blood plasma. Furthermore, because isotretinoin can cause severe birth defects, including physical abnormalities and mental retardation, a female patient taking it must not become pregnant. Female patients must obtain a negative serum pregnancy test before treatment can begin, and written consent forms must be signed. These patients should also not become pregnant for some time after the drug has been discontinued. In 1998, as a result of medical reports associating Accutane use with depression and suicide, the FDA issued new safety information regarding isotretinoin.

Newer retinoids. Medical chemists are often able to modify the structure of a drug that has unwanted side effects or problems making it difficult to administer. Even slight structural changes may result in an improved pharmacological agent that requires lower dosing, or has fewer side effects, or both. The development of adapalene is an example. A better retinoid might have enhanced stability, enhanced anti-inflammatory effects, or result in decreased skin irritation. The naphthoic-acid derivative adapalene, developed in the 1990s, works better and with less local skin irritation than earlier retinoids. The reduced side effects are attributed to the selectivity of adapalene for **nuclear** retinoic acid receptors within follicular epithelial cells. Although many persons will have acne during their teen years, effective treatment is available. SEE ALSO RETINOL.

nuclear: having to do with the nucleus of an atom

Jennifer L. Powers

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Information available from <http://www.accutaneaction.com>.

Information available from <http://www.differin.com>.

Information available from <http://www.fda.gov>.

Information available from <http://healthsquare.com/drugmain.htm>.

Actinides

The actinide elements (atomic numbers 89 through 103) involve the filling of 5f orbitals. All actinides are radioactive, but only uranium and the lighter actinides have half-lives long enough to be present in Earth's environment. The heavier actinides are produced by **nuclear** reactions and some have very short half-lives. The actinides also undergo a radius **contraction** as do the **lanthanides** with an increasing **atomic number**. They are characterized by variable **oxidation** numbers, but the importance of the +3 state and the similarities to lanthanides increase for heavier elements. American chemist Glenn Seaborg is credited with revising the Periodic Table so actinides were placed under lanthanides. SEE ALSO ACTINIUM; AMERICIUM; BERKELIUM; EINSTEINIUM; FERMIUM; LAWRENCIUM; MENDELEVIUM; NEPTUNIUM; NOBELIUM; PLUTONIUM; PROTACTINIUM; RUTHERFORDIUM; SEABORG, GLENN THEODORE.

Herbert B. Silber

nuclear: having to do with the nucleus of an atom

contraction: the shortening of a normal trend of a quantity, in this case the radius

lanthanides: a family of elements (atomic number 57 through 70) from lanthanum to lutetium having from 1 to 14 4f electrons

atomic number: the number of protons in an atomic nucleus, expressed in terms of electric charge; it is usually denoted by the symbol z

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

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Actinium

MELTING POINT: **1,050°C**
BOILING POINT: **3,200°C**
DENSITY: **10.07 g/cm^3**
MOST COMMON IONS: **Ac^{3+}**

89
Ac
ACTINIUM
227

Actinium has thirty-six **isotopes**, all of which are radioactive and which range in mass number from 209 to 234. The longest-lived isotope has a mass number of 227 and a half-life of 21.8 years. Actinium was discovered in **pitchblende** in 1899 by French chemist André-Louis Debierne, a member of the Curie laboratory. He named it *actinium*, using the Greek word *aktis*, meaning ray. It was discovered independently by Friedrich Giesel in 1902. Actinium in its ground state has an (outer orbital) electronic configuration of $5f^{0}6d7s^{2}$. Actinium exists in an **oxidation** state of 3+ in solution and in its compounds. The isotope ^{227}Ac is found in uranium ores in concentrations of approximately 0.15 mg per ton of pitchblende, and at lower concentrations, in thorium ores. Pure actinium forms a silvery-white **metal** that has a face-centered structure near its melting point.

In 1945 Glenn Seaborg proposed that actinium was the first member of a family of fifteen elements (the "actinides"), characterized by the possession of the 5*f* orbitals. His proposal was based on the similarity of the chemistry of actinium to that of lanthanum (**atomic number** 57), which is the first member of the fifteen elements of the trivalent **lanthanide** family. Actinium is somewhat more basic than lanthanum but, like lanthanum, forms compounds that have strongly ionic bonds. Many actinium compounds are

isotope: form of an atom that differs by the number of neutrons in the nucleus

pitchblende: mineral that is the principal ore of uranium

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

atomic number: the number of protons in an atomic nucleus, expressed in terms of electric charge; it is usually denoted by the symbol z

lanthanides: a family of elements (atomic number 57 through 70) from lanthanum to lutetium having from 1 to 14 4f electrons

isostructural with the corresponding compounds of lanthanum, due to the similarities in radii and electronic structures among the two set of compounds. Due to the short half-lives of the isotopes of actinium, no significant uses have been developed for these isotopes. SEE ALSO Berkelium; Einsteinium; Fermium; Lawrencium; Mendelevium; Neptunium; Nobelium; Plutonium; Protactinium; Rutherfordium; Seaborg, Glenn Theodore; Thorium; Uranium.

isostructural: relating to an arrangement of atomic constituents that is geometrically the same although different atoms are present

Gregory R. Choppin

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Active Site

Enzymes play a vital role in the majority of biochemical reactions. Not only do they allow for life as we know it, they demonstrate remarkable specificity in many cases. How do enzymes work on only one chemical process, whereas hundreds of perhaps similar processes occur in the same general vicinity? Protein structure in general provides the answers. The primary, secondary, and tertiary structures of a protein all serve to direct the specific activity of an enzyme, but the region where the specific reaction is catalyzed is referred to as the active site.

If one could place a thin skin on the surface of an enzyme, the active site would invariably look like a pocket or cave in the surface. This structural feature is the reason why many textbooks show the mechanism of enzyme specificity as a lock-and-key model. The substrate, the molecule on which the enzyme acts, is the key that fits into the enzyme, which is the lock. Like a lock, only the correct key fits into it.

intermolecular force: force that arises between molecules; generally it is at least one order of magnitude weaker than the chemical bonding force

hydrogen bonding: intermolecular force between the H of an N–H, O–H, or F–H bond and a lone pair on O, N, or F

hydrogen bond: interaction between H atoms and lone pair electrons that constitutes hydrogen bonding

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

covalent bond: bond formed between two atoms that mutually share a pair of electrons

Looking at a more detailed perspective than is provided by this model, one can see that the selectivity of the active site is associated with its geometry. **Intermolecular forces** are present between the substrate and the components of the enzyme that are present in the active site.

For example, in order for **hydrogen bonding** to be able to take place, specific atoms must be present, as shown in Figure 1. In enzymes, normally there is either an O-H bond or an N-H bond when hydrogen bonding occurs. The other component of the **hydrogen bond** is a lone pair of electrons on either a nitrogen or oxygen. The strength of this interaction depends on the specific geometry present. The atoms must be both close enough to each other and in the correct direction from each other. Essentially, a hydrogen-bonding interaction requires that the three atoms involved form a straight (or nearly straight) line.

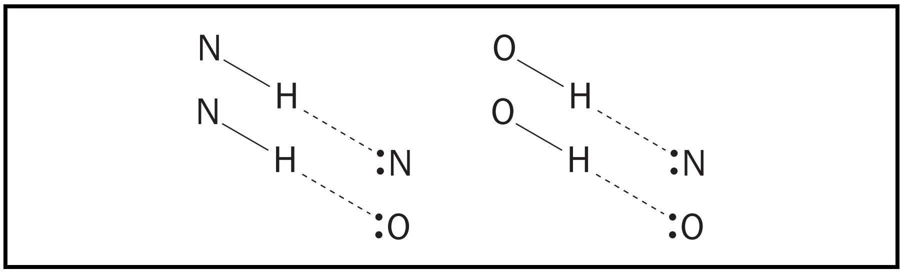

Figure 1. Atoms necessary for hydrogen bonding.

As there are many different types of active sites, it would be impossible to examine all of them here, but we can consider one important class of active sites, those that include **metal** ions. The inclusion of the metal ion in the enzyme may either be from strong coordinate **covalent bonds**, or via a looser association in the active site. When the metal is tightly bound, the protein is called a **metalloenzyme**. When the binding is not covalent, a metal-activated enzyme results. In either case, the metal ion is likely to be an important part of the active site.

One role that metal ions play in the active site of enzymes is to stabilize the charges that may be present. For example, the enzyme carbonic anhydrase, which plays the vital role of assisting the transport of carbon dioxide in the blood, is a metalloenzyme that includes zinc ions, Zn^{2+}. This enzyme catalyzes the reaction of carbon dioxide with water to form hydrogen carbonate ions

$$CO_2 + H_2O \rightarrow HCO_3^- + H^+$$

To speed this reaction, the zinc ion interacts with the water molecule to form a hydroxide, as shown in Figure 2. The small highly positively charged zinc ion is well suited to stabilize the negative charge of the hydroxide ion. Once formed, this ion reacts with carbon dioxide to form the hydrogen carbonate ion, which is released, and the Zn^{2+} is now ready to catalyze another reaction.

Most active sites operate in ways that are somehow similar to those of this example. Portions of the enzyme in the active site bind to the substrate, facilitating its reaction, and then they release the product. SEE ALSO ENZYMES; PROTEINS; RESIDUE; SUBSTRATE.

Thomas A. Holme

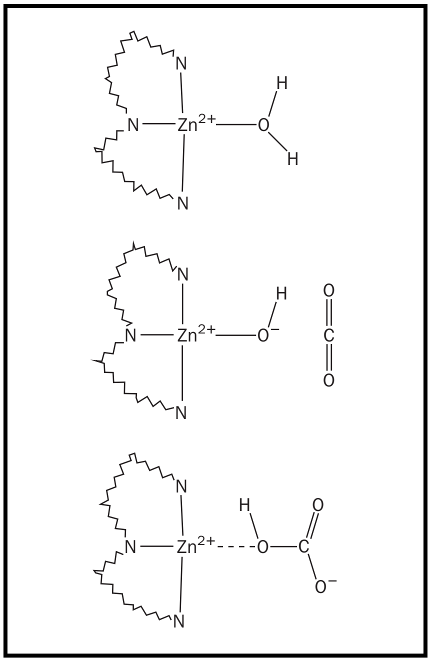

Figure 2. Zinc ions interacting with water to form a hydroxide.

metalloenzyme: a protein enzyme that contains at least one metal atom, often in an active site of the protein

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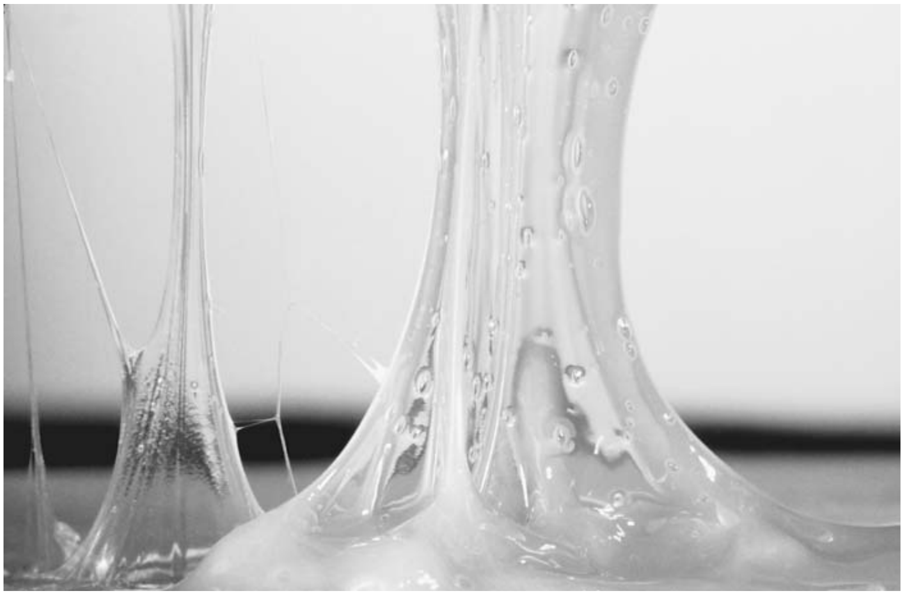
Adenine *See Nucleotide.*

Adhesives

An adhesive is a substance that sticks to the surface of an object such that two surfaces become bonded. A typical home improvement store carries many different adhesives for many different applications. Why are there so many adhesives? The answer is found in examining how an adhesive works and, in particular, what happens at the molecular level. The interaction of molecules is known as intermolecular bonding, or secondary bonding. Primary bonding, also known as intramolecular bonding, is the interaction of atoms within a molecule and includes covalent and polar covalent bonding. Secondary bonding includes dipole–dipole bonding (the interaction of molecules that have a permanent net dipole moment) and **hydrogen bonding** (an interaction that occurs when a hydrogen atom is bonded to an N, O, or F atom in a molecule).

hydrogen bonding: intermolecular force between the H of an N–H, O–H, or F–H bond and a lone pair on O, N, or F

Adhesives cure when the small resin molecules (mers) join together to form extremely large molecules known as polymers. For example, one of



Some adhesives, such as this wood adhesive, are used only with specific substrates because of the cure time needed to allow for good bonding.

the simplest polymers is polyethylene. The mer (basic building block of the polymer) is ethylene, $H_2C{=}CH_2$. The addition of an initiator ($R\cdot$) causes the formation of the radical $RCH_2CH_2\cdot$. A radical is a species that has an unpaired electron and is very reactive because it seeks the source of electrons. This radical will attach the ethylene mer (the double bond in ethylene is rich in electrons) to start a chain reaction that continues until very large polymer molecules form. This and other forms of polymerization processes are the basis for the formulation of polymers. This process is known as curing when dealing with adhesives.

electronegative: capable of attracting electrons

nonpolar: molecule, or portion of a molecule, that does not have a permanent, electric dipole

Two criteria must be met in order for a molecule to possess a permanent net dipole moment: (1) an unequal sharing of electrons within the molecule such that one or more intramolecular bonds has a partial positive end and a partial negative end, and (2) a geometry such that the vector sum of the individual dipole moments does not equal zero. The ability of an atom within a molecule to attract electrons is known as electronegativity, a concept proposed by Linus Pauling who established a table of relative electronegativities. In Pauling's table, fluorine is the most **electronegative** element and is given the value of 4.0. The greater the difference in electronegativity between two atoms within a molecule, the larger is the dipole moment in that bond. Because the bond between two atoms having unequal electronegativities has a partial positive end and a partial negative end, it is said to be a polar bond. If the geometry of the molecule is such that the vector sum of all of the dipole moments does not equal zero, then the molecule is polar. The electronegativities for carbon and oxygen are 2.5 and 3.5, respectively; therefore, the carbon–oxygen bond is a polar bond. A carbon dioxide molecule has two carbon–oxygen bonds; however, its geometry is such that the vector sum of the two dipole moments equals zero, and thus carbon dioxide is a **nonpolar** molecule. The electronegativity of hydrogen is 2.1, thus a hydrogen–oxygen bond would be polar. A water molecule has two hydrogen–oxygen bonds. The geometry of a water molecule (the H–O–H bond angle is 104.5°) is nonsymmetrical, hence the vector sum of the dipole moments is not equal to zero and water is a polar molecule.

Polar molecules will attract other polar molecules because of their net dipole moments. Water molecules, however, have an additional **attraction** for one another, based on hydrogen bonding. This attraction is so strong that, although water is a small molecule and small molecules tend to be gases, water is a liquid at room temperature. This aspect of the chemistry of water demonstrates that hydrogen bonding is a relatively strong force that can hold molecules together.

attraction: force that brings two bodies together, such as two oppositely charged bodies

So how does this relate to the many types of adhesive products that exist? In order for an adhesive to bond (hold together) two surfaces (substrates), there must be several types of interaction between the adhesive and both substrates. The first type of interaction is that the adhesive must wet the substrate, meaning that the adhesive must spread itself out into a film that covers the substrate surface. In order for this to happen, the adhesive must have a low enough viscosity so that it will flow. Viscosity is the resistance of a liquid to flow. Water has a low viscosity whereas honey has a high viscosity. Because viscosity is temperature dependent, the application of a cold adhesive to a substrate, or the application of an adhesive to a cold substrate, may result in poor wetting. Another factor that affects wetting is the relative strengths of cohesive forces (between like molecules, such as two adhesive molecules) and those of adhesive forces (between unlike molecules, such as an adhesive molecule and a substrate molecule). If the cohesive forces among adhesive molecules are weaker than the adhesive forces between the adhesive molecules and the substrate surface, then the adhesive molecules will spread out over the substrate and wet its surface. An adhesive that has a relatively low viscosity and is able to wet the substrate surface will flow into any tiny cracks or pores on the substrate surface, thus promoting what is known as mechanical bonding. Mechanical bonding increases the strength of an adhesive bond and, as a result, a forced separation of the two substrate surfaces is more apt to tear the substrate surfaces.

Mechanical bonding is one of several ways that an adhesive bonds substrates. All surfaces, except those that are highly polished, have pores. If the adhesive flows into these pores and then polymerizes, a mechanical bond is formed. It is similar to placing a wick into liquid candle wax. Once the wax solidifies the wick can not be easily removed. A mechanical bond has formed.

Because the interactions of adhesive molecules with substrates are so critical, it makes sense that some adhesives would be more appropriate for a specific substrate than others. Adhesives are designed for specific applications. For example, adhesives known as "super glues" (cyanoacrylates) are useful around the home in the bonding of common substrates (e.g., dishes, toys, etc.), which can take place in a matter of seconds. Yet their usefulness is limited when bonding wood because the cure time (the time it takes for an adhesive to undergo polymerization and become capable of holding the two substrates together) in this instance is much longer. Cyanocrylates tend to be brittle thus they are vulnerable to impact and dramatic changes in temperature. To reduce these shortcomings, small amounts of finely ground rubber has been used as filler. The rubber introduces flexibility thus reducing brittleness. In addition, cyanocrylates are attacked by polar solvents. Polar solvents will weaken cured cyanocrylate bonds over time. Therefore, applications involving water, alcohols, or other polar solvents should be avoided. Polymerization is the reaction of small molecules combining to form very

Table 1. Common adhesives and their uses.

TYPES OF ADHESIVES

Adhesive Type	Sources/Properties	Common Uses
Animal glue	Obtained from animal byproducts such as bones, blood, and hooves	Binding of abrasives in sandpaper and other grinding materials
Casein	Main protein in milk	Labels on beer bottles that do not come off in ice water, yet are recyclable
Starch	From corn and maize	Corrugated cardboard bonding
Natural rubber	Not "sticky enough" by itself but is used as an additive in other adhesives	Self-adhesive envelopes and other pressure-sensitive adhesives; adhesives that bond to substrates on contact (like tapes)
Butyl rubber/isobutylene	It is elastomeric—it stretches	Additive for hot-melt adhesives, window sealants, and pressure-sensitive adhesives
Amino resins	Water-soluble adhesives	Bonding of layers in plywood and the bonding of particles in particle board
Polyurethane	A flexible adhesive	Bonding soles to the bodies of shoes; also used in food packaging
Polyvinyl acetate	Common "white" glue	Book bindings and labels
Polyolefin/ethylene copolymer	No solvents involved	Hot melts
Acrylates or anaerobic adhesives	Cure when air is removed	Adhesive used to keep nuts tight on bolts, such as those within ATMs and heavy machinery
Silicone	Both an adhesive and a sealant and only common adhesive that is based on silicon rather than carbon	Bathtub and shower sealants; also many car applications, such as oil pans and head gaskets

large molecules. The reason for the longer cure time in the bonding of wood has to do with chemical reactions (between adhesive and substrate) that affect the rate at which the cyanoacrylate molecules polymerize. A typical cyanoacrylate product is a low viscosity liquid that readily flows over a substrate's surface. When the cyanoacrylate molecules encounter a basic environment, the small molecules within the adhesive polymerize. Many common surfaces tend to be basic, so a cyanoacrylate adhesive works fine in these instances; wood, however, tends to have an acidic surface, and because an acidic environment will inhibit polymerization, cure time is increased.

Cyanoacrylates are not appropriate for the bonding of the steel parts of an automobile, because of the environments that the car will be exposed to. Those environments include such things as rain, variations in temperature, exposure to solvents (such as gasoline, oil, and windshield washer solution), ozone, **acid rain**, salt spray, and ultraviolet light from the Sun. (A more appropriate adhesive for car parts would be an epoxy-based adhesive.) Another example of a "special" adhesive would be the one used to attach a new rearview mirror in an automobile. Because the cured adhesive in this case will be exposed to wide variations in temperature and to an extremely large amount of ultraviolet light from the Sun for prolonged periods of time, an adhesive formulated specifically for these conditions should be used.

acid rain: precipitation that has a pH lower than 5.6; term coined by R. A. Smith during the 1870s

Finally, the strength and permanence of the bond formed between adhesive and substrate must be considered when one is selecting an adhesive. Most of the time it is desirable to have maximum strength and permanence; the very common Post-it note, however, is a counterexample. Its adhesive is neither strong nor permanent. The adhesive formulation that eventually led to the Post-it was initially considered a failure because of the adhesive's weakness. It was while singing in his church choir that Arthur Fry of the Minnesota Mining & Manufacturing Company (3M) envisioned a potential use for what seemed to be a useless material.

Table 1 lists some common types of adhesives and their uses. Because of the different possible substrates and combinations of substrates, and because adhesives are subject to such a range of environmental conditions, it is no wonder that there are so many types of adhesives on the market. However, if one has some knowledge of how adhesives bond to substrates and the types of substrates being bonded, the task of selecting adhesives will not be overwhelming. SEE ALSO Bonding; Pauling, Linus.

Daryl J. Doyle

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Adrenalin *See Epinephrine*.

Agricultural Chemistry

Agricultural chemistry must be considered within the context of the soil ecosystem in which living and nonliving components interact in complicated cycles that are critical to all living things. Carbon inputs from photosynthetic organisms ultimately provide the fuel for many soil organisms to grow and reproduce. Soil organisms, in turn, promote organic carbon degradation and catalyze the release of nutrients required for plant growth. The stability and productivity of agricultural ecosystems rely on efficient functioning of these and other processes, whereby carbon and nutrients such as nitrogen and phosphorus are recycled. Human-induced perturbations to the system, such as those that occur with pesticide or fertilizer application, alter ecosystem processes, sometimes with negative environmental consequences.

Inorganic Components of the Agricultural Ecosystem

Soil is the primary medium in which biological activity and chemical reactions occur. It is a three-**phase** system consisting of solid, liquid, and gas. Approximately 50 percent of the volume in a typical agricultural soil is solid material classified chemically as either organic or inorganic compounds. Organic materials usually constitute 1 to 5 percent of the weight of the solid phase. The remainder of the soil volume is pore space that is either filled with gases such as CO_2 and O_2, or water.

phase: homogeneous state of matter

Surface area and charge characteristics of the inorganic portion of the solid phase control chemical reactivity. Soil particles are classified based on their size, with sand-sized particles having diameters of 2 to 0.05 millimeters (0.08 to 0.002 inches) and silt-sized particles from 0.05 to 0.002 millimeters (0.002 to 0.00008 inches). Clay-sized materials of less than 0.002 millimeters (0.00008 inches) in diameter have the largest surface area per unit weight, reaching as much as 800 meters (2,625 feet) squared per gram. Because of large surface areas, clay-sized materials greatly influence the sorption of chemicals such as fertilizers and pesticides and play a major role in catalyzing reactions.

Crystalline layer silicates or phyllosilicates present in the clay-sized fraction are especially important because they function as ion exchangers. Most phyllosilicates have a net negative charge and thus attract cations. This cation exchange capacity (CEC) controls whether plant nutrients, pesticides, and other charged molecules are retained in soil or if they are transported out of the soil system. In contrast, aluminum and iron oxides also present in the clay-sized fraction typically possess a net positive charge or an **anion** exchange capacity (AEC). Soils in temperate regions are dominated most often by solid phase materials that impart a net CEC, whereas soils in tropical regions often contain oxides that contribute substantial AEC.

anion: negatively charged chemical unit, like Cl^{-}, CO_{32}^{-}, or NO_{3}^{-}

Organic Components of the Agricultural Ecosystem

Organic materials contained within the solid phase, although only a small percentage of the total soil weight, are extremely important in controlling chemical and physical processes in soil. Organic matter exists in the form of recognizable molecules such as proteins and organic acids, and in large polymers called humic materials or humus. Humus is dominated by acidic **functional groups** ($-OH$ and $-COOH$) capable of developing a negative charge and contributing substantial CEC. These large polymers possess a three-dimensional conformation that creates **hydrophobic** regions important in retaining nonionic synthetic organic compounds such as pesticides. Nonionic pesticides partition into these hydrophobic regions, thereby decreasing off-site movement and biological availability (see Figure 1).

functional group: portion of a compound with characteristic atoms acting as a group

hydrophobic: a part of a molecule that repels water

A wide variety of organisms live in soil, including microorganisms not visible to the naked eye such as bacteria, fungi, protozoa, some algae, and viruses. Bacteria are present in the largest numbers, but fungi produce more **biomass** per unit weight of soil than any other group of microorganisms. Much of agricultural chemistry as it relates to nutrient cycles, pesticide transformation, plant growth, and organic matter degradation involves the participation of microorganisms. Microorganisms produce both intracellular and extracellular enzymes that increase reaction rates, oxidize and reduce organic and inorganic compounds, and synthesize organic molecules that modify soil chemical and physical properties.

biomass: collection of living matter

Additional organisms in soil such as insects, nematodes, and earthworms also alter the soil ecosystem in a manner that directly or indirectly affects chemical reactions. These organisms physically process plant-derived organic materials prior to biochemical degradation by microorganisms. Nutrient release from organic materials is thus accelerated because the meso- and macrofauna expose more organic matter surface area to microbial breakdown and redistribute such materials in soil to areas of intense microbial ac-

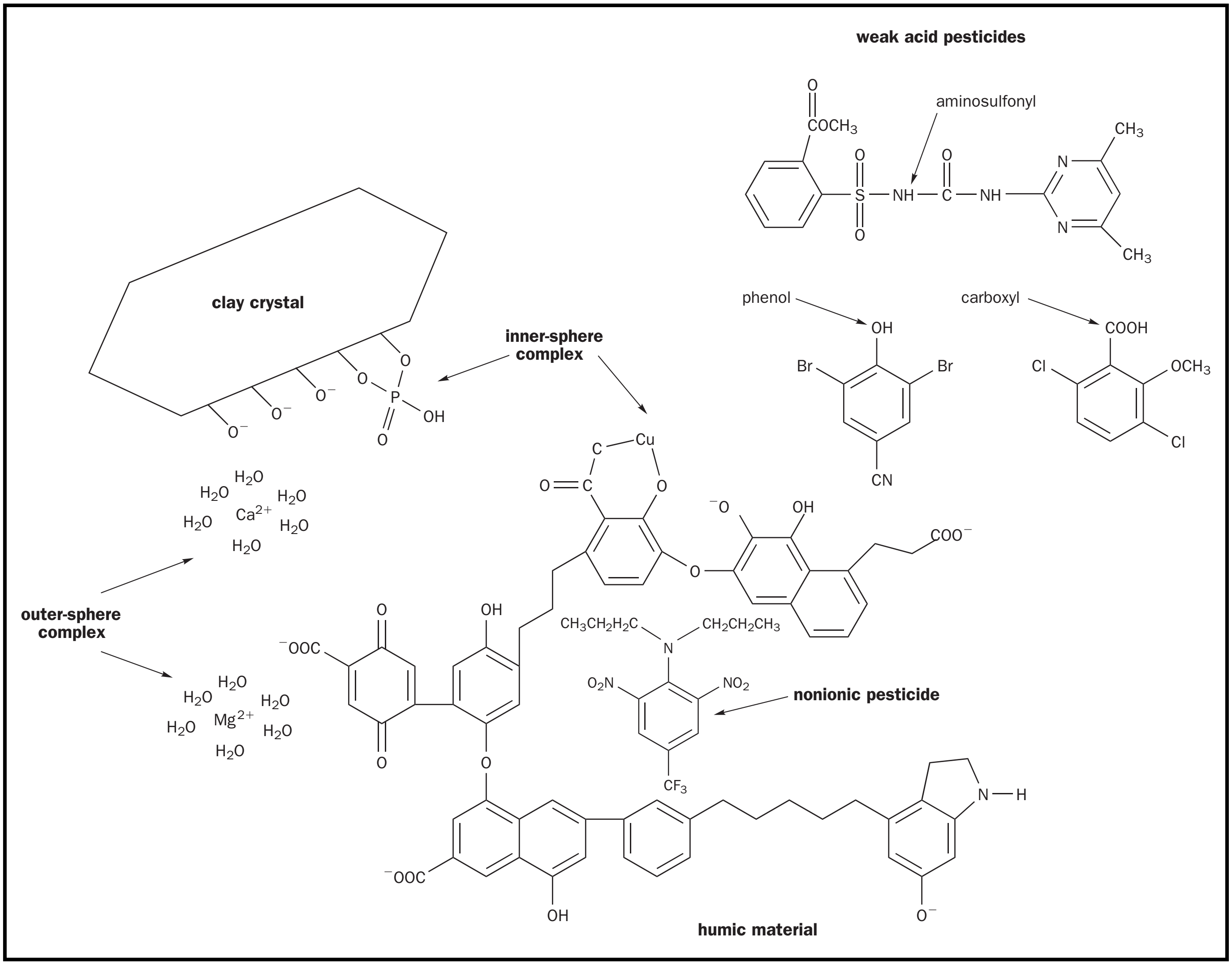


Figure 1. Interaction of ions and organic pesticides with the clays and humic materials in soil. Ions interact with clay crystals by binding directly, as in the case of the inner-sphere complex shown for PO_4^{3-}, or electrostatically in an outer-sphere mechanism, as shown for hydrated Ca^{2+}. Like clays, humic materials also have a net negative charge or a CEC that allows for inner-sphere complexation as shown for Cu^{2+} or outer-sphere interaction as shown for hydrated Mg^{2+}. In addition, humic materials will interact with nonionic pesticides by partitioning them into hydrophobic regions within the large polymeric molecule. Neither clays nor humic materials have a strong affinity for weak acid pesticides containing phenolic hydroxyls, carboxyl groups, or aminosulfonyl linkages.

tivity. In addition, bioturbation may also cause physical changes to the soil structure that increase pore space or modify water movement. Changes in O_2 concentration or soil water content will control biotic and abiotic reactions, altering rates of nutrient cycling and organic matter degradation.

Plant roots also modify soil by producing a zone of intense biological activity called the rhizosphere. This is a region of soil influenced by the root, most often delineated by comparing microbial numbers at greater distance from the root surface. Carbon compounds exuded or sloughed off from roots are used as a food source by microorganisms, thereby causing increased growth and activity. Microbial numbers above those of the bulk soil, which displays no root influence, indicate that the rhizosphere extends to 5 millimeters (0.2 inches) or less. Rhizosphere microorganisms that capitalize on carbon from the plant root interact physically and biochemically with the root, potentially producing positive or negative effects on plant growth.

Soil Chemistry

Biological availabilities and transport phenomena of ions and molecules in soil are controlled by the type of bonding that occurs with the solid phase. Ions such as those typically formed when amending soils with inorganic fertilizers interact with high surface area clay and humic colloids to form either outer- or inner-sphere complexes (see Figure 1). Outer-sphere complexes result when ions, electrostatically attracted to an oppositely charged colloidal surface, retain their shell of hydrating water molecules. These loosely held ions satisfy the excess positive or negative charge of the colloid, but are separated from the colloid's surface by one or more layers of water. In contrast, inner-sphere complexes form when the ion loses its hydration water to form a much stronger **covalent bond** with the colloid. Nutrient ions held in outer-sphere complexes are plant-available because they may be exchanged with ions of the same charge, but nutrients held by an inner-sphere mechanism are not available until the covalent bond is broken.

covalent bond: bond formed between two atoms that mutually share a pair of electrons

Most soils contain a net CEC often reported in centimoles of charge per kilogram of soil (cmol_c/kg). Biological and physical characteristics of the soil are controlled by the amount of CEC and the specific cations involved. Soils dominated by high surface area clays or humus display the highest CECs, whereas soils with large amounts of sand or silt, and only small amounts of humus, exhibit much lower CECs. Highly charged cations with small hydrated radii such as Al^{3+} are more tightly held on the CEC and less likely to exchange than larger, less highly charged cations such as Na^+. This general relationship is superseded when a specific inner-sphere complex forms such as between Cu^{2+} and humus, or K^+ and clay. An even more dramatic example is that of two plant nutrients, NO_3^- and PO_4^{3-}. Negatively charged NO_3^- readily leaches out of soil, but PO_4^{3-} is retained quite strongly because it forms an inner-sphere complex (see Figure 1).

The percentage of the CEC occupied by specific cations influences soil pH and associated characteristics relevant to plant growth and soil biological activity. Only the most strongly held cations remain in soils in high rainfall areas. Al^{3+} dominates the CEC, hydrolyzing when released from the solid phase to the soil solution to form acidic soils with pH values often below 5.

$$Al^{3+} + H_2O \longleftrightarrow AlOH^{2+} + H^+$$

In contrast, soils located in lower rainfall areas accumulate less tightly bound cations such as Ca^{2+}, Mg^{2+}, K^+, and Na^+ and have higher pH values between 5 and 7. In the most arid regions, large amounts of OH^--generating sodium and calcium salts accumulate, causing soil pH values to exceed 7. Plant growth is optimal in soils having pH values between 5.5 and 6.5 because aluminum toxicity occurring at lower pH values, and nutrient limitations caused by higher pH values, are avoided.

Soil Microbiology and Biochemistry

Biochemical transformations catalyzed largely by microorganisms are required for the sustained productivity of all ecosystems. Nutrients sequestered in organic materials and added in the form of fertilizers are cycled by mi-

Protesters pulling up genetically modified crops from a field in Banbury, U.K., during the 1990s. Crops are genetically modified to increase productivity and to produce chemicals, among other uses.

croorganisms in their quest for energy, reducing equivalents, and carbon. Microorganisms grow and reproduce by oxidizing organic or inorganic materials, thereby releasing electrons. The electrons are passed down a series of carriers aligned in a thermodynamic gradient designed to capture energy in the form of **adenosine triphosphate (ATP)**. Additional electrons originating from organic or inorganic materials are used to provide reducing equivalents necessary for synthesizing cell constituents. Carbon for cell growth is obtained from the organic materials being oxidized or captured in the form of CO_2 if inorganic materials are being oxidized.

Reduction-**oxidation** processes are therefore central to agricultural chemistry because oxidation of the electron source and reduction of the electron sink profoundly modify the respective element's chemical characteristics, and thus its behavior and biological availability in the environment. For example, microbial oxidation processes convert organic compounds to CO_2, a gas, and NH_4^+, a cation, to NO_3^-, an anion. Electrons obtained in these oxidations are passed on to a terminal electron acceptor. Microorganisms use terminal electron acceptors in a sequence that maximizes energy yield starting with O_2 and proceeding through NO_3^-, Mn^{4+}, Fe^{3+}, SO_4^{2-}, and finally CO_2, which upon reduction yield H_2O, N_2, Mn^{2+}, Fe^{2+}, H_2S, and CH_4, respectively.

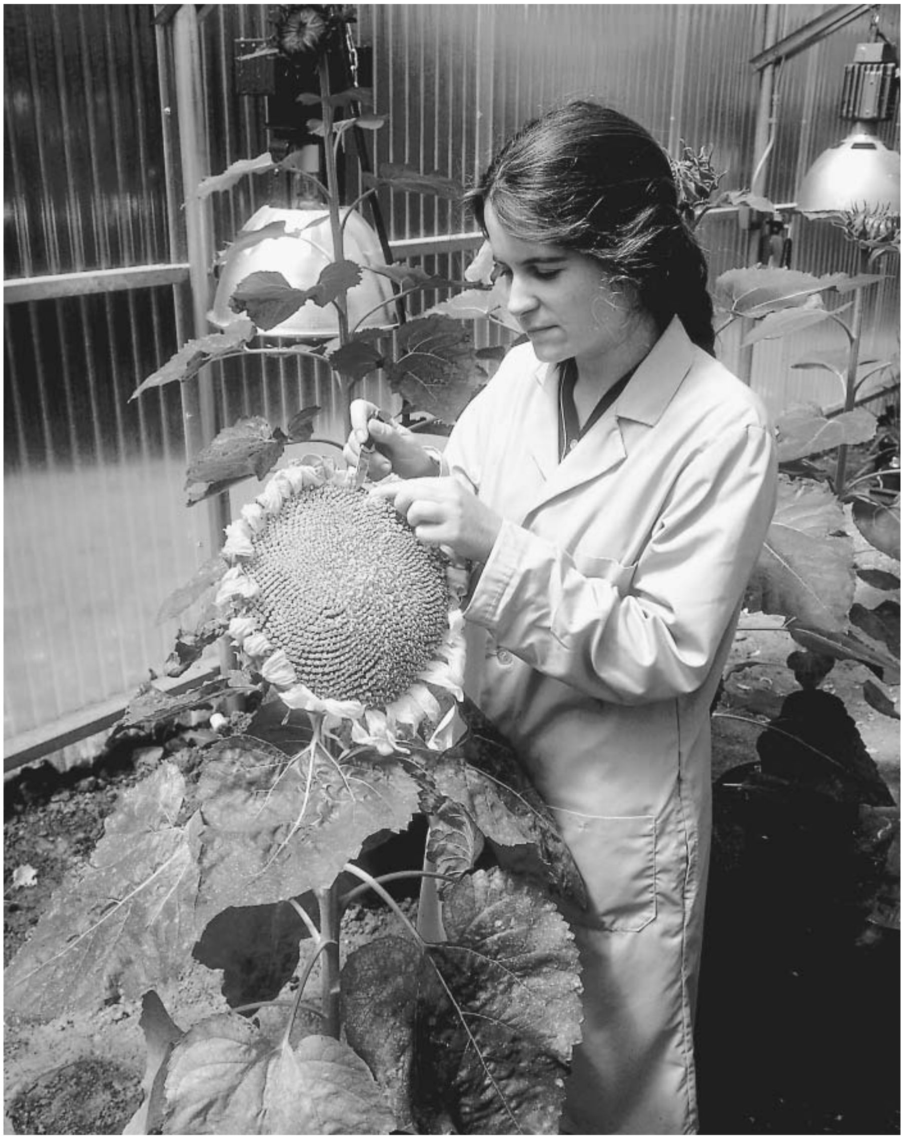
adenosine triphosphate (ATP): molecule formed by the condensation of adenine, ribose, and triphosphoric acid, HOP(O)OH–O–(O)OH–OP(O)OH–OH; it is a key compound in the mediation of energy in both plants and animals

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

Human Manipulation of Agricultural Ecosystems

Food and fiber production are typically optimized by carefully managing the agricultural ecosystem. Synthetic organic compounds are often applied

A laboratory technician at Sungene Technologies Lab in Palo Alto, California, is removing tissue from a sunflower plant for genetic engineering projects.



to control plant pests including weeds, insects, nematodes, and fungal pathogens. Pesticide fate is controlled by sorption to the solid phase and degradation rate. Because most soils have a CEC, cationic pesticides are so strongly held by soil that they are typically biologically unavailable. Weak acid pesticides containing carboxyl, phenolic hydroxyls, or aminosulfonyl functional groups are weakly retained by soil and thus most likely to leach or move off-site (see Figure 1). Weak bases, which may exist as positively charged or uncharged molecules, and nonionic compounds, are intermediate in their susceptibility to move off-site and cause environmental contamination. However, rapid degradation of some pesticides to form benign products eliminates the time available for transport, decreasing the potential for environmental problems. Both biotic and abiotic mechanisms catalyze **degradative** reactions, the rate of which is controlled by the pesticide's chemical structure.

degradative: relating to or tending to cause decomposition

With the advent of molecular techniques and the ability to transfer genes, an additional area of concern has emerged: the introduction of foreign genes into plant species for enhanced crop productivity. In addition, we have the ability to produce a variety of pharmaceutical chemicals in genetically modified plants using what has been termed "pharm crops." David Suzuki and Holly Dressel in *From Naked Ape to Superspecies* have commented on such genetic manipulations, addressing the risks of placing genes from one species into another. Not only is direct gene transfer from one living organism to another possible, but extracellular **DNA** preserved in soil systems is also potentially available for transfer, further increasing environmental risks.

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

Agricultural chemistry is most often linked to food and fiber production, specifically for human consumption. Jared Diamond in *Guns, Germs, and Steel* argues quite convincingly that it was our ability to domesticate crops and eliminate the need for hunting and gathering that allowed for the establishment of permanent settlements and the development of technologically advanced societies. The ensuing increase in human population has led to tremendous pressure to produce additional food from finite resources. Increased agricultural production, in combination with additional resource consumption and waste generation, has caused environmental degradation. By understanding key concepts in agricultural chemistry, we can utilize the soil resource to produce an adequate food supply and protect the environment. SEE ALSO FERTILIZER; HERBICIDES; INSECTICIDES.

Matthew J. Morra

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Air Pollution

Air pollution is the presence in the atmosphere of any substance at a concentration great enough to produce an undesirable effect on humans, animals, vegetation, or materials, or to significantly alter the natural balance of any ecosystem. Air pollutants can be solids, liquids, or gases, and can have local, regional, and global impacts.

At urban scales, air pollution is frequently referred to as photochemical smog. "Smog" is a contraction of the words "smoke" and "fog," and was originally used to describe air pollution caused by coal burning in London. Urban smog is photochemical because many of the chemicals found in urban air are formed by chemical reactions driven by sunlight. Among the many air pollutants in urban smog that are produced by photochemical reactions, one of the most abundant is ozone, O_3. In contrast to the ozone found in the upper atmosphere (stratospheric ozone), which protects the planet from **ultraviolet radiation**, ground level or tropospheric ozone is a lung irritant and a danger to human health. It is also responsible for crop damage and is suspected of being a contributor to forest decline in Europe

ultraviolet radiation: portion of the electromagnetic spectrum with wavelengths shorter than visible but longer than x rays and in parts of the United States. Ground level ozone and other photochemical pollutants are formed in urban atmospheres by the reactions of oxides of nitrogen (mainly NO and NO_2) in the presence of hydrocarbons. Oxides of nitrogen are byproducts of **combustion** processes. At the high temperatures generated during combustion, some of the N_2 and O_2 in air is converted to oxides of nitrogen and, in general, the higher the combustion temperature, the greater are the amounts of oxides of nitrogen produced. Hydrocarbons are emitted from natural sources and as a result of activities utilizing organic solvents, coatings, or fuel. These hydrocarbons and oxides of nitrogen participate in reactions that yield, not only ozone, but also aldehydes, hydrogen peroxide, peroxyacetyl nitrate ($C_2H_3NO_5$), nitric acid, and molecular species of low volatility that accumulate in fine particles suspended in the atmosphere. Although many of these constituents of photochemical smog have environmental impacts, fine particulate matter (PM) presents the greatest health endangerment in most urban areas.

combustion: burning, the reaction with oxygen

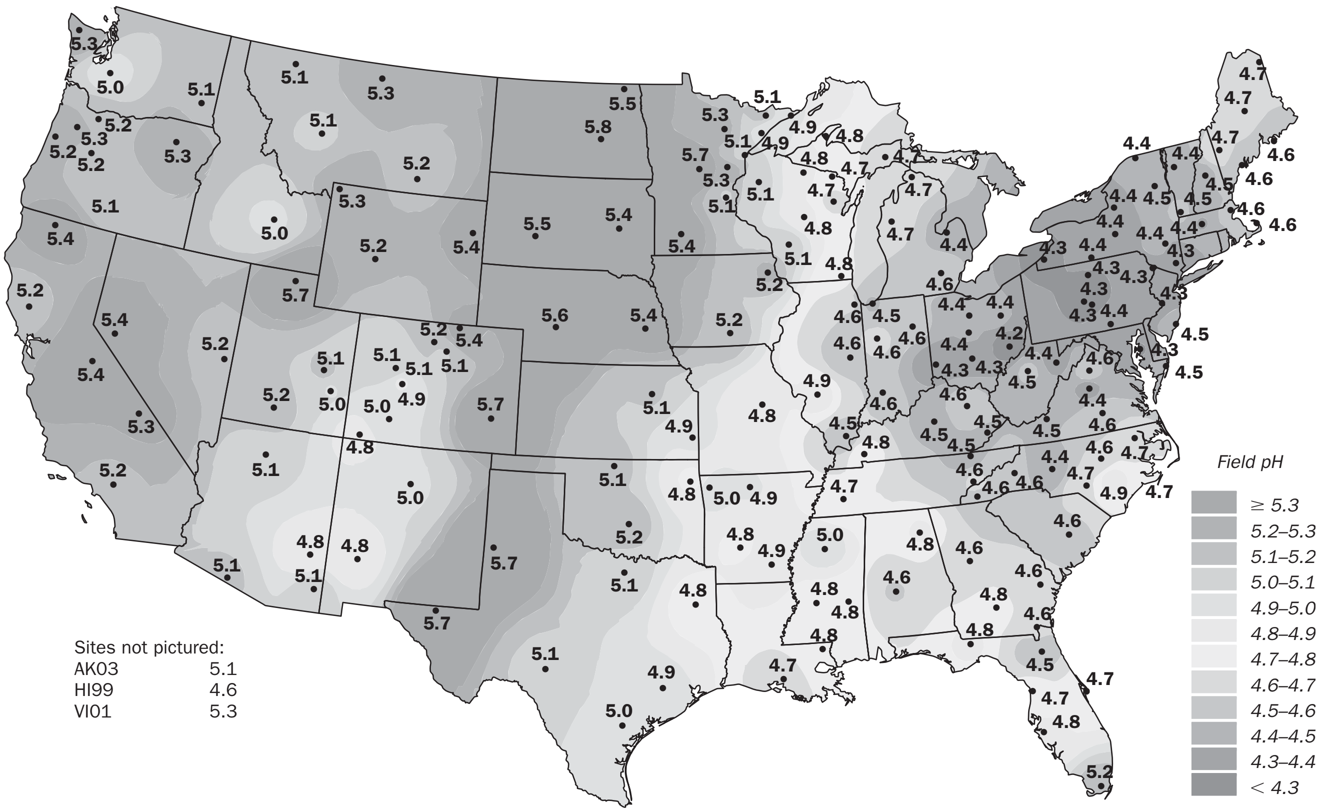
phase: homogeneous state of matter

Solid and liquid **phase** material in the atmosphere is variously referred to as particulate matter, particulates, particles, and aerosols. These terms are often used interchangeably, but all refer to particles with diameters between approximately 1 nanometer (3.9×10^{-8} inches) and 10 micrometers (39.4×10^{-5} inches) that remain suspended in the atmosphere for long periods. The greatest threats to health are associated with the smallest particles because they have the greatest likelihood of becoming deposited deep within the respiratory system.

Somewhat counterintuitively, particles of about 1 micrometer (39.4×10^{-6} inches) in size can remain suspended in the atmosphere much longer than gases. Particles much larger than 1 micrometer (39.4×10^{-6} inches) will, of course, quickly settle out of the atmosphere because of gravity. The smallest particles will coagulate and coalesce quickly, forming larger particles. But particles of approximately 1 micrometer (39.4×10^{-6} inches) in diameter do not grow as quickly as smaller particles and can remain suspended in the atmosphere for a week or more. It is not unusual, for example, for Saharan dust or particle plumes from Asia to be detected in the United States. Consequently, particulate matter is a continental to global scale air pollution problem.

Also, unlike ozone and other gas phase pollutants that are specific chemical species, particulate matter is a collection of chemical species defined mainly on the basis of particle size. The chemical constituents that make up particulate matter vary with particle size. Windblown dust is a main contributor to particles larger than 10 micrometers (39.4×10^{-5} inches) in diameter, whereas sulfates, nitrates, and organic compounds are the main constituents of smaller particles that can penetrate deeply into the respiratory system and engender health effects. Organic particles can be emitted directly as soot from combustion processes or can be formed when large hydrocarbon molecules react with oxidants in the atmosphere and form chemicals that condense onto particles. Sulfate particles are formed via a series of reactions that convert sulfur dioxide, SO_2, which is released into the atmosphere by the combustion of sulfur containing fuels, into sulfuric acid. Nitrate particles are formed via reactions that convert oxides of nitrogen, which are released into the atmosphere by combustion processes, into nitric acid. If particles containing sulfuric acid, nitric acid, and/or organic com-

HYDROGEN ION CONCENTRATION AS pH FROM MEASUREMENTS MADE AT THE FIELD LABORATORIES, 2001



Sites not pictured:

AK03	5.1
HI99	4.6
VI01	5.3

SOURCE: National Atmospheric Deposition Program/National Trends Network. <http://nadp.sws.uiuc.edu>

Figure 1. Spatial distribution of acid deposition.

pounds retain their acidity and are washed out of the atmosphere by rainfall, the rainfall becomes **acid rain**. Figure 1 shows acidity of rainfall averages in the United States and provides a sense of the continental scale of particulate matter air pollution.

The continental and global scale of air pollution problems is not limited to particulate matter. Emissions of greenhouse gases cause global climate change. The presence in the **stratosphere** of ozone-depleting compounds has created polar ozone holes. Atmospheric releases caused by volcanic eruptions and fires have global effects. Atmospheric particles also influence climate and rainfall. The challenges of reducing air pollution call for a sophisticated understanding of atmospheric chemistry, applied at local, regional, continental, and global scales. SEE ALSO Atmospheric Chemistry.

David T. Allen

acid rain: precipitation that has a pH lower than 5.6; term coined by R. A. Smith during the 1870s

stratosphere: layer of the atmosphere where ozone is found; starts about 10 km (6.2 mi) above ground

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Alchemy

The alchemical period corresponds to the span of human history that preceded the era in which fundamental understanding in the chemical sciences began to be acquired by humankind. Most scholars believe that alchemy had its roots in ancient Egypt. China has also emerged as a possible source of alchemical thought. Thus, alchemy was the practice of chemistry such as it existed over the approximately twenty-five centuries before the time of Robert Boyle (1627–1697) and Antoine Lavoisier (1743–1784), when chemistry began to develop into the science we know today. Alchemy was an early precursor to science and included many of the chemistry-related processes that have become known as the chemical arts—the working of **metals** and **alloys**, glassmaking and glass coloring, and the preparation and use of pigments, dyes, and therapeutic agents.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

alloy: mixture of two or more elements, at least one of which is a metal

In its broadest aspect, alchemy appears as a system of philosophy that strove to penetrate the mystery of life as well as to master the formation of inanimate substances. The main goals of the alchemists were the transmutation of base metals into gold and the attainment of the "Philosopher's Stone," a substance that would bring perfection to life. Other embodiments of the Philosopher's Stone were the Elixir Vitae, the Grand Magisterium, and the Red Tincture, all regarded as universal medicines. The alchemical fascination with gold emerged from the idea that gold was the perfect metal. If one could understand the essence of this perfect metal (the theory went), the essence of all substances less perfect than gold could then be understood, which, accordingly, could lead to the creation of all substances, including gold. The Philosopher's Stone incorporated the promise that the perfection of gold could somehow be transferred to life's processes. The Philosopher's Stone was the agent by which base metals could be changed to gold and, by extrapolation, could lead to greater longevity. The Chinese alchemists included these ideas in their approach to alchemistry. They sought the preparation of a liquid form of gold that would promote longevity; liquid gold would contain the essence of the Philosopher's Stone and the search for liquid gold was one route to the Philosopher's Stone. The Chinese alchemists were interested in the preparation of artificial cinnabar, which they believed to be the "life-giving" red pigment that could be used in goldmaking. They were also interested in the transmutation of base metals into gold. Thus, the focus of alchemical thought and process was the manipulation of matter in such a way as to, ultimately, increase longevity.

It is not surprising that in the early days of alchemy, much of the ancient Egyptian expertise in gold refining and goldworking as well as the Egyptian skill with respect to enamelware, the production of colored glass, and the preparation and use of pigments were highly valued by alchemists. In a sense, those Egyptian craftsmen were the first alchemists, even though

The alchemy laboratory in Powder Tower, Prague, which was used circa 1585 by John Dee and Edward Kelley.

they may not have had the same ultimate focus as the practitioners of the alchemical arts.

In the course of the evolution of the alchemical arts, the fundamental properties of matter came under consideration. Aristotle taught that all matter consisted of four fundamental constituent factors or elements—air, water, earth, and fire. All matter was supposed to incorporate these four elements in different combinations and proportions. The changes that a substance could be made to undergo, for example, the burning of wood or the boiling of water, corresponded to a change or changes in the proportions of these four elements within that substance. Thus, alchemy ultimately gave rise to modern chemical thought and, gradually, the goals of alchemy were abandoned. In a broad sense, alchemy can be regarded as a prelude to the chemistry we know today. SEE ALSO Al-Razi, Abu-Bakr Muhammed ibn Zakariya; Boyle, Robert; Lavoisier, Antoine; Paracelsus.

J. J. Lagowski

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Alkali Metals

Alkali metals are the six elements that comprise Group I in the Periodic Table: lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), and francium (Fr). Especially when dissolved in water, these elements form strong bases (alkalis) capable of reacting with and neutralizing strong acids.

inert: incapable of reacting with another substance

Each metal has the electron configuration of an **inert** (noble) gas plus one electron in the next higher *s* orbital. Thus, Na is $1s^22s^22p^63s^1$ or alternatively $(Ne)3s^1$. Virtually all alkali metal compounds are ionic in nature because this outermost single electron is readily lost, forming relatively stable monovalent ions.

isotope: form of an atom that differs by the number of neutrons in the nucleus

Sodium and potassium are abundant in Earth's crust, each comprising about 2.5 percent, and the two being the 6th and 7th most abundant elements, respectively. Other alkali metals are at least one hundred times less abundant. Francium is virtually nonexistent in the environment since all **isotopes** are radioactive with short half-lives.

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

Alkali metals are very reactive, and thus none occurs in a free state in the environment. They spontaneously react with oxygen, water, **halogens**, phosphorus, sulfur, and other substances; lithium even reacts with nitrogen. Reactions with water can be violent, with the evolution of hydrogen gas and formation of strongly alkaline solutions.

potash: the compound potassium oxide, K_2O

Compounds of various alkali metals were known in ancient times, but the great English chemist Sir Humphry Davy first isolated pure metals, purifying potassium and then sodium in 1807. Sodium is derived from "soda," a term used in the Middle Ages to characterize all alkalis, originally from the Latin *sodanum*, which was a headache remedy; its symbol Na is derived from the Latin word for soda, *natrium.* Potassium comes from the French word *potasse* (later the English **potash**), the residue produced when wood ash solutions are evaporated (so-called pot ashes); its symbol K derives from the Latin *kalium* and ultimately Arabic *qali*, meaning "alkali." The Swedish chemist J. A. Arfedson discovered lithium during his analysis of the mineral petalite in 1817, although W. T. Brande and Davy first produced the pure metal. The name is derived from the Greek word *lithos* (meaning "stony").

spectral line: line in a spectrum representing radiation of a single wavelength

During their flame spectrometry experiments on mineral waters in 1860, the German chemists Gustav Kirchhoff and Robert Bunsen determined the existence of cesium from the characteristic two blue lines in the spectrum. Likewise, extracts of the mineral lepidolite exhibited two dark red **spectral lines** from which the presence of Rb was inferred. Thus, cesium derives from the Latin *caesius*, meaning "heavenly blue," whereas rubidium derives from *rubidus*, the Latin word used to describe a very dark red color. Bunsen was able to isolate pure Rb but not Cs, later purified by C. Setterberg.

Since all isotopes of Fr are radioactive, it was not discovered until 1939 at the Curie Institute in Paris by Marguerite Perey, although the Russian chemist Dimitri Mendeleev predicted its existence. Its name derives from that of France, the country where it was discovered.

Because of their metallic and alkaline properties, potassium and especially sodium are widely used in a variety of industrial processes both as metals and as compounds with various other elements. Lithium is rarely used, but does find application in lightweight **alloys** with magnesium. Rubidium and cesium are not commonly utilized industrially, except for some applications in electronics. Sodium and potassium are essential for life, sodium being the principal extracellular and potassium the major intracellular monovalent cations. The other alkali metals have no essential biological role. SEE ALSO BUNSEN, ROBERT; CESIUM; DAVY, HUMPHRY; FRANCIUM; LITHIUM; MENDELEEV, DIMITRI; POTASSIUM; RUBIDIUM; SODIUM.

alloy: mixture of two or more elements, at least one of which is a metal

Michael E. Maguire

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Alkaline Earth Metals

Alkaline earth metals are the six elements forming Group IIa in the Periodic Table: beryllium (Be), magnesium (Mg), Calcium (Ca), Barium (Ba), Strontium (Sr), and Radium (Ra)✷. Their oxides are basic (alkaline), especially when combined with water. "Earth" is a historical term applied to nonmetallic substances that are insoluble in water and stable to heating, and also the properties of the oxides. Hence, the term "alkali earths" is often used to describe these elements.

✷See Periodic Table in the For Your Reference section of Volume 1.

Each metal has the electron configuration of an **inert** (noble) gas plus two electrons in the next higher *s* orbital. Thus, Mg is $1s^2 2s^2 2p^6 3s^2$ or alternatively (Ne)$3s^2$. The bonds of most compounds of alkali earths are ionic in nature because these outermost electrons are readily lost, forming stable divalent cations. Mg, however, can form compounds with both ionic and **covalent bonds**, whereas most compounds of Be are covalent. The heavier alkali earths are sometimes compared to Group IIb elements (zinc [Zn], cadmium [Cd], mercury [Hg]) that also have a filled s orbital ($5s^2$), but the filled $4d^{10}$ orbitals and higher **ionization** energies of the latter make compounds of Group IIb elements markedly less ionic in character than those of alkali earths.

inert: incapable of reacting with another substance

covalent bond: bond formed between two atoms that mutually share a pair of electrons

ionization: dissociation of a molecule into ions carrying + or − charges

Mg and Ca are the eighth and sixth most abundant elements in Earth's crust at 2.5 and 3.6 percent, respectively. Be, Sr, and Ba comprise 0.001, 0.025, and 0.05 percent, respectively. Ra is radioactive, and since its longest-lived **isotope** ^{226}Ra has a half-life of 1,600 years, there is very little Ra in Earth's crust. It is nonetheless present because ^{226}Ra is continuously formed by the decay of uranium (^{238}U). Alkali earth elements are

isotope: form of an atom that differs by the number of neutrons in the nucleus

very reactive and strongly reducing in character; thus, none occurs in a free state in the environment. They readily react with oxygen, and the pure metals tarnish in air, forming a surface layer of the oxide. The metals are soluble in liquid ammonia, forming covalent compounds with the general formula $M(NH_3)_6$. These solutions are strongly basic and frequently find application in industry.

Oxides of alkali earths were known in ancient times, calcium oxide being lime (from the Latin word *calx*). Magnesium oxide or magnesia was also known, its name probably deriving from a district in Asia Minor. Oxides of the other alkali earths were identified in the eighteenth century. Barium oxide or baryta was found in the mineral called heavy spar and given the name *barys* (from the Greek, meaning "heavy"). Strontia or strontianite (strontium carbonate) was found in a lead mine at Strontian in Scotland. Beryllium oxide was extracted from the mineral beryl (from the Greek word *bèryllos*). Be was originally called glucina (from the Greek *glykys*, meaning "sweet") because of its taste and is sometimes still referred to as *glucinum* in France.

The English chemist Sir Humphry Davy first isolated Mg, Ca, Sr, and Ba in 1808 by means of electrolysis. (Mg was originally called magnium since Davy had already applied the word "magnesium" to the element manganese.) Be was initially isolated from beryl by the French chemist Antoine Bussy and independently in Germany by Friedrich Wöhler in 1828. The discovery of Ra did not occur until 1898 when Marie and Pierre Curie purified it from barium using its radioactivity. They named it from the Latin word *radius* (meaning "ray") because the strength of its radioactivity was more than a million times that of uranium.

alloy: mixture of two or more elements, at least one of which is a metal

Because of their metallic properties and low mass, Be and Mg are used to form lightweight **alloys** for structural purposes. Ca sees less industrial use, although the phosphate is sometimes utilized in fertilizers. Sr and Ba have no significant industrial applications. Both Be and Ra are used in various devices, the former because it is quite transparent to x-rays and the latter because it is a ready source of both α- and γ-radiation. Mg and Ca are essential to all living systems for many reasons; the other alkali earths have no known biological roles. SEE ALSO BERYLLIUM; CESIUM; CURIE, MARIE SKLODOWSKA; DAVY, HUMPHRY; FRANCIUM; MAGNESIUM; POTASSIUM; RUBIDIUM; WÖHLER, FRIEDRICH.

Michael E. Maguire

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Allosteric Enzymes

Enzymes are biological catalysts. They accelerate the rates of reactions in cells without being changed themselves during the process of reaction. Allosteric enzymes are a subset of enzymes that are involved in the control and regulation of biological processes. The control of processes is essential to biological systems: A cell that divides out of control has undergone a kind of transformation (cancerous or precancerous) that can threaten an entire organism. There are many processes occurring inside the cell at any one time, and they must coexist in proper balance. This balance is where allosteric enzymes come into play.

Allosteric enzymes have the ability to respond to several different conditions in their environments. Every enzyme contains an active site, the location on the enzyme where it catalyzes its specific reaction. Allosteric enzymes contain a second type of site, called an allosteric site. The allosteric site, through its binding of a nonsubstrate molecule, influences (enhances or impairs) the activity of the enzyme. The word "allosteric" is derived from two Greek words: *allos*, meaning other, and *stereos*, meaning site. Another important feature of allosteric enzymes is that they consist of multiple **polypeptide** chains, with multiple active and allosteric sites.

polypeptide: compound containing two or more amide units—C(O)NH—produced by the condensation of two or more amino acids

Whereas substrates bind to the active sites of enzymes, other nonsubstrate molecules (allosteric modulators) bind to the allosteric sites. The significance and role of the allosteric site is well illustrated by the example of the enzyme aspartate transcarbamoylase, which catalyzes reaction 1.

$$\text{Aspartate} + \text{Carbamoyl Phosphate} \xrightarrow[\text{transcarbamoylase}]{\text{Aspartate}} \text{N-Carbamoylaspartate} \tag{1}$$

This is the first step of the pathway that leads to the formation of **cytosine**, a building block for **DNA synthesis**. The form of cytosine that is used to synthesize DNA (and **RNA**) is the molecule cytidine triphosphate (CTP). When intracellular CTP concentrations are high, CTP molecules bind more often to the allosteric sites on aspartate transcarbamoylase molecules, causing a change in the shape of the enzyme that slows reaction 1 down markedly. Thus, CTP is an allosteric inhibitor of this enzyme.

There are times in the life of a cell when it needs to make more N-carbamoylaspartate (and eventually more CTP), even when concentrations of CTP are high to begin with. This is particularly true just prior to cell division, because the cell is at this point rapidly synthesizing DNA. Under these conditions, a high concentration of **adenosine triphosphate (ATP)**, another building block of DNA, will be present in the cell. ATP can also bind to the allosteric site on aspartate transcarbamoylase, but, unlike CTP, it acts as an enzyme activator, overcoming the **inhibitory** effect of CTP and thereby leading to the synthesis of more CTP, when CTP concentrations are already high. SEE ALSO Enzymes; Inhibitors; Proteins.

Paul A. Craig

cytosine: heterocyclic, pyrimidine, amine base found in DNA

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

synthesis: combination of starting materials to form a desired product

RNA: ribonucleic acid, a natural polymer used to translate genetic information in the nucleus into a template for the construction of proteins

adenosine triphosphate (ATP): molecule formed by the condensation of adenine, ribose, and triphosphoric acid, HOP(O)OH–O–(O)OH–OP(O)OH–OH; it is a key compound in the mediation of energy in both plants and animals

inhibitory: relating to the prevention of an action that would normally occur

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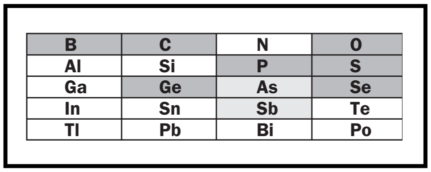

B	C	N	O
Al	Si	P	S
Ga	Ge	As	Se
In	Sn	Sb	Te
Tl	Pb	Bi	Po

Figure 1. Elements that exist as allotropes.

Allotropes

Allotropes are different forms of the same element. Different bonding arrangements between atoms result in different structures with different chemical and physical properties. Allotropes occur only with certain elements, in Groups 13 through 16 in the Periodic Table. This distribution of allotropic elements is illustrated in Figure 1.

Group 13

Boron (B), the second hardest element, is the only allotropic element in Group 13. It is second only to carbon (C) in its ability to form element-element bonded networks. Thus, in addition to amorphous boron, several different allotropes of boron are known, of which three are well characterized. These are red crystalline α-rhombohedral boron, black crystalline β-rhombohedral boron (the most thermodynamically stable allotrope), and black crystalline β-tetragonal boron. All are polymeric and are based on various modes of condensation of the B_{12} icosahedron (Figure 2).

Group 14

melting point: temperature at which a substance in the solid state undergoes a phase change to the liquid state

In Group 14, only carbon and tin exist as allotropes under normal conditions. For most of recorded history, the only known allotropes of carbon were diamond and graphite. Both are polymeric solids. Diamond forms hard, clear, colorless crystals, and was the first element to have its structure determined by x-ray diffraction. It has the highest **melting point** and is the hardest of the naturally occurring solids. Graphite, the most thermodynamically stable form of carbon, is a dark gray, waxy solid, used extensively as a lubricant. It also comprises the "lead" in pencils.

lattice: systematic geometrical arrangement of atomic-sized units that constitute the structure of a solid

The diamond **lattice** (Figure 3a) contains tetrahedral carbon atoms in an infinite three-dimensional network. Graphite is also an infinite three-dimensional network, but it is made up of planar offset layers of trigonal carbons forming fused hexagonal rings (Figure 3b). The C-C bonds within

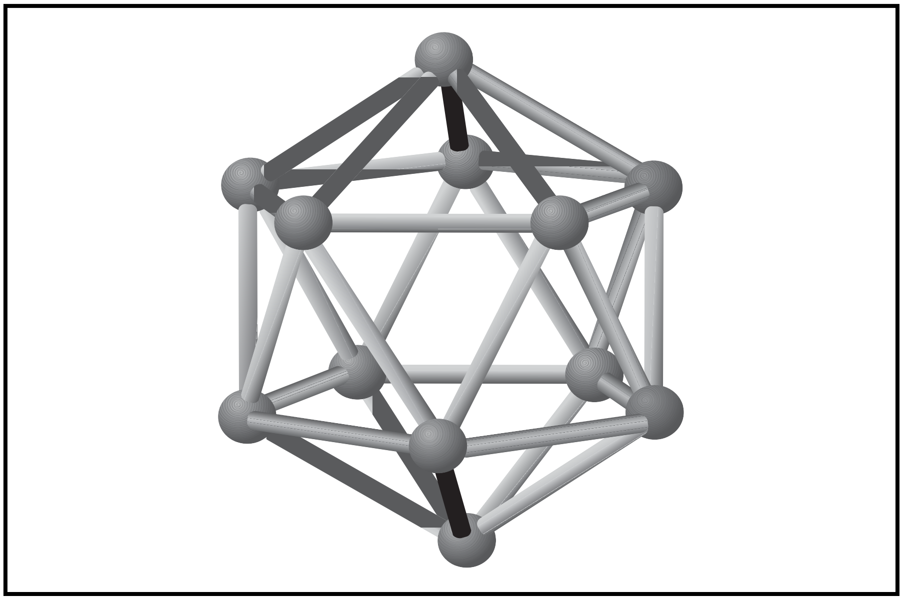

Figure 2. B_{12} icosahedron.

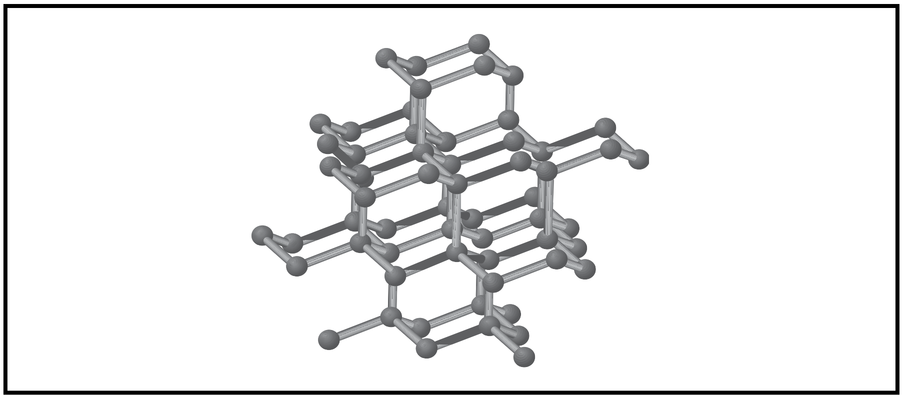

Figure 3a. Portion of the structure of diamond. This structure repeats infinitely in all directions.

a layer are shorter than those of diamond, and are much shorter than the separation between the graphite layers. The weak, nonbonding, interaction between the layers, allowing them to easily slide over each other, accounts for the lubricating properties of graphite.

Diamond and graphite are nonmolecular allotropes of carbon. A range of molecular allotropes of carbon (the fullerenes) has been known since the discovery in 1985 of C_{60} (Figure 4). The sixty carbon atoms approximate a sphere of condensed five- and six-membered rings. Although initially found in the laboratory, fullerenes have since been shown to occur in nature at low concentrations. C_{60} and C_{70} are generally the most abundant and readily isolated fullerenes.

In 1991 carbon nanotubes were discovered. They are more flexible and stronger than commercially available carbon fibers, and can be conductors or semiconductors. Although the mechanism of their formation has not been determined, they can be thought of as the result of “rolling up” a section of a graphite sheet and capping the ends with a hemisphere of C_{60}, C_{70}, or another molecular allotrope fragment. Five- or seven-membered rings can be incorporated among the six-membered rings, leading to an almost infinite range of helical, toroidal, and corkscrew-shaped tubes, all with different mechanical strengths and conductivities.

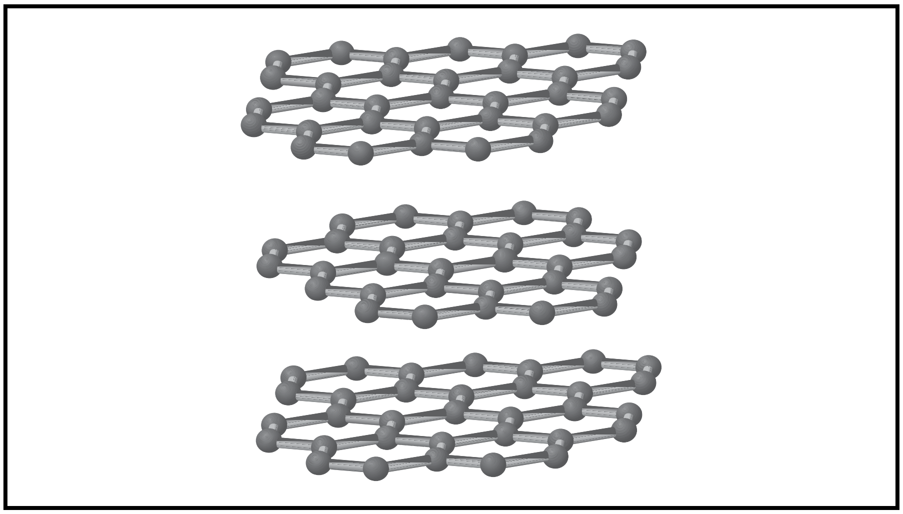

Figure 3b. Portion of the structure of graphite. This structure repeats infinitely in all directions.

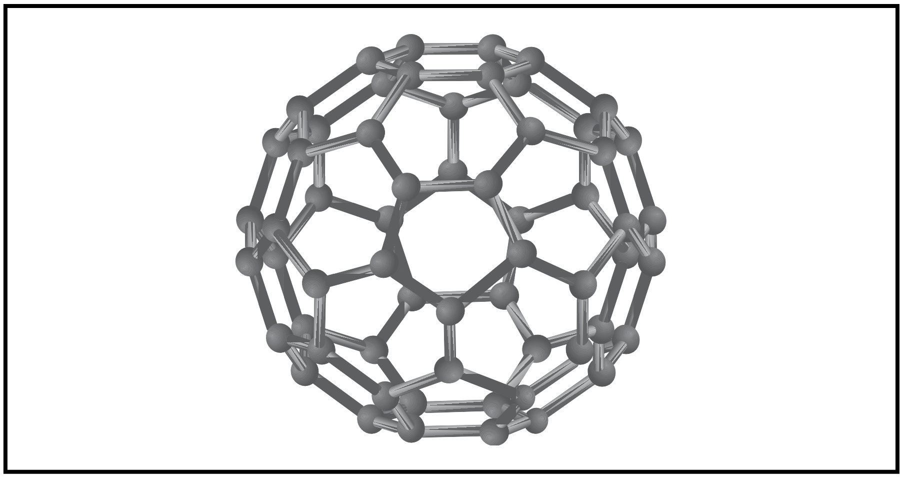

Figure 4. A fullerene allotrope of C_{60}.

Tin is a relatively low melting (232°C) material that exists in two allotropic forms at room temperature and pressure, α-Sn (gray tin) and β-Sn (white tin). α-Sn is the stable form below 13°C and has the diamond structure (Figure 3a). White, or β-Sn is metallic and has a distorted close-packed lattice.

Group 15

arsenic: toxic element of the phosphorus group

volatile: low boiling, readily vaporized

monoclinic: one of several arrangements of atoms found in crystalline solids; characterized by a unit cell of three axes each of a differing length; two axes are mutually perpendicular while the third is at an oblique angle

There are two allotropic elements in Group 15, phosphorus and **arsenic**. Phosphorus exists in several allotropic forms. The main ones (and those from which the others are derived) are white, red, and black (the thermodynamically stable form at room temperature). Only white and red phosphorus are of industrial importance. Phosphorus was first produced as the common white phosphorus, which is the most **volatile**, most reactive, and most toxic, but the least thermodynamically stable form of phosphorus, α-P_4. It coverts to a polymorphic form, β-P_4, at −76.9°C. White phosphorus is a waxy, nonconductor and reacts with air—the phosphorescent reaction of oxygen with the vapor above the solid producing the yellow-green chemiluminescent light, which gives phosphorus its name (after the Greek god, Eosphoros, the morning star, the bringer of light). The phosphorus in commercial use is amorphous red phosphorus, produced by heating white phosphorus in the absence of air at about 300°C. It melts around 600°C and was long thought to contain polymers formed by breaking a P-P bond of each P_4 tetrahedron of white phosphorus then linking the "opened" tetrahedra (Figures 5a and 5b).

A variety of crystalline modifications (tetragonal red, triclinic red, cubic red), possibly with similar polymeric structures can also be prepared by heating amorphous red phosphorus at over 500°C.

The most thermodynamically stable, and least reactive, form of phosphorus is black phosphorus, which exists as three crystalline (orthorhombic-, rhombohedral- and metallic, or cubic, and one amorphous, allotrope. All are polymeric solids and are practically nonflammable. Both orthorhombic and rhombohedral phosphorus appear black and graphitic, consistent with their layered structures.

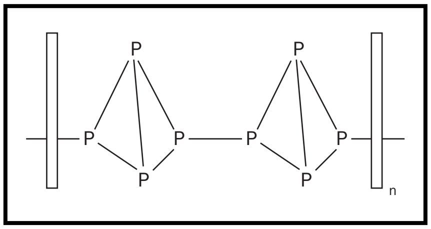

Figure 5a. Linkage of P_4 units in red phosphorus.

A violet crystalline allotrope, **monoclinic** phosphorus, or Hittorf's phosphorus, after its discoverer, can be produced by a complicated thermal and electrolytic procedure. The structure is very complex, consisting of tubes of

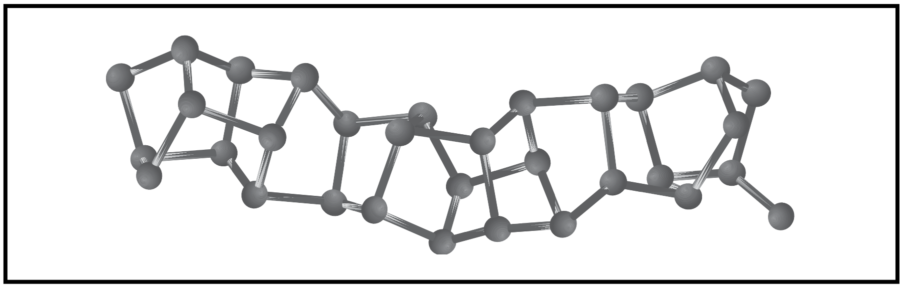

Figure 5(b). Linkage of P_4 units in red phosphorus.

pentagonal cross section joined in pairs to form double layers, which are repeated through the crystal. The tubes are formed from cagelike P_8 and P_9 groups, linked by P_2 units.

At least six forms of solid arsenic have been reported, of which three are amorphous. The most stable and most common form of arsenic at room temperature is a brittle, steel-gray solid (α-As) with a structure analogous to that of rhombohedral black phosphorus. Arsenic vapor contains tetrahedral As_4 molecules, which are thought to be present in the yellow unstable arsenic formed by condensation of the vapor. Arsenic occurs naturally as α-As and also as the mineral arsenolamprite, which may have the same structure as orthorhombic black phosphorus.

Group 16

There are only three allotropic elements in Group 16, oxygen, sulfur, and selenium. Only two oxygen allotropes are known—dinuclear "oxygen" (dioxygen, O_2) and trinuclear ozone (O_3) (Figure 6). Both are gases at room temperature and pressure. Dioxygen exists as a diradical (contains two unpaired electrons) and is the only allotrope of any element with unpaired electrons. Liquid and solid dioxygen are both pale blue because the absorption of light excites the molecule to a higher energy (and much more reactive) electronic state in which all electrons are paired ("singlet" oxygen). Gaseous dioxygen is probably also blue, but the low concentration of the species in the gas phase makes it difficult to observe.

Ozone is a V-shaped, triatomic dark blue gaseous molecule with a bond order of 1½. It is usually prepared from dioxygen by electric discharge (e.g., lightning) and can be detected by its characteristic "sharp" smell—from which it gets its name (after the Greek *ozein*: to smell). Ozone is thermodynamically unstable and reverts spontaneously to dioxygen.

The dark blue color of O_3 is important because it arises from the intense absorption of red and ultraviolet (UV) light. This is the mechanism by which ozone in the atmosphere (the ozone layer) protects Earth from the Sun's UV radiation. After F_2, ozone is the most powerful oxidant of all the elements.

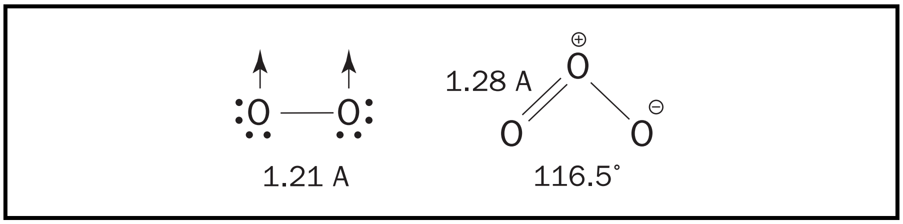

Figure 6. Dioxygen and ozone, the allotropes of oxygen.

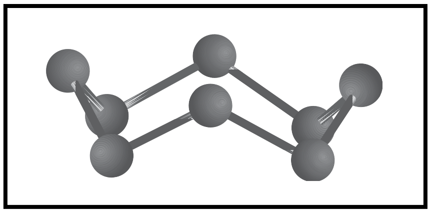

Figure 7. Sulfur allotrope, S_8.

Sulfur (S) is second only to carbon in the number of known allotropes formed. The existence of at least twenty-two sulfur allotropes has been demonstrated. The simplest allotrope of sulfur is the violet disulfur molecule, S_2, analogous to the dioxygen molecule. Unlike O_2, however, S_2 does not occur naturally at room temperature and pressure. It is commonly generated in the vapor generated from sulfur at temperatures above 700°C. It has been detected by the Hubble Space Telescope in volcanic eruptions on Jupiter's satellite, Io.

The most thermodynamically stable of all of the sulfur allotropes and the form in which sulfur ordinarily exists is orthorhombic sulfur, α-S_8, cyclooctasulfur, which contains puckered eight-membered rings, in which each sulfur atom is two-coordinate (Figure 7).

The second allotrope of sulfur to be discovered was cyclohexasulfur (sometimes called rhombohedral sulfur), first reported in 1891. It is the densest of the sulfur allotropes and forms air-sensitive orange-red crystals containing chair-shaped, six-membered rings. Sulfur forms an extensive series of generally yellow crystalline allotropes, S_n (where species with n up to 30 have been identified). The color of liquid sulfur changes from pale yellow to orange, then red and finally to black, near the boiling point (445°C). At about 159°C, the viscosity increases as polymeric sulfur is formed. The liquid is thought to contain chains of sulfur atoms, wound into helices.

Selenium (Se) also exists in several allotropic forms—gray (trigonal) selenium (containing Se_n helical chain polymers), rhombohedral selenium (containing Se_6 molecules), three deep-red monoclinic forms—α-, β-, and γ-selenium (containing Se_8 molecules), amorphous red selenium, and black vitreous selenium, the form in industrial usage. The most thermodynamically stable and the densest form is gray (trigonal) selenium, which contains infinite helical chains of selenium atoms. All other forms revert to gray selenium on warming. In keeping with its density, gray selenium is regarded as metallic, and it is the only form of selenium that conducts electricity. A slight distortion of the helical structure would produce a cubic metallic lattice.

The trend from nonmetallic to metallic character upon going down the group is exemplified by the conductivities of these elements. Sulfur is an insulator, selenium and tellurium are semiconductors, while the conductivity of polonium is typical of a true **metal**. In addition, the conductivities of sulfur, selenium, and tellurium increase with increasing temperature, behavior typical of nonmetals, whereas that of polonium increases at lower temperatures, typical of metals. SEE ALSO ARSENIC; BORON; CARBON; FULLERENES; OXYGEN; OZONE; PHOSPHORUS; SELENIUM; SULFUR; TIN.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Anthony F. Masters

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Al-Razi, Abu-Bakr Muhammed ibn Zakariya

PERSIAN PHYSICIAN AND ALCHEMIST
ca. 854 C.E.–ca. 930 C.E.

Abu-Bakr Muhammed ibn Zakariya al-Razi (also transliterated as ar-Razi) was born around 854 in Ray, near the city of Teheran (the Persian Empire, now Iran). Al-Razi (in the Latinized West, Rhazes) achieved mastery in a number of fields, including philosophy, logic, poetry, and music. Around the age of thirty he left Ray for Baghdad (now in Iraq), where he was active in the reconstruction of the city hospital. Al-Razi became famous as the most prominent physician in the Islamic world, his fame comparable only to that of another Persian physician, **Ibn Sina** (who became known in the West as Avicenna). Al-Razi's written works in medicine have been widely studied, Latin editions of which remained in use as late as the seventeenth century in Europe. From him we have the earliest distinction between smallpox and measles, and the understanding that smallpox occurs only once in a person's life. As a skilled chemist he recognized the toxicity of **arsenic** (arsenic oxide), but prescribed small doses of this compound in the treatment of many skin diseases and anemia.

Ibn Sina: given name of an Islamic scientist known in the West as Avicenna (979–1037); reputed to be the author of more than 100 books that were Europe's most important medical texts from the 12th century until the 16th century

arsenic: toxic element of the phosphorus group

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Like his predecessor, the Arabian alchemist Jabir ibn Hayyan (sometimes known as Jabir), al-Razi was influenced in his alchemical views by Aristotle's theory of the four elements. Arabic alchemists had modified the Aristotelian system with respect to the composition of minerals, whereby two elements, mercury and sulfur, were responsible for "the mercurial and sulfurous principles" of a given substance. Later called "philosophical" Mercury and Sulfur, these elements (or principles) were thought to be the substances from which all **metals** were formed. This Sulfur-Mercury theory later became highly influential among European thinkers, for example, Isaac Newton. To this Sulfur and Mercury, al-Razi added a third constituent, a salty principle (which was later reproposed by Paracelsus). In al-Razi's opinion metals were comprised of particles of these elemental constituents, while the identity of the metal depended on the relationships between these indivisible particles and the empty spaces between them.

Persian physician Abu-Bakr Muhammed ibn Zakariya al-Razi.

In contrast to Jabir, who inclined toward numerical mysticism, al-Razi became practiced in experimental work. This is apparent from his two most influential works, *Kitab al-Asrar* (*The Book of Secrets*), and *Kitab sirr al-Asrar* (*The Book of the Secret of Secrets*). In these works he gave several recipes for the alleged transmutation of common metals into precious ones, and crystal or glass into precious stones. Perhaps al-Razi's main contribution to chemistry was his attempt to systematize laboratory practices, to which end he listed contemporary laboratory equipment and techniques used in chemical experiments. Another influential contribution to chemistry was his classification of all the chemical substances he knew, for this is the earliest attempt of which we are aware. Al-Razi divided these substances into four main groups: vegetable, animal, derivative, and mineral. The last group consisted of six subgroups: (1) spirits (**volatile** substances, such as mercury, sulfur, and arsenic sulfide); (2) metals (gold, silver, copper, tin, iron, lead, and "karesin," probably a bronze composed of copper, zinc, and nickel); (3) stones (ores and minerals of iron, copper, zinc, but also glass); (4) atraments (metallic sulfates and their derivatives); (5) boraces (borax, but also sodium carbonate [confused with borax]); and (6) salts (in which categorization sodium chloride appears under four different terms, other salts being sodium carbonate, potassium carbonate, and others).

volatile: low boiling, readily vaporized

In later life al-Razi became blind, which, according to some sources, was a result of his indefatigable activity—for he is said to have written approximately 200 works. According to other sources his blindness was a result of torture, the punishment he was given when he failed to produce precious metals via alchemical transmutation. Al-Razi died in 925 or 935 in Ray. SEE ALSO NEWTON, ISAAC; PARACELSUS.

Vladimir Karpenko

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Aluminum

13
Al
ALUMINUM
26.98

MELTING POINT: **660.32°C**
BOILING POINT: **2,519°C**
DENSITY: **2.70 g/cm^3**
MOST COMMON IONS: **Al^{3+}**

Aluminum is a silvery-white metallic element discovered in 1825 by Danish chemist Hans Christian Ørsted. It is the most abundant **metal** found in Earth's crust, comprising 8.3 percent of the crust's total weight. Its content in seawater, however, is as low as 0.01 gram per metric ton (0.01 part per million). The key **isotope** of aluminum is ^{27}Al with a natural abundance of 100 percent, but seven other isotopes are known, one of which is used as a radioactive tracer (^{26}Al).

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

isotope: form of an atom that differs by the number of neutrons in the nucleus

Aluminum is not found in its metallic state in nature; it is usually found as silicate, oxide, or hydrated oxide (bauxite). Its extraction from ore is difficult and expensive; aluminum is therefore commonly recycled, the energy of recycling being a mere 5 percent of the energy needed to extract the metal.

Aluminum is lightweight, **ductile**, and easily machined. It is protected by an oxide film from reacting with air and water, and is therefore rust-resistant. It is one of the lightest metals but is quite tough and most helpful in **metallurgy**, transportation (e.g., aircraft, automobiles, railroad cars, and boats), and architecture (e.g., window frames and decorative ornaments). It is also used in the manufacture of cooking gear because it is a good conductor of heat. Aluminum foils as thin as 0.18 millimeter (0.007 inch) are a household convenience, protecting food from spoiling and providing insulation. Aluminum-made beverage cans are widely manufactured; more than 100 billion are produced each year. The average human body contains about 35 milligrams (0.0012 ounce) of aluminum, but no known biological role has been established for it; it is, however, suspected to be a factor in the development of Alzheimer's disease. SEE ALSO Electrochemistry.

ductile: property of a substance that permits it to be drawn into wires

metallurgy: the science and technology of metals

Jean-Claude Bünzli

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Americium

95
Am
AMERICIUM
243

MELTING POINT: **994°C**
BOILING POINT: **2,607°C**
DENSITY: **13.6 g/cm^3**
MOST COMMON IONS: **Am^{3+}, AmO_2^{+}, AmO_2^{2+}**

Americium is a synthetic **radioelement**, first produced in 1944 via the bombardment of plutonium with neutrons by Glenn Seaborg and coworkers as part of the **Manhattan Project**. The first isolation of a compound of americium, $Am(OH)_3$, was achieved by B. B. Cunningham in the fall of 1945. Many radioactive **isotopes** of americium have been isolated and identified, having mass numbers that range from 237 through 247. The longest-lived americium isotope has mass number 243 and a half-life of 7,380 years. The ground state (outer orbital) electronic configuration for a neutral atom is $5f^2 6d 7s^2$. The outer *d* and *s* electrons are lost to form americium in its most stable **oxidation** state, +3, in solutions and compounds. Americium is the first of the actinide elements to appear in the characteristic stable trivalent state in solution. Americium, in the V and VI oxidation states, forms the linear oxo cations AmO_2^{+} and AmO_2^{2+}—chemical behavior that is characteristic of actinide elements.

Metallic americium has a face-centered cubic structure at its melting point and a double hexagonal closed-packed structure at temperatures below its melting point. The isotope americium-241 emits **α-particles** and γ-rays in its **radioactive decay**, and is a source of γ-radiation, used to measure the thickness of **metals**, coatings, degree of soil compaction, sediment concentration, and so on. The same isotope, mixed with beryllium, is used as a neutron source in oilwell logging and other applications. Americium-241

radioelement: a radioactive element; one in which the nucleus spontaneously decomposes (decays) producing α (alpha) and β (beta) particles and gamma rays

Manhattan Project: government project dedicated to creation of an atomic weapon; directed by General Leslie Groves

isotope: form of an atom that differs by the number of neutrons in the nucleus

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

α-particle: subatomic particle with 2+ charge and mass of 4; an He nucleus

radioactive decay: process involving emission of subatomic particles from the nucleus, typically accompanied by emission of very short wavelength electromagnetic radiation

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

has been used in smoke detectors; its α-emissions ionize the surrounding air and the resulting ions provoke electronic signals when they come into contact with electrodes in the detector. SEE ALSO Actinium; Berkelium; Einsteinium; Fermium; Lawrencium; Mendelevium; Neptunium; Nobelium; Plutonium; Protactinium; Rutherfordium; Seaborg, Glenn Theodore; Uranium.

Gregory R. Choppin

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Amino Acid

In 1953, Harold Urey and Stanley Miller carried out an amazing experiment in which they produced "molecules of life" from a mixture of gases that they proposed existed in a primordial earth. The experiments simulated what would happen when lightning strikes provided energy for chemical reactions in the atmosphere and suggested a hypothesis for how life might have developed on our planet. Amino acids were the vital molecules that formed in this experiment and supported this hypothesis for the origin of life.

functional group: portion of a compound with characteristic atoms acting as a group

carboxylic acid: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the $–CO_2H$ functional group

aqueous solution: homogenous mixture in which water is the solvent (primary component)

zwitterion: molecule that simultaneously contains a positive and a negative charge

carboxyl group: an organic functional group, –C(O)– found in aldehydes, ketones, and carboxylic acids

nonpolar: molecule, or portion of a molecule, that does not have a permanent, electric dipole

synthesis: combination of starting materials to form a desired product

An amino acid is a molecule that contains two **functional groups**, an amine and a **carboxylic acid**, as shown in Figure 1. In this illustration there is an additional group called the side chain, designated with an *R.* The variation seen in naturally occurring amino acids arises from differences in this side chain. The twenty naturally occurring molecules are listed in Table 1. In an **aqueous solution**, this structure may change so that a proton from the COOH transfers to the NH_2 and a **zwitterion** is formed. This structure depends on the pH of the solution. Most physiological systems fall into such a pH range so the zwitterion form of amino acids is the most stable form in the human body.

The stereochemistry of amino acids is also an important concept. The carbon atom marked α in Figure 1 is chiral, so an amino acid can be one of two enantiomers. Note that the structure shown in the illustration has the amine group on the right and the **carboxyl group** at the top. This configuration is designated the L form, and all naturally occurring amino acids have this form.

Amino acids are categorized into three groups based on the nature of the side chain. Nine of the amino acids have side chains that are **nonpolar**. Almost 50 percent of the amino acids that are present in proteins have nonpolar side chains. The second category of amino acid contains six different molecules that have polar side chains. Finally, a group of five amino acids have side chains that are not only polar, but charged.

The key chemical characteristic of amino acids is that they link together to form proteins. Because the COOH functional group is an acid and the NH_2 functional group is a base, the two ends of amino acids can readily react with each other. Protein **synthesis** is more complicated than a simple acid-base neutralization, but consider what happens when two amino

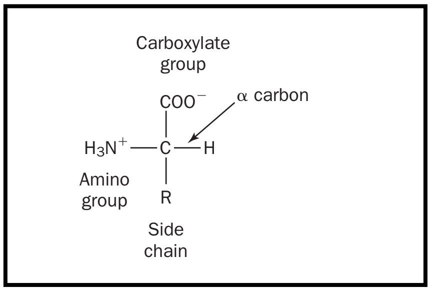

Figure 1.

THE TWENTY COMMON AMINO ACIDS FOUND IN PROTEINS

Name	One-Letter Abbreviation	Three-Letter Abbreviation
Glycine	G	Gly
Alanine	A	Ala
Valine	V	Val
Leucine	L	Leu
Isoleucine	I	Ile
Methionine	M	Met
Phenylalanine	F	Phe
Proline	P	Pro
Serine	S	Ser
Threonine	T	Thr
Cysteine	C	Cys
Asparagine	N	Asn
Glutamine	Q	Gln
Tyrosine	Y	Tyr
Tryptophan	W	Trp
Aspartate	D	Asp
Glutamate	E	Glu
Histidine	H	His
Lysine	K	Lys
Arginine	R	Arg

Table 1. The twenty common amino acids found in proteins.

acids react to form a peptide bond. The new molecule, now a dimer with two amino acid residues still has one end that is an acid and another end that is a base, so it is apparent that the process of forming a peptide bond with another amino acid could be repeated. If many amino acids are strung together, the result is a natural polymer—a protein. SEE ALSO PROTEINS; UREY, HAROLD; ZWITTERION.

Thomas A. Holme

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Analgesic ***See Acetaminophen; Acetylsalicylic Acid.***

Analytical Chemistry

Analytical chemistry is the branch of chemistry that deals with determining the identity and concentration of chemical substances (analytes). G. E. F. Lundell, an American chemist at the National Institute of Standards and Technology likened the questions that analytical chemists answer to the following one: What is the average mass of trout in this stream? To answer this question scientifically, one must devise a way to sample the population of trout in the stream in a representative way, perform the sampling (fishing), get rid of interfering species (e.g., bass, perch, walleye), weigh each trout, record the data, and calculate the average.

Analytical chemistry can be divided into subdisciplines based on the type of samples that are analyzed: atomic, molecular, or biological. Atomic analysis involves the identification and quantification of elements that often occur in complex mixtures. Analytical chemists are often asked to find the

A chemist measures concentrations in a urine sample.

concentration of manganese in a steel sample, for example. Molecular analysis involves the identification and determination of molecules. Analytical chemists are employed to assure that the caffeine concentration in soda is within the limits set by the U.S. Food and Drug Administration (FDA). Recently analytical chemists have worked with biologists to measure concentrations in biological systems. Currently research analytical chemists are working to devise techniques to determine the identity and concentration of all of the proteins in a cell.

What Analytical Chemists Do

Most analyses involve tasks similar to the above trout measurement. Chemists must reproducibly sample a population, remove interfering species, determine the concentration and record the results.

Analytical chemists use a variety of chemical and physical methods to determine identity and concentration. Purely chemical methods were developed in the nineteenth century and therefore are called classical methods. Physical methods involve determinations based on the amount of light absorbed or emitted by the analyte or on the strength of an electrical signal created by the analyte at an electrode.

Classical methods or quantitative analyses include gravimetry, where the amount of a substance is determined by the mass of product generated by a chemical reaction, and titrimetry, where concentration is determined by the volume of a **reagent** needed to completely react with the analyte. These methods are highly accurate and precise but require a sufficient amount of sample, and a concentration of analyte in the sample of at least 0.1 percent. Furthermore these analyses require the constant attention of a trained scientist.

reagent: chemical used to cause a specific chemical reaction

Physical or instrumental methods were extensively developed in the twentieth century and are gradually replacing classical methods. In *Principles of Instrumental Analysis*, three American chemists, Douglas Skoog, F. James Holler, and Timothy Nieman, detail many instrumental methods that use highly complex and often costly machines to determine the identity and concentration of analytes. While these methods often are not as accurate and precise as classical methods, they require much less sample and can determine concentrations much less than 0.1 percent. In fact, Richard Mathies, professor at the University of California at Berkeley, and coworkers recently described methods that can determine the presence of one molecule! In addition, instrumental methods often produce results more rapidly than chemical methods and are the methods of choice when a very large number of samples of the same kind have to be analyzed repetitiously, as in blood analyses.

History

Analytical chemistry began in the late eighteenth century with the work of French chemist Antoine-Laurent Lavoisier and others; the discipline was further developed in the nineteenth century by Carl Fresenius and Karl Friedrich Mohr. As a pharmacist's apprentice in Frankfurt, Germany, Fresenius developed an extensive qualitative analysis scheme that, when it was later published, served as the first textbook of analytical chemistry. He built a laboratory at his house that opened in 1848. Here he trained students in gravimetric techniques that he had developed. Mohr developed laboratory devices such as the pinch clamp burette and the volumetric pipette. He also devised a colorimetric endpoint for silver titrations. It was his 1855 book on titrimetry, *Lehrbuch der Chemisch-Analytischen Titromethode*, that generated widespread interest in the technique.

From Measurement to Concentration

Most modern analytical chemistry techniques are based on instrumental methods involving optical and electrical instruments. Elemental concentrations can be determined by measuring the amount of light absorbed or emitted by gas-phase atoms. Similarly, molecular concentrations are correlated with the emission or absorption of light by molecules in **aqueous solutions**. Electrodes, like the glass pH electrode, measure the electrical potential due to the presence of specific ions in solution. Finally, **chromatographic** methods separate the components of complex mixtures to determine the concentration of each component.

aqueous solution: homogenous mixture in which water is the solvent (primary component)

chromatography: the separation of the components of a mixture in one phase (the mobile phase) by passing it through another phase (the stationary phase) making use of the extent to which the components are absorbed by the stationary phase

Application

One application of instrumental methods is the determination of what drugs a person has taken twenty-four hours after the person took them. In a procedure detailed by Thomas P. Moyer at the Mayo Clinic, a 5-milliliter (0.17-ounce) sample of the patient's blood is analyzed by a technique called high performance liquid chromatography. The sample is treated and injected into a stream of water and methanol that is called a mobile phase. The mobile phase is pumped through a column of fine sand, where the particles of sand have been coated with a thin layer of an oil-like substance (octadecane). The molecules from the blood sample, including the drug, will spend part of their time adsorbed to the modified sand (stationary phase) and part of their time in the mobile phase. The molecules that spend the majority of their time in the mobile phase will it make through the column first.

perpendicular: condition in which two lines (or linear entities like chemical bonds) intersect at a 90-degree angle

To determine when the molecules have exited the column, an ultraviolet (UV) light is placed so that it is **perpendicular** to the flowing stream of mobile phase. The molecules in the blood sample will absorb the UV light and create a signal at the detector. The height of the signal will be proportional to the concentration of the drug in the urine. The time between the sample injection and passage through the column is reproducible and, by comparing it to the time observed when standard samples are used, permits component identification.

Recent Developments

Research is under way to develop techniques that can determine the presence of one atom or molecule in solution, to reduce the size of the instrumentation required, and to analyze the contents of a single cell. These new techniques hopefully will enable the early detection of disease, the remote sensing of a chemical spill, or the rapid analysis of water and air on space vehicles. SEE ALSO Lavoisier, Antoine; Measurement; Solution Chemistry.

G. Brent Dawson

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Androgen ***See Testosterone.***

Anfinsen, Christian

AMERICAN CHEMIST
1916–1995

Christian Boehmer Anfinsen was born in Monessen, Pennsylvania, on March 26, 1916. He earned a B.A. from Swarthmore College in 1937 and an M.S. from the University of Pennsylvania in 1939. In 1943 he received a Ph.D. in biochemistry from Harvard Medical School. He remained at Harvard for seven more years as an instructor and assistant professor of biological chemistry. In 1950 Anfinsen assumed the position of director of the Laboratory of Cellular Physiology and **Metabolism** at the National Heart Institute of the National Institutes of Health (NIH). This move led to a period of thirty years when he split his time between Harvard and the NIH until his retirement in 1981.

metabolism: the complete range of biochemical processes that take place within living organisms; comprises processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those which break down complex food molecules, thus liberating energy (catabolism)

Anfinsen began his work on the relationship between protein structure and enzyme function in the mid-1950s in collaboration with F. H. White and Michael Sela at the Weizmann Institute in Rehovot, Israel. This research on the enzyme ribonuclease led him to propose that the structure of the amino acids in sequence along the protein chain contains the information determining the tertiary structure of the enzyme. Anfinsen demonstrated that the denaturation of the enzyme was reversible. After the cleavage of **disulfide bonds** and disruption of tertiary structure, some proteins spontaneously refold to native forms and their function returns. Anfinsen's advanced explanations of this observation became widely accepted.

The pursuit of the tertiary protein structural problem led Anfinsen to the discovery of a microsomal enzyme that catalyzes sulfhydryl-disulfide interchange and accelerates the refolding of denatured proteins which contain disulfide bonds **in vitro**. The kinetics of this folding accounts for the rate of folding of newly synthesized proteins **in vivo**. It was shown, however, that the renaturation required very dilute solutions in many cases to avoid aggregation of the protein in place of proper folding.

The importance of Anfinsen's work and that of his followers is the impact it has had on understanding certain diseases that involve the folding of enzymes. Recent discoveries indicate that Alzheimer's disease, cystic fibrosis, mad cow disease, genetic emphysema, and some cancers are all based on some aspect of protein folding gone awry. These folding problems also cause difficulties with the proper naturation of synthetic proteins under development for use as pharmaceuticals. Although Anfinsen could not have known the importance of his discoveries in the 1960s, he was somewhat concerned that the breaking of the genetic **code** and discovery of the α-**helix** structure of **DNA** overshadowed the work on protein and enzyme structure and function. He was awarded the Nobel Prize in chemistry (along with American chemists Stanford Moore and William Howard Stein) in 1972 for his pioneering work on the structure of enzymes and the relationship between the **amino acid sequence** and enzyme function. Anfinsen died in 1995 at the age of seventy-nine.

Lawrence H. Brannigan

disulfide bond: bond in a complex substance that involves two bonding sulfur atoms, –S–S–

in vitro: Latin, meaning "in glass" and applied to experiments done under artificial conditions, that is, in a test tube

in vivo: Latin, meaning "in life" and applied to experiments conducted in a living cell or organism

code: mechanism to convey information on genes and genetic sequence

helix: form of a spiral or coil such as a corkscrew

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

amino acid sequence: twenty of the more than five hundred amino acids that are known to occur in nature are incorporated into a variety of proteins that are required for life processes; the sequence or order of the amino acids present determines the nature of the protein

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Antibiotics

Antibiotics are substances that inhibit the growth of microorganisms (anti**metabolites**) or their replication (a bacteriostatic effect). They were traditionally obtained by extracting them from **cultures** of microbes. However, most drugs on the market today are **semisynthetic** derivatives of natural

metabolites: products of biological activity that are important in metabolism

culture: living material developed in prepared nutrient media

semisynthetic: produced by synthesis from natural starting materials

A bottle of Amoxil, one brand name of semisynthetic penicillin amoxicillin.

products. Sulfa drugs, discovered in the 1930s, were the first antimicrobial agents put into clinical use. Unfortunately, many bacteria are not susceptible to **sulfonamides**, and with the outbreak of World War II came the need for other more potent antibacterial agents. The serendipitous discovery of penicillin is, without a doubt, the most celebrated breakthrough in the history of antibiotics. In the late 1920s, while working in a London hospital, Alexander Fleming observed a mold overtaking a culture of staphylococcus bacteria he was growing in his laboratory. He extracted juices from the mold and, in 1929, reported that the extract, which he called penicillin, had antiseptic (anti-infectious) activity. The fungus was subsequently identified as *Penicillium notatum* (now called *Penicillium chrysogenum*). It was not until the 1940s that penicillin was put into clinical use. Howard W. Florey, professor of pathology at Oxford's Sir William Dunn School of Pathology, and Ernst B. Chain are credited with culturing the fungus and producing the first significant quantities of penicillin for treating bacterial infections. In 1945 Fleming, Florey, and Chain received the Nobel Prize in physiology or medicine "for the discovery of penicillin and its curative effect in various infectious diseases."

sulfonamides: first of a series of drugs used for the prevention and cure of bacterial infections in humans; sulfanomides are amides of sulfuric acids and contain the $-SO_2NRR_1$ group

Extracts from microorganisms are still an important source of antibiotics today. Clinically, antibiotics are described as possessing either broad- or narrow-spectrum activity. Bacteria are classified based on a staining technique developed by Danish microbiologist Hans Christian Gram. The bacterial cell walls of gram-positive bacteria stain blue when treated with either crystal violet or methylene blue, while gram-negative bacteria do not retain the stain and appear red. Broad-spectrum antibiotics are capable of inhibiting both gram-positive and gram-negative bacterial cultures. Gram-positive bacteria have simpler cell walls than gram-negative strains and are susceptible to less toxic, narrow-spectrum antibiotics.

β-Lactam Antibiotics

A variety of penicillins have been produced by the fermentation of *Penicillium chrysogenum* in the presence of different nutrients. Penicillin G (benzylpenicillin; see Figure 1) predominates when the culture medium is rich in phenylacetic acid, whereas the incorporation of phenoxyacetic acid favors penicillin V (phenoxymethylpenicillin). Semisynthetic penicillins, such as ampicillin and amoxicillin, are prepared by replacing the aromatic side chain of biosynthetically derived penicillins with other chemical groups. All penicillins are *β*-lactam (see Figure 2) antibiotics and have the same mechanism of action: They inhibit bacterial cell wall **biosynthesis**.

biosynthesis: formation of a chemical substance by a living organism

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

Bacterial cell walls differ from mammalian cell walls and are therefore attractive targets for antibiotics. Bacterial cell walls contain *β*-lactam **receptors**, known as penicillin-binding proteins (PBPs). *β*-Lactam antibiotics

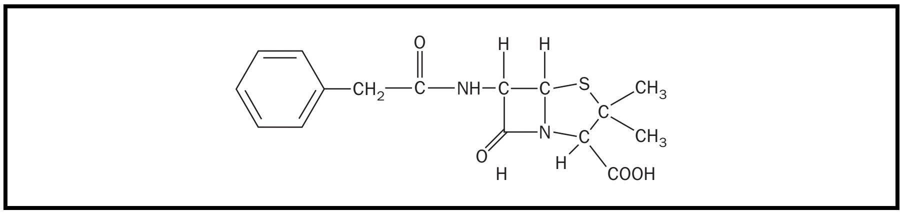


Figure 1. Penicillin G.

bind to the PBPs of bacterial cell walls and prevent their growth and repair. Widespread use of penicillin, however, has led to **drug resistance**. Because microorganisms multiply rapidly, strains of bacteria with enzymes capable of hydrolyzing β-lactam rings (β-lactamases) have evolved. β-lactamases are capable of inactivating β-lactam antibiotics before they bind to receptors on cell walls. As a result, physicians sometimes prescribe β-lactamase inhibitors to patients on penicillin therapy to circumvent drug inactivation by bacterial enzymes.

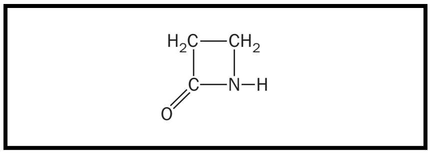


Figure 2. The β-lactam ring.

drug resistance: ability to prevent the action of a particular chemical substance

The cephalosporins comprise another important class of broad-spectrum β-lactam antibiotics. Cephalosporins were originally isolated from cultures of *Cephalosporium acremonium*. Cephalexin (Keflex) is a semisynthetic cephalosporin frequently prescribed to treat ear and skin infections caused by staphylococci or streptococci.

Antibiotics That Inhibit Protein Synthesis

There are also a large number of antibiotics structurally unrelated to penicillins and cephalosporins. These compounds exert their antimicrobial activity by inhibiting protein biosynthesis. In 1947 chloramphenicol (see Figure 3) was isolated from cultures of *Streptomyces venezuelae*. It is a broad-spectrum bacteriostatic agent that interferes with protein synthesis by binding to bacterial **ribosomes**. The use of chloramphenicol in humans is limited because of the drug's toxicity. It inhibits liver enzymes and suppresses red blood cell formation.

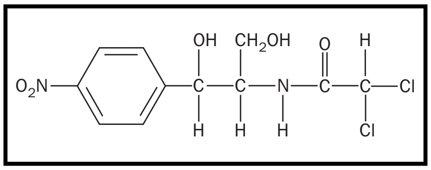


Figure 3. Chloramphenicol.

ribosome: large complex of proteins used to convert amino acids into proteins

streptomycin: antibiotic produced by soil bacteria of genus *Streptomyces*

Aminoglycosides are amino sugars with broad-spectrum antibiotic activity. **Streptomycin**, isolated from *Streptomyces griseus*, was the first aminoglycoside antibiotic discovered. Although streptomycin initially proved to be a potent agent against gram-negative bacteria, rapid microbial resistance to the drug has limited its use and today streptomycin is generally administered in combination with other antibiotics. Neomycin is a broad-spectrum aminoglycoside antibiotic isolated from *Streptomyces fradiae*. However, because of the adverse effects of neomycin on the kidneys and ear, its use in humans is restricted to topical applications, often in combination with other antibiotics or corticosteroids. Concerns over the potential risks associated with aminoglycoside therapy, chiefly nephrotoxicity (kidney disease) and ototoxicity (damage to the ear canal), have diminished their use.

erythromycin: antibiotic used to treat infections

macrolide: substance with a large ring lactone structure

ester: organic species containing a carbon atom attached to three moieties: an O via a double bond, an O attached to another carbon atom or chain, and an H atom or C chain; a compound with the general formula RC(O)OR′

In 1952 the broad-spectrum antibiotic **erythromycin** was isolated from cultures of *Streptomyces erythreus* (later renamed *Saccharopolyspora erythraea*). The erythromycins are **macrolide** antibiotics that typically have a 12-, 14-, or 16-membered cyclic backbone which is a lactone (a cyclic **ester**; see Figure 4).

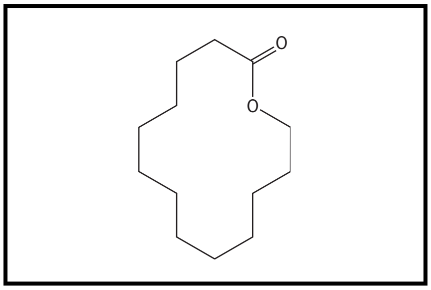
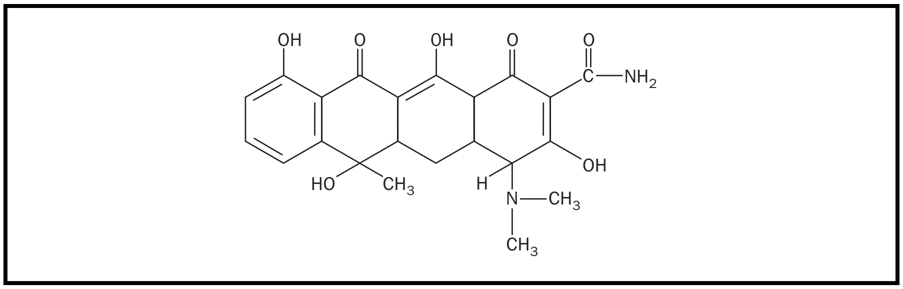


Figure 4. 14-membered lactone.

Erythromycin A, the major fermentation component of *S. erythraea*, is a 14-membered ring macrolide that is used by medicinal chemists as the foundation for building semisynthetic derivatives of erythromycin antibiotics. (Macrolides inhibit bacteria by interfering with microbial protein biosynthesis.) Semisynthetic macrolides are popular with clinicians because they can be administered orally and have relatively low toxicity. They are often used to treat respiratory tract infections, and have been especially effective against conditions such as Legionnaires' disease and community-acquired pneumonia. Erythromycin therapy is often prescribed for individuals allergic to penicillin. One of the most widely used macrolide antibiotics

Figure 5. Tetracycline.



derived from erythromycin A is azithromycin (Zithromax). Resistance to macrolide antibiotics generally involves mutations of bacterial ribosomal **RNA** that prevent macrolide binding.

RNA: ribonucleic acid, a natural polymer used to translate genetic information in the nucleus into a template for the construction of proteins

In the late 1940s and early 1950s a series of tetracycline antibiotics was isolated from cultures of streptomyces. All tetracyclines consist of four fused 6-membered rings (see Figure 5). Tetracyclines are broad-spectrum antibiotics that interfere with protein synthesis by binding to bacterial ribosomes. Unfortunately, the frequent use of tetracyclines to treat minor infections has led to resistance among previously susceptible strains of bacteria (pneumococci and staphylococci). Resistance to tetracyclines occurs when bacteria either develop proteins that prevent ribosomal binding by tetracyclines, or synthesize enzymes capable of inactivating tetracyclines.

Widespread use of antibiotics and rapid microbial evolution have led to highly resistant bacterial strains. Although most scientists no longer believe that a single drug will be developed to wipe out all infectious diseases, there is increasing demand for new antimicrobial agents. Currently, combined drug therapy appears to be the most effective means of circumventing microbial resistance to antibiotics. SEE ALSO FLEMING, ALEXANDER; PENICILLIN; SULFA DRUGS.

Nanette M. Wachter

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Anti-inflammatory *See Ibuprofen.*

51
Sb
ANTIMONY
121.75

Antimony

MELTING POINT: **630°C**
BOILING POINT: **1,750°C**
DENSITY: **6.684 g/cm^3**
MOST COMMON IONS: **Sb^{3+}, SbO^{+}**

Antimony is a **metalloid** element, or a semimetal, its chemical behavior being between those of metals and nonmetals. It is a substance that was known in the ancient world. Antimony sulfide was used as cosmetic eye paint in ancient Egypt, and artifacts composed of almost pure antimony have been found at archaeological sites. Pure antimony is silvery gray and metallic-looking. If antimony is melted and then allowed to crystallize, it manifests a characteristic pattern known as the star of antimony.

metalloid: elements that exhibit properties that are between those of metals and nonmetals; generally considered to include boron, silicon, germanium, arsensic, antimony, tellurium, and polonium

There are two stable **isotopes** of antimony: ^{121}Sb (57.25%) and ^{123}Sb (42.75%), leading to an **atomic weight** calculation of 121.75. It is not abundant in Earth's crust (an abundance of only 0.2 parts per million), but several antimony compounds occur as minerals, including stibnite, Sb_2S_3, the cosmetic mentioned above. Antimony is also a common impurity in ores of copper, lead, and silver. When antimony is heated in air it burns vigorously, forming the white oxide Sb_2O_3.

isotope: form of an atom that differs by the number of neutrons in the nucleus

atomic weight: weight of a single atom of an element in atomic mass units (AMU)

Alloys of antimony and other metals have many applications. Alloys of antimony and lead are much harder than pure lead and are used in the making of low-friction bearings, lead-acid batteries, and printing type metal. Alloys of antimony, lead, and tin have the unusual property of expanding upon **crystallization** from a melt, and thus fill all recesses of the molds used to make printing type. Antimony compounds are used as flame-retardants and in paints, glazes for ceramics, specialty glasses, and semiconductor materials. The sulfide Sb_2S_5 is a rubber additive. Tartar emetic, a complex antimony tartrate of formula $K[C_4H_2O_5Sb(OH)_2] \cdot \frac{1}{2}H_2O$ has been used medically for over three hundred years.

alloy: mixture of two or more elements, at least one of which is a metal

crystallization: process of producing crystals of a substance when a saturated solution in an appropriate solvent is either cooled or some solvent is removed by evaporation

Harold Goldwhite

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Antipyretic ***See Acetaminophen.***

Argon

MELTING POINT: **−189.3°C**
BOILING POINT: **−185.8°C**
DENSITY: **Unknown**
MOST COMMON IONS: **None known**

18
Ar
ARGON
39.948

Argon is an odorless, colorless monatomic gas at room temperature. Although it constitutes about 1 percent of the atmosphere, it was not discovered until 1894, when John William Strutt (Lord Rayleigh) and William Ramsay isolated it from the more reactive components of air. Argon is the most abundant **noble gas** and it was the first to be found. Its discovery prompted confusion over how to fit it into the periodic table: No other **inert**, monatomic gases were then known. Furthermore, its atomic weight placed it between the very reactive **metals** potassium and calcium. Ramsay suggested a new family of elements (the noble gases), and had isolated four additional members by 1898.

noble gas: element characterized by inert nature; located in the rightmost column in the Periodic Table

inert: incapable of reacting with another substance

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

The element takes its name from the Greek *argos*, meaning slow or lazy, because it is extremely unreactive. Indeed, its first stable neutral compound, argon fluorohydride (HArF), was not reported until 2000, and it exists only within a low-temperature solid matrix. Because argon in effect does not form chemical bonds, it is frequently used in the research of nonbonding chemical interactions, such as van der Waals forces and surface adsorption. Inertness makes argon useful in incandescent light bulbs: It protects the hot filament from **oxidation** and slows its evaporation. It is used to generate an inert atmosphere for other chemical reactions in industry and research. Argon is the glowing gas that occupies some fluorescent tubes, and it is an insulating filler in some double-pane thermal windows.

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

The principal **isotope** of argon is ^{40}Ar (99.6% abundance); it has two other stable isotopes, ^{36}Ar (0.3%) and ^{38}Ar (0.1%). Argon-40 is formed by β-decay of the long-lived potassium isotope ^{39}K. SEE ALSO NOBLE GASES; RAMSAY, WILLIAM; STRUTT, JOHN.

isotope: form of an atom that differs by the number of neutrons in the nucleus

Carmen Giunta

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Internet Resources

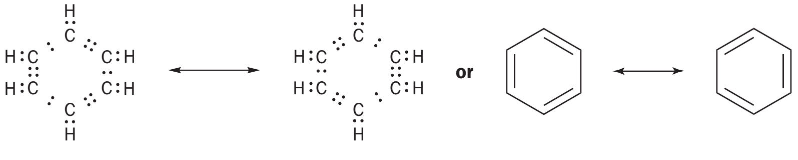
WebElements™ Periodic Table Available from <http://www.webelements.com/>.

Aromaticity

The literal meaning of "aromaticity" is "fragrance," but the word has a special meaning in chemistry. Aromaticity has to do with the unusual stability of the compound benzene and its derivatives, as well as certain other unsaturated ring compounds. The structures of these compounds are often shown to contain double bonds, but they do not actually behave like double bonds. For example, **reagents** such as bromine react with benzene by substitution rather than addition. Benzene and its derivatives had long been referred to as aromatic because of their distinctive odors.

reagent: chemical used to cause a specific chemical reaction

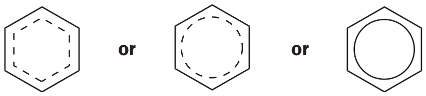
The structure for benzene is often shown as a hybrid of the two Kekulé formulas:



(1)

The double-headed "resonance arrow" does not signify an **equilibrium** in which the two structures are very rapidly shifting back and forth (as was once thought to be the case). Instead it means that the actual structure is not like either of the two Kekulé structures but is rather a *resonance hybrid* of the two. (The length of a carbon-carbon single bond is 1.54 Angstroms, and that of a double bond, 1.33 Angstroms. X-ray analysis shows that in benzene all the C-C distances are identical and equal to 1.40 Angstroms.) The C-C bonds in benzene are neither single nor double bonds, but something in between. Perhaps the benzene ring is best represented as follows:

equilibrium: condition in which two opposite reactions are occurring at the same speed, so that concentrations of products and reactants do not change



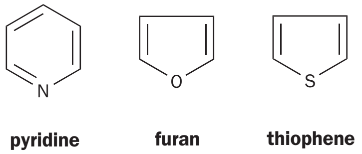
(2)

The simple circle-inscribed hexagon on the right has become a popular alternative to the classical Kekulé structure and is probably the benzene formula most widely used.

The aromaticity of the benzene ring can be assessed by measuring its "resonance energy." One way to do this is by measuring its heat of hydrogenation. When hydrogen is added to a double bond, the heat of reaction is about 120 kilojoules per mole. If benzene really had three double bonds, its heat of hydrogenation should be about 360 kilojoules per mole. In contrast, its actual heat of hydrogenation is only about 210 kilojoules per mole. This is 150 kilojoules per mole less than expected if benzene actually contained three double bonds. The 150 kilojoules per mole is a measure of the extra stability that benzene has because its π electrons are **delocalized**. (The π electrons are those involved in the second bonding pair of the double bond.)

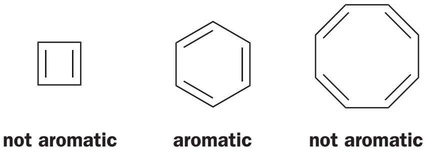
delocalized: of a type of electron that can be shared by more than one orbital or atom

Benzene is not the only compound that exhibits such unusual stability. The following heterocyclic unsaturated ring compounds also exhibit aromatic behavior:



(3)

In 1890 Eugen Bamberger was the first to suggest that six was the magic number of "potential valences" that caused an unsaturated ring to be aromatic. In 1899 Johannes Thiele suggested that any ring that had a completely conjugated set of double bonds around the ring should be aromatic; when cyclobutadiene and cyclooctatetraene were prepared, however, neither turned out to be aromatic.

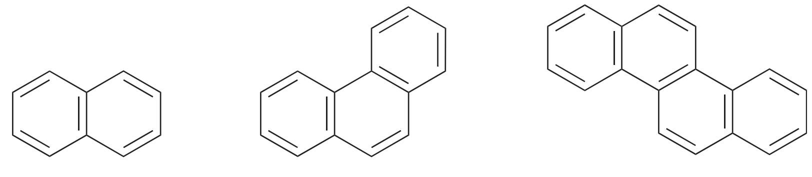


(4)

In the 1920s Armit and Robinson pointed out that it was conjugated ring systems with six multiple bonding electrons that seemed to have special stability. They spoke of an "aromatic sextet" of electrons as being necessary for aromaticity.

Hückel's Rule

German physicist Erich Hückel used the molecular orbital theory to explain the stability of benzene and other aromatic compounds. Hückel's rule determines the number of π electrons that give stability to an unsaturated planar ring according to the formula 4n + 2. For benzene and its analogs, n = 1; therefore, 4n + 2 = 6 (the aromatic sextet). The rule was calculated for single ring molecules and does not generally apply to multiring systems. Although many polycyclic aromatic molecules do follow Hückel's rule (Figure 5), some do not (Figure 6). For example, pyrene has sixteen π electrons and coronene has twenty-four, but both are aromatic.

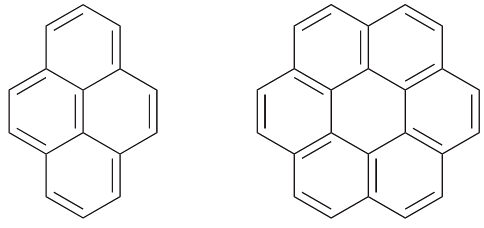


(5)

naphthalene
(n = 2)
$4n + 2 = 10$

phenanthrene
(n = 3)
$4n + 2 = 14$

chrysene
(n = 4)
$4n + 2 = 18$



(6)

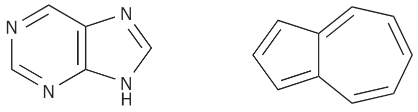
pyrene

coronene

The molecules in Figures 5 and 6 all have fused rings (in which some carbon atoms are part of two or more rings). In general, molecules with fused rings tend to be less stable than single aromatic rings.

isomer: substance with an identical molecular formula but a different structural formula

Aromatic polycyclic compounds need not contain contain benzene rings. For example, purine, which contains two fused heterocyclic rings, is aromatic. Azulene, named for its deep blue color, is also aromatic, although one ring has five carbon atoms and the other has seven. It is not, however, as aromatic as its **isomer** naphthalene, which has two fused benzene rings.



(7)

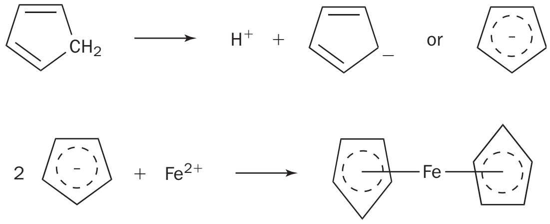
purine

azulene

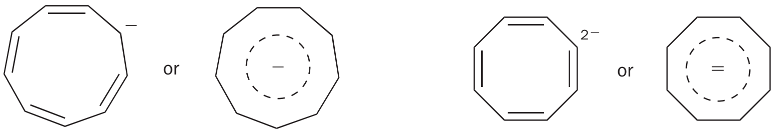
Aromatic Ions

anion: negatively charged chemical unit, like Cl^-, CO_3^{2-}, or NO_3^-

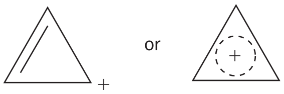
Cyclopentadiene is an acidic hydrocarbon. In 1928 English chemist Christopher Ingold suggested that this was because the cyclopentadienyl **anion** had an aromatic sextet of electrons. This was the first case of aromatic character being attributed to an ion. An interesting derivative made from this very stable carbanion was *ferrocene* (discovered in 1951).

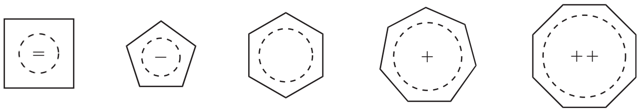


(8)


(9)

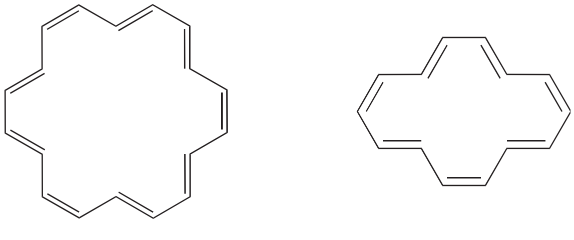
In 1945 Michael J. S. Dewar suggested that the *tropylium* ion (the cation derived from cycloheptatriene) should also be aromatic (Figure 9). This was confirmed in 1954; since then, the dianion of butadiene and the dication of cyclooctatetraene have also been shown to be aromatic. Like benzene, all four of these ions are planar rings with six π electrons. According to Hückel's rule the cyclopropene cation should also exhibit aromaticity, and it does. (In this case $n = 0$, and $4n + 2 = 2$.) The planar anion of cyclononatetraene and the dianion of cyclooctatetraene should also be aromatic ($n = 2$, and $4n + 2 = 10$), and both of them are.


(10)


(11)

Other Nonclassical Aromatic Compounds

Hückel's rule also predicted aromatic stability for certain large ring polyenes called *annulenes.* Fully conjugated [14]-annulene and [18]-annulene do have aromatic properties, especially at lower temperatures (Figure 12), as does [22]-annulene. They contain fourteen, eighteen, and twenty-two π electrons, respectively, corresponding to values of $4n + 2$ where $n = 3$, 4, and 5, and all the molecules are planar. The [12]-, [16]-, [20]-, and [24]-annulenes, on the other hand, do not obey Hückel's rule, and they are not aromatic.


(12)

[18] - annulene **[14] - annulene**

Although aromatic rings are normally planar, with uninterrupted conjugation, that is not always the case. When cyclooctatetraene is treated with acid, the *homotropylium* ion is formed. It has six electrons in a seven-membered ring that has a CH_2 group lying in a **perpendicular** plane, yet is aromatic.

perpendicular: condition in which two lines (or linear entities like chemical bonds) intersect at a 90-degree angle

What Is Aromaticity?

At one time the term "aromatic" applied only to benzene. To some chemists it still simply means "like benzene." An aromatic molecule is a planar ring with a circular cloud of delocalized π electrons. It is an unsaturated cyclic molecule stabilized by resonance. It is a very stable unsaturated ring that reacts by substitution instead of addition. Or, according to Hückel's rule, it is a fully conjugated unsaturated ring that has $4n + 2$ π electrons.

How do you know whether or not a molecule is aromatic? If an unsaturated ring compound is aromatic, its heat of hydrogenation and its heat of **combustion** will both be considerably less than they would be if double bonds were present. Its bond distances (as measured by x-ray or electron diffraction or by microwave **spectroscopy**) will be uniform. It will have longer wavelength absorption bands in the ultraviolet region of the spectrum. An aromatic compound will have **diamagnetic** anisotropy (meaning that a crystal will have more magnetic susceptibility along one axis than the other two). It will also be *diatropic*; in other words, because its π electrons are delocalized, protons attached to the ring will be shifted downfield in the nuclear magnetic resonance (NMR) spectrum from where they would be if double bonds were present. In fact, NMR can be used to measure the degree of aromaticity in a molecule by how well its ring of π electrons can sustain an induced "ring current." SEE ALSO NUCLEAR MAGNETIC RESONANCE.

combustion: burning, the reaction with oxygen

spectroscopy: use of electromagnetic radiation to analyze the chemical composition of materials

diamagnetic: property of a substance that causes it to be repelled by a magnetic field

Doris K. Kolb

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Arrhenius, Svante

COFOUNDER OF MODERN PHYSICAL CHEMISTRY
1859–1927

Swedish chemist Svante August Arrhenius, recipient of the 1903 Nobel Prize in chemistry, "in recognition of the extraordinary services he has rendered to the advancement of chemistry by his electrolytic theory of dissociation."

Svante August Arrhenius, born in Vik, Sweden, is regarded as the cofounder of modern physical chemistry. For his theory of electrolytic dissociation, Arrhenius received the Nobel Prize in chemistry in 1903. He also made important contributions to chemical kinetics and many other branches of science.

In 1884 Arrhenius obtained his Ph.D. from the University of Uppsala with a thesis on the conductivities of electrolytic solutions. Although poorly rated by his examiners, his thesis attracted the attention of the most distinguished physicists and physical chemists in Europe at the time. Arrhenius collaborated with a number of them from 1886 until 1890. Based on his international reputation, he secured a post at the Technical High School in Stockholm, first as a lecturer, then as a professor, and finally as its rector. He later became director of the new physical chemistry institute of the Nobel Foundation in 1905. By that time, his interests had already shifted toward other fields of science.

Arrhenius is mainly known for his equation describing the temperature dependence of chemical reaction rates:

$$k = A \exp(-E/RT)$$

with k being the reaction rate constant, A a preexponential factor, E the activation energy, R the gas constant, and T the absolute temperature. Although the equation was first formulated by Dutch physical chemist Jacobus Hendricus van't Hoff in 1884, Arrhenius provided the interpretation of it that is still in use today. He suggested that the crucial step in a chemical reaction was the formation of activated molecules from the reactant molecules and that both states were in **equilibrium**, separated from each other by the activation energy E. Accordingly, he explained the temperature dependence of the reaction rate as a change of equilibrium, such that with increasing temperature more activated molecules were formed to undergo reaction. Furthermore, plotting the experimental results of $\ln k$ against $1/T$ (the so-called Arrhenius plot) yielded in many cases a straight line, from the slope of which one could easily calculate the activation energy E.

equilibrium: condition in which two opposite reactions are occurring at the same speed, so that concentrations of products and reactants do not change

Arrhenius's most famous contribution, making him with the German physical chemist Friedrich Wilhelm Ostwald and van't Hoff a cofounder of modern physical chemistry, was his theory of electrolytic dissociation. Electrolytes are substances such as salts, acids, and bases that conduct electric current in solutions. Arrhenius suggested that every electrolyte, once dissolved in a solvent like water, dissociated into oppositely charged ions to a certain degree that depended on its nature and overall concentration. Before this explanation, chemists had continued to believe that electrolytes dissolved as uncharged molecules that could be separated only by strong electric forces, such as in electrolysis. Although the forces for electrolytic dissociation remained unclear for some time, Arrhenius's assumption could explain a wide range of phenomena and laws beyond electrochemistry. This included Raoult's laws of vapor pressure lowering and freezing point depression, Ostwald's dilution law, and van't Hoff's law of osmotic pressure of solutions. As Ostwald later showed in his acid-base theory, it also provided a quantitative understanding of the chemical activities of electrolytes in solution.

In his later years, Arrhenius applied the concepts of physical chemistry and physics to many other branches of science, including biochemistry, geo- and cosmic physics, and meteorology. In retrospect, his most remarkable contribution was perhaps his model of the **greenhouse effect**, according to which the temperature of Earth's lower atmosphere is determined by the concentration of carbon dioxide. Earth's surface, after being warmed by sunlight, emits energy in the form of infrared radiation, which is absorbed by molecules in the atmosphere, particularly carbon dioxide; the absorption of infrared radiation leads to heat. At that time, the greenhouse effect model was used to explain the glacial periods, rather than any climatic changes induced by the human production of carbon dioxide, as is the case today. SEE ALSO GLOBAL WARMING; OSTWALD, FRIEDRICH WILHELM; VAN'T HOFF, JACOBUS.

greenhouse effect: presence of carbon dioxide in the atmosphere prevents heat from escaping, thereby raising Earth's temperature

Joachim Schummer

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33
As
ARSENIC
74.9216

Arsenic

MELTING POINT: 817°C
BOILING POINT: 613°C
DENSITY: 5.72 g/cm^3
MOST COMMON IONS: As^{3+}, AsO_2^-

Arsenic is the twentieth most abundant element in Earth's crust, averaging a concentration of approximately 2 ppm. Arsenopyrite (FeAsS) is its most common mineral. Arsenic occurs widely in nature, and most abundantly in sulfide ores and the products of volcanic eruptions. Arsenic concentrations in rock and soil are highly variable; the highest concentrations are in hydrothermal sulfide mineralization areas.

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

isotope: form of an atom that differs by the number of neutrons in the nucleus

Arsenic has two common **oxidation** states: +5, the predominant one, and the less thermodynamically stable +3. Arsenic has twenty-three **isotopes**; of these, one (mass 75) is stable. The other isotopes have very short half-lives.

Trace amounts of arsenic occur in groundwater; it may cause human cancers at concentrations in drinking water of about 300 ppb. The U.S. Environmental Protection Agency (EPA) has proposed lowering the maximum allowable arsenic concentration in U.S. drinking water from 50 to 5 ppb. The latter lower limit is still controversial.

The properties of arsenic sulfides were known to physicians and "professional poisoners" in the fifth century B.C.E. Albertus Magnus (1193–1280) is credited with having isolated elemental arsenic by heating auripigment (As_2S_3) with soap.

metallurgy: the science and technology of metals

Beneficial effects of arsenic compounds have been known for a very long time. Arsenic was important in the development of **metallurgy** at the beginning of the Bronze Age, and later as a pigment and as an incendiary warfare ingredient. Since ancient and classical times arsenic formulations have been prescribed to cure diseases.

Historically arsenic compounds were alchemical ingredients and the art of secret poisoning was a part of the social and political life of many societies. Arsenic toxicity resulted in the deaths of painters who mixed arsenic pigments.

Between 1850 and 1950 humans were habitually exposed to arsenic in medicine, food, air, and water. Consumer products of the period that contained arsenic included pigments, medicated soaps, embalming solutions, adhesive envelopes, glass, fly-powder, and rat poison.

ferrous: older name for iron in the +2 oxidation state

alloy: mixture of two or more elements, at least one of which is a metal

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

smelting: process by which ores are reduced in the production of metals

Currently arsenic is a part of wood preservatives, some pesticides, non**ferrous alloys**, and semiconductor manufacture. Arsenic may be released into the environment from **metal smelting** and coal burning. SEE ALSO Toxicity.

Jeffrey C. Reid

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Artificial Sweeteners

There are presently four artificial, or synthetic, sweeteners that have been approved by the U.S. Food and Drug Administration (FDA): saccharin, aspartame, acesulfame-K, and sucralose. People use artificial sweeteners because they suffer from diseases such as diabetes mellitus, because they are concerned about dental caries and periodontal disease, or because they wish to lose or to avoid gaining weight. Artificial sweeteners in very small quantities give foods sweetness, and most are not metabolized, meaning that the artificial sweeteners themselves furnish zero dietary calories.

Sweetener Molecules and Sweetness

Sucrose and most artificial sweeteners are chemically quite dissimilar. Sucrose ($C_{12}H_{22}O_{11}$), the most common "natural" sweetener, is a disaccharide composed of the **monosaccharides glucose** and fructose. Saccharin has the formula $C_7H_5O_3NS$. Aspartame ($C_{13}H_{18}O_5N_2$), L-aspartyl-L-phenylalanine methyl **ester**, is the methyl ester of a dipeptide. Acesulfame-K has the formula $C_5H_6O_3NS$. Sucralose ($C_{11}H_{19}O_8Cl_3$) is prepared from sucrose via the substitution of three chloride groups for three hydroxyl groups. The molecular structures of sucrose, saccharin, aspartame, acesulfame-K, and sucralose are shown in Figure 1.

A sweetener must be soluble in water and the molecule must bind readily to a specific kind of **receptor** molecule at the surface of the tongue. The receptor is coupled to a G-protein, which dissociates when the sweetener binds to the receptor, activating a nearby enzyme, and triggering a sequence of events resulting in signals that are carried to and interpreted by the brain. The sweetness "signal" depends on this interaction between receptor and sweetener. The importance of molecular shape to sweetness is illustrated by the case of aspartame, as its stereo **isomer**, L-aspartyl-D-phenylalanine methyl ester, has a bitter, not a sweet, taste.

monosaccharide: one class of the natural products called carbohydrates with the general formula $C_x(H_2O)_y$; monosaccharides have a weak sweet taste, are readily soluble in water, and are called sugars

glucose: common hexose monosaccharide; monomer of starch and cellulose; also called grape sugar, blood sugar, or dextrose

ester: organic species containing a carbon atom attached to three moieties: an O via a double bond, an O attached to another carbon atom or chain, and an H atom or C chain; a compound with the general formula $RC(O)OR^1$

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

isomer: substance with an identical molecular formula but a different structural formula

Discovery, Sweetness, and Metabolic Products

Saccharin was the first artificial sweetener, discovered in 1879 by Constantin Fahlberg at Johns Hopkins University. The Monsanto Chemical Works was incorporated in 1901 to produce saccharin in the United States. Saccharin is easy to make, stable when heated, and is approximately 300 times sweeter than sucrose when equal quantities are compared. One common saccharin product is Sweet and Low.

Saccharin does not accumulate in body tissues. Controversy over the use of saccharin has existed for over a century. In the 1960s and early 1970s saccharin and/or its impurities were shown to cause bladder cancer in rats.

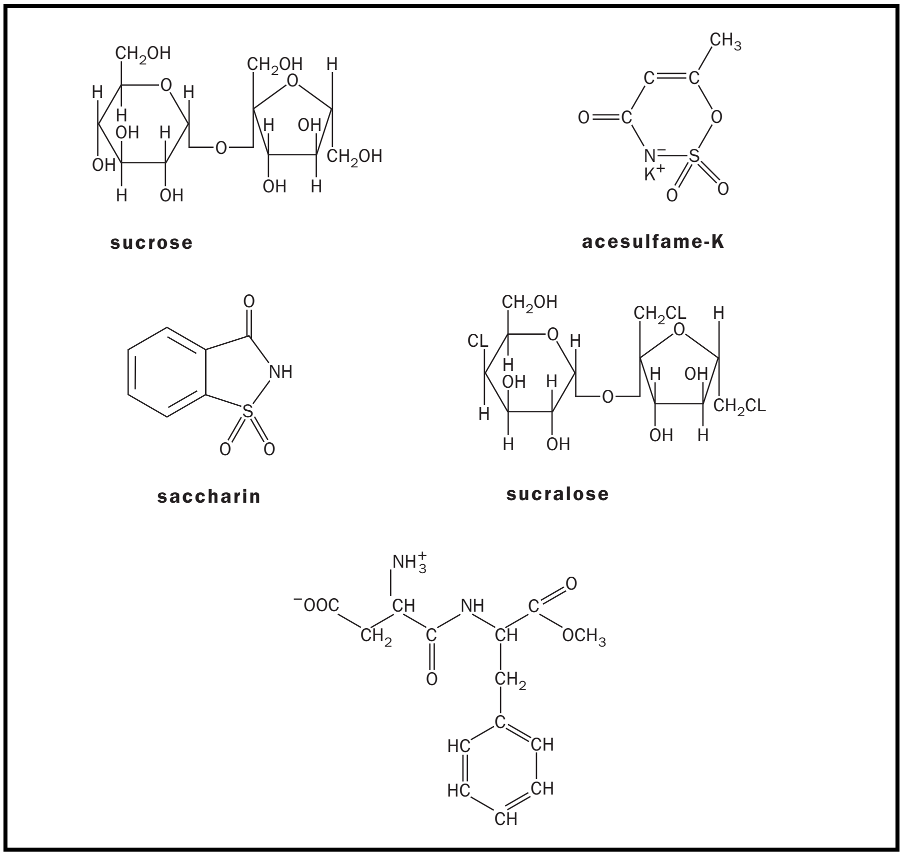

Figure 1. Molecular structures of sucrose and FDA-approved artificial sweetners.

In 1977 a Canadian study concluded that saccharin was the causative agent. Saccharin was banned in Canada. At about the same time the FDA proposed to limit the use of saccharin, but public outcry was so great that the U.S. Congress placed a moratorium on bans of saccharin until further studies were completed. The original moratorium was in effect for two years but has been continually extended to the present day.

Aspartame was discovered in 1965 by James Schlatter at G.D. Searle & Company. Aspartame is relatively easy to make and is approximately 200 times sweeter than sucrose. It is most commonly sold as NutraSweet and Equal. It is less stable than saccharin and breaks down above 29.44°C (85°F). In the body, aspartame is broken down into/absorbed as products that include aspartate, phenylalanine, and methanol. Phenylalanine is toxic to individuals who are homozygous (having identical genes in homologous chromosomes) for phenylketonuria, a genetic disease wherein individuals cannot **catabolize** phenylalanine. Phenylketonuria causes mental retardation. Products containing aspartame must therefore be labeled for phenylalanine. The FDA considers aspartame to be one of the most thoroughly studied and tested food additives and has judged it to be safe. Controversy still lingers with respect to the effects of aspartame's breakdown products—phenylalanine and aspartate, as well as methanol and its breakdown products **formaldehyde** and formate.

catabolism: metabolic process involving breakdown of a molecule into smaller ones resulting in a release of energy

formaldehyde: name given to the simplest aldehyde HC(O)H, and it contains the −C(O)H functional group

Acesulfame-K was discovered in 1967 by scientists working at Hoechst AG. It is also called Sunett. It is approximately 200 times sweeter than sugar. It has a long shelf life and does not break down in foods that are cooked or

Artificial sweeteners, such as those in diet sodas, contain no calories and are used by dieters and diabetics.

baked. Over ninety studies have been completed that have concluded that acesulfame-K is safe.

Sucralose was discovered in 1976 by researchers at Tate & Lyle PLC. It is also called Splenda. Sucralose is approximately 600 times sweeter than sugar and is stable at high temperatures. It was approved by the FDA in 1998–1999, and it is supported by a safety database of more than 110 studies. Concerns persist, including concerns over possible side effects associated with breakdown products (which include chlorine and 1,6-dichlorofructose), shrunken thymus glands (and their impacts on the immune system), and unanticipated effects that may not have manifested during the short time that sucralose has been used. SEE ALSO Toxicity.

Vivienne A. Whitworth

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Aspertame *See Artificial Sweetners.*

Aspirin *See Acetylsalicyclic Acid.*

Ascorbic Acid

Ascorbic acid or **vitamin** C is an **antiscorbutic** agent. Scurvy is a disease that potentially ranks as the second most important nutritional deficiency, after protein-calorie malnutrition. Scurvy, once common in among sailors, causes bleeding and inflamed gums, loose teeth, poor wound healing, pain in the joints, muscle wasting, etc. The structure of vitamin C is simple (see Figure 1), resembling a monosaccharide, and most animals are able to synthesize ascorbic acid. Only primates, guinea pigs, and some fruit bats have lost the ability to synthesize it.

Vitamins are organic molecules that mainly function as catalysts for reactions in the body. A **catalyst** is a substance that allows a chemical reaction to occur using less energy and less time than it would take under normal conditions.

Vitamin C is water-soluble and very important to all humans because it is vital to the production of collagen. Inside the cell, it helps form a **precursor molecule** called "procollagen" that is later packaged and modified into collagen outside the cell. Collagen is a gluelike substance that binds cells together to form tissues. It is the most abundant of the fibers contained in connective tissues. Connective tissue gives the human body form and supports its organs.

Vitamin C is also important as it helps protect the fat-soluble vitamins A and E, as well as fatty acids from **oxidation**. It is therefore a **reducing agent** and scavenger of radicals (sink of radicals). Radicals, molecules with unpaired electrons, are very harmful to the body as a result of their high reactivity, which may induce mutations and possibly cancer. Vitamin C, being an excellent source of electrons, can therefore donate electrons to free radicals such as hydroxyl and superoxide and quench their reactivity.

vitamins: organic molecules needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

antiscorbutic: substance that has an effect on scurvy

catalyst: substance that aids in a reaction while retaining its own chemical identity

precursor molecule: molecule that is the chosen starting point for the preparation of another molecule; a starting molecule in a chemical synthesis; a reactant molecule

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

reducing agent: substance that causes reduction, a process during which electrons are lost (or hydrogen atoms gained)

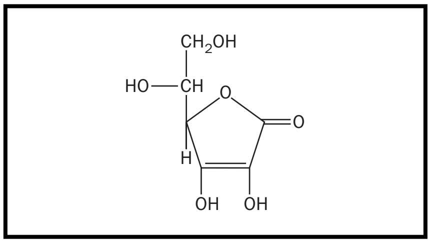

Figure 1. Ascorbic acid (vitamin C).

A debate exists over the anticancer properties of vitamin C. However, current evidence suggests that the major benefit of ascorbic acid with regard to cancer may be in reducing the risk of developing cancer, rather than in therapy. Vitamin C can work inside the cells to protect **DNA** (deoxyribonucleic acid), the hereditary material in cells, from the damage caused by free radicals. Also, it can reduce the development of nitrosamines (amines linked to the NO group) from nitrates, chemicals that are commonly used in processed foods. Once formed, nitrosamine can become carcinogenic (cancer-causing).

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

Sources of vitamin C are numerous: citrus fruits such as oranges, limes, and grapefruits and vegetables including tomatoes, green peppers, potatoes, and many others. The recommended dietary allowance (RDA) of vitamin C is 60 milligrams (0.0021 ounces) per day. An average American ingests about 72 milligrams (0.0025 ounces) a day. Some studies suggest higher daily doses especially for the elderly, women, and the infirm. For example, the late Linus Pauling, best known for his theory on chemical bonding and a two-time Nobel Prize winner, consumed several grams of vitamin C per day for the last forty years of his life and lived to age ninety-three. SEE ALSO Catalysis and Catalysts; Pauling, Linus.

Joseph Bariyanga

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Astatine

MELTING POINT: 302°C
BOILING POINT: 337°C
DENSITY: UNKNOWN
MOST COMMON IONS: At^-, AtO^-, AtO_3^-

85
At
ASTATINE
210

Astatine is a radioactive halogen (the heaviest of the halogen elements) and is a solid at room temperature. Dale R. Carson, K. R. MacKenzie, and Emilio Segrè of the University of California produced the element in 1940 by bombarding an isotope of bismuth (^{209}Bi) with alpha particles. The origin of the name "astatine" is the Greek word *astatos*, which means "unstable."

Astatine is found in only vanishingly small amounts in nature—it is believed that only 30 grams (1 ounce) of the element are present in Earth's crust at any one time. It is produced naturally when the elements uranium and thorium decay. Astatine can also be produced in a nuclear reactor by the method used by its discoverers, according to the following reaction:

$$^{209}_{83}\mathrm{Bi} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{211}_{85}\mathrm{At} + 2\,{}^{1}_{0}\mathrm{n}$$

The most stable isotope of astatine is ^{210}At, which has a half-life of 8.1 hours. Other isotopes have mass numbers ranging from 193 to 223 and half-lives ranging from 125 nanoseconds (^{213}At) to 7.2 hours (^{211}At). Astatine is known to form interhalogen compounds with bromine (AtBr), chlorine (AtCl), and iodine (AtI). Additional compounds (HAt and CH_3At) have also been detected.

Because of its scarcity and short half-life, there were no commercial uses for astatine as of 2003. Researchers are investigating astatine as a means of treating various cancers (e.g., lethal brain tumors) and diseases. Because of its similarities to iodine, which accumulates in the thyroid, it is believed that the element could be utilized to treat certain thyroid diseases. SEE ALSO HALOGENS; RADIOACTIVITY.

Stephanie Dionne Sherk

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Astrochemistry

In the night sky, the expanses of space between the stars of the Milky Way appear to be empty. In fact this space is occupied by a very thin gas that is mostly hydrogen and that has mere traces (less than 0.1% by number of atoms) of other elements such as oxygen, carbon, and nitrogen. The gas is also dusty; it contains grains of dust (particulate matter) that, like an interstellar fog, impede one's view of the stars. This gas is not evenly spread in space, but is clumpy. Although on average there is approximately one hydrogen atom for every cubic centimeter of interstellar space, a clump may be one thousand or more times as dense as a comparable volume of average density. Since about 1970 astronomers have been finding that these denser regions contain a great variety of molecules; about 120 different molecular species have been identified in the interstellar medium. A few of them are listed in the accompanying table. The study of these molecules in the Milky Way and in other galaxies is called astrochemistry.

How Do Astronomers Detect These Molecules?

spectroscopy: use of electromagnetic radiation to analyze the chemical composition of materials

Astronomers identify interstellar atoms and molecules via **spectroscopy**. For example, interstellar sodium atoms that happen to be in a line of sight going from a point on Earth's surface toward a bright star absorb light emitted by that star at a wavelength that is characteristic of sodium atoms (about 589 nanometers; 2.3×10^{-5} inches). Most interstellar molecules are detected by spectroscopic analysis that measures absorption or emission at radio wavelengths rather than those corresponding to visual light. Astronomers use large radio telescopes to detect radiation emitted by interstellar molecules. These emissions arise because the molecules are set to rotating when they collide with each other. The molecules lose energy and slow down in their rotations by emitting radiation at wavelengths that are specific for them, such that each emission is a "signature" of one type of molecule. For example, the molecule carbon monoxide, CO, may emit at various radio wavelengths, including 2.6 millimeters (0.1 inches), 1.3 millimeters (0.05 inches), 0.65 millimeters (0.03 inches), and 0.32 millimeters (0.01 inches). Interstellar gas is usually very cold (around 10 degrees above absolute zero), but even under these conditions the molecular collisions are energetic enough to keep the molecules rotating and, therefore, emitting radiation.

Sometimes these interstellar molecules may be located in warmer regions. If the gas of which they are a part is close to a star, or becomes heated

SOME MOLECULES IDENTIFIED IN THE SPACE BETWEEN THE STARS IN THE MILKY WAY

Most Abundant Molecules	Simple Hybrides	Simple Organic Molecules	Ions and Radicals	Carbon Chains
Molecular hydrogen (H_2)	Water (H_2O)	Formaldehyde (H_2CO)	CH^+	$HC_{2n+1}N$ (n=1 –5) (Cyanopolyacetylenes)
Carbon monoxide (CO)	Methane (CH_4)	Methanol (CH_3OH)	HCO^+	
	Ammonia (NH_3)	Dimethyl ether ($(CH_3)_2O$)	H_3O^+	
	Hydrogen sulfide (H_2S)	Formic acid (HCOOH)	$H_3{}^+$	
		Ethanol (C_2H_5OH)	OH	
		Benzene (C_6H_6)	CH C_nH (n=2 – 8)	

About 120 types of molecules have been identified in the space between the stars in our galaxy. Some of these molecules are listed here.

because one clump collides with another, the temperature of the molecules may rise considerably, perhaps to several thousand degrees above absolute zero. In these cases, the collisions between gas molecules are correspondingly more energetic, and molecules may be set to vibrating as well as rotating. For example, a carbon monoxide molecule, CO, vibrates to-and-fro as if the two atoms are connected by a coiled spring. A vibrating molecule also eventually slows down and loses energy (unless it is involved in further collisions) by emitting radiation that is again specific to that particular molecule. In the example of CO, that radiation has a wavelength of about 4.7 micrometers (18.5×10^{-5} inches), the detection of which necessitates the use of large telescopes that are sensitive to infrared radiation.

How Are Interstellar Molecules Formed?

The Milky Way, like all other galaxies, was formed from intergalactic gas that was essentially atomic. So where do the molecules come from? One can deduce that they are not left over from the processes that formed the Milky Way because scientists can detect molecules in regions in which they are (currently) being rapidly destroyed; therefore there must be a formation process in operation now. For example, the hydroxyl molecule, OH, can be observed in rather low density interstellar gas regions (containing about 100 H atoms per cubic centimeter) in which it is being destroyed by stellar radiation in a time frame, typically, of ten thousand years. This seems a long time but because the Galaxy has been in existence for a much longer time (about 15 billion years), the OH radicals (and many other species) must have been formed relatively recently in the Galaxy's history.

Simple collisions between O and H atoms do not lead to the formation of OH molecules, because the atoms bounce apart before they are able to form a chemical bond. Similarly, low temperature collisions between O atoms and H_2 molecules are also unreactive.

Astronomers have now determined that much of the chemistry of interstellar space occurs via ion-molecule reactions. Cosmic rays (fast-moving protons and electrons pervading all of interstellar space) ionize molecular hydrogen (H_2) and the resulting ions ($H_2{}^+$) react quickly with more H_2 to form other ions (H_3^+). The H_3^+ ions drive a chemistry that consists of simple two-body reactions. The extra proton in H_3^+ is quite weakly bound (relative to the bonding of one proton to another in H_2); in a collision an H_3^+ molecule easily donates its proton to some other species, creating a new molecule. For example, an H_3^+ ion reacts with an O atom to give OH^+, a new species:

$$O + H_3^+ \longrightarrow OH^+ + H$$

and the OH^+ then reacts with H_2 molecules to make, successively, H_2O^+ and H_3O^+ ions

$$OH^+ \longrightarrow H_2O^+ \longrightarrow H_3O^+$$

This process of H abstraction finishes here, because the O^+ ion in H_3O^+ has saturated all its valencies with respect to H atoms. However, the H_3O^+ ion has a strong **attraction** for electrons because of its positive charge, and the ion-electron recombination leads to dissociation of the ion-electron complex into a variety of products, including OH (hydroxyl) and H_2O (water).

attraction: force that brings two bodies together, such as two oppositely charged bodies

Other exchange reactions occur; for example, CO may be formed through the neutral exchange

$$C + OH \longrightarrow CO + H$$

Similar ion-molecule reactions drive the chemistries of other atoms, such as C and N, to yield ions such as CH_3^+ and NH_3^+. These ions can then react with other species to form larger and more complex molecules. For example, methanol (CH_3OH) may be formed by the reaction of CH_3^+ ions with H_2O molecules, followed by recombination of the product of that reaction with electrons

$$CH_3^+ + H_2O \longrightarrow CH_3OH_2^+$$
$$CH_3OH_2^+ + e^- \longrightarrow CH_3OH + H$$

Ion-molecule reactions, followed by ion-electron recombinations and supplemented by neutral exchanges, are capable of forming the majority of the observed interstellar molecular species. Very large gas-phase reaction networks, involving some hundreds of species interacting in some thousands of chemical reactions, are routinely used to describe the formation of the observed interstellar molecules in different locations in models of interstellar chemistry.

Does the Dust Play a Role in Astrochemistry?

The dust has several important chemical roles. Obviously, it may shield molecules from the destructive effects of stellar radiation. It also has more active roles. We have seen that free atoms in collision may simply bounce apart before they can form a chemical bond. By contrast, atoms adsorbed on the surface of a dust grain may be held together until reaction occurs. It is believed that molecular hydrogen is formed in this way (i.e., through heterogeneous **catalysis**) and is ejected from dust grain surfaces into the gas volume with high speed and in high states of vibration and rotation. Other simple molecules, such as H_2O, CH_4, and NH_3, are also likely to form in this way.

catalysis: the action or effect of a substance in increasing the rate of a reaction without itself being converted

In the denser clumps where the gas is very cold, the dust grains are also at a very low temperature (around 10 degrees above absolute zero). Gas-phase molecules colliding with such grains tend to stick to their surfaces, and over a period of time the grains in these regions accumulate mantles of ice: mostly H_2O ice, but also ices containing other molecules such as CO, CO_2, and CH_3OH. Astronomers can detect these ices with spectroscopy. For example, water ice molecules absorb radiation at a wavelength about 3.0 micrometers (11.8×10^{-5} inches), having to do with the O–H vibration in H_2O molecules; the molecules do not rotate because they are locked into the ice. In instances in which such ice-coated dust grains lie along a line of sight toward a star that shines in the infrared, this 3.0 micrometer (11.8×10^{-5} inch) absorption is very commonly seen.

Interstellar solid-state chemistry can occur within these ices. Laboratory experiments have shown that ices of simple species such as H_2O, CO, or NH_3 can be stimulated by **ultraviolet radiation** or fast particles (protons, electrons) to form complex molecules, including polycyclic aromatic hydrocarbons (PAHs) containing several benzene-type rings. The detection by astronomers of free interstellar benzene (C_6H_6) in at least one interstellar region suggests that this solid-state chemistry may be the route by which these molecules are made.

ultraviolet radiation: portion of the electromagnetic spectrum with wavelengths shorter than visible but longer than x rays

What Role Do Molecules Play in Astronomy?

The primary role that interstellar molecules play is a passive one: Their presence in regions so obscured by dust that we cannot see into them using optical telescopes is used to probe these regions. The most dramatic example of this is the discovery of the so-called giant molecular clouds in the Milky Way and other galaxies via the detection of the emission of 2.6 micrometers (10.2×10^{-5} inches) wavelength radiation by CO molecules present in these clouds. The existence of these huge gas clouds, containing up to a million times the mass of the Sun, was not suspected from optical observations because these clouds are completely shrouded in dust. However, radio astronomy has shown that these clouds are the largest nonstellar structures in the Galaxy, and that they will provide the raw material for the formation of millions of new stars in future billions of years of the Galaxy's evolution.

The radiation from molecules that we detect can represent a significant loss of energy from an interstellar cloud. Some molecules are very effective coolants of interstellar gases and help to maintain the temperatures of these gases at very low values. This cooling property is very important in clumps of gas that are collapsing inward under their own weight. If such a collapse can continue over vast stretches of time, then ultimately a star will form. In the early stages, it is important that the clumps remain cool, otherwise the gas pressure might halt the collapse. In these stages, therefore, the cooling effect of the molecules' emission of radiation is crucial. The formation of stars like the Sun is possible because of the cooling effect of molecules. Interstellar chemistry is therefore one factor determining the rate of star formation in the Galaxy. Astrochemists have shown that it takes about one million years for the molecules of a collapsing cloud to be formed; this is about the same amount of time as that required for the collapse itself to become established. The accompanying image illustrates a region of star formation in the Galaxy.

A star-forming region: pillars of gas in the Eagle Nebula (M16). A molecular cloud is eroded by the winds and radiation of nearby very bright stars (not shown, top right in figure), leaving these columns of denser and more resistant gas. Star formation is occurring in very dense globules of gas, some of which can be seen around the periphery of the pillars.

Astrochemistry also has a role that is particularly significant to the human species here on planet Earth. The planet was formed as a byproduct of the formation of the star that is the Sun, and is in effect the accumulation of dust grains that were the debris of large chunks of matter that subsequently impacted and stuck together. Earth is still subject to the occasional impacts of debris left over from the formation of the solar system. These impacts, now seen as a source of potential danger, in fact once brought prebiotic material to Earth. The oceans arose from the arrival of icy comets, and carbon, nitrogen, and elemental **metals** were brought by asteroid impacts. These elements and others are necessary for life on Earth, and a new discipline, astrobiology, is coming into being: Its aim is to study the transport of prebiological material in the Galaxy and the development of life within suitable environments in the universe.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Conclusion

Astrochemistry extends chemistry into regimes of exceptionally low density and temperature; it involves gas-phase, surface, and solid-state processes. Its products, the molecules, have opened up a new approach to astronomy. SEE ALSO Spectroscopy.

David A. Williams

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Atmospheric Chemistry

With each breath, the lungs inhale air filled with nitrogen and oxygen, the most abundant natural gases in the atmosphere. Also inhaled, however, are small quantities of gases and particles that are pollutants. Understanding the effects of these pollutants and how to control their emissions has been a continuing challenge for many centuries.

History

Humans have made a large impact on the state of the atmosphere ever since they first began using fire for light, cooking, and heat. When early populations traded their nomadic lifestyle for one based on agriculture, concentrations of air pollutants began to accumulate around permanent communities. With population growth came an increase in the use of fire, along with an increasing demand for wood.

In the twelfth and thirteenth centuries as wood became more difficult to find, growing cities began looking for alternate sources of energy. The solution was coal—plentiful, cheap, long-lasting, and hailed as the perfect new source of energy. The only "inconvenience" was the heavy black smoke that resulted from its burning. It was not long, however, before this inconvenience became a serious health concern.

As industrialization increased over the next few hundred years, the burning of coal and wood produced some of the unhealthiest air ever recorded. In some European cities, hundreds of deaths were blamed on episodes of excessive smoke and soot. London's air was especially filthy: The mixture of smoke and fog (later termed "smog") was at times so thick that it affected visibility. As little was done to control the burning of coal, many cities in Europe, Asia, and the Americas suffered from poor air quality.

Although the burning of coal remains one of the largest global sources of air pollution, the rise of automobiles in the mid-twentieth century was another major source. This was especially true on the west coast of the United States, where the ever-rising automobile population, coupled with a large petroleum industry, generated a different type of pollutant; cities became known for "brown smog," a layer of pollution that forms in sunny skies and causes irritation to the lungs and eyes.

Acid Rain

Although Earth has its own sources of naturally produced air pollutants, humans have had a far larger effect on Earth's atmosphere. One of the most striking examples of this pollution is acidic deposition, or "acid rain." Acid rain occurs when emissions of sulfur dioxide and nitrogen oxides, which typically come from coal-burning power plants and automobile emissions, react with water and oxygen to form acidic compounds such as nitric acid and sulfur-containing acids, according to the following reactions:

$$S + O_2 \rightarrow SO_2$$

$$SO_2 + O_3 \rightarrow SO_3 + O_2$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

$$SO_2 + H_2O \rightarrow H_2SO_3$$

$$2NO + O_2 \rightarrow 2NO_2$$

$$2NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

$$NO + O_2 \rightarrow NO_2$$

Once airborne, these pollutants can travel long distances before returning to Earth's surface as rain or snow, or in a dry form.

Not all atmospheric acidity is due to atmospheric pollution, as Earth also has natural sources of sulfur and nitrogen. Natural sources of sulfur dioxide include volcanoes and forest fires. Air is a natural source of nitrogen oxides, as is lightning, according to the following reactions:

$$O_2 + N_2 \rightarrow 2NO$$

$$2NO + O_2 \rightarrow 2NO_2$$

Even "normal" rain (rain that has not formed in a polluted atmosphere) is acidic because of the presence of carbon dioxide in the atmosphere:

$$CO_2 + H_2O \rightarrow H_2CO_3$$

Over the millennia, normal rain has created limestone caves because calcium carbonate is slightly soluble in solutions of H_2CO_3:

$$CaCO_3\ (s) + H_2CO_3\ (aq) \rightarrow Ca(HCO_3)_2\ (aq)$$

The additional burden of human air pollution, however, has made acid rain an important environmental concern. Acid rain may acidify lakes and streams, making the water unsuitable for some fish and other wildlife. Further damage has been reported in soil and tree vegetation, which are sensitive to the acid level of rainwater.

Acid rain also speeds the decay of buildings, statues, and other man-made structures. Natural treasures such as the Taj Mahal in India, the Acropolis in Greece, and cathedrals in Germany and Britain have suffered significant damage due to acid rain. Although large sums of money are being used to help repair these structures, some damage is beyond repair.

Many governments have enacted controls on the chemicals responsible for acid rain. Although there have been some improvements in acid levels in lakes and streams, there are still many scientists who believe that stricter controls are necessary to reduce the risk to Earth's land and water.

These statues, “Saints and Sinners” by sculptor Marshall Fredericks at Oakland University, Rochester, Michigan, were exposed to acid rain. The reaction of water with sulfur dioxide and nitrogen oxides forms acidic compounds, speeding the statues’ decay.

Fluorocarbons and Ozone Depletion

Ozone (O_3) is a gas consisting of three oxygen atoms. The ozone layer of the atmosphere acts as a shield protecting Earth’s surface from the Sun’s harmful ultraviolet (UV) radiation. When ozone absorbs UV radiation, it decomposes into an oxygen molecule (O_2) and an oxygen atom (O) as:

$$2O_3 + \text{UV radiation} \rightarrow 3O_2 + O$$

Even a relatively small decrease in the ozone layer could produce significant risks to human, animal, and plant life. For example, scientists estimated that even a 1 percent decrease in global ozone levels would produce 10,000 more cases of skin cancer each year.

Fluorocarbons are a class of chemicals widely used in various technologies, including air conditioning, aerosol cans, and fire extinguishers. While the chemicals have proved extremely useful, it was not until the 1970s (when growing concentrations of chlorine were detected in the upper atmosphere) that scientists first realized that **chlorofluorocarbons (CFCs)**, a type of fluorocarbon, could potentially destroy ozone.

chlorofluorocarbon (CFC): compound that contains carbon, chlorine, and fluorine atoms, which remove ozone in the upper atmosphere

The widespread growth of CFCs produced an unsuspecting increase in upper atmosphere chlorine. When a CFC molecule is released into the atmosphere, it can remain for many years without reacting with other chemicals. Once the CFC molecule reaches the upper atmosphere, however, it can be broken apart by UV radiation, thus releasing a chlorine atom. It is this release of chlorine that poses the serious risk to Earth's ozone layer, because it is involved in a series of ozone depleting reactions in which a chemical family or a particular species is depleted, leaving the **catalyst** unaffected. Ozone can be affected by such a cycle. In the presence of a chlorine atom (Cl), atomic oxygen and an ozone molecule are converted into molecular oxygen via the following two-step process:

catalyst: substance that aids in a reaction while retaining its own chemical identity

$$O_3 + Cl \rightarrow ClO + O_2$$

$$ClO + O \rightarrow Cl + O_2$$

A single chlorine atom can potentially destroy many thousands of ozone molecules. Notice that a chlorine atom is consumed in the first reaction and preserved in the second reaction. Chlorine atoms thus act as catalysts in the depletion of ozone.

It was not until the Antarctic ozone hole was discovered in 1985 that scientists first realized how fragile the ozone layer can be to specific chemicals. In 1987 thirty-one countries agreed to protect the ozone layer through a reduction and elimination of the chemicals that destroy ozone. This international agreement, known as the Montreal Protocol, has successfully reduced the use and production of CFCs, with the long-term goal of restoring the ozone layer to its original state.

Summary

The struggle to improve air quality has persisted for many years. Although many cities still have air pollution episodes that are classified as unhealthy, stricter emission controls mean that the air over most major cities is cleaner today than it was in the mid-twentieth century. Even so, issues such as acid rain and ozone depletion continue to pose serious environmental challenges that require cooperation between science and policy. SEE ALSO AIR POLLUTION.

Eugene C. Cordero

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Atom Bomb ***See Manhattan Project.***

Atomic Nucleus

The atomic nucleus is a tiny massive entity at the center of an atom. Occupying a volume whose radius is 1/100,000 the size of the atom, the nucleus contains most (99.9%) of the mass of the atom. In describing the nucleus, we shall describe its composition, size, density, and the forces that hold it together. After describing the structure of the nucleus, we shall go on to describe some of the limits of **nuclear** stability.

nuclear: having to do with the nucleus of an atom

The nucleus is composed of protons (charge = +1; mass =1.007 **atomic mass units** ([μ]) and neutrons. The number of protons in the nucleus is called the **atomic number** Z and defines which chemical element the nucleus represents. The number of neutrons in the nucleus is called the neutron number N, whereas the total number of neutrons and protons in the nucleus is referred to as the mass number A, where A = N + Z. The neutrons and protons are referred to collectively as nucleons. A nucleus with a given N and Z is referred to as a nuclide. Nuclides with the same atomic number are **isotopes**, such as ^{12}C and ^{14}C, whereas nuclides with the same N, such as ^{14}C and ^{16}O, are called isotones. Nuclei such as ^{14}N and ^{14}C, which have the same mass number, are isobars. Nuclides are designated by a shorthand notation in which one writes ${}^{A}_{Z}\textit{Chemical Symbol}_{N}$, that is, for a nucleus with 6 protons and 8 neutrons, one writes ${}^{14}_{6}C_8$, or, ${}^{14}_{6}C$, or just ^{14}C. The size of a nucleus is approximately 1 to 10 x 10^{-15} m, with the nuclear radius being represented more precisely as 1.2 x $A^{1/3}$ x 10^{-15} m. We can roughly approximate the nucleus as a sphere and thus we can calculate its density

atomic mass units: unit used to measure atomic mass; $\frac{1}{12}$ of the mass of a carbon-12 atom

atomic number: the number of protons in an atomic nucleus, expressed in terms of electric charge; it is usually denoted by the symbol Z

isotope: form of an atom that differs by the number of neutrons in the nucleus

$$density = \frac{mass}{volume} \cong \frac{A \bullet 1.66 \times 10^{-27}\text{kg}}{\frac{4}{3}\pi r^3} \approx \frac{A \bullet 1.66 \times 10^{-27}\text{kg}}{\frac{4}{3}\pi\left(1.2A^{1/3} \times 10^{-15}m\right)^3}$$

where 1.66 x 10^{-27} kg is the mass of the nucleon. Thus the nuclear density is about 200,000 tonnes/mm^3 and is independent of A. Imagine a cube that is 1 mm on a side. If filled with nuclear matter, it would have a mass of about 200,000 tonnes. This calculation demonstrates the enormous matter/energy density of nuclei and gives some idea as to why nuclear phenomena lead to large energy releases.

Of the 6,000 species of nuclei that can exist in the universe, about 2,700 are known, but only 270 of these are stable. The rest are radioactive, that is, they spontaneously decay. The driving force behind all **radioactive decay** is the ability to produce products of greater stability than one had initially. In other words, radioactive decay releases energy and because of the high energy density of nuclei, that energy release is substantial. Qualitatively we describe radioactive decay as occurring in three general ways: α-, β-, and γ-decay. Alpha-decay occurs in the heavy elements, and consists of the emission of a ^{4}He nucleus. Beta-decay occurs in nuclei whose N/Z ratio is different from that of a stable nucleus and consists of a transformation of neutrons into protons or vice versa to make the nucleus more stable. Gamma-decay occurs when excited nuclei get rid of some or all of their excitation energy via the emission of electromagnetic radiation, or via the radiationless transfer of energy to orbital electrons.

radioactive decay: process involving emission of subatomic particles from the nucleus, typically accompanied by emission of very short wavelength electromagnetic radiation

The force responsible for holding the neutrons and protons together within the very small nuclear volume must be unusually strong. The nuclear force, or strong interaction, is one of the four fundamental forces of nature (namely, the gravitational, electromagnetic, strong, and weak forces). The nuclear force is charge-independent, meaning that the nuclear force between two protons, or two neutrons, or a neutron and a proton, is the same. The nuclear force is short-ranged, meaning it acts over a distance of 10^{-15} to 10^{-14} m, that is, the size of nuclei. Of course the nuclear force is attractive, as it binds the nucleons in a nucleus. But some experiments have shown the nuclear force has a "repulsive core," meaning that at very short distances, the force switches from attractive to repulsive, preventing the nucleus from collapsing in on itself. The nuclear force is an "exchange" force, resulting from the virtual exchange of pions (short-lived particles with integral spin, produced normally in nuclear reactions) between interacting nucleons. More recently we have come to understand the nuclear force using a theory called quantum chromodynamics (QCD), which describes protons and neutrons as being made up of quarks. In particular, the proton is thought of as a combination of two up quarks (uu) and a down quark (d), whereas the neutron is thought to consist of one up quark (u) and two down quarks (dd). The up and down quarks are small particles with charges of +2/3 and −1/3, respectively. The quarks account for approximately 2 percent of the mass of the proton. The rest of the mass consists of gluons, which are the particles exchanged between the quarks to bind them together. The force acting between the quarks has the unusual property of being small when they are close together, and increasing as the distance between them grows. Because of this, no isolated quarks have been observed in nature.

inert: incapable of reacting with another substance

In close analogy to atomic structure, we speak of the structure of various nuclei. Many nuclear properties can be described using a nuclear shell model in which the nucleons are placed in orbitals like electrons in atoms. These orbitals and their properties are predicted by applying quantum mechanics to the problem of defining the states of the nucleons, which move under the influence of the average force in the nucleus. Like atoms, there are certain configurations of nucleons that have special stability, for example, the so-called magic numbers akin to the **inert** gas structures in chemistry. In addition to those nuclear properties that are best described in terms of a shell model, there are other properties that seem to be best explained by the large-scale collective motion of a number of nucleons. These motions lead to nuclear rotations and vibrations, which are described by a nuclear collective model.

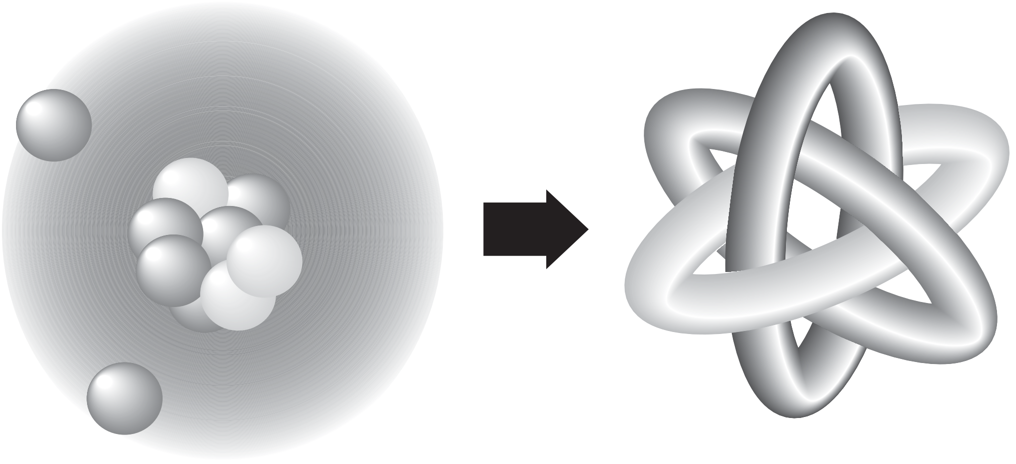
fission: process of splitting an atom into smaller pieces

synthesis: combination of starting materials to form a desired product

Current research on nuclei, their properties, and the forces that hold them together focuses on studying nuclei at the limits of stability. The basic idea is that when one studies nuclei under extreme conditions, one then has a unique ability to test theories and models that were designed to describe the "normal" properties of nuclei. One limit of nuclear stability is that of high Z, that is, as the atomic number of the nucleus increases, the repulsion between the nuclear protons becomes so large as to cause the nucleus to spontaneously **fission**. The competition between this repulsive Coulomb force and the cohesive nuclear force is what defines the size of the Periodic Table and the number of chemical elements. At present there are 112 known chemical elements, and evidence for the successful **synthesis** of elements having the atomic numbers 114 and 116 has been presented.

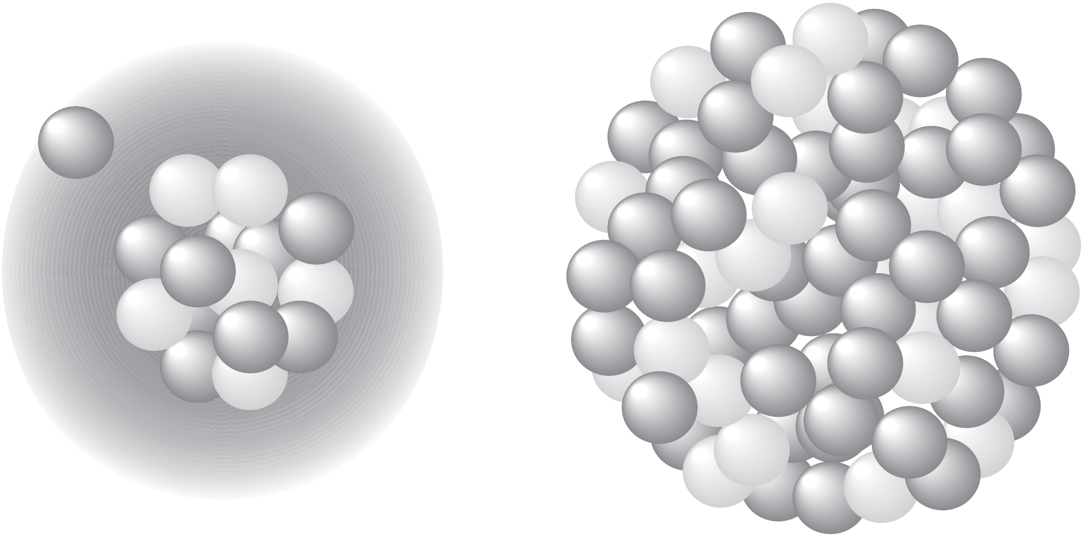
valence: combining capacity

Another limit of nuclear stability is the extreme of the neutron to proton ratio, N/Z. For certain very neutron-rich nuclei, such as ^{11}Li, an unusual halo structure has been observed. In halo nuclei, a "core" of nucleons is surrounded by a "misty cloud, a halo" of **valence** nucleons that are weakly bound and extend out to great distances, analogous to electrons surrounding the nucleus in an atom. Halo nuclei are fragile objects, are relatively large, and interact easily with other nuclei (have enhanced reaction cross sections). The halo nucleus ^{11}Li, which has a ^{9}Li core surrounded by a two-neutron halo is shown in Figure 1. ^{11}Li is as large as ^{208}Pb. ^{11}Li and other



^{11}Li: Borromean Halo Nucleus

The Borromean Rings



^{19}C: The Heaviest Known Halo Nucleus

^{208}Pb: Well Bound Heavy Nucleus

Figure 1. Schematic views of the nuclear halo nuclei ^{11}Li and ^{19}C that compares them to ^{208}Pb and the Borromean rings of medieval times. (Source: http://www.phy.anl.gov/ria/index)

two-neutron halo nuclei are three-body systems (2 neutrons and a ^{9}Li core), which pose a special challenge to nuclear theorists. They are also examples of Borromean systems, in which the nucleus is no longer bound if any one of the three components is removed. (The name derives from the heraldic emblem of medieval princes of Borromeo, which has three rings interlocked in such a way that removal of any one ring will make the others fall apart.) SEE ALSO Atomic Structure; Rutherford, Ernest.

Walter Loveland

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Atomic Structure

The ancient Greek philosophers Leucippus and Democritus believed that atoms existed, but they had no idea as to their nature. Centuries later, in 1803, the English chemist John Dalton, guided by the experimental fact that chemical elements cannot be decomposed chemically, was led to formulate his atomic theory. Dalton's atomic theory was based on the assumption that atoms are tiny indivisible entities, with each chemical element consisting of its own characteristic atoms.✷

✷See Atoms article for further discussion of Dalton's atomic theory.

Modern View of the Atom

The atom is now known to consist of three primary particles: protons, neutrons, and electrons, which make up the atoms of all matter. A series of experimental facts established the validity of the model. Radioactivity played an important part. Marie Curie suggested, in 1899, that when atoms disintegrate, they contradict Dalton's idea that atoms are indivisible. There must then be something smaller than the atom (subatomic particles) of which atoms were composed.

Long before that, Michael Faraday's electrolysis experiments and laws suggested that, just as an atom is the fundamental particle of an element, a fundamental particle for electricity must exist. The "particle" of electricity was given the name *electron*. Experiments with cathode-ray tubes, conducted by the British physicist Joseph John Thomson, proved the existence of the electron and obtained the charge-to-mass ratio for it. The experiments suggested that electrons are present in all kinds of matter and that they presumably exist in all atoms of all elements. Efforts were then turned to measuring the charge on the electron, and these were eventually successful by the American physicist Robert Andrews Millikan through the famous oil drop experiment.

The study of the so-called canal rays by the German physicist Eugen Goldstein, observed in a special cathode-ray tube with a perforated cathode, let to the recognition in 1902 that these rays were positively charged particles (*protons*). Finally, years later in 1932 the British physicist James Chadwick discovered another particle in the nucleus that had no charge, and for this reason was named neutron.

Joseph John Thomson had supposed that an atom was a uniform sphere of positively charged matter within which electrons were circulating (the "plum-pudding" model). Then, around the year 1910, Ernest Ruthorford (who had discovered earlier that alpha rays consisted of positively charged particles having the mass of helium atoms) was led to the following model for the atom: Protons and neutrons exist in a very small nucleus, which means that the tiny nucleus contains all the positive charge and most of the

GEORGE STONEY (1826–1911)

As a physical chemist, George Stoney made significant contributions to our understanding of molecular motion. However, this Irish scientist is better known for assigning a name to negative atomic charges, electrons, while addressing the Royal Society of Dublin in 1891.

—Valerie Borek

mass of the atom, while negatively charged electrons surround the nucleus and occupy most of the volume of the atom.

In formulating his model, Rutherford was assisted by Hans Geiger and Ernest Marsden, who found that when alpha particles hit a thin gold foil, almost all passed straight through, but very few (only 1 in 20,000) were deflected at large angles, with some coming straight back. Rutherford remarked later that it was as if you fired a 15-inch artillery shell at a sheet of paper and it bounced back and hit you. The deflected particles suggested that the atom has a very tiny nucleus that is extremely dense and positive in charge.

Also working with Rutherford was Henry G. J. Moseley who, in 1913, performed an important experiment. When various metals were bombarded with electrons in a cathode-ray tube, they emitted X rays, the wavelengths of which were related to the nuclear charge of the metal atoms. This led to the law of chemical periodicity, which provided refinement of the periodic table introduced by Mendeleev in 1869. According to this law, all atoms of an element have the same number of protons in the nucleus. It is called the ***atomic number*** and is given the symbol Z. Hydrogen is the simplest element and has Z = 1.

atomic number: the number of protons in an atomic nucleus, expressed in terms of electric charge; it is usually denoted by the symbol Z

Bohr Model of the Atom

Through Rutherford's work it was known that that electrons are arranged in the space surrounding the atomic nucleus. A planetary model of the atom, with the electrons moving in circular orbits around the nucleus seemed an acceptable model. However, such a "dynamic model" violated the laws of classical electrodynamics, according to which a charged particle, such as an electron, moving in the positive electric field of the nucleus, should lose energy by radiation and eventually spiral into the nucleus.

To solve this contradiction, in 1913, the Danish physicist Neils Bohr (then studying under Rutherford) postulated that the electron orbiting the nucleus could move only in certain orbits, having in each a certain "quantized" energy. It turns out that the colors in fireworks would help prove him right.

Atomic Spectra

The colorful lights of fireworks are emitted by "excited" atoms; that is, by atoms that have absorbed extra energy. Light consists of electromagnetic waves, each (monochromatic) color with a characteristic wavelength λ and frequency ν. Frequency is related to energy E through the famous Planck equation, $E = h\nu$, where h is Planck's constant (6.6256×10^{-34} J s). Note that white light, such as sunlight, is a mixture of light of all colors, so it does not have a characteristic wavelength. For this reason we say that white light has a "continuous spectrum." On the other hand, excited atoms emit a "line spectrum" consisting of a set of monochromatic visible radiations.

Each element has a characteristic line spectrum that can be used to identify the element. Note that line emission spectra can also be obtained by heating a salt of a metal with a flame. For instance, common salt (sodium chloride) provides a strong yellow light to the flame coming from excited sodium, while copper salts emit a blue-green light and lithium salts a red light. The colors of fireworks are due to this phenomenon.

Scientists in the late nineteenth century tried to quantify the line spectra of the elements. In 1885 the Swedish school teacher Johann Balmer discovered a series of lines in the visible spectrum of hydrogen, the wavelengths of which could be related with a simple equation:

$$\frac{1}{\lambda} = \mathrm{k}\left(\frac{1}{\mathrm{a}^2} - \frac{1}{\mathrm{b}^2}\right)$$

in which λ is wavelength, k is constant, $a = 2$, and $b = 3, 4, 5, \ldots$ This group of lines was called the Balmer series. For the red line $b = 3$, for the green line $b = 4$, and for the blue line $b = 5$. Similar series were further discovered: in the infrared region, the Paschen series (with $a = 3$ and $b = 4, 5 \ldots$ in the above equation), and much later in the ultraviolet region, the Lyman series (with $a = 1$ and $b = 2, 3 \ldots$). In 1896 the Swedish spectroscopist Johannes Rydberg developed a general equation that allowed the calculation of the wavelength of the red, green, and blue lines in the atomic spectrum of hydrogen:

$$\frac{1}{\lambda} = R\left(\frac{1}{\mathrm{n}_L^2} - \frac{1}{\mathrm{n}_H^2}\right)$$

where $\mathrm{n_L}$ is the number of the lower energy level to which an electron falls and $\mathrm{n_H}$ is the number of the higher energy level from which it falls. R is called the Rydberg constant ($1.0974 \times 10^{-7}\ \mathrm{m}^{-1}$). R was later shown to be equal to $2\pi^2 me^4\mathrm{Z}^2/h^3\mathrm{c}$, where m is the mass of the electron, e is its charge, Z is the atomic number, h is Planck's constant, and c is the speed of light.

Bohr's Quantum Model

As noted earlier, Bohr had suggested the quantization of Ruthford's model of the atom. Although he was not aware of the work of Balmer and Paschen when he wrote the first version of his 1913 article, he had incorporated Planck's constant h into his model, which turned out to be an important decision. Bohr assumed that the absorption or emission of radiation can occur only by "jumps" of the electron from one stationary orbit to another. (See Figure 1.) The energy differences between two such allowed orbits then provided the characteristic frequencies of the emitted light.

$$\Delta E = E_{\mathrm{n}1} - E_{\mathrm{n}2} = h\nu$$

Planck's constant h was named by Bohr the "quantum of action."

Bohr's theory was in close agreement with many experimental facts regarding one-electron atoms (the hydrogen atom and hydrogen-like atoms, such as He^+ and Li^{2+}), but it could not explain the "fine structure" of the spectral lines; that is, the fact that certain lines were actually a set of closely spaced lines. In 1915 and 1916 respectively, W. Wilson and A. Sommerfeld refined Bohr's theory by admitting elliptical orbits. However, it became evident to many physicists, including Bohr himself, that is was time for a scientific revolution.

Wave Character of Matter

To explain the photoelectric effect (the flow of electric current from a metal cathode when illuminated with visible or untraviolet light of suitable frequency), Albert Einstein attributed particulate (material) properties to light.

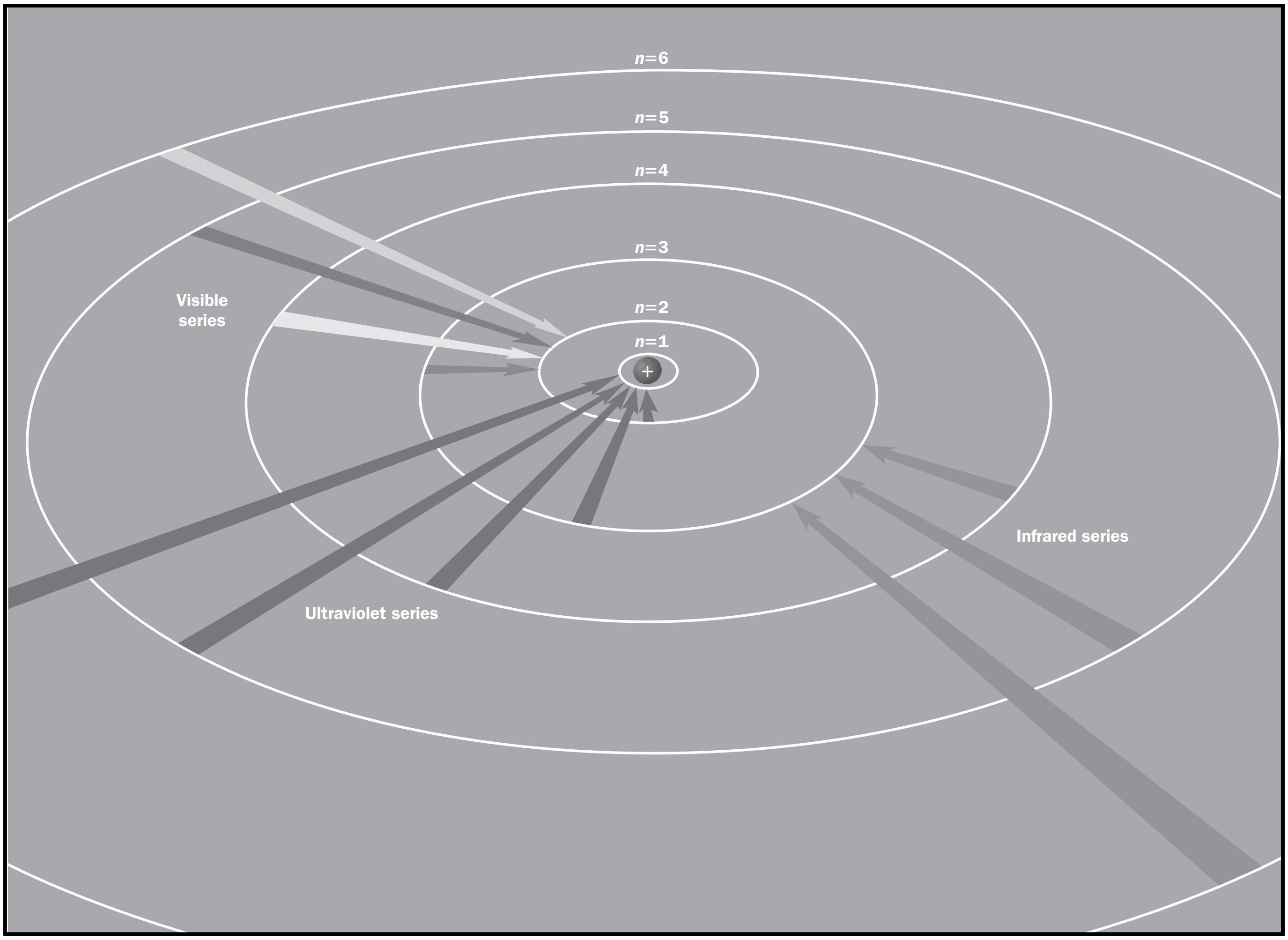


Figure 1. Diagram showing the electron jumps producing the spectral lines in the Balmer (visible) series, the Paschen (infrared) series, and the Lyman (ultraviolet) series.

Thus, besides being an electromagetic wave, light could be accounted for in terms of particles called photons. This dual property of light led the French physicist Luis Victor de Broglie to propose, in 1925, that matter should have dual character too, exhibiting both particulate and wave properties. De Broglie's genius idea was soon after (in 1927) verified by experiment.

Schrödinger's Equation: Wave Mechanics

In 1926 the Austrian physicist Erwin Schrödinger published his famous equation. He started with de Broglie's concept of matter-waves and concluded that classical mechanics is not applicable to micromechanical problems. For a single particle moving in a field that gives it a potential energy V (e.g., a one-electron atom) the Schrödinger equation takes the following form:

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V) = 0$$

where ψ is generally called the wave function, m is the particle's mass, h is Planck's constant, E is the particle's total energy, and V is its classical potential energy.

CLASSICAL AND QUANTUM PHYSICS

A fundamental difference between classical and quantum physics is that, while in classical physics the dynamic variables can be represented by ordinary algebraic variables, in quantum physics they are represented by "operators," which are expressed by mathematical matrices. This is a consequence of the fact that, while in classical physics any disturbance caused by the action of observation or measurement can, in principle, be calculated, in the submicroscopic world, the very action of observation or measurement of a dynamic variable disturbs the system. This is equivalent to the famous "uncertainty principle" of Heisenberg. The distinction between quantum (very small) and classical systems is generally made in units of *h*, Planck's contant. The size of *h* 96.6256 x 10−34 js) is extremely small for the macroscopic world, but for the sumicroscopic world of atoms, ions, molecules, etc., h is not small. Thus quantum mechanics is radically different from classical mechanics.

The Schrödinger Equation in Chemistry

The Schrödinger equation is the foundation of quantum mechanics. It is solved exactly for very few simple systems. In chemistry it is solvable without any approximation only for the hydrogen atom or hydrogen-like atoms (monoelectronic atomic cations). The mathematical solutions are called hydrogen orbitals, in general, an orbital is defined as a "one-electron wave function that obeys certain mathematical restrictions." Hydrogen orbitals depend on the values of the three quantum numbers—*n* (principal), *l* (angular momentum or "asimuthal"), and m_l (magnetic).

The principal quantum number, *n*, identifies an electron's main shell, or energy level, and assumes integer values (1, 2, 3...). The azimuthal (or angular momentum) quantum number, *l*, describes the subshell, or sublevel, occupied by the electron and has values that depend on *n*, taking values from 0 to $n-1$. For *s* orbitals $l = 0$; for *p* orbitals $l = 1$; for *d* orbitals $l = 2$; and for the more complex *f* orbitals $l = 3$. Finally the magnetic quantum number, m_l, identifies the particular orbital an electron is in and has values that depend on *l*, taking on values from 0 to $+l$ or $-l$. For a given value of *n*, there can be only one *s* orbital, but there are three kinds of *p* orbitals, five kinds of *d* orbitals, and seven kinds of *f* orbitals.

Although it does not follow from the Schrödinger equation, there is a fourth quantum number, m_s, that describes the spin of the electron. It can assume two values, +1/2 and −1/2. According to the Pauli Exclusion Principle no two electrons in an atom can have the same set of four quantum numbers. If two electrons have the same values for *n* (main shell), *l* (subshell), and m_1 (orbital), they must differ in spin. Each orbital in an atom can hold no more than two electrons, and they must be opposed in spin. Such a couple of electrons, opposite in spin, constitutes an electron pair.

For practical reasons, various graphical representations of atomic orbitals are used. The most useful are boundary surfaces, such as those shown in Figure 2. These enclose regions of space where the electron described by the corresponding wave function (orbital) can be found with high probability (e.g., 99%); *s* orbitals are spherical, *p* orbitals are dumb-bell shaped, *d* orbitals have a four-leaf-clover shape, while *f* orbitals have complex shapes.

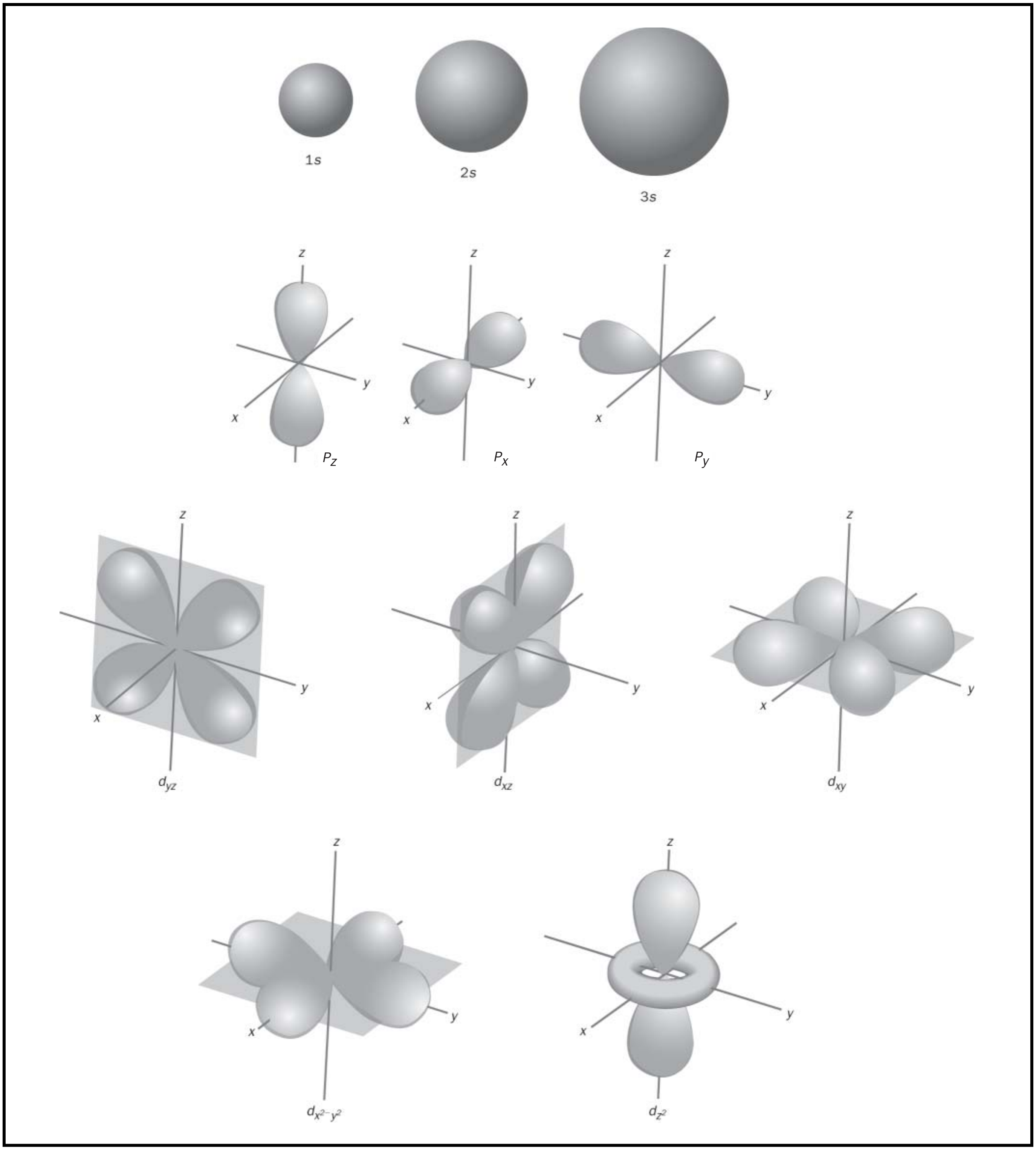


Figure 2. Orbital shapes representing boundary surfaces enclosing regions of space where electrons are most likely to be found in the first three shells.

For many-electron atoms, no exact solutions to the corresponding Schrödinger equation exist because of the electron-electron repulsions. However, various approximations can be used to locate the electrons in these atoms. The common procedure for predicting where electrons are located in larger atoms is the Aufbau (building up) principle.

The Aufbau Principle

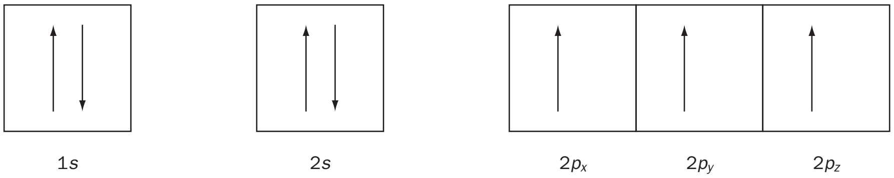
The arrangement of electrons in electron shells (K, L, M, N) is important for explaining both the chemical behavior of the elements and their placement in the periodic table. The first shell is called K ($n = 1$), the second L ($n = 2$), the third M ($n = 3$), etc. Knowing the atomic number of an element, one places that number of electrons, one after another, into the various atomic orbitals, building up the atom until all the electrons have been added.

Three basic principles are followed:

- the principle of least energy (electrons seek the lowest available energy level),
- the Pauli exclusion principle (no more than two electrons per orbital), and
- Hund's rule (electrons of the same energy spread out before pairing up).

The principle of least energy would dictate that all electrons be located in the lowest energy K shell, in the 1*s* orbital. However, the Pauli principle forbids this by requiring that no two electrons in an atom can be described by the same set of four quantum numbers. This leads to the restriction that an orbital cannot accommodate more than two electrons, and they must be of opposite spin. In this way, for a given value of *n*, the *s* orbital can accommodate no more than two electrons, the three *p* orbitals up to six electrons, the five *d* orbitals up to ten electrons, and the seven *f* orbitals up to fourteen electrons.

Hund's rule introduces one final restriction: electrons in degenerate (same energy) orbitals should spread out to fill as many orbitals as possible before pairing up. The seven electrons in the nitrogen atom would be placed in the 1*s*, 2*s*, and 2*p* sublevels as shown below. (Electrons are shown as up-pointing arrows with spin = $+\frac{1}{2}$, or down pointing arrows with spin = $-\frac{1}{2}$).



The lowest energy 1*s* orbital fills first, then the 2*s* orbital, then the last three electrons go into the three higher energy 2*p* orbitals. In a hydrogen atom all orbitals within the same main shell have the same energy, but this is not true for atoms with many electrons because of the interactions among the electrons. Within a given main shell of a large atom, the *s* orbital is the lowest in energy, followed by the *p* orbitals, then the *d* orbitals, and finally the *f* orbitals. (See Figure 3.)

electron configuration: the arrangement of electrons in an atom

The **electron configurations** of atoms are more commonly shown as follows:

$$\text{Nitrogen } (z = 7\ldots)\ 1s^2 2s^2 2p^3$$

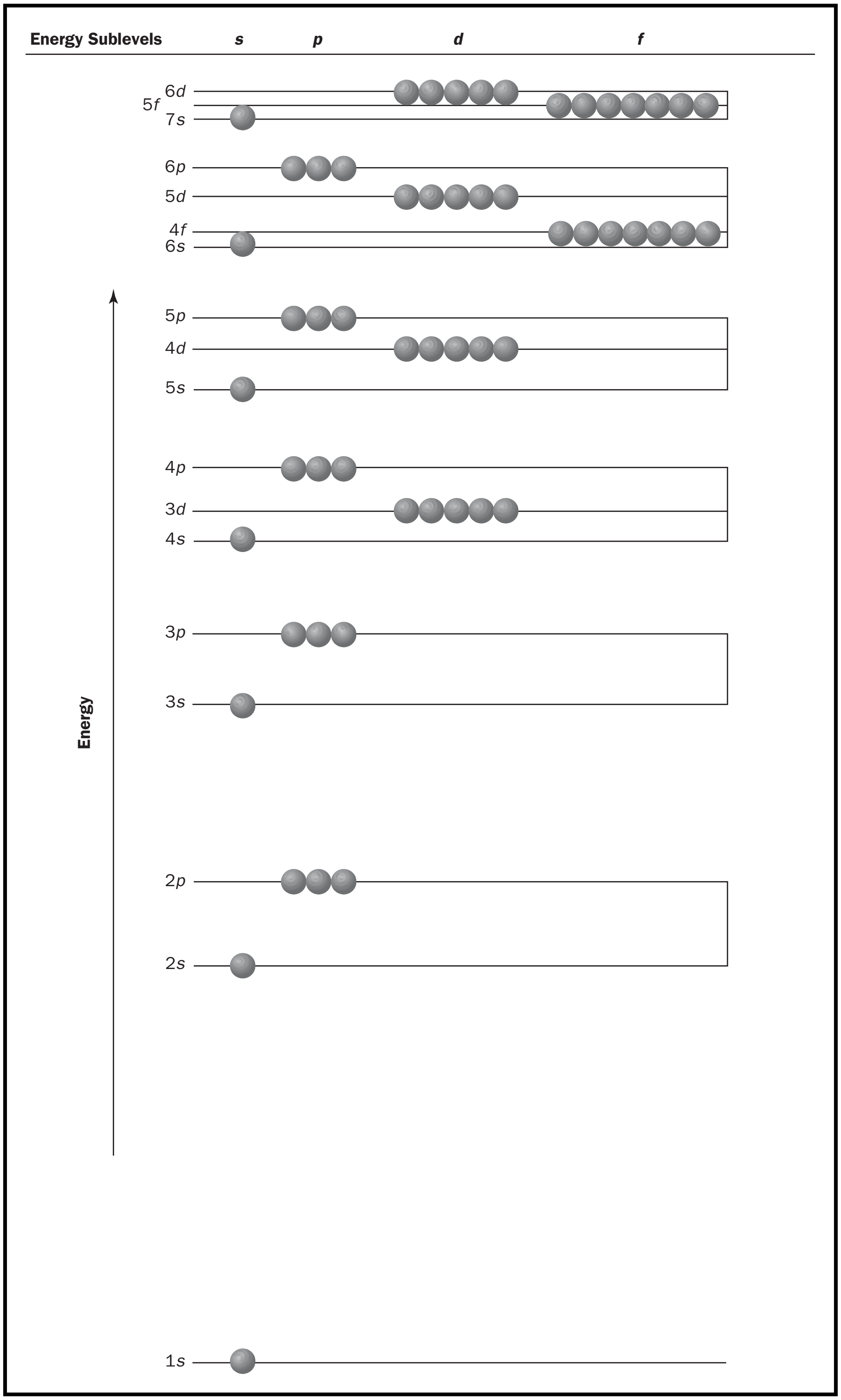


Figure 3. Relative energies of the various electron orbitals.

This shows that the nitrogen atom has a nuclear charge of +7, and it therefore has seven electrons. Two electrons are in the first main shell in an *s* orbital, and the other five are in the second main shell, two in the *s* orbital and three in the p_x, p_y, and p_z orbitals. Each can have as many kinds of orbitals (subshells) as the shell number. The first shell has one (*s*), the second has two (*s* and *p*), the third has three (*s*, *p*, and *d*), and the fourth has four (*s*, *p*, *d*, and *f*). The fifth would probably have five, if there were any atoms big enough to have a full fifth shell.

As atoms get larger, the order of filling electrons into orbitals gets more complicated. In the element Scandium (Sc), for example, the 4*s* orbital is considered filled before the 3*d* orbitals begin to fill. This may be explained in terms of the difference in shielding of the nucleus by the *s* and *d* electrons, as well as of interelectronic repulsion effects. It thus appears as if the 4*s* orbital is lower in energy than the 3*d* orbitals. (See Figure 3). The general order of filling of the various subshells is:

$$1s<2s<2p<3s<3p<4s<3d<4p<5s<4d<5p<6s<4\mathrm{f}>5d<6p<7s<5f<6d<7p$$

The *d* electrons always come in one shell late, and the *f* electrons two shells late. This can be demonstrated with the lead (Pb) atom. Using the Aufbau procedure to show the order of filling, the electron configuration for the Pb atom is:

Lead (Pb, Z = 82): $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^24f^{14}5d^{10}6p^2$

Perhaps the easiest way to determine the correct filling order is to use the periodic table. (See Figure 4). The square for each element represents the most recently added electron. In the first shell there are two *s* electrons; in the second there are two *s* and six *p* electrons; and in the third there are two *s* and six *p* electrons, and then ten more fill up the 3*d* orbitals after the fourth shell has begun. The transition elements result from electrons filling in the *d* orbitals, and the lanthanide and actinide elements from electrons filling in the *f* orbitals.

Electron configurations for the various elements in group 5A of the periodic table (but not indicating the order of the filling) are shown below:

Nitrogen (N, Z = 7): $\mathrm{ls^22s^22p^3}$
Phosphorus (P, Z = 15): $\mathrm{1s^22s^22p^63s^23p^3}$
Arsenic (As, Z = 33): $\mathrm{1s^22s^22p^63s^23p^63d^{10}4s^24p^3}$
Antimony (Sb, Z = 51): $\mathrm{1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^3}$
Bismuth (Bi, Z = 83): $\mathrm{ls^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}4f^{14}5s^25p^65d^{10}6s^26p^3}$

Note that the electron configurations for the larger atoms can get rather cumbersome, but they can be readily shortened by using the noble gas core convention.

Nitrogen	[He] $\mathrm{2s^22p^3}$
Phosphorus	[Ne] $\mathrm{3s^23p^3}$
Arsenic	[Ar] $\mathrm{3d^{10}4s^24p^3}$
Antimony	[Kr] $\mathrm{4d^{10}5s^25p^3}$
Bismuth	[Xe] $\mathrm{4f^{14}5d^{10}6s^26p^3}$

The noble gas core represents all electrons contained in an atom of noble gas. The similar chemical properties of the elements in the 5A group is attibuted to the similar arrangement of the outer shell electrons of all the members of the group: $\mathrm{ns^2np^3}$. The outermost shell is vital for determining the chemical properties of the elements and is called the *valence shell*. Similar regularities appear in the other groups of the periodic table.

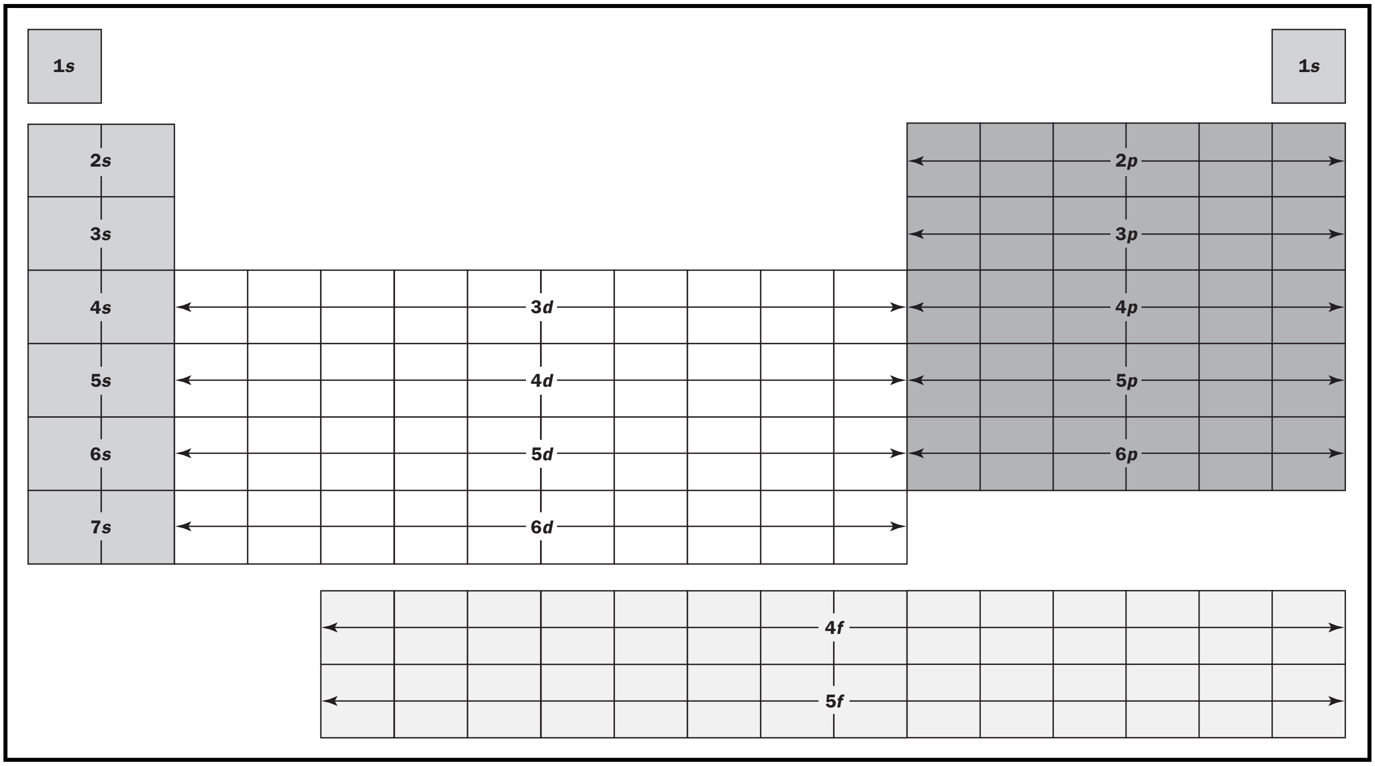


Figure 4. Diagram of the Periodic Table based on electron configurations, showing the representative elements (*s* and *p* blocks), the transition elements (*d* block), and the lanthanide and actinide elements (*f* block).

A number of elements show deviations from the predicted configurations. For instance, instead of the predicted configuration KL...$(n\text{-}1)d^4ns^2$, we have KL...$(n\text{-}1)d^5ns^1$ for the chromium (Cr) and molybdenum (Mb). In such cases, we speak of the preferred stability of the half-filled (d^5) or filled (d^{10}) *d* subshell. It might also be noted that with atoms of the heavy elements relativistic effects play a role, because of the higher velocities (approaching the speed of light) of the inner shell electrons, caused by the high Z values and the accompanying contraction of the inner shells. SEE ALSO Atomic Nucleus; Bohr, Niels.

Georgios Tsaparlis

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Atoms

An atom is the smallest possible unit of an element. Since all forms of matter consist of a combination of one or more elements, atoms are the building blocks that constitute all the matter in the universe. Currently, 110 different elements, and thus 110 different kinds of atoms, are known to exist.

Our current understanding of the nature of atoms has evolved from the ancient, untested ideas of Greek philosophers, partly as a result of modern technology that has produced images of atoms.

The Greek Atomistic Philosophy

The earliest ideas concerning atoms can be traced to the Greek philosophers, who pursued wisdom, knowledge, and truth through argument and reason. Greek scientific theories were largely based on speculation, sometimes based on observations of natural phenomena and sometimes not. The idea of designing and performing experiments rarely occurred to Greek philosophers, to whom abstract intellectual activity was the only worthy pastime.

Empedocles, a Greek philosopher active around 450 B.C., proposed that there were four fundamental substances—earth, air, fire, and water—which, in various proportions, constituted all matter. Empedocles, thus, formulated the idea of an elemental substance, a substance that is the ultimate constituent of matter; the chemical elements are modern science's fundamental substances. An **atomic theory** of matter was proposed by Leucippus, another Greek philosopher, around 478 B.C. Our knowledge of the atomic theory of Leucippus is derived almost entirely from the writings of his student, Democritus, who lived around 420 B.C. Democritus maintained that all materials in the world were composed of *atoms* (from the Greek *atomos*, meaning indivisible). According to Democritus, atoms of different shapes, arranged and positioned differently relative to each other, accounted for the different materials of the world. Atoms were supposed to be in random perpetual motion in a *void;* that is, in nothingness. According to Democritus, the feel and taste of a substance was thought to be the effect of the atoms of the substance on the atoms of our sense organs. The atomic theory of Democritus provided the basis for an explanation of the changes that occur when matter is chemically transformed. Unfortunately, the theory was rejected by Aristotle (384–322 B.C.) who became the most powerful and famous of the Greek scientific philosophers. However, Aristotle adopted and developed Empedocles's ideas of elemental substances. Aristotle's elemental ideas are summarized in a diagram (shown in Figure 1), which associated the four elemental substances with four *qualities:* hot, moist, cold, and dry. Earth was dry and cold; water was cold and moist; air was moist and hot; and fire was hot and dry. Every substance was composed of combinations of the four elements, and changes (which we now call *chemical*) were explained by an alteration in the proportions of the four elements. One element could be converted into the other by the addition or removal of the appropriate qualities. There were, essentially, no attempts to produce evidence to support this four-element theory, and, since Aristotle's scientific philosophy held sway for 2,000 years, there was no progress in the development of the atomic concept. The tenuous relationship between elements and atoms had been severed when Aristotle rejected the ideas of Democritus. Had the Greek philosophers been open to the idea of experimentation, atomic theory, indeed all of science, could have progressed more rapidly.

atomic theory: physical concept that asserts that matter is composed of microscopically tiny particles called atoms and that various elements differ from each other by having different atoms

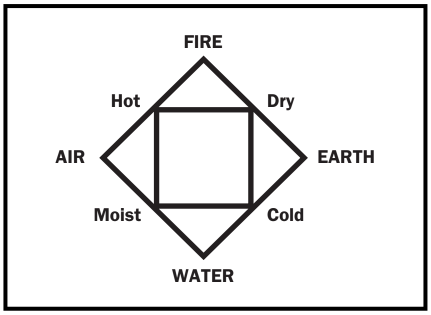


Figure 1. Aristotle's four-element diagram.

The Rise of Experimentation

The basis of modern science began to emerge in the seventeenth century, which is often recognized as the beginning of the Scientific Revolution. Conceptually, the Scientific Revolution can be thought of as a battle between three different ways of looking at the natural world: the Aristotelian, the magical, and the mechanical. The seventeenth century saw the rise of experimental science. The idea of making observations was not new. However, Sir Francis Bacon (1561–1626) emphasized that experiments should be planned and the results carefully recorded so they could be repeated and verified, an attitude that infuses the core idea of modern science. Among the early experimentalists was Robert Boyle (1627–1691), who studied quantitatively the compression and expansion of air, which led him to the idea that air was composed of particles that he called *corpuscles*, which he maintained were in constant motion. Boyle's description of corpuscular motion presages the kinetic molecular theory.

The Chemical Atom

An atomic theory based on chemical concepts began to emerge from the work of Antoine Lavoisier (1743–1794), whose careful quantitative experiments led to an operational definition of an element: An element was a substance that could not be decomposed by chemical processes. In other words, if a chemist could not decompose a substance, it must be an element. This point of view obviously put a premium on the ability of chemists to manipulate substances. Inspection of Lavoisier's list of elements, published in 1789, shows a number of substances, such as silica (SiO_2), alumina (Al_2O_3), and baryta (BaO), which today are recognized as very stable compounds. The chemists of Lavoisier's time simply did not have the tools to decompose these substances further to silicon, aluminum, and barium, respectively. The composition of all compounds could be expressed in terms of the elemental substances, but it was the quantitative mass relationship of compounds that was the key to deducing the reality of the chemical atom.

DEMOCRITUS OF ABBERA

Little is known for certain about Democritus of Abbera (c.460 B.C.E.–c.362 B.C.E. None of his writings has survived intact. It is known from others (both students and detractors) that Democritus was one of the earliest advocates of a theory that all matter exists as collections of very small, permanent, indivisible particle called atoms.

—David A. Bassett

Lavoisier's successful use of precise mass measurements essentially launched the field of analytical chemistry, which was thoroughly developed by Martin Klaproth (1743–1817). Lavoisier established the concept of mass conservation in chemical reactions, and, late in the eighteenth century, there was a general acceptance of the concept of definite proportions (constant composition) in chemical compounds, but not without controversy. Claude-Louis Berthollet (1748–1822) maintained that the composition of compounds could be variable, citing, for example, analytical results on the oxides of copper, which gave a variety of results, depending on the method of **synthesis**. Joseph-Louis Proust (1754–1826), over a period of eight years, showed that the variable compositions, even with very accurate analytical data, were due to the formation of different mixtures of two oxides of copper, CuO and Cu_2O. Each oxide obeyed the law of constant composition, but reactions that were supposed to lead to "copper oxide" often produced mixtures, the proportions of which depended on the conditions of the reaction. Proust's proof of the law of constant composition was important, because compounds with variable composition could not be accommodated within the evolving chemical atomic theory.

synthesis: combination of starting materials to form a desired product

John Dalton (1766–1844), a self-educated English scientist, was primarily interested in meteorology and is credited with being the first to describe color blindness, a condition with which he was burdened throughout his life. Color blindness is a disadvantage for a chemist, who must be able to see color changes when working with chemicals. Some have suggested that his affliction was one reason why Dalton was a rather clumsy and slipshod experimenter. Gaseous behavior had been well established, starting with the experiments of Boyle. Dalton could not help supposing, as others previously did, that gaseous matter was composed of particles. But Dalton took the next and, ultimately, most important steps in assuming that *all* matter—gaseous, liquid, and solid—consists of these small particles. The law of definite proportions (constant composition) as articulated by Proust, suggested to Dalton that a compound might contain two elements in the ratio of, for example, 4 to 1, but never 4.1 to 1 or 3.9 to 1. This observation could easily be explained by supposing that each element was made up of individual particles.

Dalton's atomic theory can be succinctly summarized by the following statements:

> Elements are composed of extremely small particles called *atoms.*
>
> All atoms of a given element have identical properties, and those properties differ from those of other elements.
>
> Compounds are formed when atoms of different elements combine with one another in small whole numbers.
>
> The relative numbers and kinds of atoms are constant in a given compound.

Dalton recognized the similarity of his theory to that of Democritus, advanced twenty-one centuries earlier when the Greek philosopher called these small particles *atoms*, and, presumably, implied by using that word that these particles were indivisible. In Dalton's representation (Figure 2) the elements were shown as small spheres, each with a separate identity. Compounds of elements were shown by combining the appropriate elemental representations in the correct proportions, to produce complex symbols that seem to echo our present use of standard chemical formulas. Dalton's symbols—circles with increasingly complex inserts and decorations—were not adopted by the chemical community. Current chemical symbols (formulas) are derived from the suggestions of Jöns Berzelius (1779–1848). Berzelius also chose oxygen to be the standard reference for atomic mass (O = 16.00 AMU). Berzelius produced a list of atomic masses that were much closer to those that are currently accepted because he had developed a better way to obtain the formulas of substances. Whereas Dalton assumed that water had the formula HO, Berzelius showed it to be H_2O. The property of atoms of interest to Dalton were their relative masses, and Dalton produced a table of atomic masses (Table 1) that was seriously deficient because he did not appreciate that atoms did not have to be in a one-to-one ratio; using more modern ideas, Dalton assumed, incorrectly, that all atoms had a **valence** of one (1). Thus, if the atomic mass of hydrogen is arbitrarily assigned to be 1, the atomic mass of oxygen is 8 on the Dalton scale. Dalton, of course, was wrong, because a water molecule contains two atoms of hydrogen for every oxygen atom, so that the individual oxygen atom is eight times as heavy as two hydrogen atoms or sixteen times as heavy as a single hydrogen atom. There was no way that Dalton could have known, from the data available, that the formula for water is H_2O.

valence: combining capacity

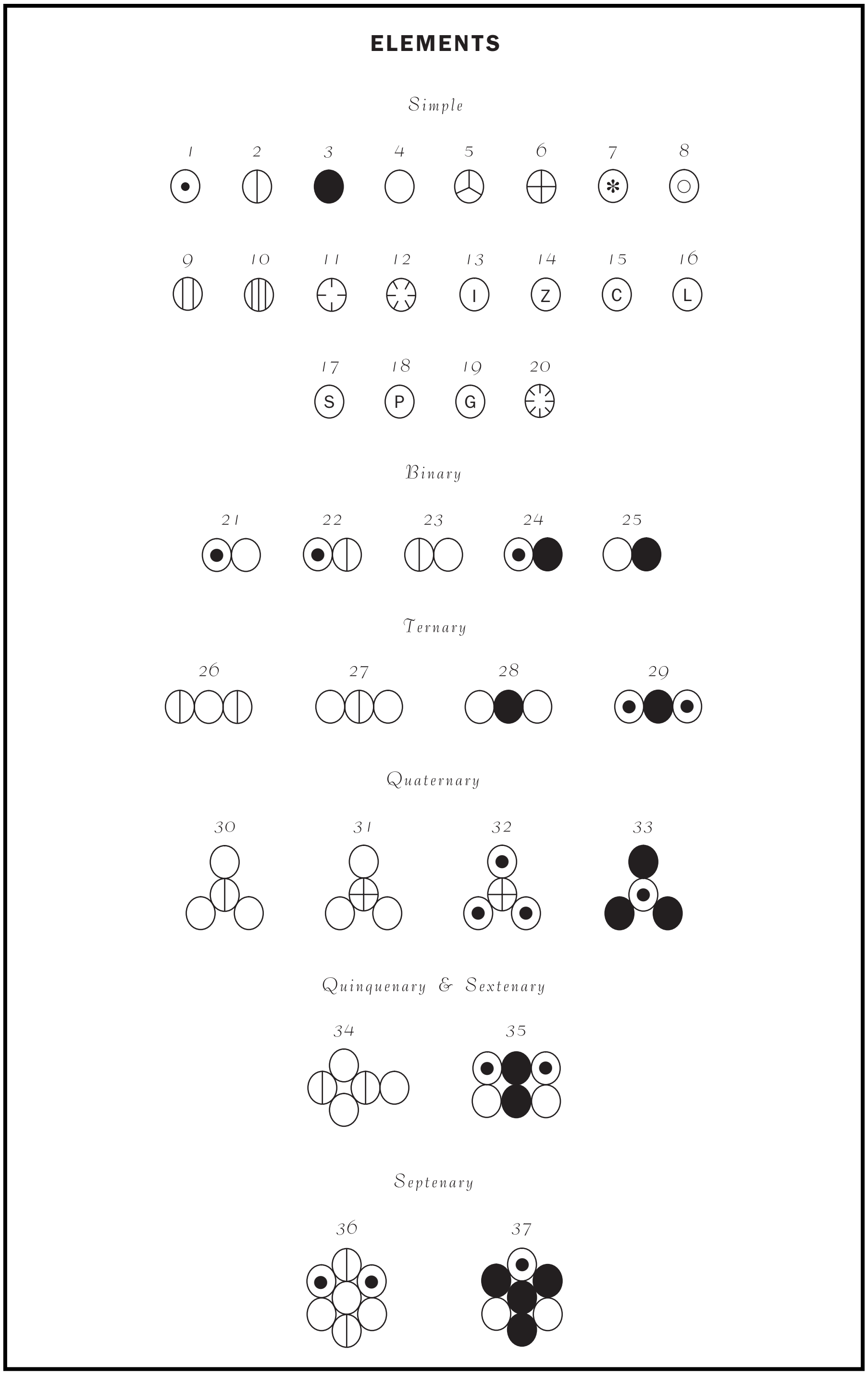


Figure 2. Dalton's atomic symbols are described as "simple." The increasingly complex combination of symbols represent binary, ternary, quaternary, etc., compounds. Thus, Number 28 is a compound atom of carbonic acid (carbon dioxide), and number 31 is a compound atom of sulphuric acid (sulphyr trioxide).

Dalton's atomic theory explained the law of multiple proportions. For example, it is known that mercury forms two oxides: a black substance containing 3.8 percent oxygen and 96.2 percent mercury, and a red compound containing 7.4 percent oxygen and 92.6 percent mercury. Dalton's theory states that the atoms of mercury (Hg) and oxygen (O) must combine in whole numbers, so the two compounds might be HgO and Hg_2O, for example. Furthermore, Dalton's theory states that each element has a characteristic mass—perhaps 9 mass units for Hg and 4 mass units for O (the

Table 1. Dalton's first set of atomic weight values (1805).

DALTON'S FIRST SET OF ATOMIC WEIGHT VALUES (1805)	
Hydrogen	1
Azot	4.2
Carbon	4.3
Ammonia	5.2
Oxygen	5.5
Water	6.5
Phosphorus	7.2
Phosphuretted hydrogen	8.2
Nitrous gas	9.3
Ether	9.6
Gaseous oxide of carbon	9.8
Nitrous oxide	13.7
Sulphur	14.4
Nitric acid	15.2
Sulphuretted hydrogen	15.4
Carbonic acid	15.3
Alcohol	15.1
Sulphureous acid	19.9
Sulphuric acid	25.4
Carburetted hydrogen from stagnant water	6.3
Olefiant gas	5.3

numbers were chosen arbitrarily, here). Given these assumptions, the relevant concepts are shown in Table 2.

The *assumed* formulas are presented in line 1. The percent composition of each compound, calculated in the usual way, is presented in line 3, showing that these two compounds, indeed, have different compositions, as required by the law of multiple proportions. Line 4 contains the ratio of the mass of mercury to the mass of oxygen, for each compound. Those ratios can be expressed as the ratio of simple whole numbers (2.25:4.5 = 1:2), fulfilling a condition required by the law of multiple proportions. Notice that Dalton's ideas do not depend upon the values assigned to the elements or the formulas for the compounds involved. Indeed, the question as to which compound, red or black, is associated with which formula cannot be answered from the data available. Thus, although Dalton was unable to establish an atomic mass scale, his general theory did provide an understanding of the three mass-related laws: conservation, constant composition, and multiple proportion. Other information was required to establish the relative masses of atoms.

The other piece of the puzzle of relative atomic masses was provided by Joseph-Louis Gay-Lussac (1778–1850), who published a paper on volume relationships in reactions of gases. Gay-Lussac made no attempt to interpret his results, and Dalton questioned the paper's validity, not realizing that the law of combining volumes was really a verification of his atomic theory! Gay-Lussac's experiments revealed, for example, that 2 volumes of carbon monoxide combine with 1 volume of oxygen to form 2 volumes of carbon dioxide. Reactions of other gaseous substances showed similar volume relationships. Gay-Lussac's law of combining volumes suggested, clearly, that equal volumes of different gases under similar conditions of temperature and pressure contain the same number of reactive particles (molecules). Thus, if 1 volume of ammonia gas (NH_3) combines exactly with 1 volume of hydrogen chloride gas (HCl) to form a salt (NH_4Cl), it is natural to conclude that each volume of gas must contain the same number of particles.

Table 2. Law of multiple proportions.

LAW OF MULTIPLE PROPORTIONS

Assumed formula	HgO	Hg_2O
Total mass of compound	9 + 4 = 13	9 + 9 + 4 = 22
% composition	% Hg 69.2; % O = 30.8	% Hg = 81.8; % O = 18.2
Mass Hg/Mass O	9/4 = 2.25	18/4 = 4.5

At least one of the implications of Gay-Lussac's law was troubling to the chemistry community. For example, in the formation of water, 2 volumes of hydrogen gas combined with 1 volume of oxygen gas to produce 2 volumes of steam (water in the gaseous state). These observations produced, at the time, an apparent puzzle. If each volume of gas contains *n* particles (molecules), 2 volumes of steam must contain 2 *n* particles. Now, if each water particle contains at least 1 oxygen atom, how is it possible to get two oxygen atoms (corresponding to 2 *n* water molecules) from *n* oxygen particles? The obvious answer to this question is that each oxygen particle contains two oxygen atoms. This is equivalent to stating that the oxygen *molecule* consists of two oxygen *atoms*, or that oxygen gas is diatomic (O_2). Amedeo Avogadro (1776–1856) an Italian physicist, resolved the problem by adopting the hypothesis that equal volumes of gases under the same conditions contain equal numbers of particles (molecules). His terminology for what we now call an atom of, for instance, oxygen, was *half molecule.* Similar reasoning involving the combining of volumes of hydrogen and oxygen to form steam leads to the conclusion that hydrogen gas is also diatomic (H_2). Despite the soundness of Avogadro's reasoning, his hypothesis was generally rejected or ignored. Dalton never appreciated its significance because he refused to accept the experimental validity of Gay-Lussac's law.

Avogadro's hypothesis—equal volumes of gases contain equal numbers of particles—lay dormant for nearly a half-century, until 1860 when a general meeting of chemists assembled in Karlsruhe, Germany, to address conceptual problems associated with determining the atomic masses of the elements. Two years earlier, Stanislao Cannizzaro (1826–1910) had published a paper in which, using Avogadro's hypothesis and vapor density data, he was able to establish a scale of relative atomic masses of the elements. The paper, when it was published, was generally ignored, but its contents became the focal point of the Karlsruhe Conference.

Cannizzaro's argument can be easily demonstrated using the compounds hydrogen chloride, water, ammonia, and methane, and the element hydrogen, which had been shown to be diatomic (H_2) by using Gay-Lussac's reasoning and his law of combining volumes. The experimental values for vapor density of these substances, all determined under the same conditions of temperature and pressure, are also required for Cannizzaro's method for establishing atomic masses. The relevant information is gathered in Table 3. The densities of these gaseous substances (at 100° C and one atmosphere pressure) are expressed in grams per liter. The masses of the substances (in one liter) are the masses of equal numbers of molecules of each substance; the specific number of molecules is unknown, of course, but that number is unnecessary for the Cannizzaro analysis. If that unknown number of molecules is called N, and if m_H represents the mass of a single hydrogen atom, then $m_H \times 2N$ is the total

CANNIZZARO'S METHOD OF MOLECULAR MASS DETERMINATION

Gaseous Substance	Density g/L[1]	Relative to Mass of an H Atom (Molecular Mass, Relative to H = 1)	% Hydrogen	Relative Mass of H Present	Number H Atoms Present in a Molecule	Formula	Mass of "Other" Atoms
Hydrogen	0.0659	2.00	100	2.00	2	H_2	H = 1
Hydrogen chloride	1.19	36.12	2.76	1.00	1	HCl	Cl = 35.2
Water	0.589	17.88	11.2	2.00	2	H_2O	O = 15,88
Ammonia	0.557	16.90	17.7	3.00	3	NH_3	N = 13.90
Methane	0.524	15.90	25.1	4.00	4	CH_4	C = 11.90

[1] Density reported for conditions of 100° C and one atmosphere pressure

Table 3. Cannizzaro's method of molecular mass determination.

mass of the hydrogen atoms in the 1 liter sample of hydrogen molecules; recall that hydrogen was shown to be diatomic (H_2) by Gay-Lussac's law. From this point of view, the relative masses of the molecules fall in the order of the masses in 1 liter (or their densities). The mass of the hydrogen *atom* was taken as the reference (H = 1) for the relative atomic masses of the elements. Thus, the mass of all the hydrogen chloride molecules in the one liter sample is $m_{\mathrm{HCl}}N$, and the ratio of the mass of a hydrogen chloride molecule to a hydrogen atom is given by:

$$\frac{m_{\mathrm{Cl}} \times \cancel{N}}{m_{\mathrm{H}} \times 2\cancel{N}} = \frac{1.19}{0.0659} = \frac{36.12}{1.00}$$

That is, if the mass of a hydrogen atom is taken to be 1 unit of mass, the mass of the hydrogen chloride molecule is 36.12 units. All the molecular masses listed in column 3 of the table can be established in the same way—twice the ratio of the density of the molecule in question to the density of hydrogen. Using experimental analytical data (column 4), Cannizzaro was able to establish the relative mass of hydrogen in each molecule (column 5), which gave the number of hydrogen atoms present in each molecule of interest (column 6), which, in turn, produced the formula of the molecule (column 7); analytical data also quantitatively indicate the *identity* of the other atom in the molecule. Thus, analysis would tell us that, for example, methane contains hydrogen and carbon. Knowing the total mass of the molecule (column 3) and the mass of all the hydrogen atoms present, the mass of the "other atom" in the molecule can be established as the difference between these numbers (column 8). Thus, if the mass of the HCl molecule is 36.12 and one atom of hydrogen of mass 1.00 is present, the mass of a Cl atom is 35.12. Relative mass units are called **atomic mass units**, AMUs.

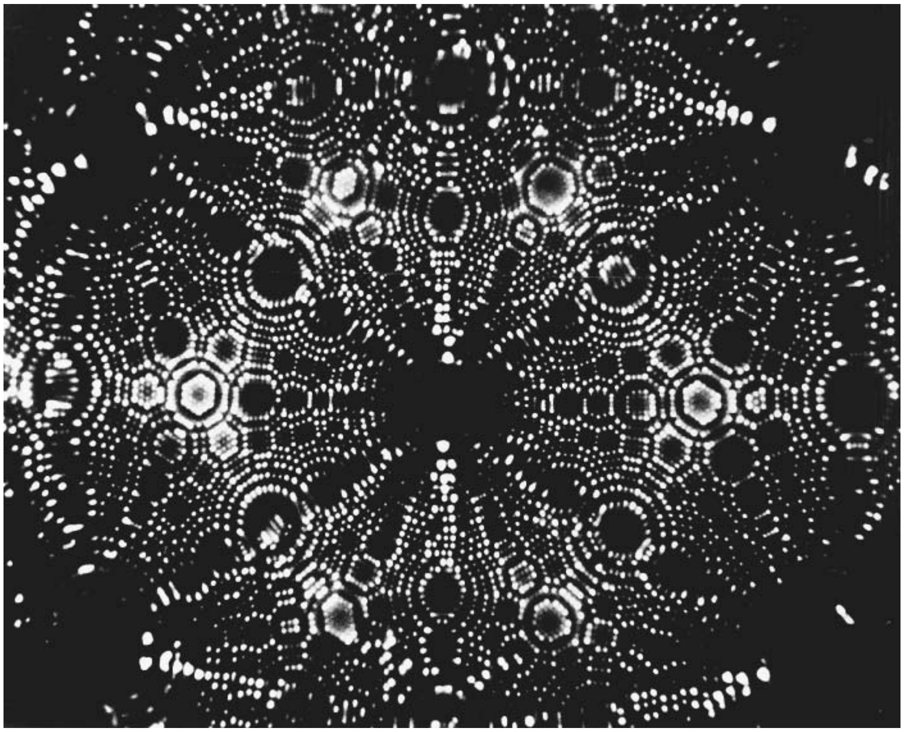
atomic mass units: unit used to measure atomic mass; $\frac{1}{12}$ of mass of a carbon-12 atom

This very convincing use of Gay-Lussac's law and Avogadro's hypothesis by Cannizzaro quickly provided the chemical community with a direct way of establishing not only the molecular formulas of binary compounds but also the relative atomic masses of elements, starting with quantitative analytical data and the density of the appropriate gaseous substances.

The long struggle to establish the concept of the chemical atom involved many scientists working in different countries using different kinds of equipment to obtain self-consistent data. All were infused with ideas of Sir Francis Bacon, who defined the classic paradigm of experimental science—results that are derived from careful observations and that are openly reported for verification. However, not all chemists equally embraced these ideas, which were to become fundamental to their craft. For example, the great physical chemist and Nobel Prize winner Friedrich Wilhelm Ostwald (1853–1932) refused to accept the existence of atoms well into the twentieth century. Ostwald held a strong personal belief that chemists ought to confine their studies to measurable phenomena such as energy changes. The atomic theory was to Ostwald nothing more than a convenient fiction.

There are, of course, other lines of observations and arguments that lead to the conclusion that matter is particulate and, subsequently, to an ultimate atomic description of matter. One of these involves the **Brownian motion** of very small particles. Robert Brown (1773–1858), a Scottish botanist, observed in 1827 that individual grains of plant pollen suspended in water moved erratically. This irregular movement of individual particles of a suspension as observed with a microscope is called *Brownian motion.* Initially, Brown believed that this motion was caused by the "hidden life" within the pollen grains, but further studies showed that even nonliving suspensions behave in the same way. In 1905 Albert Einstein (1879–1955) worked out a mathematical analysis of Brownian motion. Einstein showed that if the water in which the particles were suspended was composed of molecules in random motion according to the requirements of the kinetic molecular theory, then the suspended particles would exhibit a random "jiggling motion" arising from the occasional uneven transfer of momentum as a result of water molecules striking the pollen grains. One might expect that the forces of the water molecules striking the pollen grains from all directions would average out to a zero net force. But Einstein showed that, occasionally, more water molecules would strike one side of a pollen grain than the other side, resulting in a movement of the pollen grain. The interesting point in Einstein's analysis is that even if each collision between a water molecule and a pollen grain transfers a minuscule amount of momentum, the enormous

Brownian motion: random motion of small particles, such as dust or smoke particles, suspended in a gas or liquid; it is caused by collisions of the particle with gas or solvent molecules that transfer momentum to the particle and cause it to move



Photomicrograph of atoms in a tungsten crystal, magnified 2,700,000 times.

number of molecules striking the pollen grain is sufficient to overcome the large momentum advantage of the pollen grain (because of its considerably larger mass than that of a water molecule). Although the Swedish chemist Theodor Svedberg (1884–1971) suggested the general molecular explanation earlier, it was Einstein who worked out the mathematical details. Einstein's analysis of Brownian motion was partially dependent on the size of the water molecules. Three years later, Jean-Baptiste Perrin (1870–1942) set about to determine the size of the water molecules from precise experimental observations of Brownian motion. In other words, Perrin assumed Einstein's equations were correct, and he made measurements of the particles' motions, which Brown had described only qualitatively. The data Perrin collected allowed him to calculate the size of water molecules. Ostwald finally yielded in his objection to the existence of atoms because Perrin had a direct measure of the effect of water molecules on macroscopic objects (pollen grains). Since water was composed of the elements hydrogen and oxygen, the reality of atoms had been experimentally proved in Ostwald's view of how chemistry should be pursued.

Ostwald's reluctance to accept the chemical atom as an entity would surely have yielded to the overwhelming evidence provided by scanning tunneling microscopy (STM). Although Ostwald did not live to see it, this technique provides such clear evidence of the reality of simple atoms that even he would have been convinced. SEE ALSO Avogadro, Amedeo; Berthollet, Claude-Louis; Berzelius, Jöns JaKob; Boyle, Robert; Cannizzaro, Stanislao; Dalton, John; Einstein, Albert; Gay-Lussac, Joseph-Louis; Lavoisier, Antoine; Ostwald, Friedrich Wilhelm; Svedberg, Theodor; MOLECULES.

J. J. Lagowski

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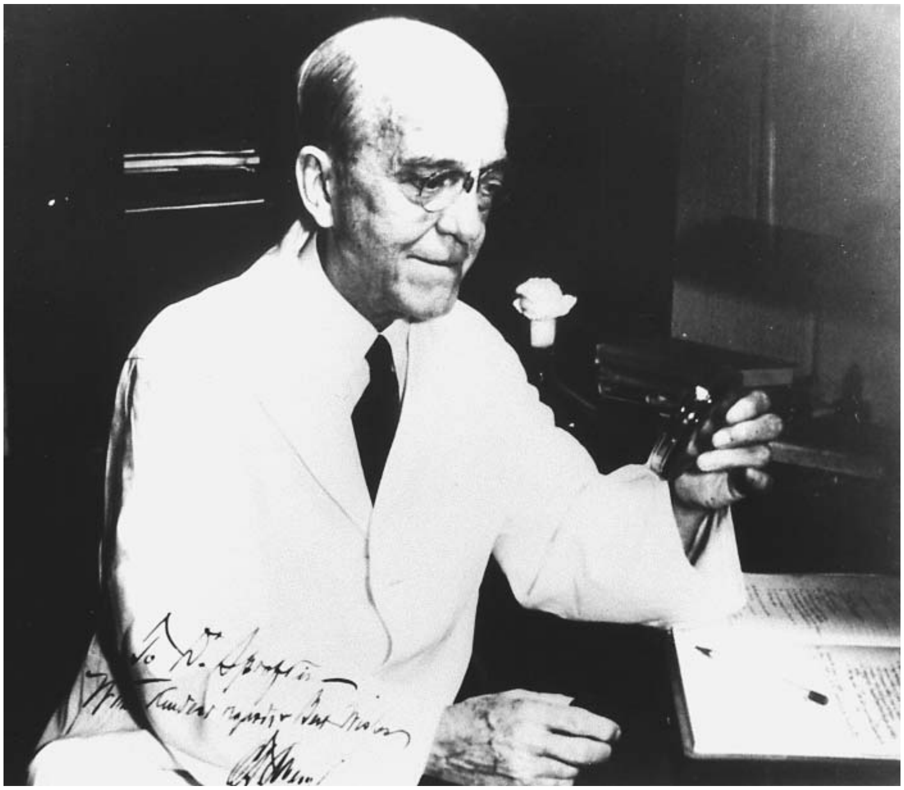
Avery, Oswald

CANADIAN-AMERICAN PHYSICIAN
1877–1955

By the early 1940s, scientists knew that chromosomes existed and that they were composed of smaller units called genes. Chemical analysis had revealed that the eucaryotic chromosome consists of about 50 percent protein and 50 percent deoxyribonucleic acid (DNA). There was no particular interest in DNA for several previous decades because no role had been assigned to it. This changed when a Canadian-born American named Oswald Avery showed that DNA is responsible for the transmission of heritable characteristics.

Avery moved from Canada to New York City in 1887. He attended Colgate University and in 1904 received his medical degree from the College of Physicians and Surgeons at Columbia University. He practiced medicine



American bacteriologist Oswald Avery, who demonstrated that DNA is the unit of genetic inheritance.

for several months before he became more interested in the transmission of infectious diseases. In 1913, Avery arrived at Rockefeller Institute, where he worked as a bacteriologist for over 43 years.

Avery and his co-workers studied the life cycle and chemical make-up of *Diplococcus pneumoniae*, or pneumococci, a species of bacteria that causes pneumonia. Avery's interest was sparked by British microbiologist Frederick Griffith's work with pneumococci. In 1928, Griffith described an experiment in which he injected mice with a mixture of a harmless strain of living pneumococci and the dead remains of a virulent strain of the bacteria. The mice died from infection by the *live* organisms of the virulent strain, though the organisms had been dead when they were administered. By 1932 Avery focused on transformation—a process by which heritable characteristics of one species are incorporated into another different species.

In an attempt to duplicate Griffith's work, Avery and his colleagues began to grow large quantities of virulent type III capsulated pneumococcus. They purified the live virulent encapsulated bacteria and then killed them by extreme heat. The bacteria's polysaccharide protein, which makes up the capsule or outer envelope, was then removed. The remaining portion of the dead bacteria, its polysaccharide gone but capsules intact, was added to living, unencapsulated bacteria. It was found that the offspring of these living bacteria had capsules. Avery had determined that the active transforming principle, as Griffith had described earlier, still remained. Because the polysaccharide protein had been removed for the test, it could not be the transforming factor.

Avery wanted to be certain that the active agent was the DNA and not a small amount of protein contamination. To verify the result, a quantity of DNase, an enzyme that would destroy the DNA without affecting the protein, was prepared and added to the sample. When a portion of bacteria was tested, it could no longer transform the unencapsulated bacteria into encapsulated bacteria. Avery and his co-workers had conclusively proven that DNA was the transforming principle responsible for the development of polysaccharide capsules in the unencapsulated bacteria.

This experiment, first published in 1944, was extremely important because, for the first time, scientists had proven that DNA controls the development of a cellular feature. It also implicated DNA as the basic genetic material of cells and stimulated James Watson and Francis Crick to later discover its structure and method of replication. Today we understand that DNA is the fundamental molecule involved in heredity. SEE ALSO WATSON, JAMES DEWEY.

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Avogadro, Amedeo

ITALIAN CHEMIST
1776–1856

atomic theory: physical concept that asserts that matter is composed of microscopically tiny particles called atoms and that various elements differ from each other by having different atoms

In 1811, just three years after John Dalton published his **atomic theory**, a brilliant theoretician named Amedeo Avogadro proposed his molecular theory. Avogadro's molecular theory related gas densities to molecular weights, explained reacting proportions by volume in terms of molecular ratios and compositions, and suggested methods for determining both molecular weights and compositions. His 1811 publication was a tour de force. Nonetheless, it was ignored for over half a century. Historians have sought reasons for the neglect of Avogadro's work in his life, his theory, and the state of chemistry at the time.

Avogadro's Life

Amedeo Avagadro was born in 1776 in Turin, a city in northwestern Italy. Avogadro spent his entire life within 80 kilometers (50 miles) of Turin, far from the cultural centers where chemistry was becoming a science. He received a classical education in the humanities, earned a doctorate in law in

1796 at the age of twenty, and practiced law for the next ten years. After auditing some courses and studying science on his own, Avogadro made a radical career change. In 1806 he became a secondary school science teacher, and in 1820 a university physics professor. He married in 1815, had seven children, and by all accounts, led a very happy family life.

During his academic career, Avogadro's publications revealed an intense curiosity, sharp intuition, vivid imagination, rigorous logic, and independent judgment—traits of an outstanding scientist. His obituary in an Italian scientific journal remarked on his retiring disposition and on the simplicity of his life, and it noted his other researches, but it did not mention the 1811 paper on his molecular theory.

Avogadro's Molecular Theory

Avogadro made two assumptions about molecules in his 1811 publication. The first assumption is now known as Avogadro's hypothesis, sometimes also called the EVEN hypothesis. It stated that equal volumes of gases contain equal numbers (thus, even) of molecules at the same temperature and pressure. The hypothesis was based on a model of the gas state in which molecules are far apart and equally spaced so that each molecule occupies the same volume. The second assumption was that gas molecules can divide during chemical reactions.

Avogadro used the EVEN hypothesis to interpret gas densities and assign molecular weights. EVEN implies that the density of a gas at a given temperature and pressure depends only on the weight of its molecules. Avogadro supposed that since the reported **gas density** of oxygen was 15 times that of hydrogen, the molecular weight of oxygen was 15 times that of hydrogen (the modern calculation of the ratio of the densities and molecular weights is actually sixteen). Consequently, he assigned oxygen a molecular weight of 15, relative to 1 for hydrogen. By this method Avogadro could determine a molecular weight for any gas, given its density.

gas density: weight in grams of a liter of gas

Avogadro needed both assumptions to explain reacting proportions and molecular compositions. For example, when water forms, the reacting proportions of hydrogen, oxygen, and water are 2:1:2 by volume. On the basis of the EVEN hypothesis, a 2:1:2 volumetric ratio should correspond to a 2:1:2 molecular ratio. Thus, two molecules of hydrogen (h) should combine with one molecule of oxygen (o) to give two molecules of water. Direct combination, however, would give only one molecule of h_2o. To fit the volumetric data, Avogadro split the h_2o water molecule into two $ho_{1/2}$ molecules. This in turn forced him to assume that oxygen molecules could divide into two "half molecules" during the reaction: $2h + o \rightarrow [h_2o] \rightarrow 2ho_{1/2}$. He expressed the composition of water as one "half molecule" of oxygen combined with one molecule of hydrogen ($ho_{1/2}$). With the aid of his two assumptions—EVEN and divisible molecules—Avogadro determined compositions for water, ammonia, hydrogen chloride, and gaseous oxides of nitrogen, carbon, and sulfur.

Early Nineteenth-Century Chemistry

The state of chemical theory and practice in 1811 was primitive by modern standards and not yet ready for Avogadro's molecular theory. Dalton's model of the gas state (atoms of different size in contact) precluded EVEN. Jöns Jakob Berzelius, another very influential chemist, believed gaseous elements like oxygen contained only indivisible atoms, not divisible molecules. Gas density and combining ratios data were limited and inaccurate. Atomic weights depended on unknown formulas and vice versa—a vicious cycle.

Conclusion

In retrospect the neglect of Avogadro's theory seems quite understandable. In 1811 he was a secondary school teacher living in a remote province. Furthermore, he was a theoretical physicist writing for practical chemists in legal language. His molecular theory was based on speculative assumptions, lacked independent experimental evidence or theoretical justification, and could only explain but not predict volumetric ratios. His molecular ratios ($2h + o \rightarrow 2ho_{1/2}$) were far removed from modern atomic ratios ($2H_2 + O_2 \rightarrow 2H_2O$) and did not solve the **atomic weight**–formula problem. Chemists in the early nineteenth century, however, needed more immediately productive theories and much more experimental information before Avogadro's theory could be truly useful. It took half a century of effort, the development of organic chemistry, and the ingenuity of another Italian, Stanislao Cannizzaro, to build a modern chemistry on the foundations laid by Avogadro. Nonetheless, as Nobel Prize winner Linus Pauling observed in a 1956 article in *Science*, Avogadro's work "forms the basis of the whole of theoretical chemistry" and is "one of the greatest contributions to chemistry that has ever been made." SEE ALSO BERZELIUS, JÖNS JAKOB; CANNIZZARO, STANISLAO; DALTON, JOHN; PAULING, LINUS.

atomic weight: weight of a single atom of an element in atomic mass units (AMU)

John D. Hostettler

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b

B_1, Vitamin ***See Thiamin.***

B_2, Vitamin ***See Riboflavin.***

Baekeland, Leo

AMERICAN CHEMIST AND INVENTOR
1863–1944

Born in St. Martens-Latem, Belgium, Leo Hendrick Baekeland was the son of a cobbler (Karel Baekeland) and a housemaid (Rosalia Merchie). He earned a B.S. in 1882 and a D.Sc.in 1884, with the highest honors, in organic chemistry from the University of Ghent. He joined the faculty at Ghent, which was then a leading center for the study of coal tar compounds. Interested in becoming an inventor, Baekeland used a traveling scholarship to visit the United States in 1889 (the year he married Celine Swart). His interest in photographic development brought him into contact with Richard Anthony of E. & H. T. Anthony and Company, who recruited Baekeland to join his American-based photographic company.

After two years Baekeland became an independent consultant, but he had little money and few prospects. Nevertheless, after experimenting with silver chloride emulsions, he developed a high-quality photographic printing paper, called Velox, sensitive enough to be used with artificial light. In 1899 the Eastman Kodak Company (located in Rochester, New York) bought the rights to Velox from Baekeland and his partner Leonard Jacobi for $750,000. This product represented a great leap forward in modern photographic technology.

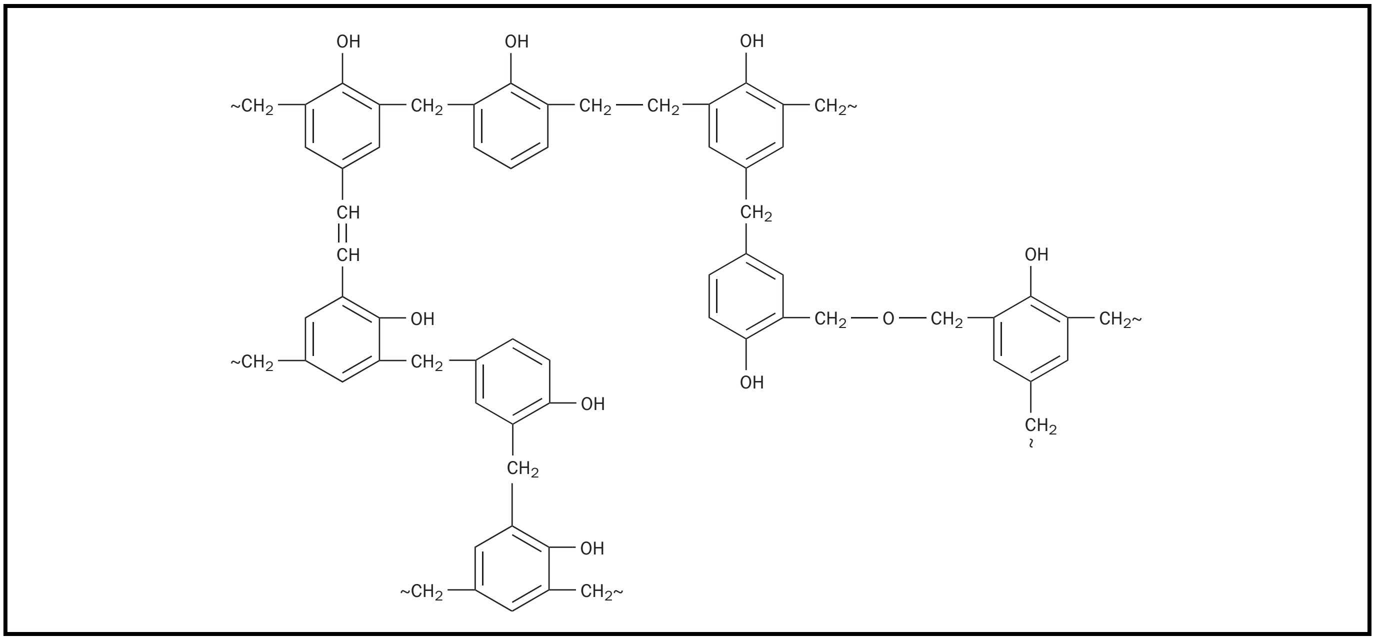

Figure 1. Structure of the phenol-formaldehyde polymer.

phenol: common name for hydroxybenzene (C_6H_5OH)

formaldehyde: name given to the simplest aldehyde, HC(O)H incorporating the −C(O)H functional group

aldehyde: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the RC(O)H functional group

catalyst: substance that aids in a reaction while retaining its own chemical identity

At his home laboratory in Yonkers, New York, Baekeland then returned to his early interest in resin chemistry. Reacting **phenol** and phenol derivatives with **formaldehyde**, he learned enough about controlling the **aldehyde**-phenol ratio with acids and alkalis to synthesize several resins. Most notable was the phenol-formaldehyde polymer resin (Figure 1) he produced with an alkali **catalyst**. Baekeland developed high pressure and high temperature techniques that greatly improved the molding of this plastic, which he named Bakelite and patented in 1909. It was a superhard, lightweight, insoluble plastic with a tensile strength of 7,000 pound force per square inch (psi). Baekeland claimed to have synthesized the first true plastic.

In 1910 Baekeland founded the General Bakelite Corporation in Perth Amboy, New Jersey, which began producing Bakelite on a commercial scale the following year. Bakelite was sold in liquid and powder form for molding to specifications. It quickly gained popularity in a variety of household and industrial uses—such as electrical insulation, billiard balls, tabletops, switchboards, and (later) automobile ignition systems—where it often replaced natural materials or earlier plastics, especially celluloid. By 1939 the factory was producing more than 50 million pounds of Bakelite a year. Baekeland and his firm controlled more than 400 patents. However, competition from major chemical companies was intensifying, and Baekeland's son George, who had worked for the company since 1923, did not wish to run it. So Baekeland, then seventy-five, sold the firm to Union Carbide and Carbon Corporation for roughly $16.5 million.

Baekeland earned many honors and awards, including the Franklin Medal of the Franklin Institute (1940), and the Perkin Medal (1916) and Messel Medal (1938) of the Society of the Chemical Industry. He was also elected president of the Chemists Club of New York (1904); the American Electrochemical Society (1909); the American Institute of Chemical Engineers (1912); and the American Chemical Society (1924). Eccentric in his old age, Baekeland spent much of his time alone, often in Coconut Grove, Florida, although he maintained a healthy correspondence with a number of colleagues on a broad range of subjects. He died in Beacon, New York, on February 23, 1944.

David B. Sicilia

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Bakelite ***See Baekeland, Leo.***

Balmer, Johann Jakob

SWISS MATHEMATICIAN
1825–1898

The name of Johann Jakob Balmer is immortalized in the Balmer series of **spectral lines** emitted from the hydrogen atom. Atoms that are excited to higher energies return to lower energies by emitting electromagnetic radiation at specific frequencies. Gustav Kirchhoff had shown in 1859 that each element has its own unique spectrum, but attempts to predict the frequencies of these spectral lines were unsuccessful until Balmer.

spectral line: line in a spectrum representing radiation of a single wavelength

After receiving a doctorate in mathematics from the University of Basel in Switzerland in 1849, Balmer taught at a girls' secondary school in Basel for the rest of his life; he was also a part-time university lecturer for many years. In 1885 he proposed an empirical formula for the wavelengths (l) of four hydrogen spectral lines in the visible region. The modern form of this equation is

$$\frac{1}{\lambda} = R\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

where R is a constant. With the values $n = 2$, and $m = 3, 4, 5, 6$, the equation predicts the wavelengths of the four lines with considerable accuracy.

Aware of only these four lines, Balmer calculated l for a fifth line ($m = 7$). A line with a wavelength very close to the predicted value was observed experimentally. Balmer suggested that his formula might also predict wavelengths of other series of spectral lines by using integer values for n other than 2 and $m^3\ n + 1$. Other series of hydrogen lines were not known then, but were subsequently discovered (the Lyman, Paschen, Brackett, and Pfund series of lines).

There was no obvious reason why Balmer's formula should be so successful. Not until Niels Bohr proposed his atomic model in 1915 could line spectra be explained in terms of electrons moving from higher-energy orbits to lower-energy ones. SEE ALSO Bohr, Niels.

Richard E. Rice

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Bardeen, John

AMERICAN PHYSICIST
1908–1991

In 1972 John Bardeen did something that no other physicist, not even Albert Einstein, had ever done. He won his second Nobel Prize in physics. The first was awarded to him (and to Walter H. Brattain and William Shockley) in 1956 for "investigations on semiconductors and the discovery of the transistor effect."

Their pioneering efforts ushered in the age of modern electronics and the integrated circuit, which eventually spawned the computer chip and the cell phone. Arguably, the transistor (and all of the devices it has made possible) is the single most important invention of this modern age and ranks with fire for its effects upon society and civilization.

Bardeen (along with Leon Neil Cooper and John Robert Schrieffer) won a second Nobel Prize in 1972 for "their jointly developed theory of superconductivity," usually called (using the last initials of the three scientists) the BCS theory. In essence, BCS theory explains the phenomenon of superconductivity in Type I superconductors—**metals**, such as mercury, lead, and niobium.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

lattice: systematic geometrical arrangement of atomic-sized units that constitute the structure of a solid

Fermi conduction level: vacant or partially occupied electronic energy level resulting from an array of a large number of atoms in which electrons can freely move

According to BCS theory, at extremely low temperatures the **lattice** structures in these metals are very well-ordered and have little intrinsic vibrational motion. As an atom in a Type I superconductor gives up electrons to the **Fermi conduction levels**, it becomes a positively charged point in a sea of electrons. Below the critical temperature (the temperature at which a metal becomes superconducting), electrons in this Fermi level interact with the lattice atoms, producing vibrational motion that, in turn, interacts with a second electron. The result is the passage of electrons in the metal as "Cooper pairs," which move through the metal with zero resistance. Although Type I superconductors have not found extensive use because of their extremely low critical temperatures, the Type II or "alloy based" superconductors have radically changed science and technology, as they have enabled the construction of superconducting magnets, used in a range of devices, including magnetic resonance imaging (MRI) devices. SEE ALSO EINSTEIN, ALBERT; SUPERCONDUCTORS.

Todd W. Whitcombe

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Barium

MELTING POINT: 729°C
BOILING POINT: 1,640°C
DENSITY: 3.51 g/cm^3
MOST COMMON IONS: Ba^{2+}

56
Ba
BARIUM
137.33

The fifty-sixth element in the Periodic Table, barium has been known in various mineral forms since the 1600s. However, it was not until the 1770s that Carl W. Scheele and J. G. Gahn independently began separating barium compounds from other components of various minerals, isolating barium oxide (BaO) and barium sulfide ($BaSO_4$). The latter compound was isolated from the heavy feldspar and eventually named barite, from the Greek word *barys*, meaning "heavy." It was not until 1808 that elemental barium was isolated by Sir Humphry Davy, using his famous electrolysis system.

In its elemental form, barium is a relatively soft, silvery-white **metal**. As a highly reactive member of the alkaline-earth family, metallic barium will oxidize readily in water to form barium hydroxide, evolving hydrogen gas. It will also react readily and vigorously with oxygen in air to form BaO. As with other alkaline-earth elements, barium's most common **oxidation** state is +2.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

As the fourteenth most abundant element in Earth's crust, barium is the most common of all elements with an **atomic number** greater than 26 (iron). Barium and its compounds are used in a variety of ways, including in electronics, fireworks (where barium burns with its well-known yellow-green flame), paint pigments, and insecticides. Although barium compounds are highly toxic, doctors sometimes have patients ingest a special barium sulfate solution when it is necessary to x-ray their digestive tracts. The $BaSO_4$ is insoluble enough that it is not absorbed and so passes through the body without causing harm. In the process, the $BaSO_4$ can deflect X rays, thus making it possible to clearly image the soft tissue of the digestive tract. SEE ALSO ALKALINE EARTH METALS; DAVY, HUMPHRY; SCHEELE, CARL.

atomic number: the number of protons in an atomic nucleus, expressed in terms of electric charge; it is usually denoted by the symbol Z

David A. Dobberpuhl

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Base Pairing

James Watson and Francis Crick proposed the molecular structure of deoxyribonucleic acid (**DNA**) in 1952. Gathering a number of experimental findings on DNA, including x-ray diffraction patterns of DNA fibers, they proposed that DNA was a double-stranded helical molecule, with its **hydrophobic** bases occupying the interior of the molecule, and its **hydrophilic**

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

hydrophobic: a part of a molecule that repels water

hydrophilic: a part of a molecule having an affinity for water

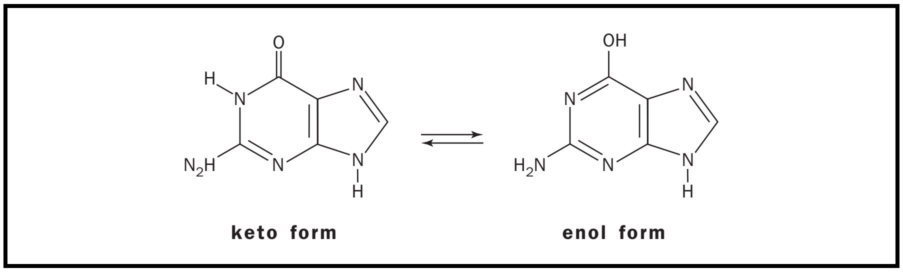

Figure 1. The tautomeric pair for guanine.

deoxyribose and phosphates groups occupying (or being oriented toward) the outer surfaces, interacting with water. The 20-angstrom (7.9×10^{-8}-inch) diameter of the **helix** was consistent with the presence of two adjacent strands and supported the hypothesis that a **purine base** resided on one strand and a **pyrimidine base** on the equivalent (homologous) site of the complementary strand.

Biochemist Erwin Chargaff had shown that the numbers of **adenine** and **thymine** units found in DNA were identical, and likewise for **guanine** and **cytosine** units. The ways in which the individual bases in the complementary A–T and G–C base pairs interacted to produce this one-to-one correspondence were not understood. The heterocyclic bases contain **functional groups**: ring nitrogens, carbonyl groups, and exocyclic amino groups that define much of the character of the bases. Interestingly, each base can occur in two structural forms, called *tautomers.* For example, the tautomeric pair that describes guanine, referred to as the *keto* and the *enol* forms, is shown in Figure 1. They are in **equilibrium**, with the keto form being favored by a factor of (approximately) 1,000 to 1. Once Watson and Crick had determined the correct tautomeric forms for each base, the nature of the phenomenon of pairing became clear.

A G–C base pair contains three specific **hydrogen bonds** within itself, whereas an A–T base pair contains two hydrogen bonds. (See Figure 2.) It is important to note that the presence of an incorrect tautomeric form in DNA would engender very different **hydrogen bonding** interactions, and the structural **complementarity** of base pairs would, in this instance, not exist. This simple yet elegant complementarity of the A–T and G–C base pairs also provides a mechanism to ensure that the proper bases are in-

helix: form of a spiral or coil such as a corkscrew

purine base: one of two types of nitrogen bases found in nucleic acids

pyrimidine base: one of two types of nitrogen bases found in nucleic acids

adenine: one of the purine bases found in nucleic acids, $C_5H_5N_5$

thymine: one of the four bases that make up a DNA molecule

guanine: heterocyclic, purine, amine base found in DNA

cytosine: heterocyclic, pyrimidine, amine base found in DNA

functional group: portion of a compound with characteristic atoms acting as a group

equilibrium: condition in which two opposite reactions are occurring at the same speed, so that concentrations of products and reactants do not change

hydrogen bond: interaction between H atoms and lone pair electrons that constitutes hydrogen bonding

hydrogen bonding: intermolecular force between the H of an N–H, O–H, or F–H bond and a lone pair on O, N, or F

complementarity: basis for copying the genetic information, where each nucleotide base has a complementary partner with which it forms a base pair

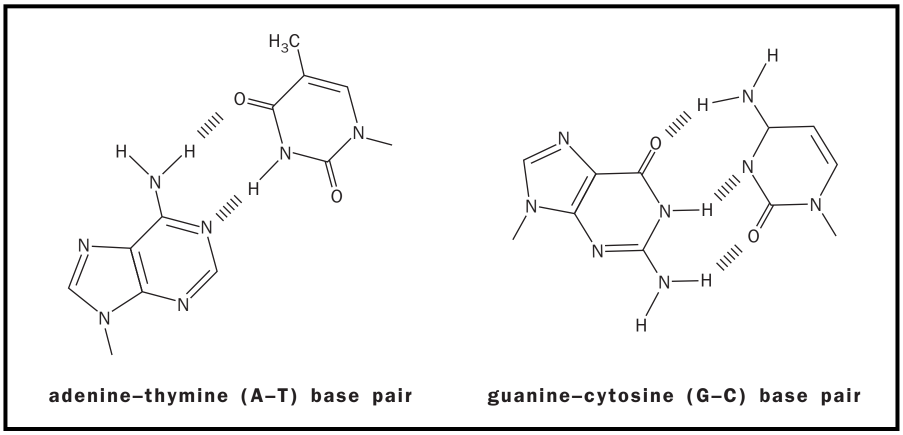

Figure 2. The complementary Watson-Crick base pairs, A–T and G–C.

corporated into DNA during DNA replication. SEE ALSO DNA REPLICATION; WATSON, JAMES DEWEY.

William M. Scovell

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Bases

Bases are considered the chemical opposite of acids because of their ability to neutralize acids. In 1887 the Swedish physicist and chemist Svante Arrhenius defined a base as the chemical substance that produces hydroxide ions (OH^-) and cations. A typical base, according to the Arrhenius definition, is sodium hydroxide (NaOH). The neutralization of an acid with a base to yield salt and water may be represented as

$$\mathrm{HCl}\ (aq) + \mathrm{KOH}\ (aq) \leftrightarrows \mathrm{H_2O}\ (l) + \mathrm{KCl}\ (aq) \qquad (1)$$

A major problem with Arrhenius's definition of bases is that several chemical compounds, such as $NaHCO_3$, Na_2CO_3, Na_3PO_4, which produce basic solutions when dissolved in water, do not contain hydroxide ions. The Brønsted-Lowry theory, which was proposed independently by Danish chemist Johannes Brønsted and English chemist Thomas Lowry in 1923, states that a base accepts hydrogen ions and an acid donates hydrogen ions. This theory not only includes all bases containing hydroxide ions, but also covers any chemical species that are able to accept hydrogen ions in **aqueous solution**. For example, when sodium carbonate is dissolved in solution, the carbonate ion accepts a hydrogen ion from water to form the bicarbonate ion and hydroxide ion.

aqueous solution: homogenous mixture in which water is the solvent (primary component)

$$\underset{\text{base}}{\mathrm{CO_3}^{2-}\ (aq)} + \underset{\text{acid}}{\mathrm{H_2O}\ (l)} \leftrightarrows \underset{\text{conjugate acid}}{\mathrm{HCO_3}^{-}\ (aq)} + \underset{\text{conjugate base}}{\mathrm{OH}^{-}\ (aq)} \qquad (2)$$

The Brønsted-Lowry theory includes water as a reactant and considers its acidity or basicity. In reaction (2) a new acid and base are formed, which are called the conjugate acid and conjugate base, respectively.

The strength of a base is determined by the extent of its **ionization** in aqueous solution. Strong bases, such as NaOH, are 100 percent ionized in aqueous solution and weak bases, such as ammonia, are only partially ionized in aqueous solution.

ionization: dissociation of a molecule into ions carrying + or − charges

$$\underset{\text{base}}{\mathrm{NH_3}\ (aq)} + \underset{\text{acid}}{\mathrm{H_2O}\ (l)} \leftrightarrows \underset{\text{conjugate acid}}{\mathrm{NH_4}^{+}\ (aq)} + \underset{\text{conjugate base}}{\mathrm{OH}^{-}\ (aq)} \qquad (3)$$

The partial ionization is a dynamic **equilibrium**, as indicated by the double arrow in equation (3).

equilibrium: condition in which two opposite reactions are occurring at the same speed, so that concentrations of products and reactants do not change

The strength of acids and bases also determines the strength of their conjugate bases and conjugate acids, respectively. Weak acids and bases have strong conjugate bases and acids. For example, when ammonium chloride is dissolved in water, it gives an acidic solution because ammonium ion is a strong conjugate acid of the weak base ammonia, but chloride ion is a weak conjugate base of the strong acid hydrochloric acid.

$$NH_4^+ \ (aq) + H_2O \ (l) \rightarrow NH_3 \ (aq) + H_3O^+ \ (aq) \qquad (4)$$

The carbonate ion in equation (2) yields a basic solution because it is the strong conjugate base of the weak acid HCO_3^-.

When $NaHCO_3$ is dissolved in water, it gives a basic solution, even though a hydrogen ion is available. Predicting this requires one to consider the strength of carbonic acid, H_2CO_3, which is a very weak acid.

$$H_2CO_3 \ (aq) + H_2O \ (l) \leftrightarrows HCO_3^- \ (aq) + H_3O^+ \ (aq) \qquad (5)$$

However, HCO_3^- will act as an acid if a strong base is added.

$$HCO_3^- \ (aq) + OH^- \ (aq) \rightarrow H_2O \ (l) + CO_3^{2-} \ (aq) \qquad (6)$$

anion: negatively charged chemical unit, like Cl^-, CO_{32}^-, or NO_3^-

This ability to act as a base or an acid is called amphoterism. Any **anions** of polyprotic acids, such as HCO_3^-, $H_2PO_4^-$, and HPO_4^{2-}, which contain replaceable hydrogen ions, are amphoteric. Some hydroxides, such as $Al(OH)_3$ and $Zn(OH)_2$, are also amphoteric, reacting with a base or acid, as illustrated by the following equations:

$$Al(OH)_3 \ (s) + OH^- \ (aq) \rightarrow Al(OH)_4^- \ (aq) \qquad (7)$$

$$Al(OH)_3 \ (s) + 3 \ H_3O^+ \ (aq) \rightarrow Al^{3+} \ (aq) + 6 \ H_2O \ (l) \qquad (8)$$

Equations (7) and (8) can also be explained by American chemist Gilbert Lewis's acid-base theory. A Lewis acid is a substance that can accept a pair of electrons to form a new bond, and a Lewis base is a substance that can donate a pair of electrons to form a new bond.

$$\underset{\text{acid}}{A} + \underset{\text{base}}{:B} \rightarrow \underset{\text{adduct}}{A{-}B} \qquad (9)$$

metal cation: positively charged ion resulting from the loss of one or more valence electrons

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

All Arrhenius and Brønsted-Lowry bases are also Lewis bases. All **metal cations** are potential Lewis acids. Complexes of **metal** ions with water, ammonia, and hydroxide ion are examples of Lewis acid-base reactions. For example, $[Al(H_2O)_6]^{3+}$ may be regarded as a combination of the Lewis acid, Al^{3+}, with six electron pairs from six H_2O molecules.

Buffer solutions contain a base and an acid that can react with an added acid or base, respectively, and they maintain a pH very close to the original value. Buffers usually consist of approximately equal quantities of a weak acid and its conjugate base, or a weak base and its conjugate acid. For example, one of the buffers used to keep the pH of the blood near 7.45 is the $H_2PO_4^-/HPO_4^{2-}$ acid/conjugate base system. Small amounts of an acid or base react with one of the components of the buffer mixture to produce the other component as follows:

$$H_2PO_4^- \ (aq) + OH^- \ (aq) \rightarrow H_2O \ (l) + HPO_4^{2-} \ (aq) \qquad (10)$$

$$HPO_4^{2-} \ (aq) + H_3O^+ \ (aq) \rightarrow H_2O \ (l) + H_2PO_4^- \ (aq) \qquad (11)$$

SEE ALSO Acid-Base Chemistry; Arrhenius, Svante; Brønsted, Johannes Nicolaus; Chemical Reactions; Lewis, Gilbert N.; Solution Chemistry.

Melvin D. Joesten

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Batteries *See New Battery Technology.*

Becquerel, Antoine-Henri

FRENCH PHYSICIST
1852–1908

Antoine-Henri Becquerel was born the son of the physicist Alexandre-Edmond Becquerel, and the grandson of the physicist Antoine-César Becquerel, and it is not surprising that he followed in their footsteps. It is also not surprising that his research interests centered around solar radiation and phosphorescence, as these are phenomena that his father had investigated. He entered the École Polytechnique, in Paris, in 1872, which he left in 1874 and to which he subsequently returned. Becquerel received a doctorate degree from the Faculty of Sciences of Paris in 1888. In 1892, he was appointed professor of applied physics in the Department of Natural History at the Paris Museum, and in 1895, professor of physics at the École Polytechnique.

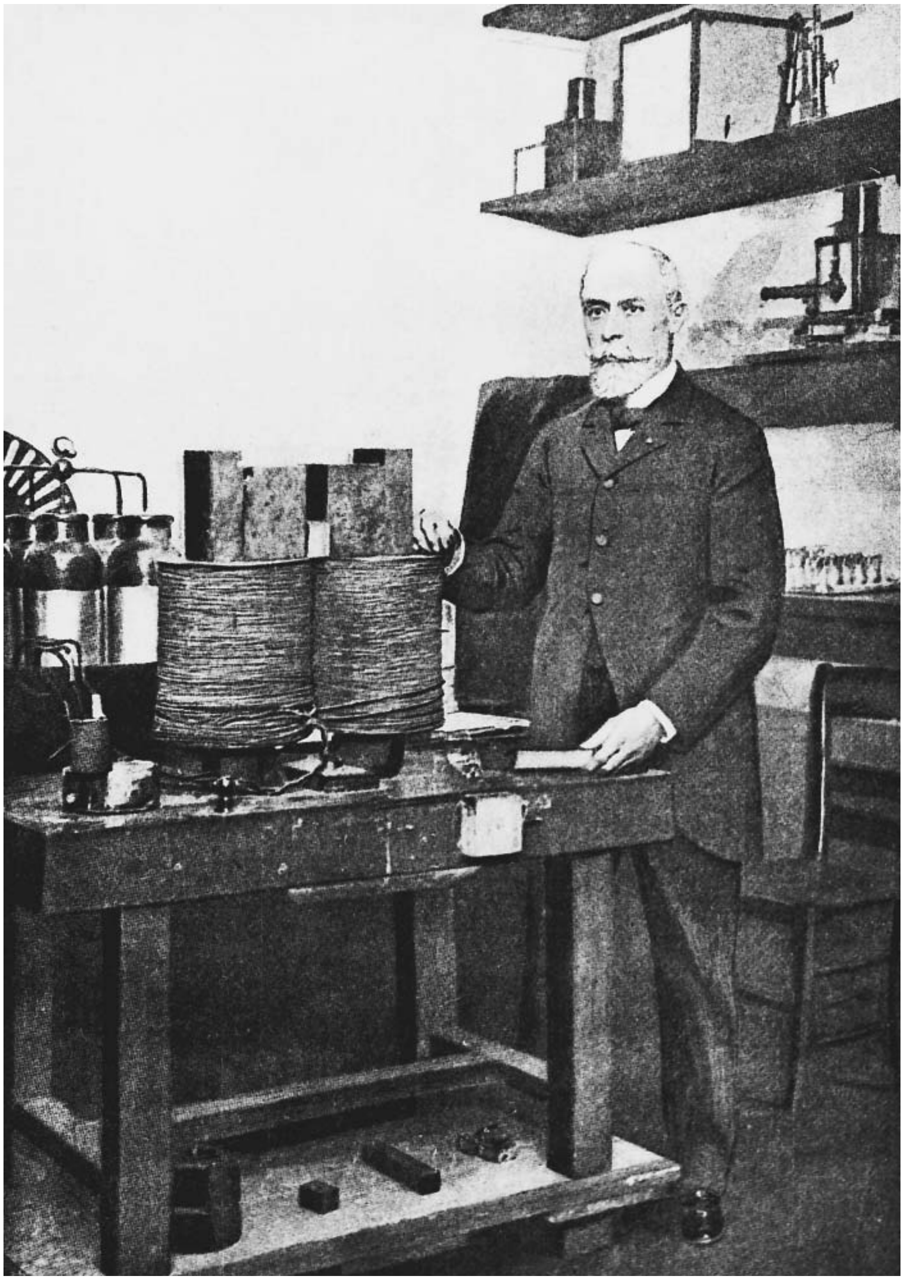
Becquerel's early work focused on plane-polarized light, the phenomenon of phosphorescence (in which certain compounds glow after being exposed to direct light), and the absorption of light by crystals. But all of his early research became overshadowed by his discovery of natural radioactivity. Although Becquerel did not initially comprehend what he was observing, his landmark discovery of radioactivity paved the way for a new understanding of the atom and atomic structure.

On February 24, 1896, Becquerel attended a meeting of the French Academy of Science and presented a short paper (one of the quickest methods in France at that time for disseminating results). One can well imagine Becquerel's excitement as he reported his results to the members of the academy.

> One wraps a Lumiere photographic plate with a bromide **emulsion** in two sheets of very thick black paper, such that the plate does not become clouded upon being exposed to the Sun for a day. One places on the sheet of paper, on the outside, a slab of the phosphorescent substance, and one exposes the whole to the Sun for several hours. When one then develops the photographic plate, one recognizes that the silhouette of the phosphorescent substance appears in black on the negative. (Becquerel *Comptes Rendus*)

emulsion: immiscible two-phase mixture in which one phase is dispersed (as small droplets) in the other phase

From this simple experiment, Becquerel concluded that the phosphorescent substance had to be emitting a type of ray that was passing through the paper and reducing the silver in the emulsion. This would seem to make sense, as the production of X rays, discovered a few years earlier by Wilhelm Röntgen, is accompanied by a soft glowing spot at the surface of the cathode ray tube. Becquerel decided to probe his unusual rays a little further. One week later, on March 2, 1896, Becquerel was back before the French Academy with the results of his further experiments. He had continued his experiments using a double sulfate salt of uranium and potassium



French physicist Antoine-Henri Becquerel, co-recipient of the 1903 Nobel Prize in physics, "in recognition of the extraordinary services he has rendered by his discovery of spontaneous radioactivity."

(potassium uranium sulfate monohydrate), which has a strong but short-lived phosphorescence.

He carefully wrapped his photographic plates in black paper, coating the paper with a crust of the uranium double salt, and upon exposure to sunlight he once again observed the "signature" of the phosphorescence-induced rays. However, repeating the experiment on Wednesday, February 26, and Thursday, February 27, he was frustrated by two days of only intermittent sunlight. And because the Sun made no appearance on the two days following, on March 1 he developed his plates. Expecting to see only a faint silhouette resulting from the wrapped plates' intermittent exposure to sunlight, he was surprised to see that the silhouettes appeared with great intensity.

Becquerel suspected that the rays that produced the silhouettes emanated from the uranium salt itself, and that the small amount of sunlight was of no consequence. He arranged three more experiments, in which photographic plates were kept completely in the dark but put in direct contact with: (1) the salt; (2) a thin sheet of glass; and (3) a thin sheet of aluminum. He surmised that the glass would eliminate any possibility that a silhouette was the consequence of a chemical reaction, and that the aluminum would block the mysterious rays.

Developing the photographic plates, Becquerel observed an intensely defined silhouette on the first two plates, and a clear but considerably weaker silhouette on the third. Because he had double-boxed his plates inside his dark room and had placed the ensembles inside a drawer that he then closed, he was able to conclude that his mysterious rays were not related to phosphorescence and were not induced by sunlight.

It was another four years before Becquerel's radiation became understood as the production of β-rays (high energy electrons), but by then there was no question that Becquerel had discovered the instability of some atomic nuclei, and that he was richly deserving of the 1903 Nobel Prize that he shared with Pierre and Marie Curie. SEE ALSO CURIE, MARIE SKLODOWSKA; RÖNTGEN, WILHELM.

Todd W. Whitcombe

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Berg, Paul

AMERICAN BIOCHEMIST
1926–

Paul Berg is considered to be one of the few pioneers in molecular biology, which is essentially the application of chemistry to biological systems. His work with recombinant DNA provided scientists with a very valuable laboratory technique. Berg worked with cloning genes from two different organisms. These hybrid DNA molecules could be produced in larger amounts and the DNA sequence could then be determined. It was also possible to change the genes and put them back into the cells from which they were obtained to determine the effects these specific changes would have on the gene function. Genes from one organism, such as a bacterium, virus, or yeast cell, could be introduced into the cells of another simple organism by the same technique, thus adding new functions to organisms. Later, microorganisms were developed that would synthesize compounds useful in research, commerce, and medicine. Today, insulin and factor VIII are two common drugs produced by recombinant organisms that help treat diabetes and hemophilia, respectively. Bacteria that feed on oil have been designed to assist in cleaning up oil spills. The applications are endless.

Berg understood the darker side of this technology too. He knew that it was theoretically possible to create new organisms with new pathogenic abilities which may be able to infect humans with new diseases. These diseases could be potentially deadly since the body would not have a chance to build up any immunity against them. In 1975, Berg and others working in recombinant DNA technology recommended a set of regulations, known as the "Berg Letter" to prevent such problems. These research guidelines are still in place today, although some rules have been relaxed as control over such experimentation has increased.

Dr. Berg's interest in science began early. He graduated from Pennsylvania State University in 1948 and obtained his doctorate from Case Western Reserve University in 1952. He spent several years as a research fellow at the Institute of Cytophysiology in Denmark and later at Washington University in St. Louis, Missouri. He was eventually promoted to chairman of the microbiology department at Washington University. By 1959, Berg moved west to Stanford University where he served as professor of biochemistry. In February of 1975 he helped organize the Asilomar Conference, an international forum on advances in DNA technology. Paul Berg has earned many prestigious awards and honors, including election into the American Academy of Arts and Sciences and the National Academy of Sciences. Perhaps the highlight of his career came in 1980 when he shared the Nobel Prize in chemistry with Walter Gilbert and Frederick Sanger for his work with DNA. SEE ALSO Genes; Genetic Engineering; Recombinant DNA.

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radioelement: a radioactive element; one in which the nucleus spontaneously decomposes (decays) producing α (alpha) and β (beta) particles and gamma rays

isotope: form of an atom that differs by the number of neutrons in the nucleus

α-particle: subatomic particle with 2+ charge and mass of 4; an He nucleus

Berkelium

97
Bk
BERKELIUM
247

MELTING POINT: 986°C
BOILING POINT: Unknown
DENSITY: Unknown
MOST COMMON IONS: Bk^{3+}, Bk^{4+}

Berkelium, element 97, is a synthetic **radioelement**, first synthesized by Glenn Seaborg's group in 1949. A target of a few milligrams of an **isotope** of americium (^{241}Am) was bombarded with **α-particles** within a cyclotron at the University of California at Berkeley. An α-emitting species with a half-life of 4.5 hours was isolated via **ion exchange chromatography** and identified as being an isotope of element 97 with mass number 243. The first isolation of a berkelium compound was accomplished by Stanley Thompson and B. B. Cunningham in 1958. The known isotopes of berke-

ion exchange chromatography: form of liquid-solid chromatography based on the reversible formation of bonds between the fixed ions bound to an insoluble matrix of an ion exchanger and mobile counter ions present in the liquid phase passing over the insoluble matrix lium have mass numbers that range from 240 to 251, and are all radioactive. The longest-lived isotope has a mass number of 247 and a half-life of 1,380 years. The ground state electronic configuration of the outer orbitals of berkelium is $5f^8 6d^1 7s^2$. In compounds and in **aqueous solution**, berkelium is present in **oxidation** states III (the more stable) and IV.

aqueous solution: solution in which water is the solvent (primary component)

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

lanthanides: a family of elements (atomic number 57 through 70) from lanthanum to lutetium having from 1 to 14 4f electrons

Berkelium was named for the city in which it was discovered, in part to emphasize its relationship to its analog in the **lanthanide** series, terbium, which was named for the city of Ytterby in Sweden (where many of the rare earth minerals had been discovered). Metallic berkelium has a face-centered cubic structure—something it has in common with the actinide elements americium though einsteinium. Due to the very high level of radioactivity of even the long-lived isotopes, berkelium is usually studied at tracer level concentrations. The most commonly studied isotope is ^{249}Bk, with a half-life of 320 days. This nuclide has been isolated at milligram levels and undergoes β-decay. SEE ALSO ACTINIUM; EINSTEINIUM; FERMIUM; LAWRENCIUM; MENDELEVIUM; NEPTUNIUM; NOBELIUM; PLUTONIUM; PROTACTINIUM; RUTHERFORDIUM; SEABORG, GLENN THEODORE; THORIUM; URANIUM.

Gregory R. Choppin

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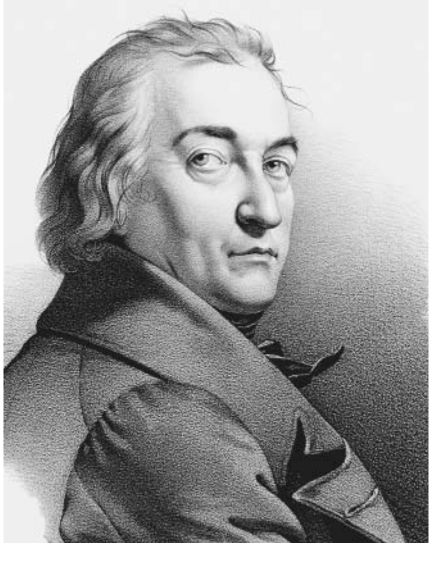
Berthollet, Claude-Louis

FRENCH CHEMIST
1748–1822



French chemist Claude-Louis Berthollet, developer of a chlorine-based bleach.

Claude-Louis Berthollet was influential in four areas: theoretical chemistry, experimental chemistry, practical chemistry, and chemical writing. He was also a chemistry teacher and, with his contemporary Pierre-Simon de Laplace, a patron of young French scientists. Born in 1748 in the town of Talloire, near Annecy, France, Berthollet studied medicine at the University of Turin. Arriving in Paris in 1772, he soon found a medical patron in one of the great Parisian aristocrats, Louis-Philippe, duke of Orléans. To consolidate his professional status, Berthollet obtained a medical degree at the University of Paris and continued to practice medicine until the mid-1780s. During the 1770s he had acquired an active interest in chemistry. By 1780 he had presented eighteen mémoires to the Académie des Sciences. He was admitted to the Académie as an *adjoint* in 1780, promoted to *associé* in 1785, and promoted to its highest position, *pensionnaire*, in 1792.

By the early 1780s, Berthollet had gained entrance to the circle of chemists that surrounded Antoine-Laurent Lavoisier, who had been developing his new oxygen-based, antiphlogistic theory of chemistry. Although Berthollet at first criticized features of the new chemistry (and never did accept Lavoisier's oxygen-based theory of acidification), he was the first chemist of Lavoisier's circle to formally and publicly become a supporter. In 1787 he joined with Lavoisier's other close associates (including Antoine

Fourcroy and Louis-Bernard Guyton de Morveau) to forge a chemical nomenclature that would be coordinated with the new chemistry.

In 1784 Berthollet was appointed to the post of inspector of the dye works and director of manufacture at the Gobelin tapestry works. While studying the properties of newly discovered chlorine gas ("dephlogisticated marine acid"), Berthollet recognized its superior bleaching properties, and he developed a chlorine-based bleach. In 1791 Berthollet published *Élémens de l'art de la teinture*, a systematic study and scientific discussion of the nature of dyeing. Berthollet also contributed to another scientific study of a major industry of the 1780s: ironmaking and steelmaking. In this study an attempt was made to provide a scientific explanation of the different kinds of iron (cast, wrought) and steel based on degrees of reduction (removal of oxygen) of the ore and subsequent combination with carbon. A third area of practical chemistry in which Berthollet was active was munitions. His most significant work in this area was the development of a potassium chlorate–based explosive (which turned out to be too powerful for use as a munition).

During the French Revolution and the Napoleonic era, Berthollet came to play active civic and political roles in France. During the Revolution, he was one of the scientists entrusted by the Committee of Public Safety with the emergency amplification of munitions production. He taught at the École Normale and was one of the founders of the École Polytechnique. He became a friend of Napoleon Bonaparte, whom he accompanied to Egypt in 1798, and in Egypt helped to set up a scientific institute along the lines of the Parisian *Académie.* Under the aegis of Napoleon, Berthollet was made a count, a senator of Montpellier, and a *grand officier* of the Légion d'Honneur.

Although Berthollet never published a textbook of chemistry, he did publish the *Essai de statique chimique* (1803), an ambitious work that attempted to provide a systematic theoretical foundation for chemistry. Like his predecessors, Berthollet conceived of the microscopic-level forces by which chemical substances "attracted" one another as being the same as or analogous to gravity. But Berthollet challenged his predecessors' view that the strengths of chemical affinity forces were determined solely by the nature of the reagents and were invariant under all physical and chemical condition. He held that factors such as the masses of the reagents, their physical states before and after the reaction, and general physical circumstances could affect the directions of reactions and even the combining proportions of their products.

Regarding combining proportions, Berthollet asserted that chemical reagents in continuous ranges of weight proportions could combine, depending on the masses of the reagents and the physical circumstances of the reactions. By this time, Joseph-Louis Proust had already set forth his general assertion that true chemical combination was always marked by fixed-weight proportions of the reagents. Berthollet and Proust argued the issue in print for several years without any resolution of the argument. What "settled" the issue was the ascendancy of John Dalton's chemical atomic theory (1808), which in its laws of definite and multiple proportions supported Proust's position. SEE ALSO DALTON, JOHN; LAVOISIER, ANTOINE.

Seymour Mauskopf

Beryllium

MELTING POINT: 1,285°C
BOILING POINT: 2,500°C
DENSITY: 1.848 g/cm^3
MOST COMMON IONS: Be^{2+}

4
Be
BERYLLIUM
9.0121

Beryllium was identified as a unique element and as a constituent of the mineral beryl and the gem emerald by the French chemist Louis Vauquelin in 1797. Metallic beryllium was isolated in 1828 by the scientists (working independently of one another) Antoine Bussy and Friedrich Wöhler. Beryllium usage was not common until a 1920s discovery that the 2 percent addition of beryllium to copper resulted in an **alloy** six times stronger than the original material. Beryllium has a melting point of 1,285°C (2,345°F), a boiling point of 2,500°C (4,532°F), and a density of 1.848 g/cm^3. Its most common **oxidation** state is +2. It has a high heat adsorption capacity and is nonmagnetic and corrosion-resistant.

alloy: metallic mixture of two or more elements, at least one of which is a metal

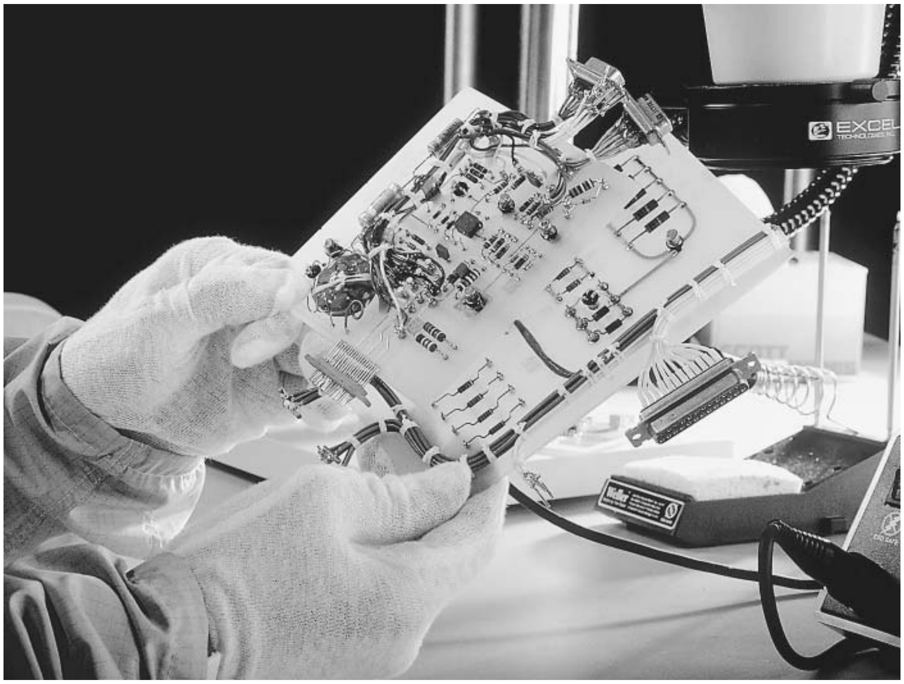
oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

Beryllium is one of the most toxic elements in the Periodic Table. It is the agent responsible for chronic beryllium disease (CBD), an often-fatal lung disease, and is a Class A carcinogen (as determined by the U.S. Environmental Protection Agency). The primary route of human exposure to beryllium and beryllium compounds is inhalation.

Approximately fifty beryllium minerals occur in nature and over half of these minerals are silicates. Beryllium is mined primarily from these silicates, including beryl, $Al_2Be_3Si_6O_{18}$, 5 percent (wt.) beryllium, and bertrandite, $Be_4(OH)_2Si_2O_7$, 15 percent (wt.) beryllium. The world resources of beryllium are estimated at approximately 80,000 tons. Other common beryllium silicates include chrysoberyl, $BeAl_2O_4$, and phenacite, Be_2SiO_4.

Beryllium is a key component of materials used in the aerospace, electronics, aviation, telecommunications, automotive, and **nuclear** power

nuclear: having to do with the nucleus of an atom



Circuit board assembly for a satellite transmitter. Beryllium is mined for the silicate beryl, which is used in aerospace electronics due to its high thermal conductivity.

industries. It is used in aircraft bearings and bushings; fuel containers for solid propulsion jet and rocket fuel systems; gyros, reentry vehicles, springs, switches, and relays and connectors in electronic systems; fiber optics and cellular network communication systems; optical laser scanners; automobile air bag sensors, ignition switches, and power steering systems; and to moderate nuclear reactions in power plants. Beryllium oxide ceramics have a thermal conductivity second only to that of diamond among electrically insulating materials, dissipating nearly 300 watts/millikelvin (W/mK) at room temperature. SEE ALSO TOXICITY; WÖHLER, FRIEDRICH.

Tammy P. Taylor
Nancy N. Sauer

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Berzelius, Jöns Jakob

SWEDISH CHEMIST
1779–1848

Before the early 1800s the symbols used to denote chemical elements and compounds were obscure. Alchemists wanted to keep their work secret and so devised symbols for the chemicals they used that would not reveal anything about them. This all changed with the work of Jöns Jakob Berzelius.

Berzelius was born in Linköping, Sweden, in 1779. Both of his parents died while he was young, yet he still managed to finance his education by tutoring. He became interested in nature at school, and while he was a medical student at the University of Uppsala, his interests became more focused on experimental chemistry. Berzelius was so taken with experimental work, he bribed a caretaker in order to gain extra access to the university's laboratory.

In addition to devising a new language of chemistry, Berzelius was also keenly interested in the analysis of minerals. In 1800 Berzelius was apprenticed to a physician at the Medivi mineral springs in Sweden. Here, he analyzed the mineral content of the spring water. It was while working at Medivi that he developed his quantitative analysis skills.

Berzelius's analytical skills were put to the test when he and a colleague, Johan Gottlieb Gahn (1745–1818), noticed a residual substance while studying a method of producing sulfuric acid in 1817. They at first thought the substance was tellurium, but after careful quantitative analysis, they realized that they had isolated a new element. They named this element selenium.

atomic theory: physical concept that asserts that matter is composed of microscopically tiny particles called atoms and that various elements differ from each other by having different atoms

The most notable of Berzelius's contributions to chemistry was his development of a rational system of atomic symbols. Around 1810 Berzelius was working to confirm John Dalton's **atomic theory** as well as Proust's law showing that separate elements always combined in whole-number proportions. At the same time, he was also compiling the new Swedish *Pharmacopoeia*. While working on these three projects, Berzelius came to the conclusion that the existing system of denoting elements and compounds was a hindrance. In establishing his own atomic symbols, he stated that "it is easier to write an abbreviated word than to draw a figure which has little analogy with words" (Jaffe 108). Instead of using obscure symbols like circles with arrows extending from their sides, or collections of dots arranged in a specific pattern, Berzelius opted to use the first letter of the Latin name for each element as its symbol. For example, carbon would be denoted as C and oxygen as O. If elements had the same first letter, such as gold (*aurum*) and silver (*argentum*), Berzelius decided that the symbol would be the first two letters of the name: Thus, gold would be known as Au and silver as Ag.

Berzelius then extended his development to represent compounds, for example, copper oxide was identified as CuO and zinc sulfide as ZnS. And, conforming to Proust's law and Dalton's theory, Berzelius added algebraic exponents (later to become subscripts) to his system of atomic symbols—for example, water was denoted as H_2O and carbon dioxide as CO_2.

Even though his atomic symbols were introduced in 1814, it was quite a few years before Berzelius's symbols were adopted by the chemistry community. But once accepted, they became the new international language of chemistry.

Berzelius published more than 250 papers in his lifetime covering every aspect of chemistry. He was devoted to the entire field of chemistry, as can be seen by his efforts to bring order to the language of chemistry and to insist on quantitative excellence in all its areas. He died in 1848 and is buried in Stockholm, Sweden. SEE ALSO ATOMS; DALTON, JOHN.

Lydia S. Scratch

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Bioluminescence

Bioluminescence is the emission of visible light by biological systems, which arises from enzyme-catalyzed chemical reactions. Bioluminescence can be distinguished from chemiluminescence in that it occurs in living organisms and requires an enzyme **catalyst**. These chemical-dependent emissions of light differ from fluorescence and phosphorescence, which involve the absorption of light by a compound followed by emission of light at a lower energy (higher wavelength) from the excited state of the molecule. The excited molecule produced during bioluminescence reactions, however, is

catalyst: substance that aids in a reaction while retaining its own chemical identity

The jellyfish is among many bioluminescent species.

analogous to that produced during fluorescence, and consequently the luminescence emission spectrum can often be related to the fluorescence emission spectrum. It should also be noted that the processes of fluorescence and phosphorescence also occur in living organisms and should not be confused with bioluminescence.

Bioluminescence has been observed in many organisms and phyla throughout the terrestrial and aquatic worlds, with the majority of luminescent organisms being found in the ocean. Because of the ease with which light can be detected, recorded observations of bioluminescence extend back several thousand years. Both the ancient Chinese and the ancient Greeks recorded luminescence sightings. Aristotle, in the fourth century B.C.E., wrote that "some things, though they are not in their nature fire, nor any species of fire, yet seem to produce light."

Luminescent species are found among marine and terrestrial bacteria, annelids or segmented worms (e.g., fireworms), beetles (e.g., fireflies, click beetles, railroad worms), algae (e.g., dinoflagellates), crustaceans (e.g., shrimp, ostracod), mollusks (e.g., squid, clams, limpets), coelenterates (e.g., jellyfish, sea pansies, hydroids), bony fish (e.g., hatchet fish, flashlight fish, pony fish), and cartilaginous fish (e.g., sharks). Luminescent vertebrates (except for certain fish), mammals, higher plants, and viruses do not exist—except for those versions created by recombinant technology.

Most, if not all, bioluminescence reactions have oxygen as a common reactant and a conjugated system as part of one of the substrates—both needed to generate molecules in an excited state, leading to the emission of light in the visible region. However, the bioluminescence reactions in some organisms are quite different from those in other organisms, and consequently the enzymes catalyzing the reactions (luciferases) and the substrates (often but not always referred to as luciferins) are also quite

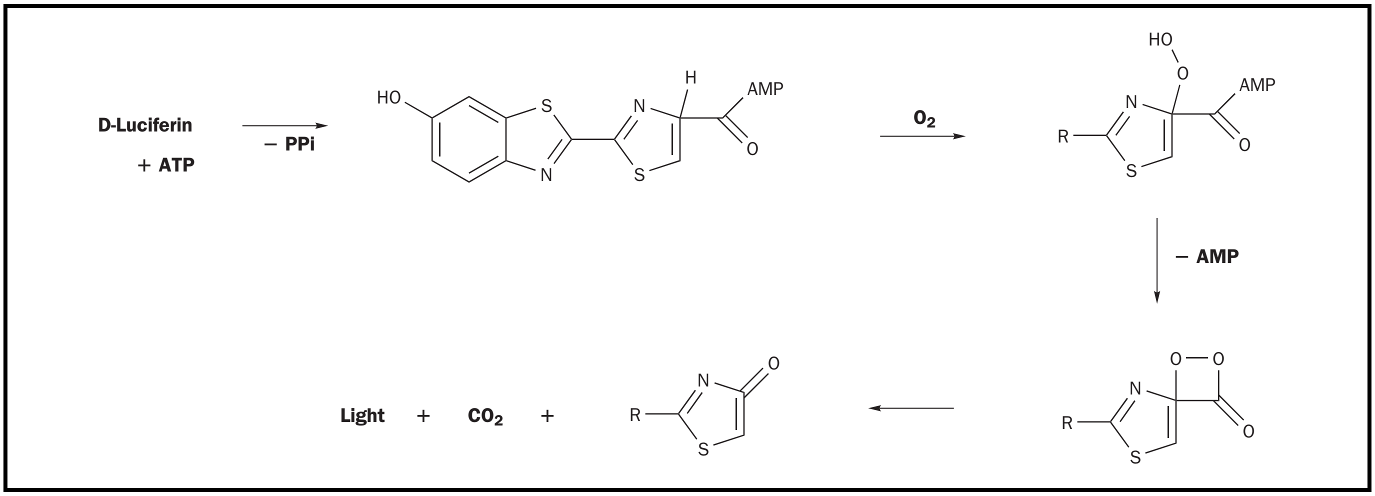


Figure 1. Bioluminescence reaction in fireflies.

distinct. Four bioluminescence systems (fireflies, dinoflagellates, bacteria, and imidazolopyrazine-based e. g., coelenterates) have been studied in greatest detail, and their chemical reactions reflect both their differences and their common features.

Beetles/Fireflies

Luciferases from click beetles, fireflies, and railway worms catalyze the ATP-dependent decarboxylation of luciferin (Figure 1). An AMP derivative of luciferin is formed, which subsequently reacts with O_2. Cleavage of this dioxy derivative results in the emission of light characterized by wavelengths ranging from 550 nanometers (2.17×10^{-5} inches; green) to 630 nanometers (2.48×10^{-5}; red, depending on the particular luciferase), and the release of CO_2. Fireflies generally emit in the yellow to green range, as part of a courtship process; click beetles emit green to orange light; whereas railway worms emit red light, with green light being emitted on movement.

Dinoflagellates

Much of the brightness that is observed on the surface of the oceans is due to the bioluminescence of certain species of dinoflagellates, or unicellular algae, and this bioluminescence accounts for many of the recorded observations that have described the apparent "phosphorescence" of the sea. Dinoflagellates are very sensitive to motion induced by ships or fish, and respond with rapid and brilliant flashes, thus causing the glow that is sometimes seen in the wake of a ship. The luciferin in these instances is a tetrapyrrole containing four five-member rings of one nitrogen and four carbons, and its **oxidation**, catalyzed by dinoflagellate luciferase, results in blue-green light centered at about 470 nanometers (1.85×10^{-5} inches; Figure 2).

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

Bacteria

Bacterial luciferase catalyzes the reaction of reduced flavin mononucleotide ($FMNH_2$) with O_2 to form a 4a-peroxyflavin derivative that reacts with a

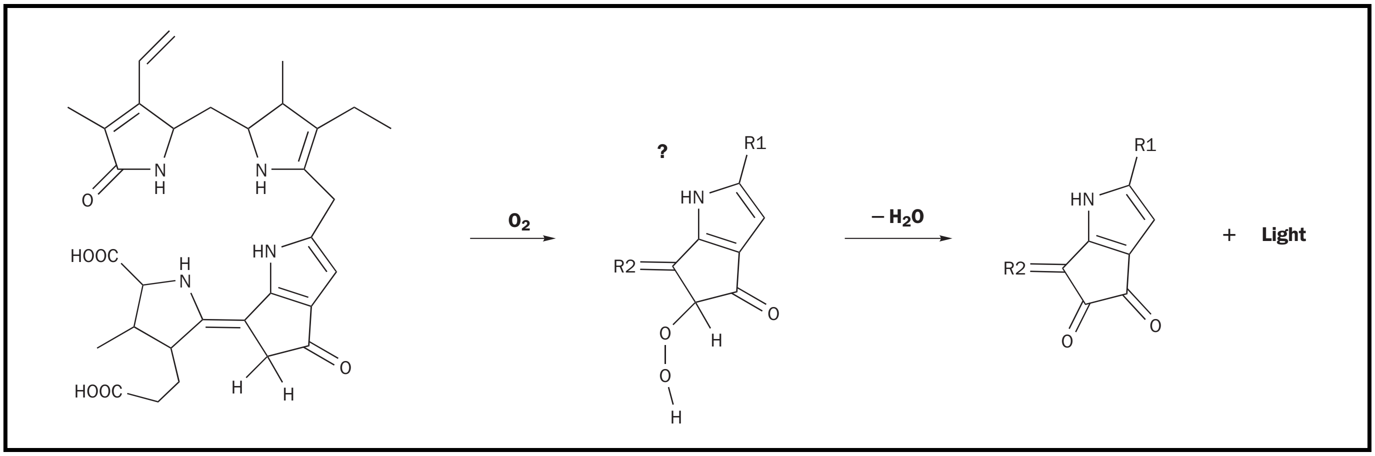


Figure 2. Bioluminescence reaction in dinoflagellates.

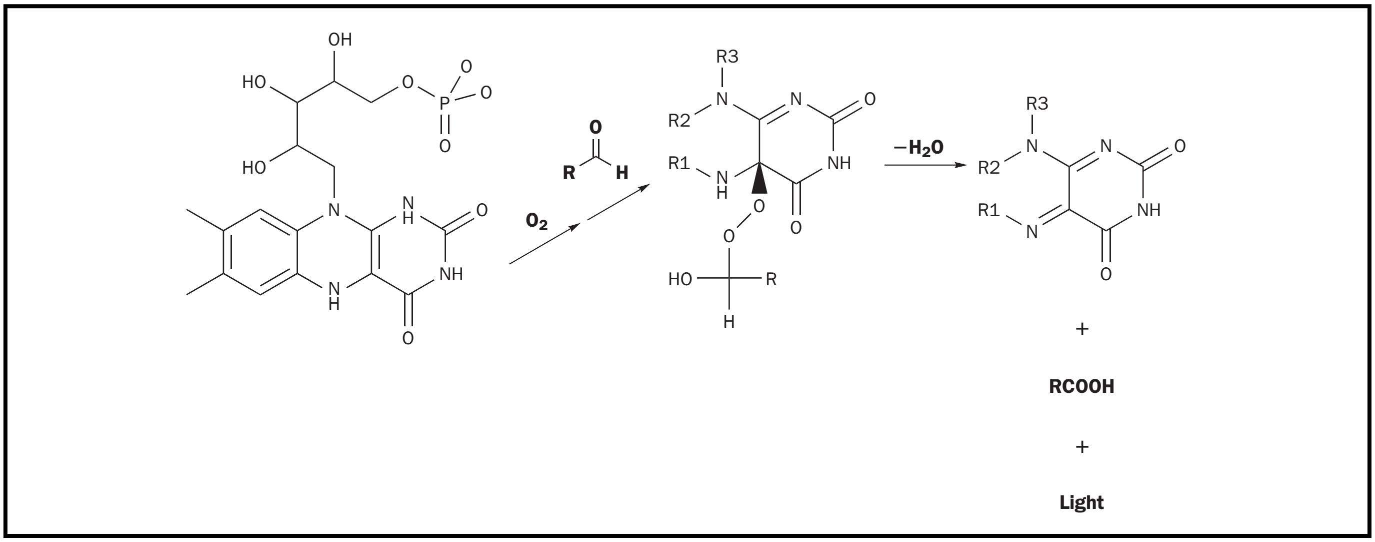
aldehyde: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the RC(O)H functional group

vitamins: organic molecules needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

long chain **aldehyde** leading to the emission of blue-green light (490 nanometers, or 1.93×10^{-5} inches) and the formation of riboflavin phosphate (FMN; the phosphorylated form of **vitamin** B_2), H_2O, and the corresponding fatty acid (Figure 3). Luminescent bacteria are found throughout the marine environment, living free, in symbiosis, or in the gut of marine organisms (including many fish and squid), as well as in the terrestrial environment as symbionts of nematodes.

The luciferins believed to be the most widespread among phyla living in the ocean have structures based on imidazolopyrazine, for example, coelenterazine, found in luminescent coelenterates contains imidazolopyrazine as its central bicyclic ring (Figure 4). The typical reaction involves the oxidation of the imidazolopyrazine ring with the emission of blue light (460–480 nanometers, or 1.81×10^{-5}–1.89×10^{-5} inches), and proceeds according to a mechanism that is very similar to that of the oxidation of firefly luciferin. Among the most commonly studied imidazolopyrazine-utilizing organisms are species of *Renilla* (sea pansy) and *Aequorea* (jellyfish) both of which utilize coelenterazine. The luciferin of a crustacean (*Cypridina* or

Figure 3. Bioluminescence reaction in bacteria.



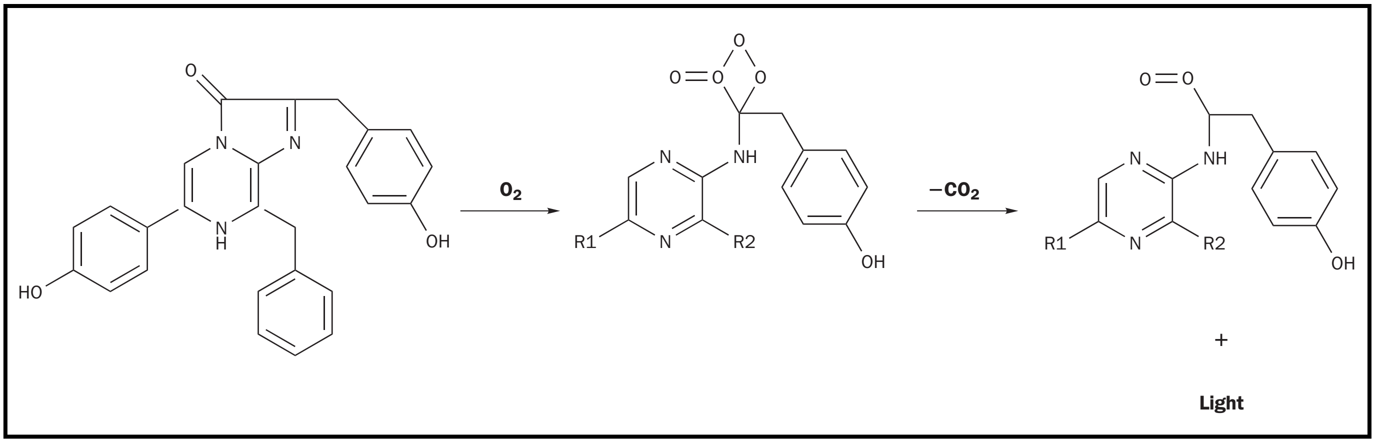


Figure 4. Bioluminescence reaction in coelenterates.

Vargula) also is an imidazolopyrazine-based compound related to coelenterazine. The luciferases of the luminescent species, however, vary widely. Recent evidence suggests that some, and possibly many, marine luminescent organisms (including the jellyfish) acquire luciferins via the ingestion of other luminescent organisms, which would account for the widespread distribution of imidazolopyrazine-based luciferins. Many luminescent species also have a binding protein that releases the luciferin upon Ca^{++} uptake, while some have a fluorescence protein that absorbs and then emits light at a higher wavelength.

Although other luminescent systems have been studied (including those of the fireworm and the limpet, both of which use aldehydes as luciferins), bioluminescence remains somewhat mysterious. Elucidation of the chemical and biological bases for luminescence systems in other organisms should improve understanding of why the remarkable and beautiful phenomenon of bioluminescence appears in so many species. SEE ALSO CHEMILUMINESCENCE.

Edward A. Meighen

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83
Bi
BISMUTH
208.9804

Bismuth

MELTING POINT: 271.4°C
BOILING POINT: 1,564 ±5°C
DENSITY: 9.747 g/cm^3
MOST COMMON IONS: Bi^{3+}, Bi^{4+}

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

heavy metal: by convention, a metal with a density greater than 5 g/cm^3; 70 elements are thus classified as heavy metals

isotope: form of an atom that differs by the number of neutrons in the nucleus

Bismuth is a brittle, crystalline **metal** that is white with a pinkish tint. It is the heaviest and only nontoxic member of the **heavy metals**. Its name is derived from the German *Wismut* ("white metal"), which was Latinized to *bisemutum* by G. Bauer in 1530. In early years it was confused with tin and lead. Bismuth has only one naturally occurring **isotope**, ^{209}Bi (the heaviest stable isotope of any element).

Peru, Japan, Mexico, and Canada are the main producers of bismuth. It can be found in several ores: bismuthinite (Bi_2S_3), bismite (Bi_2O_3), and bismutite $(BiO_2)CO_3$. It is also obtained as a by-product of the refining of silver and gold ores in the United States. Bismuth has an abundance in Earth's crust of 0.008 parts per million.

Bismuth commonly forms cations of +3 charge. It forms the basic oxide Bi_2O_3 and salts of oxoacids such as $Bi_2(SO_4)_3$ and $Bi(NO_3)_3$. Reaction of the metal with halides such as fluorine and chlorine results in a salt with the formula of BiX_3. Because of the size of the metal atom, the linkages are more ionic than those found for other group members.

diamagnetic: property of a substance that causes it to be repelled by a magnetic field

Bismuth is the most **diamagnetic** of all metals and has low thermal conductivity. Since bismuth expands upon solidification, it is used to make castings for objects subjected to high temperatures. It is used as a replacement for lead in solders, shot for hunting, fishing sinkers, ceramic glazes, and brasses for plumbing applications. It is also used as a carrier for ^{235}U (an isotope of uranium) fuel in atomic reactors. Ionic compounds of bismuth are used in cosmetics and medicine.

Catherine H. Banks

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Black, Joseph

SCOTTISH CHEMIST AND PHYSICIST
1728–1799

Joseph Black was trained as a medical doctor. One of his early scientific undertakings was investigating means of treating "the stone" (kidney stones and gallstones). The investigation prompted him to make a study of how to dissolve stones found in nature. Black found that certain stones, such as limestone, dissolved in mild acids, giving off large volumes of a gas. He called this gas "fixed air," as it had been "fixed" in a small volume of solid stone.

Following the practice of the **pneumatic chemists** (chemists who were studying the properties of gases or "airs"), he trapped and characterized this new gas. "Fixed air" was found to be mildly acidic. It would later be called carbon dioxide, and stones that generated this gas would be defined as carbonates. Black also discovered that the chemical nature of the gas that had been produced in these experiments was determined by the stone it came from, not by the acid used.

pneumatic chemist: early chemist who studied primarily the properties of gases

Black was the first to distinguish between the temperature of an object and the heat contained in that object. He characterized "specific heat" as the amount of heat required to increase the temperature of a sample by a given amount. He recognized that it is dependent on the identity of and the amount of the material in the sample. If the sample being heated is at its melting or boiling temperature prior to the application of heat, it will absorb heat as it is going through a **phase** change (from solid to liquid or liquid to gas), but the temperature of the sample does not increase. The amount of heat absorbed during such a transition is also dependent on the amount of material in the sample and is characteristic of the type of material in the sample. Black termed this heat "latent heat" because it is "latent" in the sample and does not increase the temperature of the sample.

phase: homogeneous state of matter

Although trained as a medical doctor, Joseph Black spent most of his professional career as an instructor in chemistry at the University of Edinburgh. His lecture notes were edited by one of his students and published as a textbook in chemistry in 1803, four years after his death.

David A. Bassett

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Bleaches

When chlorine gas is bubbled through a cylinder of tomato juice, the chlorine/tomato juice mixture turns almost completely white within five minutes. This spectacular change is a result of the chemical action of chlorine, acting as an oxidizing bleaching agent, on the pigments in tomato juice. When old newspaper clippings, discolored through aging and exposure to light, are treated with 1 percent aqueous sodium borohydride solution, the paper is dramatically whitened within twenty minutes. In this instance, the paper has been restored to its original white color by the action of sodium borohydride acting as a reducing bleaching agent.

A bleaching agent is a substance that can whiten or decolorize other substances. Colored substances generally contain groups of atoms, called **chromophores**, that can absorb visible light having specific, characteristic wavelengths, and reflect or transmit the part of light that is not absorbed. For example, if a chromophore absorbs blue light, it will reflect light of the complementary color, and the chromophore-containing substance will appear yellow. Bleaching agents essentially destroy chromophores (thereby removing the color), via the **oxidation** or reduction of these absorbing groups. Thus, bleaches can be classified as either oxidizing agents or **reducing agents**.

chromophore: part of the molecule that yields characteristic colors

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

reducing agent: substance that causes reduction, a process during which electrons are lost (or hydrogen atoms gained)

Some of the use of bleaching agents are:

- The bleaching of textiles and fabrics
- The bleaching of wood pulp
- The removal of stains
- Commercial and household laundering and cleaning
- As ingredients in scouring cleansers and dishwashing products
- The bleaching of hair

Oxidizing Bleaches

A large number of oxidizing bleaches were reviewed by Jules A. Szilard in *Bleaching Agents and Techniques* (1973). The oxidizing bleaches (and bleaching agents) in common use today are: chlorine, chlorine dioxide, alkaline hypochlorites, hydrogen peroxide, peroxygen compounds, and sunlight and artificial light.

Chlorine (Cl_2). The discovery of chlorine by the Swedish chemist Carl Wilhelm Scheele in 1774 marked the beginning of the modern era of bleaching. According to Sidney M. Edelstein in a 1948 journal article titled "The Role of Chemistry in the Development of Dyeing and Bleaching," French chemist Claude-Louis Berthollet was the first to use chlorine to bleach cotton and linen fabrics.

Chlorine has been used to bleach wood pulp. Many pulp mills employing the Kraft pulping process prepare sodium hydroxide (needed to digest wood chips) on-site via the electrolysis of **brine**, a concentrated **aqueous solution** of sodium chloride.

brine: water containing a large amount of salts, especially sodium chloride (NaCl)

aqueous solution: solution in which water is the solvent (primary component)

$$2NaCl + 2H_2O \rightarrow 2NaOH + H_2 + Cl_2 \qquad (1)$$

Chlorine is a side product. Subsequent chlorine bleaching of the brown pulp gives a product that can be used for the manufacture of writing and printing paper. Unfortunately, organic compounds in the pulp are both oxidized and chlorinated, yielding small quantities of organochlorine compounds, in-

BLEACHING AGENTS AND USES

Bleaching Agent	Commercial Use in Bleaching
Chlorine	Bleaching pulp and paper; making hypochlorites
Chlorine dioxide	Bleaching kraft paper and flour
Sodium hypochlorite	Household laundering and sanitizing
Calcium hypochlorite	Solid bleach used in sanitizing
Sodium dichloroisocyanurate	Sanitizing and dishwashing agents
Hydrogen peroxide	Bleaching textiles, fur, pulp and paper, and hair
Sodium perborate	Milder bleach for laundering; dry cleaning; denture cleaning; tooth powder; replacement for phosphates in detergents
Light	Bleaching paper artifacts
Sulfur dioxide	Preserving grapes, wine, and apples; removal of color during refinement of sugar
Sodium sulfite; sodium bisulfite	Anti-chlor (a reducing agent for removing oxidizing bleaches)
Sodium dithionite	Bleaching textiles, pulp and paper; removing rust stains
Sodium borohydride	Bleaching pulp and paper

Table 1. Bleaching agents and their commercial uses.

cluding dioxins. In fact, the most abundant dioxin produced by the pulp and bleaching process, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD), has been found to be both a carcinogen and a deadly **toxin**. Thus, chlorine as a bleaching agent is being replaced by the safer bleaching agents chlorine dioxide and hydrogen peroxide. In fact, the trend in the pulp and paper industries is toward totally chlorine free (TCF) bleaching. Chlorine is now used in the bleaching industry mainly to prepare hypochlorite solutions and dry bleaches such as calcium hypochlorite.

toxin: poisonous substance produced during bacterial growth

Chlorine Dioxide (ClO_2). Chlorine dioxide has been used as a bleaching agent both in its gaseous **phase** and in aqueous solution. Because of its explosive nature, chlorine dioxide in the gaseous phase is often diluted with nitrogen or carbon dioxide. If stored or shipped, chlorine dioxide is passed through cold water and kept under refrigeration.

phase: homogeneous state of matter

Chlorine dioxide is prepared industrially via the reduction of sodium chlorate by sulfur dioxide in aqueous solution.

$$2NaClO_3 + SO_2 + H_2SO_4 \rightarrow 2ClO_2 + 2NaHSO_4 \qquad (2)$$

A relatively safe method for the preparation of ClO_2 involves the reaction between sodium chlorite ($NaClO_2$) and **formaldehyde** (H_2CO).

formaldehyde: name given to the simplest aldehyde HC(O)H, incorporating the −C(O)H functional group

$$H_2CO + H^+ + ClO_2^- \rightarrow HOCl + HCOOH \qquad (3)$$

As reaction 3 proceeds, the pH of the solution drops (due to the production of formic acid [HCOOH]). The increased acidity of the solution promotes the formation of ClO_2, shown in equation 4.

$$HCOOH + HOCl + 2ClO_2^- \rightarrow 2ClO_2 + Cl^- + H_2O + HCOO^- \qquad (4)$$

In acidic solution, chlorine dioxide behaves as an oxidizing agent. The complete reduction of ClO_2 is shown in equation 5.

$$ClO_2 + 4H^+ + 5\,e^- \rightarrow Cl^- + 2H_2O \qquad (5)$$

The individual steps of this overall reduction reaction produce $HClO_2$, HOCl, and Cl_2, which all behave as oxidizing agents. An acidic medium is required, as ClO_2 disproportionates in alkaline solution, as shown in equation 6.

$$2ClO_2 + 2OH^- \rightarrow ClO_3^- + ClO_2^- + H_2O \qquad (6)$$

Chlorine dioxide is mainly used for pulp bleaching.

Hypochlorites (OCl^-). Hypochlorite bleach solutions are made from NaOCl and, to a lesser extent, $Ca(OCl)_2$. Hypochlorites are used in laundering, as disinfectants, in the bleaching of pulp and textiles, and in the removal of ink from recycled paper. Commercial bleaching solutions are obtained by passing chlorine gas through cold, dilute, aqueous sodium hydroxide, as shown in equation 7.

$$Cl_2 + 2OH^- \rightarrow OCl^- + Cl^- + H_2O \qquad (7)$$

Alternatively, the hypochlorite ion can be generated by the hydrolysis of organic nitrogen-chlorine compounds. Some of the more important nitrogen-chlorine compounds used in this way are the chlorinated isocyanurates. These find use in cleansing and dishwasher products.

To be an effective bleach, the hypochlorite solution should be kept alkaline ($pH > 9.0$), in order to suppress the hydrolysis of OCl^- (see equation 8) and prevent the formation of unstable HOCl.

$$OCl^- + H_2O \rightarrow HOCl + OH^- \qquad (8)$$

In acidic solutions, HOCl forms and decomposes.

$$3HOCl \rightarrow HClO_3 + 2HCl \qquad (9)$$

HOCl will also react with HCl, one of the decomposition products.

$$HOCl + HCl \rightarrow H_2O + Cl_2 \qquad (10)$$

heavy metal: by convention, a metal with a density greater than 5 g/cm^3; 70 elements are thus classified as heavy metals

Hypochlorite bleaching solutions must not contain **heavy metal** cations, as these cations (like light or heat) promote the decomposition of HOCl, as shown in equation 11.

$$2HOCl \rightarrow 2HCl + O_2 \qquad (11)$$

The active ingredients in hypochlorite bleaches vary with pH. At $pH < 2$, Cl_2 is the main component in solution; at pH 4 to 6, HOCl is the dominant species; at $pH > 9$, OCl^- is the only component present. It is the hypochlorite ion in basic solution that is the active ingredient in household bleach, which is typically about 5 to 6 percent NaOCl. The OCl^- ion oxidizes chromophores in colored materials, and is itself reduced to chloride and hydroxide ions.

$$OCl^- + H_2O + 2\ e^- \rightarrow Cl^- + 2OH^- \qquad (12)$$

The whitening process effected by commercial hypochlorite bleach is often enhanced by the use of optical brighteners, compounds that absorb incident ultraviolet light and emit visible light, making the fabric appear brighter and whiter.

Hydrogen Peroxide (H_2O_2). Hydrogen peroxide can be prepared by the reaction of barium peroxide and sulfuric acid (see equation 13). As barium sulfate precipitates out, hydrogen peroxide is easily separated.

$$BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2 \qquad (13)$$

Hydrogen peroxide, as a bleaching agent used in the pulp and paper industry, has the advantage that it is nonpolluting. Because of the instability of pure hydrogen peroxide, aqueous solutions are employed in bleaching. At room temperature, hydrogen peroxide very slowly decomposes to water and oxygen.

$$2H_2O_2 \rightarrow H_2O + O_2 \qquad (14)$$

transition metals: elements with valence electrons in d-sublevels; frequently characterized as metals having the ability to form more than one cation

However, the presence of **transition metal** cations (particularly Fe^{3+}, Mn^{2+}, and Cu^{2+}) and other catalysts dramatically accelerates this reaction. As a result, aqueous hydrogen peroxide must be stabilized with complexing agents that sequester transition metal cations.

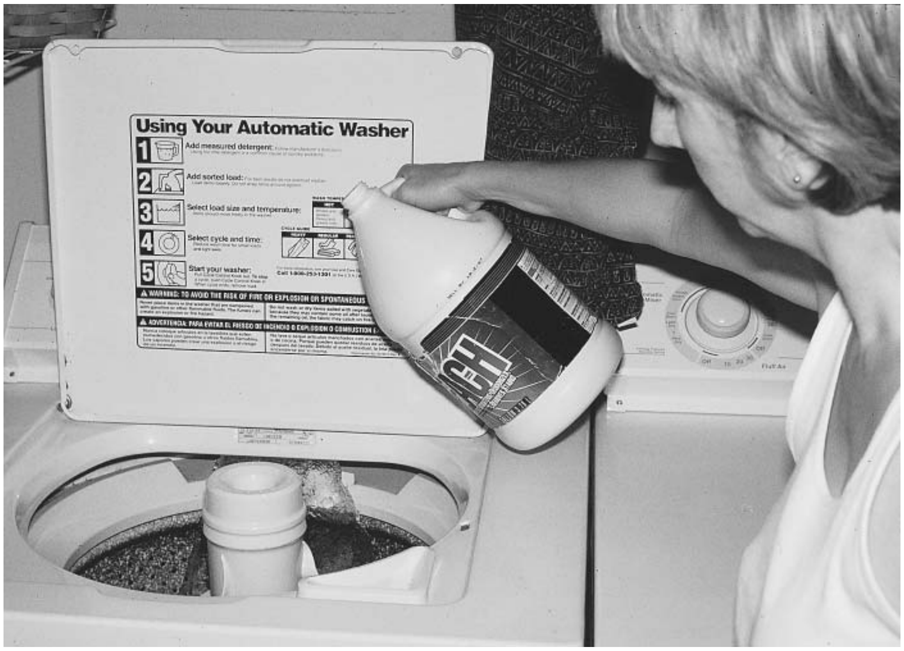
anion: negatively charged chemical unit, like Cl^-, $CO_{32}{}^-$, or $NO_3{}^-$

ionization: dissociation of a molecule into ions carrying + or − charges

The active bleaching species in hydrogen peroxide is the perhydroxyl **anion**, OOH^-, formed through the **ionization** of H_2O_2.

$$H_2O_2 + H_2O \rightarrow H_3O^+ + OOH^- \qquad (15)$$

The acid ionization constant of hydrogen peroxide is very low ($K_a = 2 \times 10^{-12}$) with the result that solutions of H_2O_2 must be made alkaline in or-



This woman is using bleach to launder clothing. Not only can bleach remove stains, but it can act as an agent to remove color.

der to raise the concentration of OOH^-. In the absence of an alkaline medium, hydrogen peroxide is no longer effective as a bleaching agent. For example, the bleaching stage of hair dyeing often employs hydrogen peroxide (5–6%), but also ammonia to provide an alkaline medium.

At the same time the pH must not rise above 11, as at this point the decomposition of OOH^- begins to occur.

$$2OOH^- \rightarrow O_2 + 2OH^- \qquad (16)$$

Peroxygen Compounds. A number of solid peroxygen compounds that release hydrogen peroxide when dissolved in water exist. These include sodium perborate ($NaBO_3 \cdot 4H_2O$ or $NaBO_2 \cdot H_2O_2 \cdot 3H_2O$) and sodium carbonate peroxyhydrate ($2Na_2CO_3 \cdot 3H_2O_2$). The structure of sodium perborate contains the peroxoanion $B_2(O_2)_2(OH)_4^{2-}$, which contains two O–O linkages that join two tetrahedral $BO_2(OH)^{2-}$ groups. These peroxygen compounds are used in detergents, denture cleaners, and tooth powders.

Bleaching with Light. Bleaching that involves either natural sunlight or artificial light has been used to remove stains from paper artifacts and to treat textiles. The material to be bleached is first immersed in an alkaline solution of either calcium or magnesium bicarbonate, and then protected from **ultraviolet radiation** by covering it with Plexiglas, Lexan, or Mylar. Exposure to light is then allowed to take place for two to four hours, for natural sunlight, and two to twelve hours, for artificial light.

ultraviolet radiation: portion of the electromagnetic spectrum with wavelengths shorter than visible but longer than x rays

Reducing Bleaches

Reducing agents used in bleaching include sulfites, bisulfites, dithionites, and sodium borohydride, all of which are used in pulp and textile bleaching.

Sulfites (SO_3^{2-}) and Bisulfites (HSO_3^-). The oxidation state of sulfur in both SO_3^{2-} and HSO_3^- is +4, and oxidation to +6 occurs readily, with the formation of SO_4^{2-} and HSO_4^-, respectively, making sulfites and bisulfites good reducing agents.

Dithionites ($S_2O_4^{2-}$). Both sodium and zinc dithionite have found use in the bleaching of mechanical pulps and textiles. The preparation of the dithionite ion is accomplished via the reduction of the bisulfite ion and sulfur dioxide with Zn dust.

$$2HSO_3^- + SO_2 + Zn \rightarrow Zn^{2+} + S_2O_4^{2-} + SO_3^{2-} + H_2O \quad (17)$$

The dithionite ion, $S_2O_4^{2-}$, which has sulfur in the +3 oxidation state, behaves as a strong reducing agent in alkaline solution.

$$S_2O_4^{2-} + 4OH^- \rightarrow 2SO_3^{2-} + 2H_2O + 2\ e^- \quad (18)$$

As the pH is lowered, the reducing power of the dithionite ion drops off, as predicted by LeChatelier's principle.

Dithionites are useful in removing rust stains, and neutral citrate solutions of $Na_2S_2O_4$ were used to remove iron corrosion products from objects recovered from the *Titanic.*

Sodium Borohydride ($NaBH_4$). Sodium borohydride has been used mainly in the industrial bleaching of mechanical pulps. The BH_4^- ion is a strong reducing agent in alkaline solution.

$$BH_4^- + 10OH^- \rightarrow BO_3^{3-} + 8\ e^- + 7H_2O \quad (19)$$

One problem with using sodium borohydride is that the BH_4^- ion slowly decomposes in aqueous solution.

$$BH_4^- + 4H_2O \rightarrow B(OH)_4^- + 4H_2 \quad (20)$$

As an alternative method, BH_4^- salts may be dissolved in either CH_3OH or the less toxic C_2H_5OH. The decomposition of the BH_4^- ion in alcohols occurs at a much slower rate:

$$BH_4^- + 4ROH \rightarrow B(OR)_4^- + 4H_2 \qquad (R = CH_3, C_2H_5) \quad (21)$$

Conclusion

A bleaching agent can whiten or decolorize a substance by reacting with the chromophores that are responsible for the color of the substance. Depending on the nature of the chromophores, the bleaching agent will either be an oxidizing or reducing agent. That is, the chromophore is either oxidized or reduced to produce a colorless or whitened substance. Bleaching agents and their commercial uses are summarized in Table 1. SEE ALSO BERTHOLLET, CLAUDE-LOUIS; CHLORINE; DETERGENTS; SCHEELE, CARL.

Henry A. Carter

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Blood *See Hemoglobin.*

Bohr, Niels

DANISH PHYSICIST
1885–1962

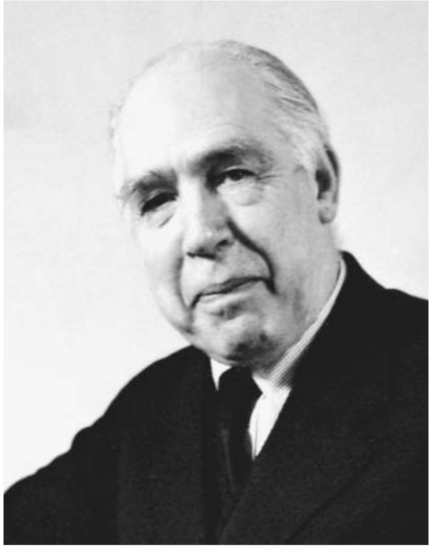
Niels Bohr was one of the founders of modern atomic and **nuclear** physics. He was born into a family of intellectual and academic distinction. His father, Christian Bohr (1855–1911), was a professor of physiology; his brother, Harald Bohr (1887–1951), was a professor of mathematics; and his son, Aage Bohr (b. 1922), a professor of physics—all of them at the University of Copenhagen.

Niels Bohr studied at the University of Copenhagen and earned a master of science degree in 1909 and a doctorate degree in 1911 (at the age of twenty-six). He then went to England and worked with Joseph John Thomson at Cambridge University and with Ernest Rutherford at Victoria University in Manchester. In 1914 Bohr returned to the University of Copenhagen, where, at the age of twenty-nine, he became an assistant professor of physics (he became a full professor in 1916 and held that post until 1956). From 1920 onward he was the director of the university's Institute for **Theoretical Physics** (renamed the Niels Bohr Institute in 1965). The institute became a focal center for theoretical physics for a generation.

In 1913 Bohr (while still in England) published three papers on the quantum theory of atoms. He explained that atoms exist in "stationary" states, and that when an atom changes from one state to another, there has

nuclear: having to do with the nucleus of an atom

theoretical physics: branch of physics dealing with the theories and concepts of matter, especially at the atomic and subatomic levels



Danish physicist Niels Henrik David Bohr, recipient of the 1922 Nobel Prize in physics, "for his services in the investigation of the structure of atoms and of the radiation emanating from them."

been an emission (or absorption) of electromagnetic radiation of frequency ν, determined by the energy difference between the two states.

$$\Delta E = E_2 - E_1 = h\nu.$$

The constant h is Planck's constant. With this theory Bohr combined the atomic model of Rutherford with existing quantum theory, and he made it clear that classical physics was not sufficient to describe atoms or their behaviors. At first the Bohr theory was a theory that explained the behavior of hydrogen atoms. In the years to come he extended the theory to encompass all elements and to provide an explanation of the Periodic Table. The Bohr radius (52.9×10^{-12} m) and the Bohr magneton (9.27×10^{-24} J/T) are today used as units of measure. In 1922 Bohr received the Nobel Prize in physics.

Bohr deduced the correspondence principle: A quantum description of atoms must tend to the classical description for larger dimensions. He also deduced the complementarity principle: There are interactions between objects and the instruments used to observe them. Using the complementarity principle he concluded that there is always a limit to the ability of scientists to observe (and to know) atoms. With this concept he acquired an influence beyond the world of physics.

fission: process of splitting of a heavy atom into smaller pieces

Manhattan Project: government project dedicated to creation of an atomic weapon; directed by General Leslie Groves

In the 1930s Bohr turned to nuclear physics. In 1936 he described an atomic nucleus as resembling a liquid drop existing in different states. In 1940 he and John Archibald Wheeler devised a theory of the **fission** of atoms, in it explaining the phenomenon of the accompanying release of atomic energy. In that same year Denmark was occupied by German military forces, and in 1943 Bohr fled to the United States via Sweden and England. In the United States he became a member of the **Manhattan Project**. After the war he returned to Denmark, where he continued to conduct research in atomic and nuclear physics.

In 1950 Bohr wrote an open letter to the United Nations warning of the horrors of nuclear war. In 1955 he organized the first Atoms for Peace Conference. Niels Bohr was one of the greatest scientists of the twentieth century. SEE ALSO RUTHERFORD, ERNEST; THOMSON, JOSEPH JOHN.

Ole Bostrup

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Boltzmann, Ludwig

AUSTRIAN PHYSICIST
1844–1906

kinetic theory: theory of molecular motion

Ludwig Edward Boltzmann is one of the foremost theoretical physicists of the latter nineteenth century. A vigorous advocate for the existence of atoms, he made monumental contributions to the **kinetic theory** of gases and established the statistical nature of the second law of thermodynamics.

Boltzmann was born in Vienna, Austria, and graduated from high school in Linz. He entered the University of Vienna in 1863, and he received his doctorate in physics three years later. Then, for two years, he served as assistant professor at the university, where he was strongly influenced by the atomistic thinking of physicists Josef Loschmidt and Josef Stefan.

In 1869 Boltzmann became professor of mathematical physics at the University of Graz, the first of his many academic appointments. After leaving Graz in 1873, he held chairs in mathematics at Vienna (1873–1876), experimental physics at Graz (1876–1890), and **theoretical physics** at Munich (1890–1893), Vienna (1893–1900), Leipzig (1900–1902), and finally Vienna again for the remaining four years of his life. According to many of his students, Boltzmann was an outstanding teacher, and his lectures were often filled to overflowing. He displayed a congenial attitude toward students and their learning, something rather rare among Austrian and German professors at that time.

Austrian physicist Ludwig Boltzmann, who established the statistical nature of the second law of thermodynamics.

theoretical physics: branch of physics dealing with the theories and concepts of matter, especially at the atomic and subatomic levels

equilibrium: condition in which two opposite reactions are occurring at the same speed, so that concentrations of products and reactants do not change

Boltzmann's first significant contribution to physics was the generalization of James Clerk Maxwell's distribution of velocities and energies for a sample of gaseous atoms. Although Maxwell had deduced this distribution, he provided no physical basis for it. Boltzmann showed that as atoms move toward **equilibrium** they assume the Maxwell distribution—later known as the Maxwell-Boltzmann distribution—and further that this is the only statistically possible distribution for a system at equilibrium.

Boltzmann connected his ideas with those of Rudolf Clausius, who had introduced the concept of entropy in 1865. Somehow related to heat, entropy was known to increase during irreversible processes, but its exact nature was unknown. From the distribution of gas atoms, Boltzmann described a quantity—later symbolized by the letter H—which is a minimum when atoms assume a Maxwell-Boltzmann distribution. He recognized his H function as the negative of entropy, which is a maximum when the atoms reach thermal equilibrium. Thus Boltzmann offered a kinetic explanation for entropy and, more generally, a connection between the behavior of atoms and thermodynamics.

One of the serious problems with Boltzmann's statistical treatment arose from the reversibility of the laws of mechanics, which holds true for a particle moving in one direction just as they do for a particle moving in the opposite direction. How then could a given set of atomic motions cause H to tend toward a minimum (or entropy toward a maximum), rather than away from it? This was a vexing question for Boltzmann and a serious criticism of kinetic theory.

In response, Boltzmann considered the number of different ways that a sample of gaseous atoms could achieve a particular distribution. The more ways the atoms can arrange themselves to achieve some distribution, the more likely it becomes for that distribution to occur. This connection between entropy (S) and the number of ways (W) that a given distribution can occur is embodied in the equation $S = k \ln W$ (k is now known as Boltzmann's constant, and ln is the natural logarithm). This famous relationship, which is engraved on Boltzmann's gravestone in Vienna, indicates that maximum entropy is associated with the distribution that has the most ways of occurring, that is, with the Maxwell-Boltzmann distribution. Although it is possible for a system of atoms to move away from a Maxwell-Boltzmann distribution, it is not probable, since it is statistically unlikely for the system to move from a distribution with more ways of achieving it to one with fewer ways. Much of Boltzmann's work in this area was formalized somewhat differently under the name of statistical mechanics by Josiah Willard Gibbs, an American physicist who was well known and well respected in Europe, but not in his own country.

Boltzmann's achievements in theoretical physics are all the more remarkable in view of the considerable opposition to his ideas and in view of his own declining health. He had increasingly severe bouts of mental depression, and he tried to commit suicide several times during his life. In 1906 he succeeded in hanging himself while vacationing with his wife and family at Duino, near Trieste, on the Adriatic Sea. SEE ALSO GIBBS, JOSIAH WILLARD; MAXWELL, JAMES CLERK.

Richard E. Rice

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Bonding

In the everyday world around us, we observe three very different types of materials: gases, liquids, and solids. Closer examination of the physical properties of **homogeneous** crystalline solids shows that they can be subdivided into four distinct categories according to their physical properties and the different forces holding them together. For each category, we must develop a bonding picture, based on electrons, that will lead to an understanding of the physical properties exhibited. We can classify the solids according to the distribution of the **valence** electrons of the atoms (as shown in Figure 1), which explains their physical properties.

homogeneous: uniform throughout

valence: combining capacity

Types of Solids

Metallic. A **metal** is a substance that can conduct electricity both as a solid and when it is molten. The range of melting points for metals is very large, from −39°C for mercury to 1,083°C for copper and 3,200°C for tungsten. The outermost valence electrons of the atoms belong to the crystal as a whole, **delocalized** as a "sea" in which they are freely mobile to flow from

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

delocalized: of a type of electron that can be shared by more than one orbital or atom

atom to atom. The positive nuclei of the atoms are embedded in the sea as a close-packed three-dimensional array.

Ionic. Ionic materials are those that are brittle and that conduct electricity when molten but not as solids. Melting points range upwards from about 500°C. Examples are CaO (quicklime), MgF_2, and NaCl (common table salt). The electrons are constrained about each atom, some atoms with excess positive charge (cations) and some with excess negative charge (**anions**). The ions are packed closely together, held by coulomb (electrostatic) forces of **attraction**.

Covalent network. A solid that is extremely hard, that has a very high **melting point**, and that will not conduct electricity either as a solid or when molten is held together by a continuous three-dimensional network of **covalent bonds**. Examples include diamond, quartz (SiO2), and silicon carbide (SiC). The electrons are constrained in pairs to a region on a line between the centers of pairs of atoms.

Van der Waals molecular. A material that has a very low melting point and that will not conduct electricity either as a solid or when molten consists of molecules that are close-packed, bump-in-hollow and that are attracted to each other by weak van der Waals attractions. Examples include carbon dioxide (CO_2, dry ice), iodine (I_2), and naphthalene (mothballs). The electrons are constrained to the well-defined groups of atoms that constitute the molecules. The atoms within the molecules are linked together by strong covalent bonds. The weak attractions between the molecules, termed London forces, arise from the charge asymmetry in the molecules that result from the polarizability of their electron clouds.

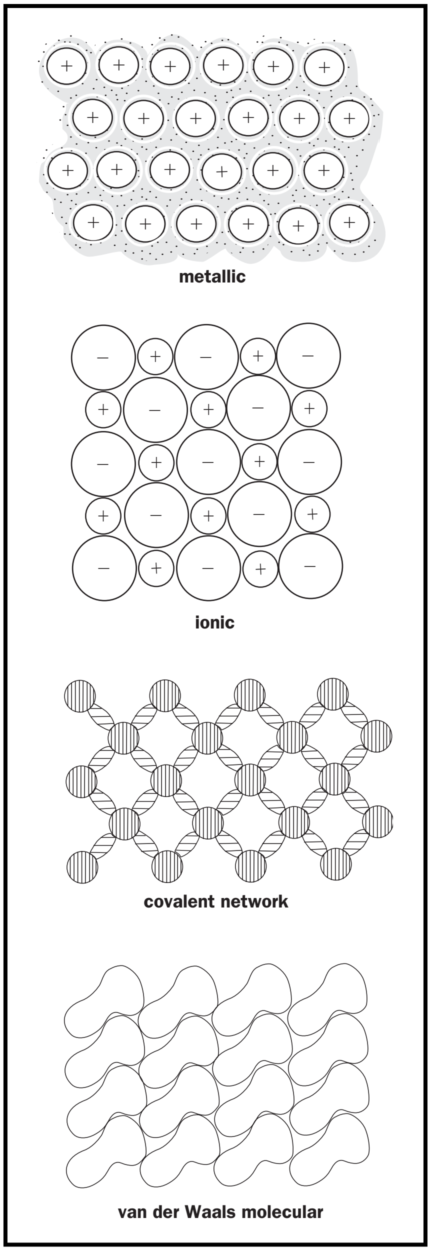


Figure 1. Schematic representation of the packing of the atoms and the electron distribution in the four types of solids.

The Tetrahedron of Bonding Types

These four extreme types of bonding can be represented on the four apexes of a tetrahedron. (See Figure 2.)

The various intermediate types of bonding lie along the edges. Choosing examples that exemplify the extreme types of bonding is straightforward. It is far more difficult to identify appropriate solids to illustrate the six intermediate cases (those that lie along the edges of the tetrahedron), yet it is these very materials that are the most interesting and that often have important applications. The criteria for selecting them must include

- Melting point;
- Conductance as a solid;
- Conductance when molten;
- Pattern and number of close contacts in the solid; and
- Atom-atom distances in the solid

because these are the properties that characterize the four extreme types of bonding.

Metallic Bonding

Metals are unique in that they can conduct electric current in the solid state. (Examples include aluminum high **voltage** transmission cables and copper

voltage: potential difference expressed in volts

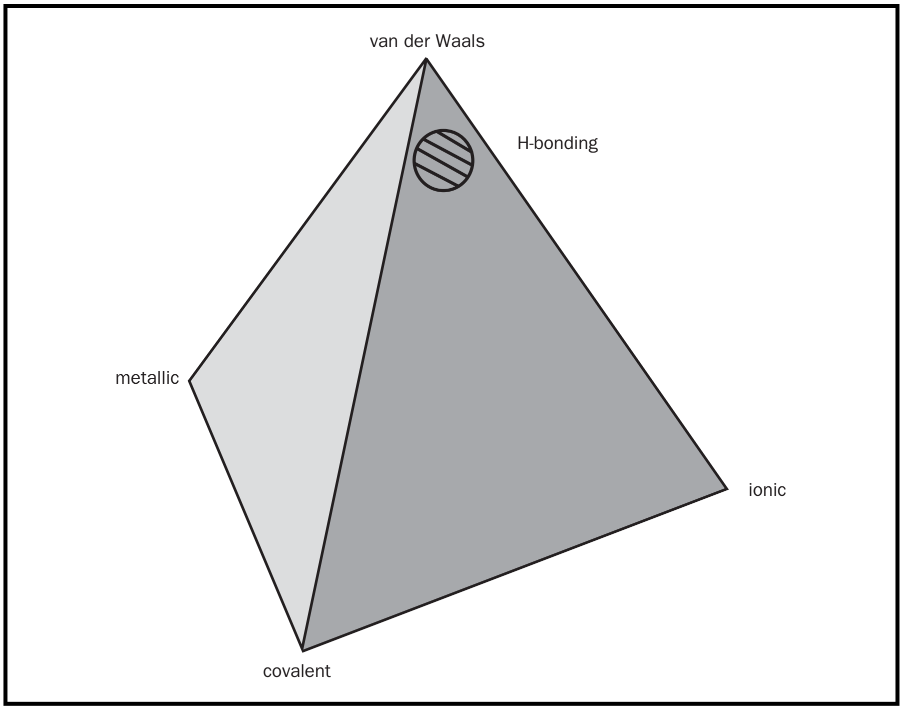


Figure 2. The tetrahedron of bonding types. Typical examples are: metallic-copper; ionic-NaCL; covalent network-diamond; van der Waals, molecular-iodine. Hydrogen bonding would be represented by the cross-hatched area near to van der Waals types of bonding.

ductile: property of a substance that permits it to be drawn into wires

wire in domestic wiring.) Also, metals are **ductile** and malleable; they can be hammered into sheets, such as the pressed steel used as body parts for a car. The layers of atoms can slide past each other on a cushion of electrons, yet the solid remains whole. (See Figure 1.)

In many metals, each atom is in contact with twelve others: six in a plane, three above, and three below. These are termed close-packed hexagonal (e.g., magnesium), or face-centered cubic (e.g., copper). In other metals (e.g., iron), each atom is in contact with eight others at the corners of a cube; such structures are called body-centered cubic.

To a first approximation, we expect that the melting point of the metal should be related to the number of valence electrons that each atom contributes to the "sea." Two series of metals, as outlined in Table 1, illustrate the effect.

alloy: mixture of two or more elements, at least one of which is a metal

The simple model fits observation remarkably well for pure metals. However, this model begins to fail for **alloys** (solutions of one metal in another), such as brass and bronze, where for certain stoichiometries the material has anomalous physical properties and behaves almost as a compound (e.g., CuZn and Cu5Sn, termed Hume-Rothery electron phases).

MELTING POINTS OF METALS

Group in the Periodic Table	1	2	3	4
Metal	K	Ca	Sc	Ti
Melting point (°C)	64	850	1,539	1,875
Metal	Rb	Sr	Y	Zr
Melting point (°C)	39	770	1,509	1,852

Table 1. Melting points of metals.

PROPERTIES OF IONIC COMPOUNDS

Compound	$q^+ \times q^-$	Lattice Energy (kJ/mole)	Melting Point (°C)	Solubility in Water
NaCl	$1 \times 1 = 1$	770	808	Soluble
CaF_2	$2 \times 1 = 2$	2,610	1,418	Insoluble
MgO	$2 \times 2 = 4$	3,906	3,070	Insoluble

Table 2. Properties of ionic compounds.

Ionic Bonding

When two elements of very different groups in the Periodic Table react (e.g., the metals Na and Mg from Groups 1 and 2 on the left side with the nonmetals O_2 and Cl2 from Groups 6 and 7 on the right side), the product is a solid (usually colorless) that has a high melting point. The product is an insulator but will conduct electricity in the molten state. The solid is built of alternating positively charged cations and negatively charged anions, packed tightly together, the exact pattern depending on the charges on the ions, q^+ and q^-, and on their relative sizes—the radius ratio r_+/r_-. In general, the metal atom loses electrons to leave a cation with a closed shell—an octet, at the cost of the **ionization** energy (IE): $Na° - e^- \rightarrow Na^+$. A **halogen** atom will acquire an electron to form an anion with a closed shell, releasing energy, the electron affinity (EA): $F + e^- \rightarrow F^-$.

ionization: dissociation of a molecule into ions carrying + or − charges

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

The attractive forces within the crystalline ionic structure are of the form $M\,(q^+ \times q^-)/(r_+ + r_-)^2$, where the value of M, the Madelung constant, depends on the pattern of packing of the ions. We can expect that the product $(q^+ \times q^-)$ should give an indication of the cohesive energy of the solid. (See Table 2.)

A large value of the **lattice** energy indicates very strong bonding in the solid, hence a high melting point, and insolubility in water. The face-centered cubic structure adopted by the ionic compounds NaCl and MgO is shown in Figure 3. The small spheres represent the cations, and the large spheres represent the anions.

lattice: systematic geometrical arrangement of atomic-sized units that constitute the structure of a solid

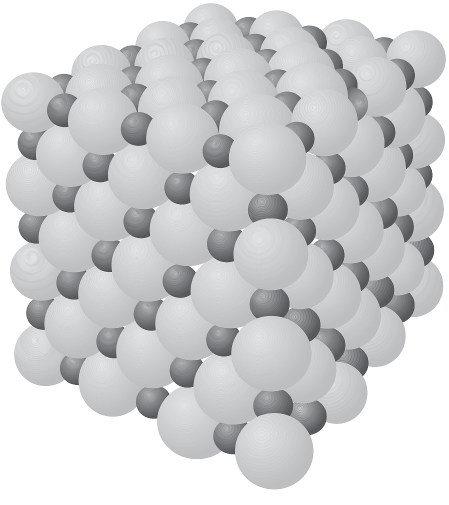


Figure 3. Face-centered cubic structure of NaCl and MgO crystals.

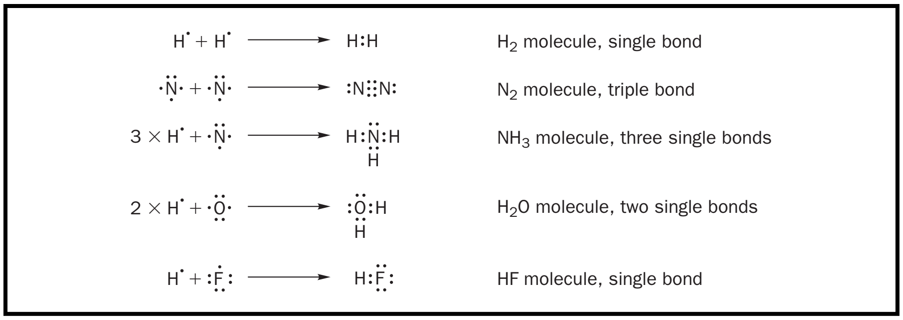


Figure 4. Electron pair bonding in simple molecules. Each H atom shares two electrons, each of the other atoms has four pairs.

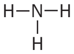
Covalent Bonding

This type of bonding is found between pairs of similar atoms, especially among those in the upper right hand corner of the periodic table. For example, C—C in hydrocarbons, S—O in sulfur dioxide, C—F in Freons. The bonds can give rise to three-dimensional structures like diamond, and are found in simple molecules like H_2S. These bonds are strong, and result in molecules with fixed geometry, such as methane, and give rise to optical activity in molecules such as lactic acid where the C atom is rigidly bonded to four different groups.

Pairs of electrons. Covalent bonding occurs between two atoms as a result of the sharing of a pair of electrons between the atoms. An example is provided in Figure 4.

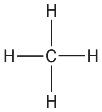
Octets and Lewis Structures When bonded, atoms of the elements C, N, O, and F always tend to be associated with eight electrons in the valence shell—the "octet." The simultaneous attaining of a pair of electrons per covalent bond and an octet around the heavy atom is a powerful bookkeeping method of accounting for the bonding in molecules of the lighter main group elements in the periodic table. The diagrams are termed Lewis structures. The three-dimensional network structures are built around atoms with four bonds in a tetrahedron. For example, in diamond each carbon atom shares electrons with four neighbors to give four covalent bonds in a tetrahedral array. (See Figure 5.)

The diamond crystal can thus be imagined as a huge carbon molecule (C_x). If the pairs of electrons in the diagrams are replaced by lines to represent the covalent bonds, ammonia becomes



$$\begin{array}{c} H-N-H \\ | \\ H \end{array}$$

and methane becomes



$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$$

Each straight line represents a localized two-center two-electron bond. In the ammonia molecule, one pair of electrons on the nitrogen atom is not involved in directly bonding to the H atoms; this is termed a lone pair. Unfortunately these Lewis diagrams can say nothing about the shape of the

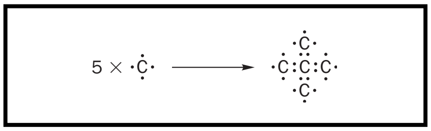


Figure 5. Octet of electrons about the carbon atom in diamond.

molecule. This comes much later by the Sidgwick-Powell/Gillespie-VSEPR approach to molecular geometry.

If we apply the Lewis formalism to the diatomic molecules of nitrogen, oxygen, and fluorine, we get

N≡N, a triple bond O=O, a double bond F—F, a single bond

The three molecules obey the octet rule, and in each case all of the electrons are paired. The experimental facts show that for oxygen this bonding picture is wrong: Oxygen is paramagnetic; that is, the molecule has two unpaired electrons. This simplistic picture has failed, and a new approach to covalent bonding is required.

There are two other approaches to understanding covalent bonding: the molecular orbital (MO) theory and the valence bond (VB) theory. The VB approach is useful when considering molecular geometry. The MO approach is important when considering electronic spectra and other energy properties of the molecule. These topics are discussed separately.

Hybrid atomic orbitals and shapes of molecules. The valence electrons of the light elements lithium to fluorine are distributed in **atomic orbitals** 2s, $2p_x$, $2p_y$, and $2p_z$, whose shapes are given in Figure 6.

atomic orbital: mathematical description of the probability of finding an electron around an atom

If they are close in energy, the s and p orbitals of an atom can interact to give combinations of different geometry, called hybrid atomic orbitals. This is nicely seen in the simple hydrocarbons, because the energy gap between the 2s and 2p orbitals in the carbon atom is relatively small, about 4 electron volts compared to 16 electron volts in the oxygen atom. The combination of one s plus three p orbitals gives four sp^3 hybrid orbitals oriented in a tetrahedron, with an interorbital angle of $109\frac{1}{2}°$. The combination of one s plus two p orbitals gives three sp^2 hybrid orbitals arranged in a trigonal plane, with an interorbital angle of 120°. The combination one s plus one p orbital gives two collinear sp hybrid orbitals. (See Figure 7.)

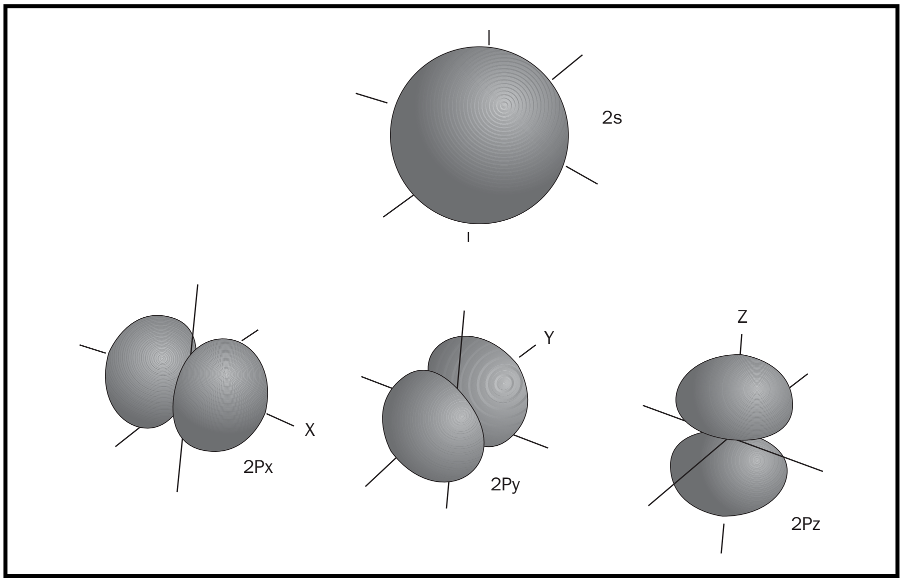


Figure 6. Shapes of atomic orbitals: s, p_x, p_y, and p_z.

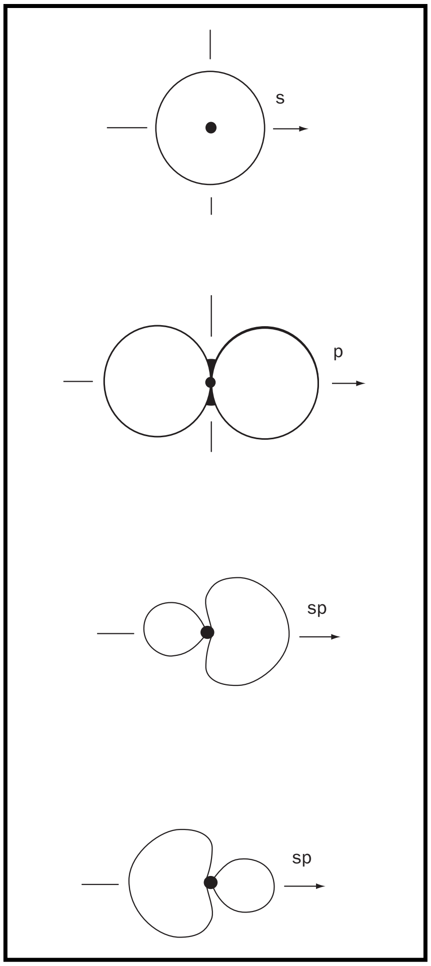


Figure 7. Formation of two sp hybrid orbitals resulting from the combination of one s and one p atomic orbital.

phase: homogeneous state of matter consisting of gases, liquids, or solids

The sp^3 hybrids about the C atom are used to form the four bonds in diamond, methane, and all alkanes. The sp^2 hybrids are used to form the double bond in all alkenes. The sp hybrids are used in the triple bond in acetylene. The shapes of the molecules of the simple gases ethane, ethylene, and acetylene are well described by the hybrid model. (See Table 3.)

All three compounds burn in air. Acetylene is used for welding; ethylene is polymerized to give polyethylene, a plastic common in every kitchen.

Coordinate Bond

Molecules, such as ammonia, that have a lone pair of electrons are able to donate these two electrons to an empty orbital on a metal atom, to form a coordinate or dative bond. A typical example is the deep blue coordination complex of copper, $[Cu(NH_3)_4]2+$, which has four Cu(N bonds in a square plane.

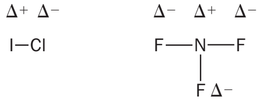
Similarly, a proton will attach itself to the lone pair of electrons on the ammonia molecule to give the tetrahedral NH_4^+ ammonium cation. The lone pair on the N atom in $N(CH_3)_3$ will bond to the empty orbital on the B atom in $B(CH_3)_3$ to give the compound $(CH_3)_3N-B(CH_3)_3$.

The F^- anion will donate a pair of electrons to the B atom in the BF_3 molecule to form the tetrahedral BF_4^- anion. This type of bonding where one atom, the donor, supplies both electrons to form the bond to the second atom, the acceptor, is termed Coordinate, or sometimes Dative.

Van der Waals Attractions

Materials held together by van der Waals attractions often have a smell at room temperature (e.g., camphor and menthol). This is caused by the molecules escaping from the solid and subliming directly into the gas **phase**. The attractive forces between the molecules are weak. These forces arise from distortions in the electron cloud around the molecule, which cause some parts to be relatively positively charged, while other parts are relatively negative.

Polar bonds. When a covalent (electron pair) bond is formed between two different atoms, the pair of electrons is concentrated nearer the atom with the larger power to attract electrons. This power is termed electronegativity. The charge asymmetry generates a bond moment. For example,



$$\overset{\Delta+}{\mathrm{I}}-\overset{\Delta-}{\mathrm{Cl}} \qquad \begin{array}{c}\overset{\Delta-}{\mathrm{F}}-\overset{\Delta+}{\mathrm{N}}-\overset{\Delta-}{\mathrm{F}}\\ | \\ \mathrm{F}\;\Delta-\end{array}$$

PHYSICAL PROPERTIES OF THREE SIMPLE HYDROCARBONS

	Ethane	Ethylene	Acetylene
Formula	H_3C-CH_3	$H_2C=CH_2$	$HC\equiv CH$
Molecular mass	30	28	26
Boiling point (°C)	−88.6	−103.7	−84.0
Shape	3H's, part of a tetrahedron about each C	4H's and 2C's coplanar, HCH angle = 120°	H's and C's collinear
C—C bond, orbitals	Single, sigma	Double, sigma + pi	Triple, sigma + two pi

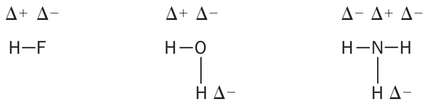
Table 3. Physical properties of three simple hydrocarbons.

Depending on its shape, the molecule as a whole can have a dipole moment μ. For instance, for BF_3, $\mu=0$ because BF_3 is trigonal planar, while for NF_3, $\mu=0.23$ D, because NF_3 is **pyramidal**. The presence of a dipole moment in a molecule results in attractions between pairs of molecules, termed Keesom forces.

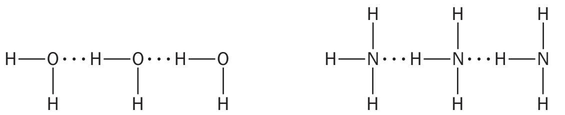
pyramidal: relating to a geometric arrangement of four electron-donating groups located at the four vertices of a pyramid

Polarizability. More interestingly, neutral molecules with a zero dipole moment are mutually attracted to give liquids (such as CCl_4) and solids (such as naphthalene). These attractions, termed London forces or dispersion forces, arise from the ease of distortion of the electron cloud of the molecule as a whole. This is termed polarizability and is related to the volume of the molecule and the number of electrons in the valence shells of the atoms on the exposed surface of the molecule. The net effect (surprisingly, perhaps) is large and accounts for the relatively high melting points of iodine, CO_2 (dry ice), and naphthalene. These London forces are important; they are the attractions between the long-chain polymeric molecules in solid polyvinyl chloride (PVC) and polyethylene.

Hydrogen bonding. The effect of polarity of a covalent bond is magnified in the case of a hydrogen atom bonded to an atom of either fluorine, oxygen, or nitrogen. In simple molecules, the distortion of the electron cloud is large, causing the hydrogen atoms to be slightly positively charged. For instance,



This results in a strong attraction between pairs of molecules:



These strong intermolecular attractions are termed **hydrogen bonds** and, unlike London forces, are directional. They would be represented in the cross-hatched area in Figure 2. It is this intermolecular hydrogen bonding that causes boiling points to be considerably higher than might be expected for molecules with low molecular masses, such as HF, H_2O, and NH_3. (See Table 4.)

hydrogen bonding: intermolecular force between the H of an N–H, O–H, or F–H bond and a lone pair on O, N, or F

hydrogen bond: interaction between H atoms and lone pair electrons that constitutes hydrogen bonding

inert: incapable of reacting with another substance

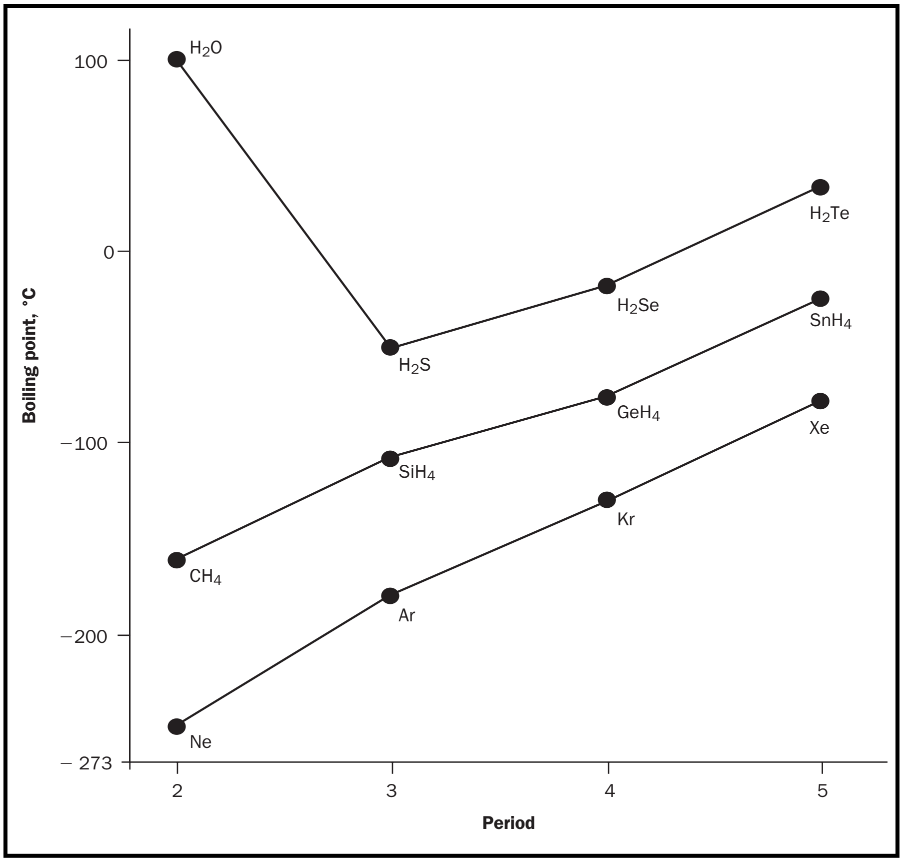
Figure 8 compares the boiling points of the series CH_4, SiH_4, GeH_4, and SnH_4 with those of H_2O, H_2S, H_2Se, H_2Te, and the **inert** gases, and it shows the very high boiling point of water. It is these same OH···O hydrogen bonds

Table 4. Physical properties of simple compounds.

PHYSICAL PROPERTIES OF SIMPLE COMPOUNDS

Compound	CH_4	NH_3	H_2O	HF	SiH_4	PH_3	H_2S	HCl
Molecular mass	16	17	18	20	32	34	34	36
Boiling Point (°C)	−161	−33	+100	+20	−111	−88	−60	−85
μ (D)	0	1.46	1.84	1.82	0	0.58	0.97	1.08

Figure 8. Plot of the boiling points of simple molecules MH_x, versus the position of M in the Periodic Table.



DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

that hold water on a cotton facecloth and that are the forces between the base pairs in the **DNA** in our bodies.

Intermediate Cases

There are many homogeneous materials in which the bonding cannot be described simply as one of the four extreme types. The bonding in these materials is intermediate in character. For example, tin at room temperature is metallic in nature, but on cooling, it totally changes its electronic structure and adopts the diamond structure. A small change in energy nudges the tin atoms over the edge as the bonding teeters on the brink between metallic and covalent. It was this change that caused the tin buttons on the great coats of the soldiers of Napoleon's *Grande Armée* to crumble, during the terrible retreat from Moscow in the winter of 1812.

The element gallium is not truly metallic. In the solid, each gallium atom has one short bond of covalent character, and six other much longer contacts to neighboring atoms, intermediate in character between metallic and van der Waals, similar to the structure of crystalline iodine. The six intermediate types of bonding are not easy to describe, but in fact they are often the most important and certainly are very interesting.

Alloys. Many alloys have structures in which the atoms of the different metals are ordered. Hence they behave like compounds (e.g., $AuCu_3$ and Cu_5Zn_8). CsAu has the NaCl structure (see Figure 3) and behaves almost as if it were ionic, $Cs^+Au^($. This corresponds with the low ionization energy of Cs, 376 kilojoules per mole, and the favorable electron affinity of Au, 223 kilojoules per mole. CsAu's bonding would lie along the metal/ionic edge of the tetrahedron of bonding types.

Semiconductors. Semiconducting materials are of great practical importance in electronics. Ge, GaAs, ZnSe, and CuBr, are examples and they have bonding that can be described as intermediate between ideal covalent and ideal ionic. Each atom is bonded to four others in a tetrahedron, the zinc blende structure.

Silicate minerals. The bonding within a solid is always reflected in its physical properties, and this relationship to its internal structure is beautifully displayed in the morphology of the series of silicate minerals: quartz, mica, and asbestos. In quartz there is a three-dimensional network of Si—O bonds. In mica there are negatively charged infinite sheets consisting of a two-dimensional network of SiO_4 units, with the sheets linked by cations. In asbestos, there are infinite negatively charged chains of tetrahedral SiO_4 units with strong covalent Si—O—Si bonds. The chains are attached to each other via cations. These latter two solids are each held together by two types of bonds, and the difference between the very strong covalent bonding and the other weaker attractions is evident: Mica is easily split into sheets, whereas asbestos consists of fibers.

Glass. Ordinary glass is an amorphous solid, constructed of negatively charged fragments of nets of SiO_4 units that are linked by Na^+ and $Ca2^+$ cations. There is no internal order. As a result, glass shatters to give curved surfaces; and it gradually softens on heating and does not have a sharp melting point. The bonding in ceramic materials (such as bricks, tiles, pottery, and insulators) is similar, predominantly ionic.

Conclusion

It is important to remember that bonding is always accompanied by a reduction in energy, and that all bonding theory is but an intellectual model, a mental scaffolding on an atomic scale, on which to hang our ideas in hopes of giving a self-consistent explanation of observed reality. SEE ALSO Molecular Orbital Theory; Valence Bond Theory.

Michael Laing

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5

B

BORON

10.8115

Boron

MELTING POINT: 2,300°C
BOILING POINT: 2,550°C
DENSITY: 2.46g cm^3
MOST COMMON IONS: B^{3+}

Boron occurs in nature as part of oxygenated compounds, or borates, that have been known since ancient times for their use in glass and metal production. In 1808 Joseph-Louis Gay-Lussac and Louis Jacques Thenard of France and Humphry Davy of England discovered the element boron almost concurrently. Another century passed before boron was successfully isolated in pure form. Elemental boron in its amorphous form is a dark brown powder; it is a yellowish-brown, hard, brittle solid in its **monoclinic** crystalline form. It melts at 2,300°C (4,172°F). Boron is unreactive to oxygen, water, acids, and alkalis. Boron compounds burn yellow-green during the flame test.

monoclinic: one of several arrangements of atoms found in crystalline solids; characterized by a unit cell of three axes each of a differing length; two axes are mutually perpendicular while the third is at an oblique angle

There are 217 minerals that contain the element boron but few are found in great enough quantities to make them commercially valuable. The few that are found in some quantity are white in color. Some boron-containing minerals, their percentages of boron, and the countries of their production in 2000 are: colemanite (51%), the United States and Turkey; datolite (25%), Russia; kernite (51%), Turkey and the United States; probertite (50%), Turkey and the United States; tincal (36%), Argentina, Turkey, and the United States; and ulexite (53%), Argentina, Bolivia, Peru, Turkey, and the United States. From these minerals, chemical compounds such as borax (sodium borate) and boric acid of various grades are manufactured. These compounds are clear or white. Commercial products, in order of the total quantity of boron consumed, are: fiberglass, borosilicate glass, soaps and detergents, fertilizers, enamels, fire retardants, and **alloys**.

alloy: mixture of two or more elements, at least one of which is a metal

Sodium borohydride is marketed in powdered or pellet form, and in solution, for use in fuel cells. Boron nitride can withstand temperatures of up to 650°C (1,202°F); when subjected to high pressures and temperatures, it forms cubic crystals whose hardness rivals that of diamond. Boron carbide, produced by reacting coke and boric acid at 2,600°C (4,712°F), is a highly refractory material and one of the hardest substances known. It has both abrasive and abrasion-resistant applications, and is used in **nuclear** shielding. SEE ALSO Davy, Humphry; Gay-Lussac, Joseph-Louis; Nuclear Chemistry.

nuclear: having to do with the nucleus of an atom

Phyllis A. Lyday

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Boyle, Robert

BRITISH PHYSICIST AND CHEMIST
1627–1691

Robert Boyle was born in 1627, the youngest son of a large upper-class English family with significant landholdings in Ireland and ties to both sides of the English Civil War (1642–1651). Boyle’s literary and religious interests

British physicist and chemist Robert Boyle (r.) and Denis Papin (l.) inspect Papin's steam digester.

turned to **natural philosophy** as early as 1647. Boyle was active within the Baconian group called "the Invisible College," which would later become the **Royal Society**, chartered by King Charles II after the Restoration.

Among Boyle's earliest scientific work were studies involving the air pump. At the time, Robert Hooke was Boyle's laboratory assistant. Starting with the German physicist Otto von Guericke's description of an air pump, Hooke improved on its design, reducing its size and increasing its performance while making it easier to use. Utilizing this improved air pump, Boyle devised experiments to explore the properties of air. He examined the behavior of sound, heat, light, electricity, magnetism, chemical reactions (such

natural philosophy: study of nature and the physical universe

Royal Society: The U.K. National Academy of Science, founded in 1660 as a flame), and living systems (such as small animals or plants) in a vacuum. He also considered the behavior of the air itself under extension or compression. The result of this study was the relationship now known as Boyle's law, which states that the pressure and volume of a confined air (gas) are inversely related. Mathematically, this is expressed as pressure times volume equals a constant

$$PV = \text{constant}$$

In 1661 Boyle published the first edition of *The Sceptical Chymist*. A second, expanded edition was published in 1680. It has earned him the title "the father of chemistry" among some British historians. Many point to this as the work in which Boyle examined numerous alchemical procedures and ultimately rejected the classically derived notion of the four elements (earth, air, fire, and water); also dismissed the Paracelsian notion of three essences: salt, sulfur, and mercury; and articulated a relatively modern working definition of atoms. Modern scholarship has questioned some of the details of this interpretation of Boyle's work, but his importance cannot be denied.

metallurgy: the science and technology of metals

alchemy: medieval chemical philosophy having among its asserted aims the transmutation of base metals into gold

Boyle was among the first chemists not primarily trained in medicine and medicinal chemistry, in mining and **metallurgy**, or interested in those applications. He was also among the first to recognize chemistry as an intrinsically important subject for natural philosophy. In pursuing such a line of thought, he had to convince natural philosophers that chemistry was something other than the disreputable **alchemy** it was known as and chemists that the experimental principles of natural philosophy might offer them a valuable area of practice.

reagent: chemical used to cause a specific chemical reaction

Boyle refocused the study of chemistry in two important ways. First, he shifted attention away from questions surrounding the source and history of a material to its identity and purity. Second, he redirected the interest in desired byproducts to an examination of the chemical reaction itself. In doing this, Boyle promoted the use of chemical identity tests and a control arm in an experiment. Among the measures of identity and purity were color, specific gravity, crystal shape, flame tests, solubility, precipitates, and reaction to standardized **reagents**. In these ways, Boyle helped frame the important questions for succeeding chemists until the seminal work of Antoine-Laurent Lavoisier. SEE ALSO ALCHEMY.

David A. Bassett

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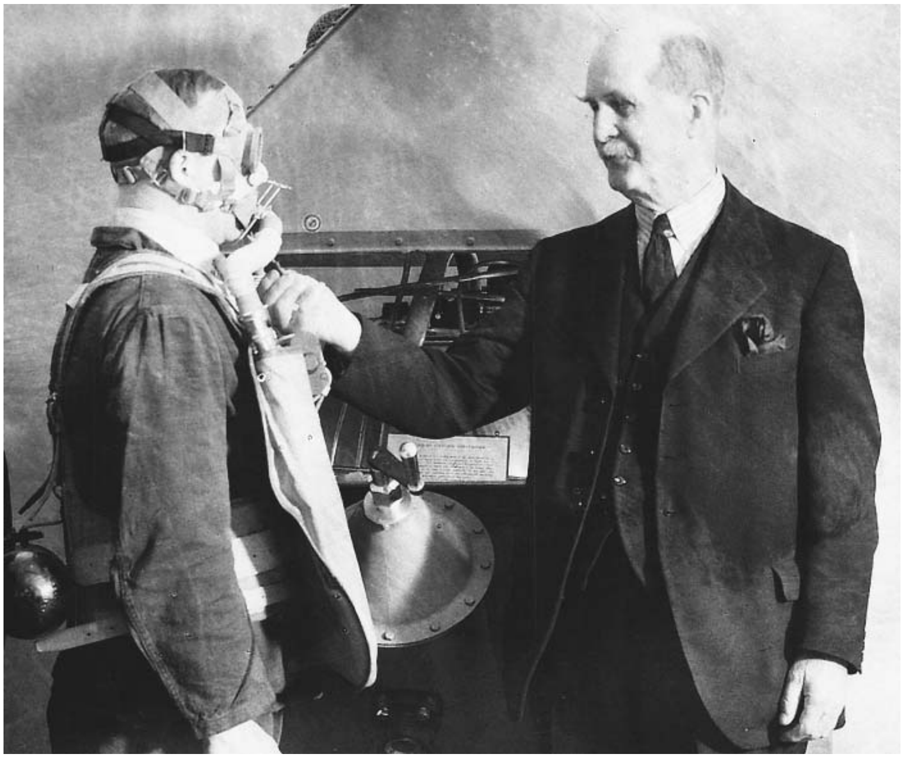
Bragg, William Henry

ENGLISH PHYSICIST
1862–1942

Sir William Henry Bragg was born on July 2, 1862, near Wigton in the northwest of England, the son of an officer in the merchant navy. He attended King William's College on the Isle of Man, before studying for the mathematical degree at Trinity College, Cambridge, in 1884. Two years later he



English physicist Sir William Henry Bragg examining liquid oxygen at a 1936 science exhibition.

was appointed professor of mathematics and physics at the University of Adelaide in South Australia. It was not until nearly twenty years later that Bragg began serious scientific research, concentrating first on **α-particles** and then x rays, in which he was critical of certain aspects of the then accepted theories on both. The significance of his work was such that it warranted his return to England, where he was appointed professor of physics at the University of Leeds in 1909. In 1912 to 1913, working with his son William Lawrence Bragg, a research student at the Cavendish Laboratory, Cambridge, he discovered how to use x rays to determine the molecular structure of crystals. This turned out to be one of the key scientific discoveries of the twentieth century for which the two shared the Nobel Prize for physics in 1915.

α-particle: subatomic particle with 2+ charge and mass of 4; an He nucleus

During World War I, Bragg moved to University College, London, and worked for the admiralty, developing the submarine detection systems ASDIC (Allied Submarine Detection Investigation Committee) and SONAR (Sound Navigation and Ranging). After the war Bragg became disenchanted with University College, and following the death of James Dewar in 1923, he moved to the Royal Institution. There Bragg created a major British center for x-ray crystallography. The scientists at the laboratory established a distinctive approach to x-ray crystallography that later formed the basis of the British school of molecular biology. Bragg trained such figures as Kathleen Lonsdale, the first woman fellow of the **Royal Society**), J. D. Bernal (who went to Birkbeck College), W. T. Astbury (University of Leeds), and, of course, William Henry Bragg's son, (William) Lawrence Bragg. The Braggs came to a tacit agreement that the work in the Royal Institution would concentrate on organic crystals, whereas Lawrence's independent efforts would explicitly focus on minerals.

Royal Society: The U.K. National Academy of Science, founded in 1660

Bragg, knighted for his work during World War I, played a major role in scientific popularization and administration during the interwar period. He was one of the earliest scientists to take advantage of the new medium of radio that he used to full effect to emphasize the value of science for society at large and for industry in particular. From 1935 to 1940 he served as president of the Royal Society, in which capacity he played a major role in helping scientists fleeing from fascist regimes to find employment, in establishing the committee that became the scientific advisory committee to the war cabinet, and in determining what scientific resources would be available for the looming conflict with Germany. During the blitz (the German bombing of London during World War II), the Royal Institution was a designated bomb shelter, and often Bragg would go down to the shelter at night to help boost the morale of people taking refuge there, actions for which he is still remembered. He died, in office, on March 10, 1942. SEE ALSO BRAGG, WILLIAM LAWRENCE; DEWAR, JAMES; LONSDALE, KATHLEEN.

Frank A. J. L. James

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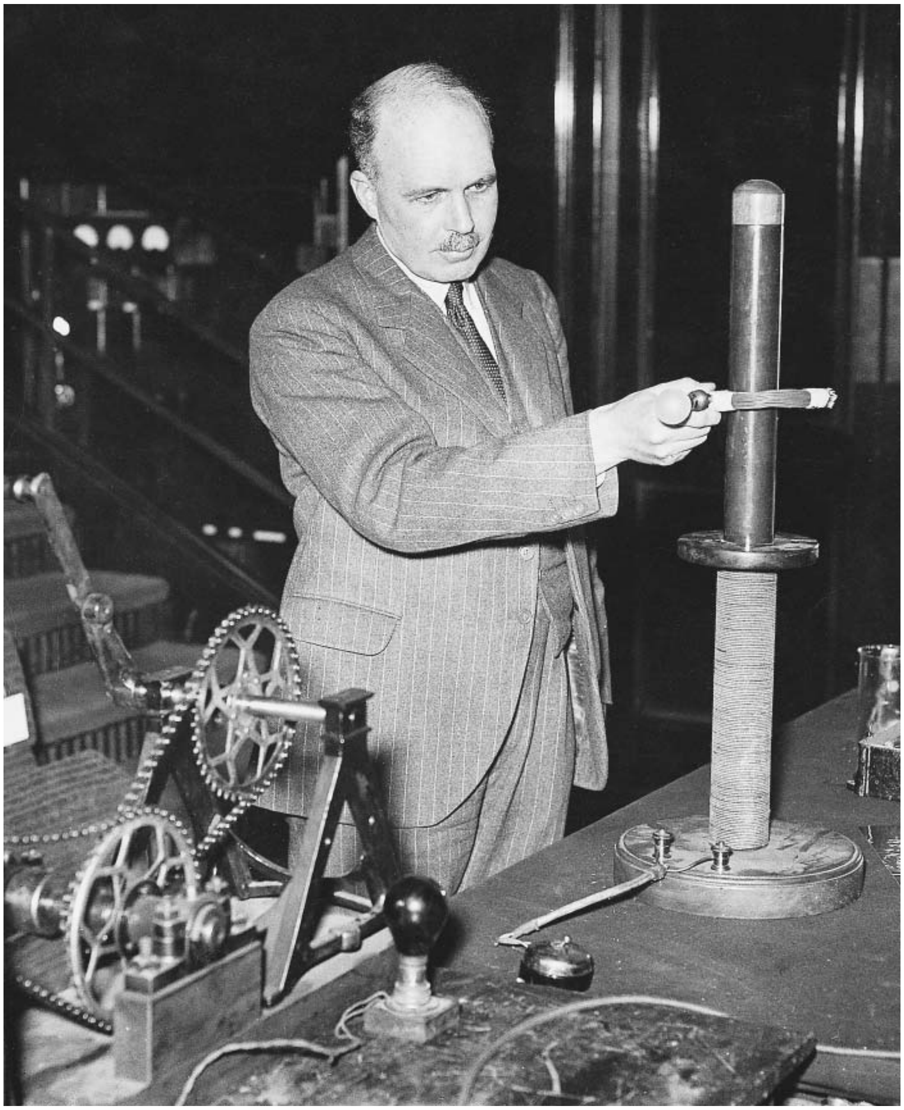
Bragg, William Lawrence

ENGLISH PHYSICIST
1890–1971

Sir William Lawrence Bragg was born on March 31, 1890, in Adelaide, South Australia, where his father, William Henry Bragg, was professor of mathematics and physics. Lawrence attended St. Peter's College, Adelaide, and studied mathematics at the university. The family moved to England in 1909, and Bragg continued his studies at Trinity College, Cambridge, taking first place in the natural sciences degree in 1912. He then began research studies at the Cavendish Laboratory and during 1912 and 1913, in conjunction with his father, he discovered how to use x rays to determine the molecular structure of crystals. Lawrence also determined Bragg's law, $n\lambda = 2d \sin\theta$ the equation that links the wavelength of x rays with the distance between two crystal planes and the angle of incidence. For this work, one of the crucial discoveries of twentieth-century science, the Braggs were jointly awarded the Nobel Prize for physics in 1915; sharing the award at the age of twenty-five, Lawrence remains the youngest-ever winner of the esteemed prize.



English physicist William Lawrence Bragg, co-recipient, with Sir William Henry Bragg, of the 1915 Nobel Prize in physics, "for their services in the analysis of crystal structure by means of X-rays."

During World War I, Bragg served in Flanders in a sound-ranging unit of the Royal Artillery. After demobilization he succeeded Ernest Rutherford as professor of physics at the University of Manchester. There he worked on problems such as the structure of silicates and of **metals**. After briefly directing the National Physical Laboratory, Bragg in 1938 became director of the Cavendish, once again succeeding Rutherford. At the Cavendish, Bragg established a major crystallographical research group despite some opposition from former members of Rutherford's group who wanted the laboratory to continue to concentrate on **nuclear** physics. Bragg held the laboratory together during the World War II years (1939–1945) and served on a number of government scientific committees; as a result of his efforts, he was knighted in 1941.

After the war Bragg established at the Cavendish Laboratory, with funding from the Medical Research Council, a unit for the study of molecular structure of biological systems. It was here in 1953 that Francis Crick (whom Bragg did not like) and James Watson determined the double helical structure of **DNA**. At the start of 1954 Bragg moved to the Royal Institution to

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

nuclear: having to do with the nucleus of an atom

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

try to repair the scientific capacity of the institution after it had been poorly managed by another scientist. Bragg was the only scientist of repute willing to take on this position, and it undoubtedly did him harm within the scientific community, especially the **Royal Society**.

Royal Society: The U.K. National Academy of Science, founded in 1660

Bragg revived the fortunes of the Royal Institution, both by increasing its public programs, especially its schools' lectures, and developing a major research group. This group included Max Perutz and John Kendew, who, working at both the Royal Institution and the Cavendish Laboratory, determined the structures of hemoglobin and myoglobin, for which they won the Nobel Prize for chemistry in 1962. Working with Bragg during the 1960s at the Royal Institution, David (later Lord) Phillips determined the structure of an enzyme, lysozyme, for the first time. On his retirement in 1966, Bragg was able to hand over a Royal Institution now in reasonably good shape to his successor George Porter. Bragg died five years later on July 1, 1971. SEE ALSO Bragg, William Henry; Rutherford, Ernest; Watson, James Dewey.

Frank A. J. L. James

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35
Br
BROMINE
79.9

Bromine

MELTING POINT: −7.3°C
BOILING POINT: 59°C
DENSITY: 3.12 g/cm^3 (liq. at 20°C)
MOST COMMON IONS: Br^-, BrO^-, BrO_3^-, BrO_4^-

Bromine is a member of a family of elements known as **halogens** that are found in group 7A of the Periodic Table. Bromine was discovered in 1826 in Montpellier, France, by French chemist Antoine J. Balard.

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

Bromine is one of two elements (the other being mercury) that is liquid at normal temperatures. As with the other halogens, bromine is very reactive, corrosive, and poisonous. Both the liquid and vapor of bromine are deep red in color. Bromine has a pungent, irritating odor that is the source of the element's name (the Greek word *bromos* means "stench").

Elemental bromine is a diatomic molecule (Br_2). Bromine will combine with most other elements. Reaction with metallic elements leads to salts such as silver bromide (AgBr), in which the bromine atom has a −1 charge and **oxidation** number. Bromine forms many interesting covalent compounds as well, including two oxides: bromine (IV) oxide (BrO_2) and bromine (I) oxide (Br_2O).

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

Bromine is produced commercially from natural brines and from seawater either by electrolysis or with displacement by chlorine, a somewhat more reactive halogen. The concentration of bromine in seawater is approximately 67 parts per million (ppm) by weight; it is found in Earth's crust at an average level of 3 ppm.

Bromine compounds have a variety of uses. Methyl bromide (CH_3Br) is a common agricultural soil fumigant; other bromohalocarbon compounds have been used as refrigerants and fire suppressants. Inorganic bromides are important components of photographic emulsions. Bromine reacts with liquid water to produce hypobromite ion (BrO^-), a powerful bleaching agent. There are also many dyes and pharmaceutical agents that contain bromine. SEE ALSO Halogens.

John Michael Nicovich

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Brønsted, Johannes Nicolaus

DANISH CHEMIST
1879–1947

Johannes Nicolaus Brønsted was a physical chemist whose work resulted in a new theory of acids and bases. He was born in the town of Varde in Jutland (Denmark), where his father was an engineer for the Danish Heath Society. His mother died shortly after his birth. When his father died in 1893, young Brønsted relocated to Copenhagen, where he was admitted to the old Latin school (high school), the Metropolitanskolen. He passed the school's final examinations in 1897.

Brønsted studied chemistry at the University of Copenhagen. He received a master of science degree in 1902 and a doctorate degree in 1908. After receiving temporary appointments at the University of Copenhagen, he became an assistant professor there in 1905, and full professor in 1908. Brønsted studied chemical affinity, electrolytes, **isotope** separation, reaction kinetics, thermodynamics, and acid-base **catalysis**.

isotope: form of an atom that differs by the number of neutrons in the nucleus

catalysis: the action or effect of a substance in increasing the rate of a reaction without itself being consumed

On May 4, 1923, the Dutch chemical journal *Receueil des Travaux Chimiques des Pays-Bas* (42:718) received a paper from Brønsted on existing concepts of acids and bases. In this paper Brønsted demonstrated how useful it was to define an acid as a proton donor and a base as a proton acceptor. In the Brønsted scheme, acid-base reactions are proton transfer reactions. Every acid is related to a conjugate base, and every base to a conjugate acid. Also in this paper he pointed out that there is an analogy between the proton transfer that is characteristic of acid-base reactions and the electron transfer that is characteristic of **oxidation**-reduction reactions.

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

On January 19, 1923, an article by Thomas Martin Lowry (1874–1936) was published in the English journal *Chemistry and Industry*, in which the idea of proton transfer between acids and bases was launched. In spite of this, Brønsted's theorizing work has been recognized, and the terms Brønsted acid and Brønsted base have had wide usage. SEE ALSO Acid-Base Chemistry.

Ole Bostrup

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Brønsted Acids ***See Acid-Base Chemistry.***

Bunsen, Robert

GERMAN CHEMIST
1811–1899

German chemist Robert Wilhelm Bunsen, the co-developer of the science of spectroscopy.

Robert Wilhelm Bunsen, born in Göttingen, is often identified with the laboratory burner that bears his name. But to think of him only in relation to the Bunsen burner is to do him a disservice. Bunsen contributed widely to the development of many laboratory instruments, some of which helped to dramatically advance chemistry. His most important work was developing several techniques used to analyze chemical substances.

Born into an academic family and well-versed in many disciplines, Bunsen made chemistry his field of choice. After receiving his doctorate at the age of nineteen, Bunsen went on a partially government-funded tour throughout Europe, where he met many chemists and engineers. His travels provided him with a network of contacts that he used throughout his career. Upon his return and after teaching at several universities, he settled into a professorship at the University of Heidelberg in 1852, where he stayed until his retirement in 1889.

arsenic: toxic element of the phosphorus group

Bunsen was an avid experimentalist. He spent much of his time in the laboratory trying to discover the composition of chemical substances. His early research concerned the properties of **arsenic** and its compounds. In particular, the chemical composition of a certain class of chemicals, called cacodyls, was unknown. His experiments showed that cacodyls were oxides of arsenic. But Bunsen's work with arsenic nearly cost him his life—he nearly killed himself through arsenic poisoning and lost the sight in one eye during his experiments with cacodyls.

galvanic: relating to direct current electricity especially when produced chemically

atomic weight: weight of a single atom of an element in atomic mass units (AMU)

As his research advanced to the studies of gases and alkali metals, Bunsen recognized the importance of developing new methods to analyze and identify chemical substances. The importance of quantitative analysis was realized in the late eighteenth century. Chemists needed to probe further into a substance's composition in order to help explain the physical world. Bunsen recognized this need and worked to develop new instruments for this purpose. For example, he invented new types of **galvanic** and carbon-zinc electrochemical cells, or batteries, to isolate barium and sodium. He also constructed a new type of ice calorimeter that measured the volume, rather than the mass, of melted water. This allowed Bunsen to measure a metal's specific heat in order to find its **atomic weight**.

spectroscopy: use of electromagnetic radiation to analyze the chemical composition of materials

Bunsen's most lasting contribution to chemistry though was **spectroscopy**, which he developed in collaboration with the German physicist

Gustav Kirchhoff. Bunsen became interested in analyzing the colors given off by heating chemicals to the point that they glowed. He heard that Kirchhoff was involved in similar work, and in 1854, Kirchhoff joined Bunsen at the University of Heidelberg. When Kirchhoff suggested that they observe the light being emitted from the elements by dispersing the light with a **prism**, the science of spectroscopy was born. When viewed through a prism, they found that the light was broken down into a series of lines, called **spectral lines**. Bunsen and Kirchhoff determined that the light emitted by each substance had its own unique pattern of spectral lines—a discovery that led to the spectroscopic method of chemical analysis.

prism: triangular-shaped material made from quartz or glass used to diffract light

spectral line: line in a spectrum representing radiation of a single wavelength

It was during the process of developing spectroscopy that the Bunsen burner came into being. Bunsen realized that the spectral patterns observed were being contaminated by the light coming from the burner they were using to heat the elements. He modified the burner he was working with by mixing air into the gas before burning in order to obtain a high temperature, nonluminous flame.

Using the new burner, Bunsen and Kirchhoff were able to clearly see the spectra of all the chemicals they were studying. Together, they catalogued the spectra of all the known elements. This aided chemists enormously, because by identifying their spectral patterns, chemists could determine the composition of any unknown substance. In the process of cataloguing the spectra of the elements, Bunsen and Kirchhoff discovered two new elements that they named after the colors of their spectral lines: cesium (blue) and rubidium (red). Using Bunsen and Kirchhoff's new analytical technique and the spectroscope they next developed, many new elements were subsequently discovered. But spectroscopy not only opened the door to the further analysis of earthly substances, the composition of the stars could also now be deduced.

Bunsen was a very modest man, despite being honored by some of Europe's most prestigious scientific institutions. In 1853 he was elected to the Chemical Society in London and to the Academie des Sciences in Paris. He was named a fellow of the **Royal Society** of London in 1858 and received its Copley Medal in 1860. Bunsen and Kirchhoff were together awarded the first Davy Medal in 1877 for their development of spectroscopy.

Royal Society: The U.K. National Academy of Science, founded in 1660

On his retirement in 1889, Bunsen turned his attention to another of his lifelong interests, geology. Bunsen's contributions to chemistry included not just the Bunsen burner, but also many other instruments that allowed the physical world to be seen in new and informative ways. SEE ALSO SPECTROSCOPY.

Lydia S. Scratch

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C, Vitamin *See Ascorbic Acid.*

Cadmium

48
Cd
CADMIUM
112.40

MELTING POINT: 320.9°C
BOILING POINT: 767°C
DENSITY: 8.642 g/cm^3
MOST COMMON IONS: Cd^{2+}

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Cadmium is a silver-white, malleable **metal** that exists as crystals having the hexagonal close-packed arrangement, and is usually found combined with other elements in mineral compounds (e.g., cadmium oxide, cadmium chloride, cadmium sulfate, and cadmium sulfide). Cadmium dust can ignite spontaneously in air and is both flammable and explosive when exposed to heat, flame, or oxidizing agents. Toxic fumes are emitted when cadmium metal is heated to high temperatures. Cadmium lacks a definite taste or odor. It was discovered as an impurity in zinc carbonate by Friedrich Strohmeyer in Germany in 1817. Most cadmium is obtained as a byproduct of the chemical treatment of copper, lead, and zinc ores, although it is a naturally occurring element in Earth's crust.

alloy: mixture of two or more elements, at least one of which is a metal

Industrial uses of cadmium include electroplating and the manufacture of batteries, metal coatings, and **alloys**. Cadmium is also used as a pigment in paints and plastics. Some fertilizers also contain cadmium.

Food and cigarette smoke are the most likely sources of cadmium exposure for the general population. The total daily intake of cadmium from food, water, and air for an adult living in North America or Europe is estimated to be between 10 and 40 micrograms (3.53×10^{-7} and 1.41×10^{-6} ounces). The U.S. Environmental Protection Agency has established oral reference doses for cadmium: 0.0005 mg/kg/day (from water) and 0.001mg/kg/day (from food). The reference dose is the level that may be consumed over a lifetime with minimal risk of adverse effects. Occupational exposure may occur in individuals who work with cadmium or in industries that produce cadmium. About 15 percent of inhaled cadmium is absorbed by the body, whereas 5 to 8 percent is absorbed from the gastrointestinal tract following cadmium ingestion. Cadmium is transported in the blood by hemoglobin, as well as by albumin and other large molecular weight proteins. The half-life for cadmium in the body is about thirty days, with most of the excess cadmium accumulating in the liver and kidneys. Cadmium is **excreted** primarily in the urine.

excrete: to eliminate or discharge from a living entity

Acute toxicity may result from the ingestion of cadmium. Symptoms that follow cadmium ingestion may include abdominal pain, nausea, and vomiting; symptoms that follow inhalation include acute respiratory irritation and/or inflammation. Epidemiologic studies in humans have found associations between cadmium exposure and lung cancer, and between cadmium exposure and prostate cancer. Other evidence of the carcinogenic potential of cadmium has been found in the results of animal studies. SEE ALSO Toxicity.

Ronald Brecher

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Caffeine

Caffeine belongs to the family of heterocyclic compounds known as purines. It has the systematic name 3,7-dihydro-1,3,7-trimethyl-1H-purine-2,6-dione; it is also known as 1,3,7-trimethylxanthine, and 1,3,7-trimethyl-2,6-dioxopurine. Caffeine can be classified as an **alkaloid**, a term used for substances produced as end products of nitrogen **metabolism** in some plants. The chemical formula is $C_8H_{10}N_4O_2$. Caffeine has a molar mass of 194.19 grams (6.85 ounces). It is soluble in water and in many organic solvents, and it appears in pure form as white crystals. Caffeine can be prepared by extraction from natural sources or by **synthesis** from uric acid.

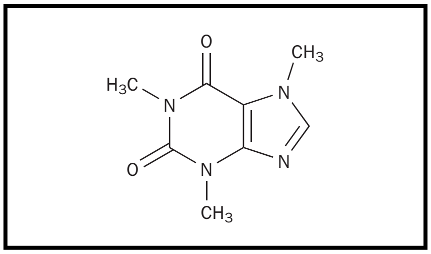

Figure 1. The molecular structure of caffeine.

alkaloid: alkaline nitrogen-based compound extracted from plants

metabolism: all of the biochemical processes that take place within living organisms; comprises processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those that break down complex food molecules, thus liberating energy (catabolism)

synthesis: combination of starting materials to form a desired product

analgesic: compound that relieves pain, e.g., aspirin

More than sixty plants, including those that give us coffee, tea, cola, and cacao, produce caffeine from the purine xanthine. Whereas caffeine is a natural constituent in coffee, tea, chocolate, and some cola drinks, it is added to consumer products such as soft drinks, diet pills, and **analgesics**. Caffeine is said to be the most widely used drug in the world, and more than 100 million people in the United States consume caffeine each day. It has pharmacological uses: as a cardiac and respiratory stimulant and as an agent that promotes kidney diuresis. A therapeutic dose of caffeine is about the same as the amount found in an average cup of coffee, between 100 and 200 milligrams (0.0071 ounces). Decaffeinated coffee can be prepared through extraction with a solvent (such as methylene chloride), water extraction, or steam extraction.

Caffeine enters the bloodstream about ten minutes after its ingestion and stays in the body for up to twelve hours. Like other alkaloids, caffeine has powerful physiological effects on humans and animals. It stimulates heart muscle and relaxes certain structures that contain smooth muscle, including the coronary arteries and the bronchi. It is a diuretic. Theophylline and theobromine, two other plant alkaloid derivatives of xanthine, have physiological effects similar to those of caffeine.

Caffeine acts as a stimulant of the central nervous system (CNS) through several proposed mechanisms. The most important seems to be its interference with the ability of the neurotransmitter adenosine to bind to its nerve cell **receptor**. Also, caffeine inhibits the enzyme cyclic nucleotide phosphodiesterase, which breaks down intracellular cyclic adenosine monophosphate (cAMP), another messenger involved in the transmission of nerve signals from hormones originating outside the central nervous system

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

Coffee drinks are among the most popular sources of caffeine, believed to be the most commonly used drug worldwide.

such as epinephrine and glucagon—hormones that initiate the "fight or flight" response in animals. Other proposed mechanisms have to do with effects on CNS intracellular calcium ion concentrations.

Caffeine is moderately habit-forming, but because caffeine users can usually control its use, it is not listed as an addicting stimulant by the American Psychiatric Association. Caffeine is not regarded as being harmful to the average healthy adult. In fact there are beneficial effects to be derived from moderate caffeine intake (about three cups of coffee per day). It relieves tiredness, improves thought processes, increases alertness, and enhances physical performance. It may be used to treat respiratory depression and, because it constricts blood vessels in the brain, is often an ingredient in headache remedies. There is some evidence that caffeine may help to mitigate symptoms of migraine headache and lower the risk of gallstones. Some studies show that caffeine may protect against Parkinson's disease, perhaps by inhibiting the depletion of the neurotransmitter dopamine in brain cells.

There may be some adverse effects due to excessive caffeine intake, such as restlessness, headaches, heart palpitations, heartburn, and insomnia. Some individuals may have a toxic reaction to it. Ingestion by pregnant women and nursing mothers may have adverse effects on fetuses and babies; caffeine crosses the placenta and gets into breast milk. Caffeine has a wide margin of safety. A lethal dose for most people would be the amount of caffeine found in about one hundred cups of coffee.

Some investigations into caffeine-related health issues are inconclusive. Studies have shown no correlation between caffeine intake and increased risk of osteoporosis or increased risk of spontaneous abortion. There is no conclusive evidence linking caffeine intake (as coffee) with bladder, pancreatic, breast, or colon cancer. There is also no conclusive evidence that moderate caffeine intake contributes to heart disease or heart arrhythmias; however, one study has shown that relatively high coffee consumption elevates blood levels of homocysteine (an amino acid)—a situation that may contribute to heart attack or Alzheimer's disease. There is continuing controversy over whether heavy caffeine intake increases blood pressure, a woman's risk of developing breast lumps, or the incidence of miscarriage. SEE ALSO Dopamine; Epinephrine; Stimulants.

Sharron W. Smith

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Calcium

20
Ca
CALCIUM
40.08

MELTING POINT: 839°C
BOILING POINT: 1,484°C
DENSITY: 1.55 g/cm^3
MOST COMMON IONS: Ca^{2+}

Calcium is the fifth most abundant element in Earth's crust, with calcium oxide, CaO (lime), being among the most common of all terrestrial compounds. Calcium is very important from a biological standpoint, being critical to bones, teeth, and shells of various animals, most often appearing in the form of insoluble calcium phosphate, $Ca_3(PO_4)_2$. Thus calcium is an important part of a healthy diet.

This worker is spraying a lake in Sweden with agricultural lime (calcium oxide), in an attempt to counteract the inflow of acidic materials.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

In elemental form, calcium is a relatively soft, silvery **metal**. Like other alkaline earths, it is too reactive to be found as a free element in nature. It was not until 1808 that Sir Humphry Davy isolated it by doing electrolysis on a mixture of lime (CaO) and mercuric oxide. Calcium's name comes from the Latin word *calx*, which means lime, a substance used since ancient Roman times in various ways, including as plasters for construction.

In addition to its biological role, calcium's presence is widespread in both nature and industry. As lime, it has many important commercial uses including in the treatment of drinking water and in the production and purification of iron and lead. Because of its usefulness, global consumption of lime exceeds 100 million tons annually. Other calcium compounds include calcium carbonate ($CaCO_3$), which is better known as limestone and is the principal component of stalactites and stalagmites in underground caves. Because it is a weak base, calcium carbonate is also used as an antacid. Calcium silicates (Ca_2SiO_4 and Ca_3SiO_5) are major ingredients in Portland cement, named because it resembles natural calcium minerals found on the Isle of portland in England. Calcium chloride ($CaCl_2$) is an excellent deicing and drying agent. In short, calcium is a very important and useful element. SEE ALSO ALKALINE EARTH METALS; DAVY, HUMPHRY.

David A. Dobberpuhl

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Caldwell, Mary

AMERICAN BIOCHEMIST
1890–1972

During the early part of the twentieth century, women were rarely able to find a career related to chemistry. However, there were three particular fields that were havens for women: crystallography (to which physicist Dorothy Hodgkin contributed); radioactivity (a field that physicist Lise Meitner and chemist Marie Curie excelled in); and biochemistry, where Mary Caldwell was able to pursue a lifelong career.

Caldwell was born in 1890 in Bogota, Colombia, to American parents. Her parents strongly supported the concept of higher education, and all five children in her immediate family became scholars or educators. In the United States, women's colleges were a major avenue for young women to obtain a degree, and Caldwell attended Western College for Women in Oxford, Ohio. She received a B.S. in 1913 and was hired by the same institution as an instructor the following year. In 1917 she was promoted to the rank of assistant professor. Caldwell remained only one more year at Western College, deciding that she needed to acquire more specialized knowledge if she was going to follow her dreams.

In 1918 Caldwell entered Columbia University, in New York, from which she received an M.S. in 1919 and a Ph.D. in 1921. Caldwell was so talented that she was immediately hired by Columbia as an instructor. The only woman in a department at a time when the very idea of women serving as chemistry faculty was almost totally unheard of beyond women's colleges, she rose through the ranks to full professorship in 1948.

Besides carrying a heavy teaching load, Caldwell developed a strong research program in nutrition and biochemistry. Her particular interest was the amylase family of enzymes. Enzymes dramatically speed up the rate at which chemical reactions occur in biological systems. Without enzymes, the complex human body would be unable to function. The amylase enzymes are those that break down starch into sugars; Caldwell's specific interest was pancreatic amylase, the version of the enzyme present in the mammalian pancreas. When she started her research, she was dissatisfied with the purity of the then commercially available enzyme. Over the next two decades she developed methods for producing pure crystalline amylase. Today, purified amylases are used in industry for fermentation, for wallpaper sizing, and in preprepared foods.

The methods Caldwell developed were applicable to other enzymes, and they were used by laboratories in the United States and Europe as a general enzyme purification procedure. Having isolated the pure enzyme, subsequent research in her laboratory showed for the first time that amylases were proteins.

Caldwell served as an important role model for aspiring women chemists. At a time when there were very few women chemists, she encouraged her women students to further pursue their education and research and become chemists and biochemists themselves. She retired in 1959, and the following year she was awarded the Garvan Medal by the American Chemical Society. This medal was awarded to a woman chemist for outstanding achievement, and for Caldwell, receiving the medal was the high point of her life. Outside of her work, she was an avid hiker until a muscular disease afflicted her. She died in Fishkill, New York, in 1972. SEE ALSO Curie, Marie Sklodowska; Enzymes; Hodgkin, Dorothy; Meitner, Lise; Radioactivity.

Marelene Rayner-Canham
Geoffrey W. Rayner-Canham

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Californium

MELTING POINT: 900°C
BOILING POINT: Unknown
DENSITY: Unknown
MOST COMMON IONS: Cf^{2+}, Cf^{3+}

98
Cf
CALIFORNIUM
252

Element 98, named after the state of California, was first synthesized by the research group of Glenn Seaborg in 1950 at the University of California at

The radioactive element californium is used in airport x-ray equipment.

isotope: form of an atom that differs by the number of neutrons in the nucleus

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

aqueous solution: solution in which water is the solvent (primary component)

tetravalent oxidation state: bonding state of an atom that can form four bonds

radioactive decay: process involving emission of subatomic particles from the nucleus, typically accompanied by emission of very short wavelength electromagnetic radiation

nuclear: having to do with the nucleus of an atom

fission: process of splitting of a heavy atom into smaller pieces

activation analysis: technique that identifies elements present in a sample by inducing radioactivity through absorption of neutrons

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Berkeley. A target of microgram amounts of an **isotope** of curium (^{242}Cm) was bombarded with accelerated helium ions in a cyclotron, to produce approximately 5,000 atoms of a californium isotope of mass 245 and a half-life of 44 minutes.

Californium, like all the actinide elements heavier than plutonium, exists in a stable trivalent **oxidation** state in **aqueous solutions**. It has also been found to exist in the (less stable) **tetravalent oxidation state** in solution. The ground state electronic configuration for the atom is $5f^{10}7s^2$. Metallic californium has a face-centered cubic structure near its melting point and a double hexagonal close-packed structure at temperatures below its melting point. Californium has eighteen isotopes, all of which are radioactive. The longest-lived isotope has a mass number of 251 and a half-life of 900 years. The isotope having mass number 252 and a half-life of 2.65 years undergoes **radioactive decay**, a fraction of which (3%) is via spontaneous **nuclear fission**; it releases neutrons in the fission event. Californium-252 has been used as a neutron source in a variety of analytical techniques, in medical diagnostic tests that require **activation analysis**, and in the production of short-lived nuclides. Californium neutron sources are used to image low density materials (especially hydrogenous materials). The compactness and portability of ^{252}Cf neutron sources has resulted in their use in such areas as the detection of **metals** in deep wells, lunar exploration, and nuclear weapons monitoring. SEE ALSO ACTINIUM; BERKELIUM; EINSTEINIUM; FERMIUM; LAWRENCIUM; MENDELEVIUM; NEPTUNIUM; NOBELIUM; PLUTONIUM; PROTACTINIUM; RUTHERFORDIUM; SEABORG, GLENN THEODORE; THORIUM; URANIUM.

Gregory R. Choppin

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Calvin, Melvin

AMERICAN CHEMIST
1911–1997

Melvin Calvin was born to immigrant parents on April 8, 1911, in St. Paul, Minnesota. Calvin's family subsequently moved to Detroit, where young Calvin attended high school. With the help of a scholarship he attended the Michigan College of Mining and Technology (now Michigan Technological University) during the years 1927 to 1931 as its first chemistry major. He received a bachelor of science degree in 1931. Because offerings in chemistry were few, he took courses in disciplines such as mineralogy, geology, paleontology, and civil engineering, which helped him in his later interdisciplinary research.

Calvin continued his studies at the University of Minnesota, where he investigated the electron affinities of **halogen** atoms. He received a Ph.D. degree in 1935. As a Rockefeller Foundation fellow at the University of Manchester in England (1935–1937), Calvin worked with Michael Polanyi, who introduced him to the interdisciplinary approach, on coordination **catalysis**, the activation of molecular hydrogen, and metalloporphyrins. In 1937 he joined the faculty of the University of California, Berkeley, as an instructor, and remained there for the balance of his career.

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

catalysis: the action or effect of a substance in increasing the rate of a reaction without itself being converted

During the early 1940s Calvin worked on molecular genetics. He proposed that **hydrogen bonding** was involved in the stacking of nucleic acid bases within chromosomes. During World War II he produced an oxygen-generating apparatus that used cobalt complexes that bond reversibly with oxygen, for use in submarines and on destroyers. As a member of the **Manhattan Project**, he used chelation and solvent extraction to purify and **isolate** plutonium from the **fission** products of irradiated uranium.

hydrogen bonding: intermolecular force between the H of an N–H, O–H, or F–H bond and a lone pair on O, N, or F

Manhattan Project: government project dedicated to creation of an atomic weapon; directed by General Leslie Groves

isolate: part of a reaction mixture that is separated and contains the material of interest

fission: process of splitting an atom into smaller pieces

In 1942 Calvin married Genevieve Jemtegaard. After their first child Elin's death, related to Rh factor incompatibility, Calvin and his wife were part of an interdisciplinary project that investigated the etiology of the disease. They helped to determine the composition and structure of the Rh factor, named elinin for their daughter.

In 1946 Calvin began to investigate **photosynthesis**. He added carbon dioxide containing the radioactive **isotope** carbon-14 (as a tracer) to a suspension of the single-celled green alga *Chlorella pyrenoidosa*. By stopping the plant's growth at various stages and then isolating and identifying the radioactive compounds (present in minute amounts), he determined most of the reactions that comprise the intermediate steps of photosynthesis, by which carbon dioxide is converted into carbohydrates. He found that the so-called dark reactions of photosynthesis (now known as the Calvin cycle) is driven by compounds produced in the "light" reactions, which occur as a result of the absorption of light by **chlorophyll** (producing oxygen). This first use of carbon-14 to elucidate a chemical pathway earned Calvin the Nobel Prize in chemistry in 1961. Using isotopic tracer techniques he also traced the path of oxygen in photosynthesis.

photosynthesis: process by which plants convert carbon dioxide and water to glucose

isotope: form of an atom that differs by the number of neutrons in the nucleus

chlorophyll: active molecules in plants undergoing photosynthesis

When his bioorganic research group outgrew its quarters (at Berkeley), Calvin himself designed the Laboratory of Chemical Biodynamics. His design of a circular building included spacious laboratories, many windows, and few walls. He directed the laboratory until his retirement (1980), at which time it was renamed the Melvin Calvin Laboratory. He died in Berkeley, California, on January 8, 1997, after several years of declining health. SEE ALSO MANHATTAN PROJECT; NUCLEIC ACIDS; PHOTOSYNTHESIS.

George B. Kauffman

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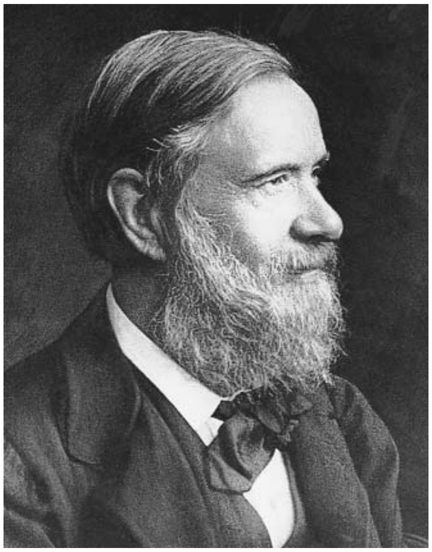
Cancer *See Carcinogen; Mutagen.*

Cannizzaro, Stanislao

ITALIAN CHEMIST
1826–1910



Italian chemist Stanislao Cannizzaro, known for his theories on atomic weight.

Born in Palermo, Sicily, in 1826, Stanislao Cannizzaro began medical studies at the University of Palermo before moving to Pisa to study chemistry. However, when the Sicilian revolt broke out in 1848, Cannizzaro took part in the capture of Messina. The failure of the revolt forced Cannizzaro to flee to France, where he continued his studies in chemistry at the laboratory of Michel-Eugène Chevreul. In 1851, he returned to Italy and accepted a teaching position in Alessandro.

It was at Alessandro that Cannizzaro completed his studies of the reaction in which the action of alkali on benzaldehyde generates benzoic acid and benzyl alcohol, which came to be known as the Cannizzaro reaction. Further studies on the reaction revealed that it could employ any aldehyde without a hydrogen atom on the carbon closest to the carbonyl group.

Cannizzaro was a talented organic chemist and an early leader in the discipline, but it is his contribution to the then-existing debate over atoms, molecules, and atomic weights for which he is best known. He championed Amedeo Avogadro's notion that equal volumes of gas at the same pressure and temperature held equal numbers of molecules or atoms, and the notion that equal volumes of gas could be used to calculate atomic weights. In so doing, Cannizzaro provided a new understanding of chemistry.

atomic theory: physical concept that asserts that matter is composed of tiny particles called atoms, the specific characteristics of which determine the form and type of the matter

During the early 1800s, many chemists were weighing in on **atomic theory** debates, including the debate over the actual, corporeal existence of atoms, with varying degrees of cogency. One difficulty arose from the fact that chemical formulas could be written in any one of a number of ways, if the atomic weights were unknown. For example, the formula for ordinary water, which we know is H_2O, was often written "HO." Use of the latter formula required a belief that oxygen was only eight times as massive as hydrogen, and not sixteen times. The establishment of atomic weights was an important goal of chemists, as all chemical formulas were determined by ratios of elements, leading to empirical and not molecular formulas. Further, some of the leading chemists of the day had their own idiosyncratic theories on how atoms interacted, and there remained the belief that atoms did not actually exist.

In 1858 Cannizzaro published his "Sketch of a Course in Chemical Philosophy" in the journal *Il Nuovo Cimento*, in which he undertook to resolve many of chemistry's outstanding issues, basing his arguments on the work of Avogadro. Cannizzaro felt strongly that a consensus on these issues needed to be achieved. But the paper had little effect at the time of its publication. In 1860 August Kekulé, with the help of Adolphe Wurtz and Carl Weltzien, presided over the first international congress of chemists in Karlsruhe, Germany. Over 140 chemists, including Cannizzaro, attended the three days of discussion and debate. It was the organizers' hope that the congress would resolve some of the aforementioned issues. A participant posed the basic question: "Shall a difference be made between the expressions 'molecule' and 'atom' such that a molecule be named the smallest particle of bodies which can enter into chemical reactions . . . atoms being the smallest particles of those bodies which are contained in molecules?" (DeMilt, p. 38). Cannizzaro was present at the conference and spoke at length on virtually every subject that was debated.

Little was resolved at Karlsruhe. Still, in the words of attendee Dimitri Mendeleev, Jean-Baptiste-André Dumas made a brilliant speech proposing to use the new atomic weights only in organic chemistry, leaving the old for inorganic. Against this Cannizzaro spoke heatedly, showing that all should use the same new **atomic weight**. There was no vote on this question, but the great majority took the side of Cannizzaro.

atomic weight: weight of a single atom of an element in atomic mass units (AMU)

It was after his departure from the conference that Cannizzaro finally made his point and settled the atomic weight debate. Angelo Pavesi, professor of chemistry at the University of Pavia and Cannizzaro's friend, distributed a pamphlet at the conference that contained Cannizzaro's 1858 "Sketch of a Course in Chemical Philosophy." The time was right for those in attendance to at last recognize that a systematic approach to atomic and molecular weights based on the work of Avogadro would resolve many of the outstanding disagreements. The Karlsruhe conference and Cannizzaro's paper are inevitably linked and represent a major turning point in our understanding of chemistry. SEE ALSO Atoms; Avogadro, Amedeo; Chevreul, Michel; Kekulé, Friedrich August, Mendeleev, Dimitri; Periodic Table.

Todd W. Whitcombe

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Carbohydrates

Carbohydrates are the most abundant natural organic compounds on Earth. The term "carbohydrate" derives from their general formula of $C_n(H_2O)_n$, first determined in the nineteenth century, and indicates that these compounds are hydrates of carbon. Carbohydrates are more specifically defined as polyhydroxy aldehydes or **ketones** and the products derived from them. Carbohydrates are synthesized via **photosynthesis** by plants, algae, and some bacteria. Animals feeding on these organisms then use the energy stored in these compounds.

Energy storage is not the only function of carbohydrates. They have a variety of functions in living organisms, including their contribution to the structure of cell walls and their vital role in communication at the site of cell membranes. Carbohydrates form part of the backbone of **RNA** and **DNA** molecules, and they are also found linked to proteins and **lipids** as glycoproteins and glycolipids. The three basic groups of carbohydrates based on size are: **monosaccharides**, oligosaccharides, and polysaccharides (saccharide from the Greek *sakcharon*, or "sugar"). The oligosaccharides and polysaccharides are composed of a few and many monosaccharides, respectively. Monosaccharides have two major groups: the aldoses and the ketoses.

ketone: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the RC(O)R functional group

photosynthesis: process by which plants convert carbon dioxide and water to glucose

RNA: ribonucleic acid, a natural polymer used to translate genetic information in the nucleus into a template for the construction of proteins

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

lipid: a nonpolar organic molecule; fatlike; one of a large variety of nonpolar hydrophobic (water-hating) molecules that are insoluble in water

monosaccharide: one class of the natural products called carbohydrates with the general formula $C_x(H_2O)_y$; monosaccharides have a weak sweet taste, are readily soluble in water, and are called sugars

Aldoses

The simplest of the aldoses is glyceraldehyde, which is a triose, or three-carbon sugar. Glyceraldehyde has one chiral carbon and therefore two stereoisomers, designated D and L. In nature, only D sugars occur in abundance. Other aldoses can be derived from glyceraldehyde via insertion of additional hydroxy carbons between the carbonyl carbon and the molecule's other carbons. In this way, tetroses, pentoses, and hexoses are formed. Although glyceraldehyde and the tetroses can occur only as simple linear struc-

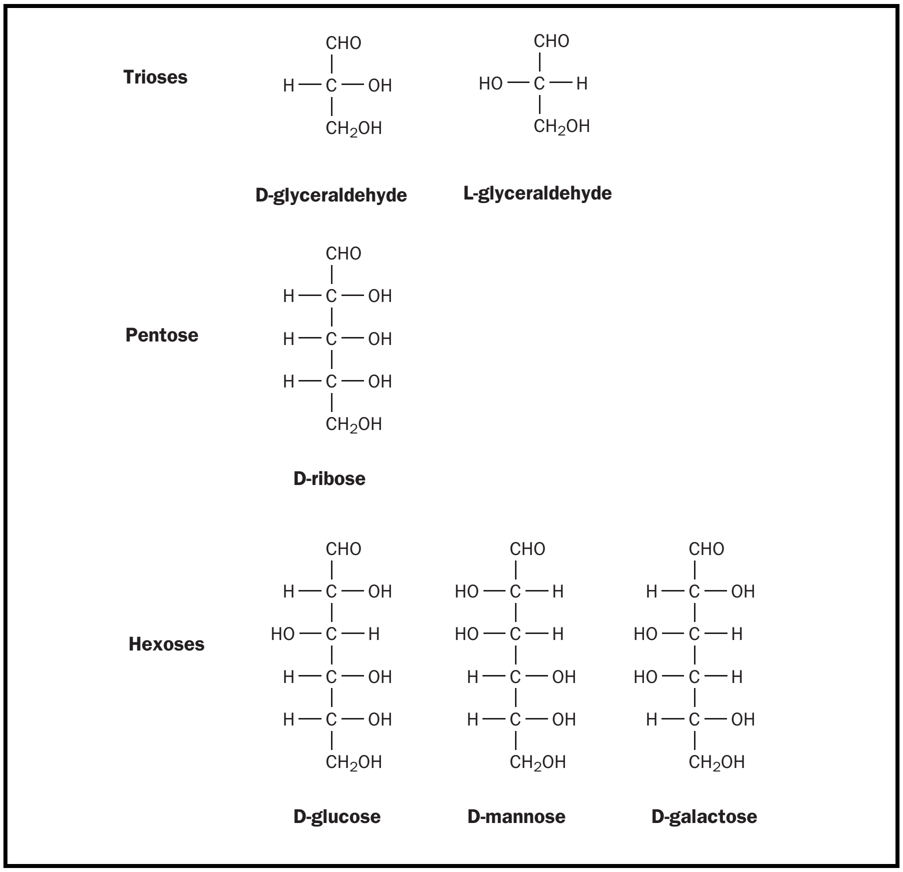


Figure 1. The structure of selected aldoses.

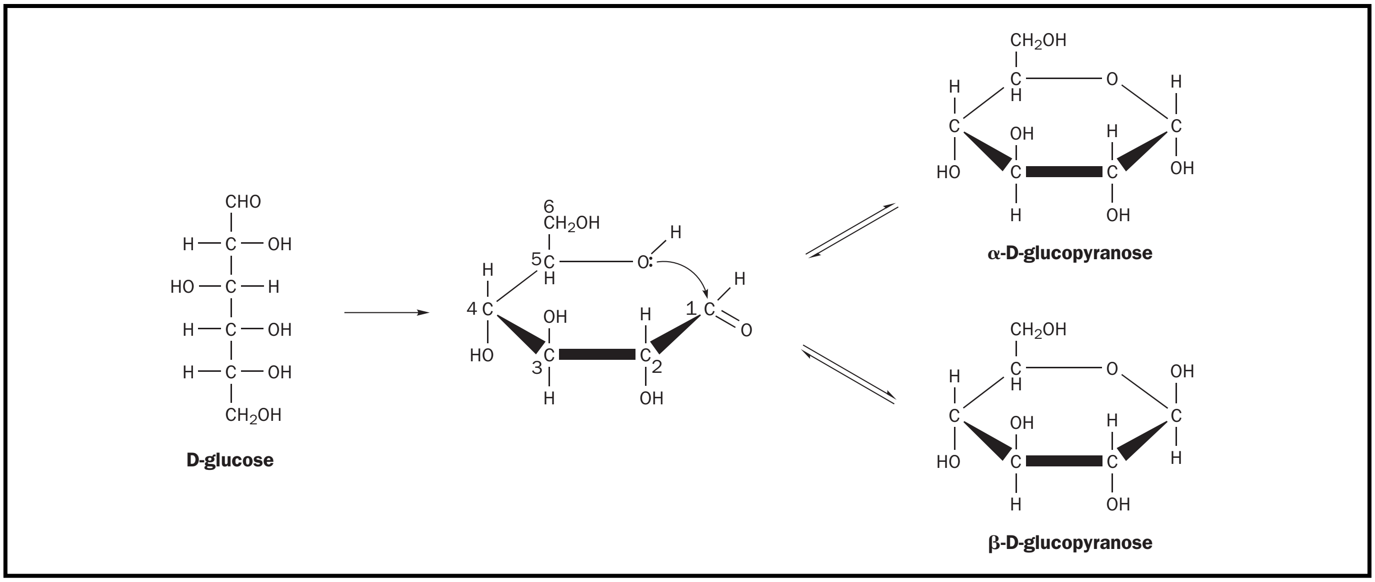


Figure 2. The ring formation of glucose. The rings are shown as Haworth projections.

tures, the pentoses and the hexoses can also form rings. The ring formation has important effects on the properties of these molecules.

Glucose, an aldohexose, is the most common of the monosaccharides. In various combinations and permutations, it forms starch, cellulose, sucrose (table sugar), and lactose (milk sugar), among other things. When metabolized via the glycolytic pathway, it is the major energy source for many living things. Most commonly, glucose forms a ring, its fifth hydroxyl group reacting with the aldehyde carbonyl group to form a **hemiacetal** (see Figure 2). As a result of this reaction, the sugar forms a six-membered ring and the carbonyl carbon becomes chiral. The two new stereoisomers of glucose that revolve on the aldehyde carbon are designated *α* and *β* and are considered anomers of one another. The now chiral carbon is called the "anomeric" carbon. These six-membered ring structures are called pyranoses, as they resemble the compound pyran. Thus, in its ring forms, glucose is properly designated *α*-D-glucopyranose, or *β*-D-glucopyranose.

glucose: common hexose monosaccharide; monomer of starch and cellulose; also called grape sugar, blood sugar, or dextrose

hemiacetal: a compound formed from an alcohol and a carbonyl-containing molecule

These pyranose rings are not flat and can assume several different conformations. In general, the most stable conformation is the "chair" conformation, in which the bulky atomic groups (e.g., the hydroxyl and hydroxymethyl groups) are equatorial or within the plane of the ring (see Figure 3). The hydrogens would then be axial or **perpendicular** to the plane of the ring. Only in *β*-D-glucopyranose are all of the bulky groups equatorial; thus, *β*-D-glucopyranose is more stable than *α*-D-glucopyranose, in which the C-1 hydroxyl group is axial to the ring. The *α* and *β* forms of

perpendicular: condition in which two lines (or linear entities like chemical bonds) intersect at a 90-degree angle

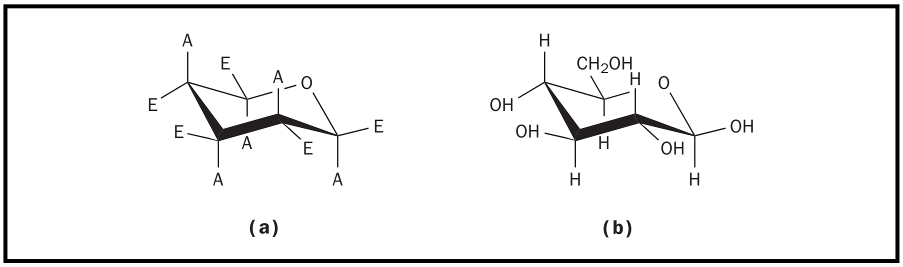


Figure 3. Chair conformations. (a) Axial (A) and equitorial (E) positions of a boat conformation; (b) β-D-glucose in one possible boat conformation.

glucose are freely interconvertible in solution. At equilibrium, a solution of glucose contains about two-thirds α-D-glucopyranose, one-third α-D-glucopyranose, and small amounts of the linear and five-membered ring forms of glucose.

galactose: six-carbon sugar

Other widely occurring aldoses include mannose, **galactose**, and ribose (see Figure 1). Mannose and galactose are, like glucose, aldohexoses and can form six-membered rings. Mannose is an important part of the complex sugars, or oligosaccharides, that attach to proteins in the formation of glycoproteins. Galactose combines with glucose to form lactose or milk sugar. Structurally, each of these sugars differs from glucose only in the stereochemistry that revolves on one carbon: mannose on C-2 and galactose on C-4. Sugars that differ from one another only in respect to the stereochemistry at one carbon are considered epimers of each other. Thus mannose is the C-2 epimer of glucose, and galactose the C-4 epimer. Mannose and galactose are not epimers; they differ from each other in respect to the stereochemistry revolving around two carbons.

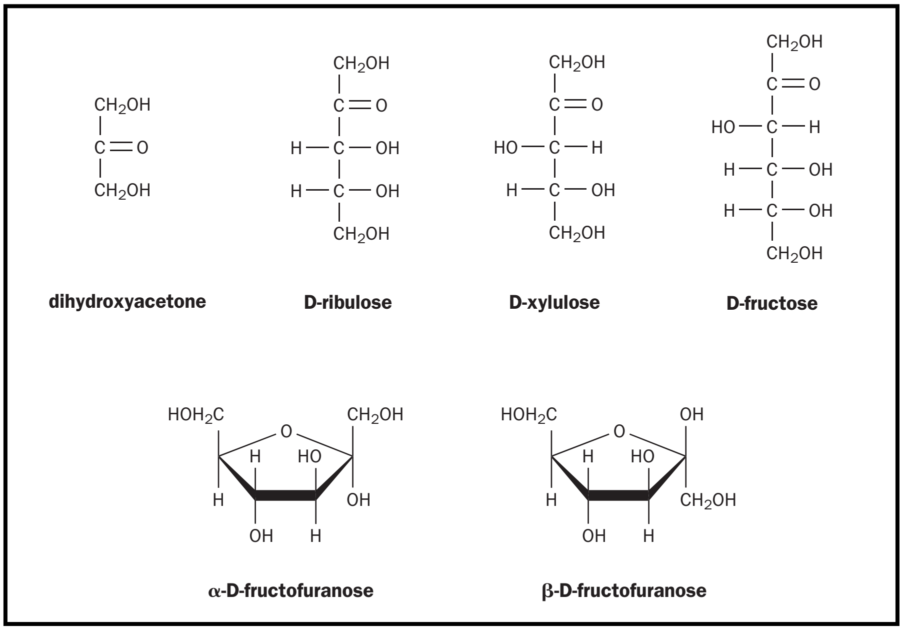
Ribose is an aldopentose. It composes the carbohydrate portion of the ribonucleotides that form a cell's RNA. Ribose, like the aldohexoses, can form a ring. However, ribose forms a five-membered ring, called a "furanose" because of its similarity to the compound furan. Once again, there are two possible forms this ring can have: α-D-ribofuranose and β-D-ribofuranose. RNA contains β-D-ribofuranose.

intermediate: molecule, often short-lived, that occurs while a chemical reaction progresses but is not present when the reaction is complete

metabolism: all of the biochemical processes that take place within living organisms; comprises processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those that break down complex food molecules, thus liberating energy (catabolism)

Ketoses

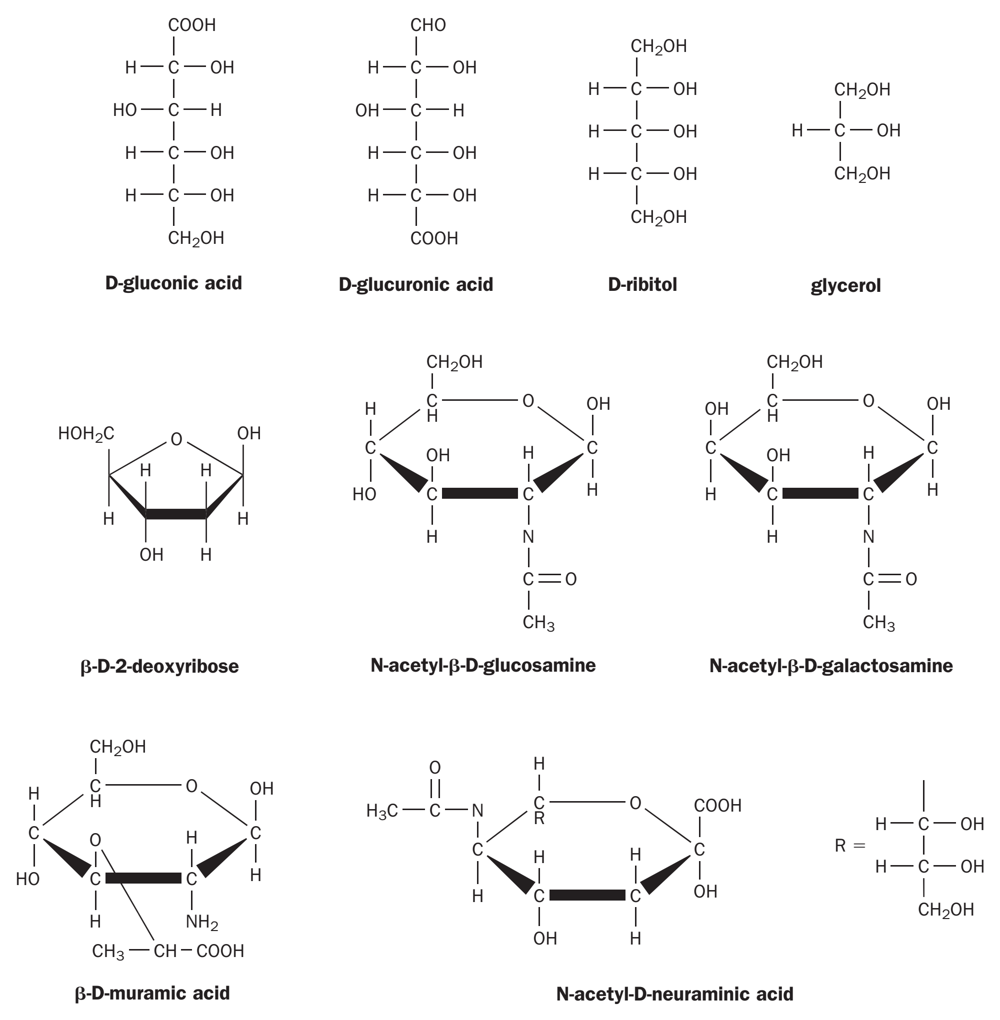
There are fewer ketoses than there are aldoses because ketoses have one less chiral carbon. The most prevalent of the ketoses are dihydroxyacetone, ribulose, xylulose, and fructose (see Figure 4). All four of these sugars are important **intermediates** in **metabolism**. Fructose is, along with glucose, part of sucrose or table sugar. Fructose is a ketohexose, and the only one of the four ketoses that can assume a ring structure. Like ribose, fructose forms a five-membered (or furanose) ring and has α and β anomers.



dihydroxyacetone **D-ribulose** **D-xylulose** **D-fructose**

α-D-fructofuranose **β-D-fructofuranose**

Figure 4. The structures of selected ketoses. Note that dihydroxyacetone does not have a chiral carbon and so does not have D and L variants.



D-gluconic acid   **D-glucuronic acid**   **D-ribitol**   **glycerol**

β-D-2-deoxyribose   **N-acetyl-β-D-glucosamine**   **N-acetyl-β-D-galactosamine**

β-D-muramic acid   **N-acetyl-D-neuraminic acid**

Figure 5. Selected derivatives of monosaccharides.

Monosaccharide Derivatives

Monosaccharides undergo incorporation into oligo- and polysaccharides. Individual monosaccharides can also undergo a variety of transformations. One important modification of monosaccharides is the formation of deoxy sugars. The most biologically significant of the deoxy sugars is *β*-D-2-deoxyribose (see Figure 5), in which the C-2 hydroxyl group of ribose has been replaced with hydrogen. This deoxy sugar is the sugar component of DNA.

In the amino sugars, an amino group replaces one or more of the hydroxyl groups. The most common of these sugars are D-glucosamine and D-galactosamine, both of which have an amino group in place of the hydroxyl group on the second carbon. Often, these amino groups are acetylated to give N-acetyl sugars, such as N-acetylglucosamine and N-acetylgalactosamine. These sugars are important components of larger polysaccharides. Other important amino sugars are muramic acid and N-acetylneuraminic acid, which are components of the oligosaccharides of glycoproteins and glycolipids, and of bacterial cell walls. Muramic acid and N-acetylneuraminic acid are glucosamines, which have been linked at either C-3 or C-1 to three-carbon acids. Muramic acid is formed via an ether linkage between the C-3 of glucosamine and the hydroxyl group of lactic acid.

N-acetyl-D-neuraminic acid results from the formation of a C–C bond between the C-1 of N-acetyl-D-mannosamine and the C-3 of phosphoenolpyruvate. This and other derivatives of neuraminic acid are collectively called sialic acids and are widely found in bacteria and animals.

ester: organic species containing a carbon atom attached to three moieties: an O via a double bond, an O attached to another carbon atom or chain, and an H atom or C chain; a compound with the general formula RC(O)OR′

Finally, monosaccharides often form **ester** linkages with phosphate and sulfate ions. In fact it is rare to find free monosaccharide in cells. Glucose is the only unmodified monosaccharide that exists in substantial quantities in living things, in which it exists primarily extracellularly. SEE ALSO CHIRALITY; GLYCOLYSIS.

Stephanie E. Dew

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International Union of Pure and Applied Chemistry. Information available from <http://www.chem.qmw.ac.uk/iupac/>.

6
C
CARBON
12.01

Carbon

MELTING POINT: 3,500°C
BOILING POINT: 4,827°C
DENSITY: 2.62 g/cm^3
MOST COMMON IONS: CO_3^{2-}, HCO_2^-

Carbon is the sixth most abundant element in the universe and possibly the most widespread element on earth. Named from the Latin word *carbo*, meaning charcoal, it has been known since ancient times, although not recognized as an element until more modern times. It is found in all living things, but is also commonly found in minerals such as limestone and marble and as a small but important constituent of the atmosphere, as carbon dioxide.

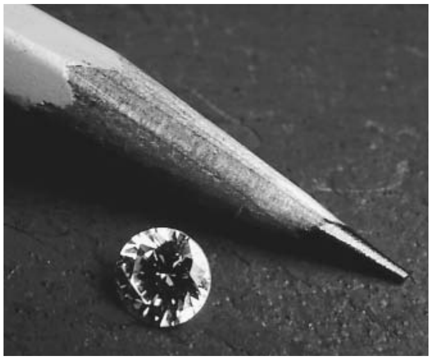
isotope: form of an atom that differs by the number of neutrons in the nucleus

biomass: collection of living matter

photosynthesis: process by which plants convert carbon dioxide and water to glucose

In its elemental form, carbon can be found as diamond, the hardest naturally occurring substance; graphite, an excellent lubricant; or as a fullerene (or "buckyball"). Although five **isotopes** are known, only C-12 (98.9 percent natural abundance) and C-13 (1.1 percent) are stable. Nevertheless, the presence of trace amounts of C-14, a radioactive isotope (with a half-life of 5,730 years), permits "carbon dating" of historical objects.

Carbon is unique among the elements in that carbon atoms can form bonds with other carbon atoms. This property, known as "concatenation," is the reason that there are more than several million known organic (containing carbon) compounds.



Diamonds and graphite are allotropes of carbon.

Carbon is a major constituent of most of our fuels—natural gas, petroleum, coal, wood, and other **biomass**. When burned for their heat content, these fuels produce carbon dioxide, which escapes into the atmosphere. In the "carbon cycle," this carbon dioxide is trapped by plants and reincorporated into useful substances such as cellulose and starch via **photosynthe-**

sis. Since the **Industrial Revolution** of the nineteenth century, which greatly increased the quantity of fuel **combustion**, the concentration of carbon dioxide in the atmosphere has increased. This atmospheric change has been implicated as the cause of global warming.

Carbon is a major constituent of most polymers, both naturally occurring ones such as cellulose, starch, **RNA**, **DNA**, silk, and wool, as well as synthetic ones, including nylon, Teflon, polyethylene, and polystyrene. Some of the strongest and most modern materials replacing **metals** are made of carbon fibers. SEE ALSO Allotropes; Global Warming; Organic Chemistry.

George H. Wahl Jr.

Industrial Revolution: widespread replacement of hand tools by power-driven machines, beginning about 1750 (especially in England)

combustion: burning, the reaction with oxygen

RNA: ribonucleic acid, a natural polymer used to translate genetic information in the nucleus into a template for the construction of proteins

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

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Carboxylic Acids *See Fats and Fatty Acids; Lipids.*

Carcinogen

A carcinogen is a substance that can cause cancer in humans or animals. Carcinogens bring about molecular and biochemical disturbances in cells, resulting in **dedifferentiation** (the loss of cells’ morphological and functional specializations, such that they behave like immature cells capable of resuming cell division) and uncontrolled growth (neoplasia).

Some common substances that are known to be carcinogenic are asbestos, pesticides, lead, cadmium, **arsenic**, benzene, polyvinyl chlorides (PVC), soot, crystallized silica, glass wool (often a component of fiberglass), tobacco smoke, and smokeless tobacco. Most of these chemical carcinogens are called “procarcinogens,” requiring metabolic conversion into “ultimate carcinogens” capable of damaging deoxyribonucleic acid (**DNA**, the genetic material in cells). **Ultraviolet radiation** (UVA, UVB, and UVC) from the Sun is also carcinogenic and can lead to different types of skin cancer.

For a substance to be declared a carcinogen there must exist sufficient evidence of a relationship between exposure to that substance and cancer in humans or animals. Because the use of human test subjects is deemed unethical, testing is done on animals (e.g., mice and rats) and on animal and human cell **cultures** (specialized nutrient-rich growth media); the data are then extrapolated to humans. An agent’s potential carcinogenicity in humans is also determined from what is known of that agent’s effect at the molecular level (i.e., damage to DNA/protein) or from anecdotal evidence (e.g., UV exposure and cancer).

The potency of a carcinogen is expressed as the dose rate that, when administered chronically throughout the standard life span of a test species, will reduce the probability of the population remaining tumorless for that period by 50 percent. Called the TD50 value, the rate is measured in milligrams per kilogram [mg/kg] body weight per day. Hence, the lower the TD50 value, the more potent the carcinogen. Caution is necessary in extrapolating TD50 values from animal systems to humans, however, because

dedifferentiation: the opposite of the biological process of differentiation by which a relatively unspecialized cell undergoes a progressive change to a more specialized form or function

arsenic: toxic element of the phosphorus group

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

ultraviolet radiation: portion of the electromagnetic spectrum with wavelengths shorter than visible but longer than x rays

culture: living material developed in prepared nutrient media the pathway through which that substance becomes carcinogenic may be absent in humans. SEE ALSO Mutagen; Teratogen.

Hiranya S. Roychowdhury

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Careers in Chemistry

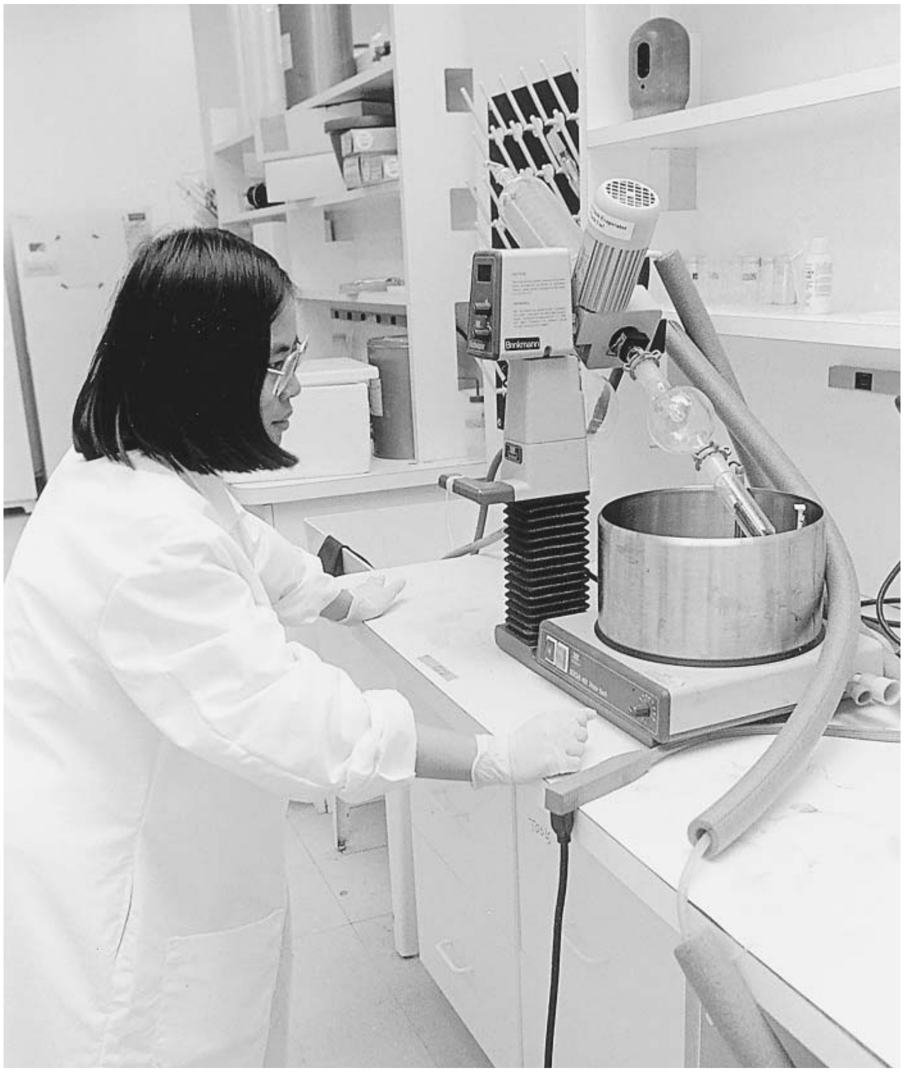
An undergraduate program in chemistry prepares the ground for many possible career paths, including industry, graduate work, and professional programs.

Choosing a college is beyond the scope of this discussion, but any U.S. school being considered for chemistry studies should offer a degree in chemistry approved by the American Chemical Society, the major professional association of chemists in the United States. Another critical criterion for college selection is the availability of undergraduate research work, a very valuable experience for a chemistry undergraduate; summer research at another college is a possible alternative, as is summer employment related to chemistry. The size of the educational institution is a matter of personal preference. Some students prefer the faculty contact that is available to them at a small liberal arts college, and others desire the wider social and academic choices that they have at a large institution.

Most colleges have a basic curriculum that gives students a broad background, but it is still possible for those students to pick courses that support future career plans. For the student leaning toward science, composition and speech courses are always valuable, as are computer courses (including courses in spreadsheet and database fundamentals, computer electronics, and computer networking). Business courses are a useful preparation for management or chemical sales positions. Most chemistry programs require several mathematics courses. Even if not required, courses in statistics, differential equations, and matrix mathematics are, for chemistry students, valuable assets. The same is true for biology and biochemistry courses.

What Does a Chemist Do in Industry?

Very often, graduates with bachelor of science degrees begin industrial careers as bench chemists, that is, individuals who work directly with chemicals under the supervision of a chemist with a Ph.D. or M.S. degree. Entry-level jobs are usually either quality control jobs (chemical analysis work) or research assistant jobs (one helps to develop new products or to improve existing products). Relatively few chemists remain at these bench jobs for their entire careers (which is why a good undergraduate program includes preparation for other job options—such as sales, customer service, or instrument development).



Many chemists begin their careers as bench chemists, in quality control, or as research assistants.

Many companies support employees who pursue further education, with partial or full payment of graduate tuition, released time (with or without pay), and even the option of doing joint research at the company (which may fulfill the graduate research requirement). When interviewing, job seekers should check on the availability of graduate programs. They should be warned that going to graduate school while working full time requires tremendous organization and motivation.

Graduate School in Chemistry and Biochemistry

A doctoral program in chemistry often lasts more than five years. Money is not usually a deciding factor, as matriculation within a chemistry graduate school usually includes an assistant teaching position that pays tuition and living costs. The Ph.D. degree is normally a research degree, and so it requires a commitment to doing research. A master's degree is all that some students will desire. It is also the way to go for students who wish to remedy academic deficiencies before doing advanced work.

Research advisers usually expect students pursuing doctorate degrees to spend at least forty to sixty hours a week on research. Graduate courses can be tremendously challenging and can require a heavy time commitment. Most graduate students doing research view college vacation time as the best time to get work done (graduate students do not have the long vacations they knew as undergraduates).

Although graduates who obtain doctorate degrees from well-known schools have an advantage when looking for employment, a great many other factors are important in a job search. Some departments or individual faculty members have relationships with particular companies (which also helps when one is looking for a position after graduation). Graduate programs in polymer chemistry, analytical chemistry, or materials sciences provide excellent job opportunities, but are often found at schools that are not highly ranked overall.

The main areas of graduate research correspond to the subject matter of typical undergraduate courses: biochemistry, analytical chemistry, inorganic chemistry, organic chemistry, and physical chemistry. One can tentatively identify areas of interest based on one's experience of these courses. One can then look for graduate schools that have advisers working in one's chosen area (or areas). Selecting a research adviser is one of the most important decisions of a career. Looking up graduate departments in the *American Chemical Society Directory of Graduate Research*, one can easily find out the research fields and publications records of faculty members. Faculty members who have published a small number of articles in refereed journals within the preceding five years may not be still active in research.

Alternative Careers

The applications of chemistry within biology are so important that many chemistry departments have become departments of chemistry and biochemistry, or departments of biological chemistry, and some offer both chemistry and biochemistry majors. Biochemistry is one of the major growth areas in chemistry. Although mergers in the pharmaceutical industry have eliminated some research laboratories, this contraction has been offset by an expansion of startup biotechnology companies.

A strong undergraduate program in chemistry or biochemistry is an excellent preparation for professional programs in medicine, optometry, chiropractic, and osteopathy. The combination of chemistry and law school is a powerful one, but one that is not often thought of. Other areas to be considered by chemistry undergraduates are food chemistry, textile and fabric chemistry, forensic science, industrial hygiene, and **toxicology**. Although the number of jobs available in these fields may be limited, there are few students who have acquired credentials in them, and so the employment opportunities can be excellent. The World Wide Web may be used to obtain more information about these fields and to locate a school with the desired program.

toxicology: division of pharmacology dealing with poisons, their identification, detection, effects on the body, and remedies

Some graduates will not want to limit their job searches to the chemical industry. The analytical thinking and organizational skills typical of successful chemistry majors make them strong candidates for positions as patent examiners or stock analysts. The combination of chemistry with computer science is attractive to many employers. Chemistry majors interested in art or writing may want to consider careers in science journalism or science illustration (although finding training and employment in these areas can be difficult).

A researcher is spraying decontamination foam in a laboratory to test the neutralization of chemical weapons.

Those who wish to teach chemistry will find opportunities at all levels, from middle school to universities. In general, the higher the level of the educational institution, the more education required. High school teachers usually start out with a secondary education degree, and then earn a master's degree while teaching. Teaching at a four-year college typically requires a Ph.D. degree. Because research is not emphasized at two-year colleges, an M.S. degree is often the appropriate certification for teaching at this level. Postdoctoral work is typically a requirement for teaching at a doctoral institution, and at some four-year colleges. SEE ALSO CHEMICAL ENGINEERING; FORENSIC CHEMISTRY; INDUSTRIAL CHEMISTRY, INORGANIC; INDUSTRIAL CHEMISTRY, ORGANIC.

Harry E. Pence

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FRENCH PHYSICIST AND ENGINEER
1796–1832

Nicolas-Léonard-Sadi Carnot was born in 1796 in Paris. He is known as the father of thermodynamics. Originally a military engineer, he developed a keen interest in industry and especially the steam engine. He took a leave of absence from the military to devote more time to pursuing these interests.

mechanical energy: energy of an object due to its position or motion

Carnot published only one work in his lifetime—an essay that detailed the industrial, political, and economic importance of the steam engine. This essay also introduced the concept of the ideal steam engine and reported on the factors involved in the production of **mechanical energy** from heat. Carnot used the analogy of a waterfall to understand the ideal steam engine, positing that, as height and quantity of water determine the power of a waterfall, temperature drop and quantity of heat determine the power of a steam engine. Although his theory was not completely accurate, Carnot did make the correct observation that the power produced in a steam engine is dependent on a change in temperature.

Carnot died of cholera at a relatively young age, and this effectively ended the study of thermodynamics for almost two decades. It was not until 1850, when the English physicist William Thomson confirmed some of Carnot's theories, that his ideas on thermodynamics were more broadly applied. In fact, both the first and second laws of thermodynamics can be derived by extending Carnot's early theories. SEE ALSO THERMODYNAMICS.

Lydia S. Scratch

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Carothers, Wallace

AMERICAN CHEMIST
1896–1937

Wallace Hume Carothers, one of the founders of the modern synthetic materials industry, was born in Burlington, Iowa, on April 27, 1896. At first, his

A nylon-fiber manufacturing plant. Wallace Carothers was part of the team that first produced nylon, a material used in the manufacturing of carpeting.

education was directed not toward chemistry, but toward accounting. In 1915 he graduated from the Capital City Commercial College in Des Moines, Iowa, where his father was an instructor. He then attended Tarkio College in Missouri, where he taught accounting while studying for a bachelor's degree in science. For a brief time during World War I, he was actually the head of the chemistry department there. Carothers graduated in 1920 and went on to receive a master's degree at the University of Illinois at Urbana in 1921. After teaching for a year at the University of South Dakota, where he began serious work on organic chemistry, he returned to his studies at the University of Iowa, where he earned his doctorate in chemistry in 1924. Carothers taught for several years at Iowa and was then recruited by Harvard University. He found that he liked research better than teaching, however, and when the E. I. du Pont de Nemours & Co. asked him to direct its research in organic chemistry, he accepted the post in 1928. His principal area of interest was in polymers (long-chain molecules), particularly high molecular weight compounds, both their fundamental properties and their suitability for commercial exploitation.

Carothers's early research at Du Pont focused on products related to acetylene, whose molecules were known to form long chains. With Arnold Collins, in 1931, he produced polychlorobutadiene, better known by its commercial name Neoprene, the first wholly synthetic rubber to be manufactured commercially (beginning in 1933).

Du Pont was particularly interested in developing synthetic fibers. Because of political and trade problems resulting from Japan's war in China, the United States's main source of silk was restricted, so work was directed toward producing an artificial substitute. Carothers believed that polycondensation, in which polymers are formed by condensation and the elimination of small molecules such as water, would yield interesting new materials. His work with **dibasic acids** (acids with two hydrogen atoms, such as sulfuric acid [H_2SO_4]) and **dihydroxy compounds** (compounds with two OH- ions, such as tartaric acid [2,3-dihydrobutanedioic acid] produced different

dibasic acid: acidic substance that incorporates two acidic hydrogen atoms in one molecule, such as sulfuric (H_2SO_4) acid

dihydroxy compound: compound with molecules that incorporate two hydroxyl groups (–OH) in its structure, such as 1,2 dihydroxy ethane (sometimes called glycol) and the three dihydroxy benzene compounds kinds of polyesters, but because they had low melting points and were either water-soluble or dissolved in dry cleaning fluids, they were not commercially viable. Part of the problem with polyesters was that they were chemically related to fats and oils, and were not particularly stable.

Carothers turned to another group of chemicals, collectively known as polyamides. Silk, produced by the silkworm, is the best-known natural polyamide fiber. Synthetic polyamides were made by mixing dibasic acids with **diamines**. (Amines are compounds that replace one or more of the hydrogen atoms in ammonia with organic groups. Diamines contain two amino [-NH_2] groups, and are found in many important organic molecules such as glutamine [$C_5H_{10}N_2O_3$].) The products of these reactions were synthetic proteins and tended to be very stable molecules. A number of different materials with good qualities were produced, but because of the cost of their base materials, were not manufactured commercially. Then Carothers and his team attempted to use adipic acid and hexamethylenediamine (1,6-diaminohexane), which could be made from benzene, a widely available material. This produced long fibers of 6,6′-polyamide, later named Nylon 66. Patented in 1937, nylon went into commercial production in 1939 and was an immediate success. To promote the new fiber, Du Pont showed nylon stockings at the New York World's Fair that same year, advertising it as a material made from coal, air, and water. During World War II nylon production was shifted to meet wartime needs, especially for parachutes. When the war ended and Du Pont resumed commercial production, there was such a high demand for nylon stockings that fights actually broke out in stores for the limited supplies.

diamine: compound, the molecules of which incorporate two amino groups (–NH_2) in their structure, such as 1,2 diamino ethane (sometimes called ethylenediamine) and the three diamine benzene compounds

Carothers published over sixty scientific papers and held numerous patents, and was the first organic chemist elected to the National Academy of Sciences. Nylon was and continues to be an important product, but Carothers did not live to see its success. Throughout his life, he had suffered from bouts of severe depression. Early in 1937 his sister died suddenly and he subsequently went into a deep depression. On April 29, 1937, Carothers committed suicide, prematurely ending one of the most productive careers in chemistry. SEE ALSO NYLON; POLYMERS, SYNTHETIC.

Andrew Ede

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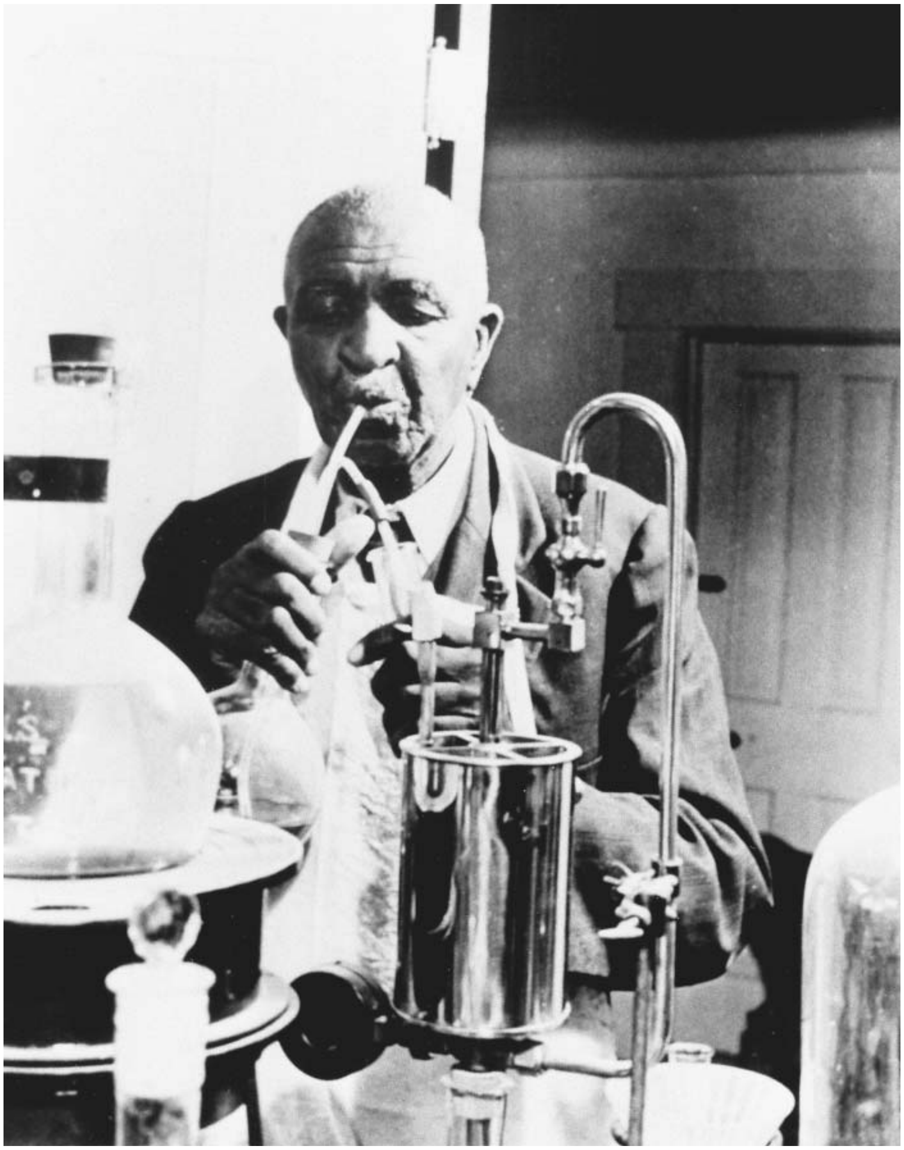
Carver, George Washington

AMERICAN BOTANIST
c. 1864–1943

George Washington Carver was born on a Missouri farm near Diamond Grove sometime toward the end of the U.S. Civil War. The exact date of



American botanist George Washington Carver was interested in industrial applications for organic raw materials. He developed hundreds of products—from shaving cream to synthetic rubber—from agricultural products.

his birth was never recorded, although later in life Carver gave the year as 1864. His father died in an accident prior to or shortly after Carver's birth. His mother Mary was kidnapped with her infant son by slave raiders shortly after his birth. Although Carver was eventually returned to Moses and Susan Carver in exchange for a horse, his mother was never heard from again.

Carver was not a strong child and this prevented him from working the fields. Instead, he helped with household chores and gardening. It is likely that these duties and the hours spent exploring the woods surrounding his home induced his keen interest in plants and led to his life of study and scholarly pursuits. He gathered and cared for a wide variety of plants from throughout the region and frequently helped friends and neighbors treat ailing plants.

As an adolescent, Carver was sent to Neosho, Missouri, where he worked as a farmhand and studied in a one-room schoolhouse. From there, he moved to Kansas and attended Minneapolis High School. In 1885, as a young adult, Carver was accepted to Highland University in Kansas on scholarship. However, when he showed up the first day of class, the president of the university is said to have denied him entrance because of his race. Other colleges rejected him for the same reason, but that did not stop Carver from attempting to seek a higher education.

In 1890 Carver entered Simpson College, a Methodist school in Indianola, Iowa, to study piano and art. While he excelled at both, his art instructor Etta Budd recognized his horticultural talent. She persuaded him to pursue a more pragmatic career in scientific agriculture. In 1891 Carver transferred to the Iowa State College of Agriculture and Mechanic Arts, which is now Iowa State University. Carver was the first African-American student accepted by the college.

As an undergraduate student, Carver was a leader. He became involved in all facets of university life; his poetry was published in the student newspaper and his paintings exhibited at the 1893 World's Fair in Chicago. It was for his excellence as a botanist, however, that he earned his B.S. in agriculture in 1894. Joseph Budd (Etta's father and a professor of horticulture) and Louis Pammel (a botany professor) encouraged Carver to stay on as a graduate student. His proficiency in plant breeding soon led to his appointment as a member of the Iowa State faculty. Over the next two years, Carver's extensive work in plant pathology and mycology (the branch of botany that studies fungi) prompted him to publish several articles, and, as a consequence, he gained national respect as a scientist. In 1896 he earned his M.S. in agriculture from Iowa State and was invited by Booker T. Washington to join Alabama's Tuskegee Institute.

At Tuskegee, Carver found his intellectual home. As the director of its Agricultural Experiment Station, he was given a barren 21-acre plot to work on. Carver and his students conducted experiments on crops requiring low input and capable of fixing nitrogen, such as the cowpea and the peanut. The resulting soil enrichment substantially increased crop production and became an accepted agricultural practice for both cotton and tobacco growers.

biomass: collection of living matter

It was working with the surplus of peanuts that this practice produced that led to Carver's reputation as a "chemurgist," a chemist interested in the industrial applications of organic raw materials and particularly farm products. His research resulted in the creation of over 325 different products from peanuts, ranging from buttermilk to shaving cream to synthetic rubber. He generated 108 products from the sweet potato and invented countless other products from a wide variety of agricultural plants—everything from pecans to soybeans. Indeed, Carver pursued **biomass** conversion with a zeal that is only now being matched as contemporary society searches for alternatives to fossil fuel consumption.

Toward the end of his life, Carver received numerous accolades and honors; a feature film about his life was even produced in 1938. He died on January 5, 1943. In 1994 Iowa State posthumously awarded Carver the degree of Doctor of Humane Letters. This was a fitting tribute to a life spent in the pursuit of knowledge. SEE ALSO AGRICULTURAL CHEMISTRY.

Todd W. Whitcombe

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Catalysis and Catalysts

Catalysis is an acceleration or **retardation** of the rate of a chemical reaction, brought about by the addition of a substance (the **catalyst**) to the reaction medium. The catalyst, usually present in small amounts, is not consumed in the reaction. Catalysis today is almost always associated with rate acceleration, and is very important in industry because rate acceleration usually means that a chemical compound can be made more cheaply and cleanly. It is hard to envision what modern society would be like without its use of myriad chemicals, polymers, and pharmaceuticals, most of which are prepared industrially by catalytic chemistry.

retardation: to slow down a chemical reaction

catalyst: substance that aids in a reaction while retaining its own chemical identity

The rate of reaction refers to the amount of reactant consumed or product formed per unit of time at a given temperature and pressure. Generally speaking, the rate of reaction goes up as the temperature of the reaction is raised. This is related to the fact that most reactants have to "climb" over one or more energy barriers to reach the product stage. This can be likened to one's climbing a hill. The taller the hill, the more energy one expends in reaching its top. Reactants must become energetic enough to "reach" the top of an energy barrier if a reaction is to occur. Raising the reaction temperature ultimately imparts more energy to the reactants, creating a greater probability that more of them will be energetic enough to traverse the barrier, and this results in a faster rate.

What does a catalyst do? First of all, a catalyst does not change the energetic characteristics of the reactants and products and the barriers between them. It instead finds an alternate reaction pathway that bridges reactants and products, and one that has lower (and thus easier-to-traverse) energy barriers. An alternate pathway means a faster reaction rate. Although a catalyst can itself be considered a reactant, it is regenerated, unchanged, at a later stage in the catalytic process. The regenerated catalyst can then be used to catalyze another like reaction. Thus, in principle, only a very small amount of catalyst is needed to generate copious amounts of product. This is desirable, as many catalysts that are used industrially are very expensive.

Homogeneous catalysis refers to catalytic reactions in which the catalyst is in the same **phase** as the reactant. This is most often the liquid phase, although gas phase examples are known. Ozone in the **stratosphere**, for example, is converted into oxygen via the catalytic action of chlorine atoms formed as a result of the photochemical destruction of **chlorofluorocarbon** refrigerants.

The Fischer **esterification**, named after the eminent German chemist Emil Fischer, is the Brønsted acid–catalyzed reaction of an alcohol with a **carboxylic acid** to form an **ester** (see Table 1). Sulfuric acid is often the catalyst. Esters are widely used in the soap, perfume, and food industries.

homogeneous: relating to a uniform mixture of substances

phase: homogeneous state of matter consisting of gases, liquids, or solids

stratosphere: layer of the atmosphere where ozone is found; starts about 10 km (6.2 mi) above ground

chlorofluorocarbon (CFC): compounds that contains carbon, chlorine, and fluorine atoms; CFCs remove ozone in the upper atmosphere

esterification: chemical reaction in which esters (RCO_2R') are formed from alcohols (R_1OH) and carboxylic acids (RCO_2H)

carboxylic acid: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the $–CO_2H$ functional group

ester: organic species containing a carbon atom attached to three moieties: an O via a double bond, an O attached to another carbon atom or chain, and an H atom or C chain; a compound with the general formula RC(O)OR′

EXAMPLES OF CATALYTIC REACTIONS

Type	Reaction Phase(s)	Reaction	Catalyst	Name of Process/Reaction
homogeneous	gas	ozone → oxygen	chlorine atom	ozone depletion
	liquid	alcohol + acid → ester	sulfuric acid	Fischer esterification
	liquid	arene + acid chloride → ketone	aluminum chloride	Friedel-Crafts acylation
	liquid	methanol + CO → acetic acid	rhodium salts $+1^-$	Monsanto process
heterogeneous	gas-solid	$3H_2 + N_2 \rightarrow 2NH_3$	iron	Haber process
	gas-liquid-solid	alkene + H_2 → alkane	transition metals such at Pt and Pd	catalytic hydrogenation
	gas-solid	crude oil → gasoline	zeolite	catalytic cracking
	liquid-solid	waste water + H_2O_2 (O_2) → clean water	titanium dioxide	photocatalysis
enzyme	water	starch → D-glucose	α-Glucosidase	hydrolysis
	water	cellulose → D-glucose	β-Glucosidase	hydrolysis

Table 1. Examples of catalytic reactions.

ketone: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the RFC(O)R functional group

The Friedel–Crafts acylation reaction, named after the French and American chemists who discovered it, used to prepare aryl **ketones**, is catalyzed by the Lewis acid aluminum chloride. Although aluminum chloride is a catalyst, it must be used (in Friedel–Crafts reactions) in stoichiometric amounts, as the portion of aluminum chloride that is catalytically inactive strongly binds to the product. Because aluminum chloride is corrosive and difficult to handle and must be destroyed when the reaction is complete, chemists continue to seek more environmentally friendly catalysts for this reaction.

transition metals: elements with valence electrons in d-sublevels; frequently characterized as metals having the ability to form more than one cation

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Transition metal salts and complexes also serve as homogeneous catalysts. In the Monsanto process, rhodium salts plus iodide convert methanol and carbon monoxide into an industrially useful carboxylic acid, acetic acid. The rhodium **metal** serves as the primary reaction site; it binds the reactants and subsequently unbinds the products. The key reactions at the metal reaction site are called oxidative addition and reductive elimination.

Heterogeneous catalysis describes reactions in which the catalyst and the reactants are in different phases. In these reactions the catalyst is most often an insoluble solid and the reactants are in the gaseous or liquid/solution phase. A key feature of this type of catalysis is that the reactants must adsorb to the catalyst's surface. Large catalyst surfaces, then, ensure that the desired reaction occurs rapidly.

feedstock: mixture of raw materials necessary to carry out chemical reactions

synthesis: combination of starting materials to form a desired product

In the Haber process, named after its German discoverer, gaseous hydrogen and nitrogen are converted into ammonia over an iron catalyst under pressure and elevated temperature. Ammonia is a **feedstock** for the **synthesis** of fertilizers, explosives, and dyes. L-dopa, a drug used in the treatment of Parkinson's disease, is prepared via a hydrogenation reaction (the addition of hydrogen) over a solid transition metal catalyst. Margarine is, likewise, synthesized via a hydrogenation reaction.

Crude oil is converted into gasoline in cracking reactions that transform large molecules into smaller ones. The catalytic reactions occur in the interiors of porous inorganic solids called zeolites. The actual catalysts are protons that exist on the interior walls of the zeolites. Titanium dioxide, a photocatalyst, is an interesting solid because it functions as a catalyst only when it is exposed to light. This is environmentally advantageous, as the combination of titanium dioxide and light can be used to catalyze the removal of pollutants from water via their oxidization with hydrogen peroxide or oxygen.

Most useful compounds require more than one reaction for their syntheses, all of which may be catalytic. A good illustration of this is the three-step synthesis of the **analgesic** agent ibuprofen. The first reaction of the synthesis of ibuprofen is a homogeneous, hydrogen fluoride–catalyzed, Friedel–Crafts acylation reaction; the second, a heterogeneous, palladium-catalyzed, hydrogenation reaction; and the third, a homogeneous, palladium-catalyzed, carbonylation reaction (addition of carbon monoxide).

analgesic: compound that relieves pain, e.g., aspirin

Enzyme catalysis, a form of homogeneous catalysis, refers to the catalytic chemistry that controls the rates of virtually all reactions occurring in living systems. Enzymes, which serve as biological catalysts, are high molecular weight polymers made up from twenty different monomers called amino acids. The linked amino acids have a common backbone, but differing side chains of great structural and chemical variety, and an overall confirmation of great complexity.

An enzyme, in general, functions by first binding the reactant to a site on its surface called the active site. It is here that the catalytic chemistry occurs. The bound reactant then interacts and reacts with the side chains of the amino acids that make up the enzyme, and it is this interaction that brings about the chemical transformation. When the reaction is complete, the bound product diffuses away from the active site. Enzyme reactions take place in water, the biological solvent, at ambient temperatures. They often occur at rates a million or more times faster than those of uncatalyzed reactions. Hundreds of thousands of reactions can occur at the site of a single enzyme in one second. Many enzymes require the assistance of a molecule called a coenzyme if the catalytic reaction is to occur. Other enzymes require **metal cations**, such as Zn^{+2}, at their active sites.

metal cation: positively charged ion resulting from the loss of one or more valence electrons

When we eat, our mouths very often experience a sweet taste. This sweetness is due to the conversion of starch polymer molecules into the sugar D-glucose by the enzyme α-glucosidase, present in saliva. The polymer cellulose, structurally related to starch, is converted into D-glucose by the enzyme β-glucosidase (but only in bacteria). There are enzymes in the stomach and gut that aid digestion. The liver produces enzymes that are instrumental in removing toxic compounds from blood. Yeast organisms contain enzymes that convert sugar into ethanol and carbon dioxide—important in the making of bread and alcoholic beverages. Even the genetic material **DNA** (and its ancillary material **RNA**) is made by and functions by participation in enzyme-catalyzed reactions. Interestingly, DNA and RNA are also instrumental in synthesizing these very same enzymes. SEE ALSO KINETICS; REACTION RATES.

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

RNA: ribonucleic acid, a natural polymer used to translate genetic information in the nucleus into a template for the construction of proteins

Richard Pagni

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Cavendish, Henry

ENGLISH PHYSICIST AND CHEMIST
1731–1810

English chemist and physicist Henry Cavendish, who discovered hydrogen.

Henry Cavendish, born in Nice, France to an aristocratic English family, was an avid and excellent experimenter. At the age of forty, he inherited an immense fortune that afforded him the luxury of pursuing his scientific interests (he was described by some as the "richest of all the learned and the most learned of all the rich"). He was an extraordinarily odd man, whose extreme shyness rendered him a virtual recluse. Despite this, he is remembered as a great, albeit humble, man who devoted his life to science.

Cavendish explored all areas of science, including astronomy, optics, electricity, geology, and pure mathematics. Among his accomplishments are the first calculation of Earth's mass (his results were just 10% off modern measurements) and the introduction of the concept of **voltage**. His principal interest nevertheless was experimental chemistry. His most famous contribution to science was the discovery and description of the properties of hydrogen and its status as a constituent element in water.

voltage: potential difference expressed in volts

Cavendish, like many before him, noticed that a gas was produced when zinc or iron was dropped into an acid. He called this gas "inflammable air" (known today as hydrogen). Using his exacting experimental skills, Cavendish was the first to distinguish this inflammable air from ordinary air and to investigate its specific properties. He presented a paper detailing his findings in 1766.

The importance of inflammable air became clear about fifteen years after Cavendish presented his paper. Joseph Priestley (1733–1804) was also interested in gases, and in 1781 told Cavendish of the results of some of his own experiments. When Priestley used an electrostatic machine to spark ordinary air with inflammable air, he noticed that water was formed. Cavendish repeated this experiment, as well as others like it, but using oxygen (or, as he called it, "dephlogisticated air") in place of ordinary air.

Cavendish's results were the same as Priestley's, but he did not publish or present his findings. Sometime before 1783, however, Cavendish did advise Priestley of his results. Priestley told Charles Blagden, secretary of the **Royal Society** in London, and Blagden in turn informed Antoine Lavoisier (1743–1794) in France.

Royal Society: The U.K. National Academy of Science, founded in 1660

Cavendish did eventually publish his findings on the formation of water in 1784. But Lavoisier claimed that *he* had discovered how water was formed—in fact, it was Lavoisier who coined the name "hydrogen," which means "water former." It was not until the mid-nineteenth century, when Cavendish's notebooks were published, that he was given sole credit for discovering that water is composed of inflammable air and dephlogisticated air, or hydrogen and oxygen.

As may be seen in his collaborative work with Priestley in the investigation of the composition of water, Cavendish did not allow his natural shyness to impede his work. The relationship between him and Priestley demonstrates not only Cavendish's devotion to science, but the general cooperative nature of scientific investigation. By sharing the results of their separate experiments, these two great scientists were able to discover the composition of water.

For all of his scientific genius, Cavendish was a pronounced eccentric. He rarely left his house except for weekly meetings of the Royal Society, and even there, despite being one of the most famous scientists of his time, he was known to linger outside the meeting room and enter only when he thought no one would notice. He could barely tolerate the company of women; if any of his female servants happened to cross his path, she was likely to be fired. Though enormously wealthy, he was reputed to own but one suit, and an old-fashioned one at that.

Cavendish lived a lonely and humble life, committed to the cultivation of science. To him, science was measurement, and he showed himself to be one of the most respected experimentalists of the time. His death was as lonely as his life; when he sensed that the end was near, he instructed his servant to leave the room and not come back until a certain time. When the servant returned, he found that Cavendish had died. SEE ALSO Hydrogen; Lavoisier, Antoine; Priestley, Joseph.

Lydia S. Scratch

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Cellulose

Cellulose is the most abundant organic molecule in nature. It is a polysaccharide assembled from **glucose** monomer units, and it (together with other materials such as hemicellulose and lignin) is the main constituent of plant cell walls. Along with several undigestible polysaccharides, cellulose constitutes the main part of dietary fiber. Specifically cellulose is one of the components of insoluble fiber.

glucose: common hexose monosaccharide; monomer of starch and cellulose; also called grape sugar, blood sugar, or dextrose

The glucose units in cellulose are combined in a way that results in the formation of very linear, flat molecules that can, in turn, form sheets that possess extensive networks of **hydrogen bonds**. The hydrogen bonds are both within individual sheets and between successive sheets. As a result of these bonds, sheets of cellulose are particularly strong—a property critical to the function of plant cell walls. Cellulose shows a variable degree of polymerization, with anywhere from 1,000 to 14,000 glucose residues comprising a single cellulose polymer. Because of its high molecular weight and crystalline structure, cellulose is insoluble in water and has a poor ability to absorb water.

hydrogen bond: interaction between H atoms and lone pair electrons that constitutes hydrogen bonding

Human beings lack the enzyme cellulase and are therefore unable to break cellulose down to individual glucose molecules. Although many fungi are able to break down cellulose to glucose, only a few types of bacteria have

rumina: multiple stomachs found in grass-eating animals; digestion of cellulose is carried out in these stomachs

this ability. In the **rumina** of cows, sheep, and goats, two different types of bacteria produce the enzyme that breaks down cellulose.

Cellulose and its derivatives are used in a number of food products to modify those foods in different ways (e.g., as a thickener, stabilizer, or texturizer). The fibrous form is a basic material that is used to make both textiles and paper. Cellulose is also used to make nitrocellulose (an ingredient in explosives and lacquers) and as a binder in the manufacture of medicinal tablets. SEE ALSO Fibers; Polymers, Natural; Polysaccharides.

Matthew A. Fisher

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Ceramics

Ceramics can be defined as heat-resistant, nonmetallic, inorganic solids that are (generally) made up of compounds formed from metallic and nonmetallic elements. Although different types of ceramics can have very different properties, in general ceramics are corrosion-resistant and hard, but brittle. Most ceramics are also good insulators and can withstand high temperatures. These properties have led to their use in virtually every aspect of modern life.

The two main categories of ceramics are traditional and advanced. Traditional ceramics include objects made of clay and cements that have been hardened by heating at high temperatures. Traditional ceramics are used in dishes, crockery, flowerpots, and roof and wall tiles. Advanced ceramics include carbides, such as silicon carbide, SiC; oxides, such as aluminum oxide, Al_2O_3; nitrides, such as silicon nitride, Si_3N_4; and many other materials, including the mixed oxide ceramics that can act as superconductors. Advanced ceramics require modern processing techniques, and the development of these techniques has led to advances in medicine and engineering.

crystallization: process of producing crystals of a substance when a saturated solution in an appropriate solvent is either cooled or some solvent removed by evaporation

Glass is sometimes considered a type of ceramic. However, glasses and ceramics differ in that ceramics have a crystalline structure while glasses contain impurities that prevent **crystallization**. The structure of glasses is amorphous, like that of liquids. Ceramics tend to have high, well-defined melting points, while glasses tend to soften over a range of temperatures before becoming liquids. In addition, most ceramics are opaque to visible light, and glasses tend to be translucent. Glass ceramics have a structure that consists of many tiny crystalline regions within a noncrystalline matrix. This structure gives them some properties of ceramics and some of glasses. In general, glass ceramics expand less when heated than most glasses, making them useful in windows, for wood stoves, or as radiant glass-ceramic cooktop surfaces.

Composition

Some ceramics are composed of only two elements. For example, alumina is aluminum oxide, Al_2O_3; zirconia is zirconium oxide, ZrO_2; and quartz is

Ceramics are good insulators and can withstand high temperatures. A popular use of ceramics is in artwork.

silicon dioxide, SiO_2. Other ceramic materials, including many minerals, have complex and even variable compositions. For example, the ceramic mineral feldspar, one of the components of granite, has the formula $KAlSi_3O_8$.

The chemical bonds in ceramics can be covalent, ionic, or polar covalent, depending on the chemical composition of the ceramic. When the components of the ceramic are a **metal** and a nonmetal, the bonding is primarily ionic; examples are magnesium oxide (magnesia), MgO, and barium titanate, $BaTiO_3$. In ceramics composed of a **metalloid** and a nonmetal, bonding is primarily covalent; examples are boron nitride, BN, and silicon carbide, SiC. Most ceramics have a highly crystalline structure, in which a three-dimensional unit, called a unit cell, is repeated throughout the material. For example, magnesium oxide crystallizes in the rock salt structure. In this structure, Mg^{2+} ions alternate with O^{2-} ions along each **perpendicular** axis.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

metalloid: element that exhibits properties that are between those of metals and nonmetals; generally considered to include boron, silicon, germanium, arsensic, antimony, tellurium, and polonium

perpendicular: condition in which two lines (or linear entities like chemical bonds) intersect at a 90-degree angle

Manufacture of Traditional Ceramics

Traditional ceramics are made from natural materials such as clay that have been hardened by heating at high temperatures (driving out water and allowing strong chemical bonds to form between the flakes of clay). In fact, the word "ceramic" comes from the Greek *keramos*, whose original meaning was "burnt earth." When artists make ceramic works of art, they first mold clay, often mixed with other raw materials, into the desired shape. Special ovens called kilns are used to "fire" (heat) the shaped object until it hardens.

Clay consists of a large number of very tiny flat plates, stacked together but separated by thin layers of water. The water allows the plates to cling together, but also acts as a lubricant, allowing the plates to slide past one another. As a result, clay is easily molded into shapes. High temperatures drive out water and allow bonds to form between plates, holding them in place and promoting the formation of a hard solid. Binders such as bone ash are sometimes added to the clay to promote strong bond formation, which makes the ceramic resistant to breakage. The common clay used to make flowerpots and roof tiles is usually red-orange because of the presence of iron oxides. White ceramics are made from rarer (and thus more expensive) white clays, primarily kaolin.

The oldest known ceramics made by humans are figurines found in the former Czechoslovakia that are thought to date from around 27,000 B.C.E. It was determined that the figurines were made by mixing clay with bone, animal fat, earth, and bone ash (the ash that results when animal bones are heated to a high temperature), molding the mixture into a desired shape, and heating it in a domed pit. The manufacture of functional objects such as pots, dishes, and storage vessels, was developed in ancient Greece and Egypt during the period 9000 to 6000 B.C.E.

An important advance was the development of white porcelain. Porcelain is a hard, tough ceramic that is less brittle than the ceramics that preceded it. Its strength allows it to be fashioned into beautiful vessels with walls so thin they can even be translucent. It is made from kaolin mixed with china stone, and the mixture is heated to a very high temperature (1,300°C, or 2,372°F). Porcelain was developed in China around C.E. 600 during the T'ang dynasty and was perfected during the Ming dynasty, famous for its blue and white porcelain. The porcelain process was introduced to the Arab world in the ninth century; later Arabs brought porcelain to Spain, from where the process spread throughout Europe.

Bone china has a composition similar to that of porcelain, but at least 50 percent of the material is finely powdered bone ash. Like porcelain, bone china is strong and can be formed into dishes with very thin, translucent walls. Stoneware is a dense, hard, gray or tan ceramic that is less expensive than bone china and porcelain, but it is not as strong. As a result, stoneware dishes are usually thicker and heavier than bone china or porcelain dishes.

Manufacture of Advanced Ceramics

The preparation of an advanced ceramic material usually begins with a finely divided powder that is mixed with an organic binder to help the powder consolidate, so that it can be molded into the desired shape. Before it is fired, the ceramic body is called "green." The green body is first heated at a low temperature in order to decompose or oxidize the binder. It is then heated to a high temperature until it is "sintered," or hardened, into a dense, strong ceramic. At this time, individual particles of the original powder fuse together as chemical bonds form between them. During sintering the ceramic may shrink by as much as 10 to 40 percent. Because shrinkage is not uniform, additional machining of the ceramic may be required in order to obtain a precise shape.

Sol-gel technology allows better mixing of the ceramic components at the molecular level, and hence yields more **homogeneous** ceramics, because the ions are mixed while in solution. In the sol-gel process, a solution of an **organometallic compound** is hydrolyzed to produce a "sol," a colloidal suspension of a solid in a liquid. Typically the solution is a metal alkoxide such as tetramethoxysilane in an alcohol solvent. The sol forms when the individual formula units polymerize (link together to form chains and net-

homogeneous: relating to a uniform mixture of substances

organometallic compound: compound containing both a metal (transition) and one or more organic moieties works). The sol can then be spread into a thin film, precipitated into tiny uniform spheres called microspheres, or further processed to form a gel inside a mold that will yield a final ceramic object in the desired shape. The many crosslinks between the formula units result in a ceramic that is less brittle than typical ceramics.

Although the sol-gel process is very expensive, it has many advantages, including low temperature requirements; the ceramist's ability to control porosity and to form films, spheres, and other structures that are difficult to form in molds; and the attainment of specialized ceramic compositions and high product purity.

Porous ceramics are made by the sol-gel process. These ceramics have spongelike structures, with many porelike lacunae, or openings, that can make up from 25 to 70 percent of the volume. The pore size can be large, or as small as 50 nanometers (2×10^{-6} inches) in diameter. Because of the large number of pores, porous ceramics have enormous surface areas (up to 500 square meters, or 5,382 square feet, per gram of ceramic), and so can make excellent catalysts. For example, zirconium oxide is a ceramic oxygen sensor that monitors the air-to-fuel ratio in the exhaust systems of automobiles.

Aerogels are solid foams prepared by removing the liquid from the gel during a sol-gel process at high temperatures and low pressures. Because aerogels are good insulators, have very low densities, and do not melt at high temperatures, they are attractive for use in spacecraft.

Properties and Uses

For centuries ceramics were used by those who had little knowledge of their structure. Today, understanding of the structure and properties of ceramics is making it possible to design and engineer new kinds of ceramics.

inert: incapable of reacting with another substance

Most ceramics are hard, chemically **inert**, refractory (can withstand very high heat without deformation), and poor conductors of heat and electricity. Ceramics also have low densities. These properties make ceramics attractive for many applications. Ceramics are used as refractories in furnaces and as durable building materials (in the form of bricks, tiles, cinder blocks, and other hard, strong solids). They are also used as common electrical and thermal insulators in the manufacture of spark plugs, telephone poles, electronic devices, and the nose cones of spacecraft. However, ceramics also tend to be brittle. A major difficulty with the use of ceramics is their tendency to acquire tiny cracks that slowly become larger until the material falls apart. To prevent ceramic materials from cracking, they are often applied as coatings on inexpensive materials that are resistant to cracks. For example, engine parts are sometimes coated with ceramics to reduce heat transfer.

Composite materials that contain ceramic fibers embedded in polymer matrices possess many of the properties of ceramics; these materials have low densities and are resistant to corrosion, yet are tough and flexible rather than brittle. They are used in tennis rackets, bicycles, and automobiles. Ceramic composites may also be made from two distinct ceramic materials that exist as two separate ceramic phases in the composite material. Cracks generated in one phase will not be transferred to the other. As a result, the resistance of the composite material to cracking is considerable. Composite ceramics made from diborides and/or carbides of zirconium and hafnium mixed with silicon carbide are used to create the nose cones of spacecraft. Break-resistant cookware (with outstanding thermal shock resistance) is also made from ceramic composites.

Although most ceramics are thermal and electrical insulators, some, such as cubic boron nitride, are good conductors of heat, and others, such as rhenium oxide, conduct electricity as well as metals. Indium tin oxide is a transparent ceramic that conducts electricity and is used to make liquid crystal calculator displays. Some ceramics are semiconductors, with conductivities that become enhanced as the temperature increases. For example, silicon carbide, SiC, is used as a semiconductor material in high temperature applications.

High temperature superconductors are ceramic materials consisting of complex ionic oxides that become superconducting when cooled by liquid nitrogen. That is, they lose all resistance to electrical current. One example is the material $YBa_2Cu_3O_{7-x}$, which crystallizes to form "sheets" of copper and oxygen atoms that can carry electrical current in the planes of the sheets.

Some ceramics, such as barium ferrite or nickel zinc ferrites, are magnetic materials that provide stronger magnetic fields, weigh less, and cost less than metal magnets. They are made by heating powdered ferrite in a magnetic field under high pressure until it hardens. Ceramic magnets are brittle, but are often used in computers and microwave devices.

voltage: potential difference expressed in volts

The properties of piezoelectric ceramics are modified when **voltage** is applied to them, making them useful as sensors and buzzers. For example, lead zirconium titanate is a piezoelectric ceramic used to provide "muscle action" in robot limbs in response to electrical signals.

Some ceramics are transparent to light of specific frequencies. These optical ceramics are used as windows for infrared and ultraviolet sensors and in radar installations. However, optical ceramics are not as widely used as glass materials in applications in which visible light must be transmitted. An electro-optic ceramic such as lead lanthanum zirconate titanate is a material whose ability to transmit light is altered by an applied voltage. These electro-optic materials are used in color filters and protective goggles, as well as in memory-storage devices.

Still other ceramics are important in medicine. For example, they are used to fabricate artificial bones and to crown damaged teeth. The fact that many ceramics can be easily sterilized and are chemically inert makes ceramic microspheres made of these materials useful as biosensors. Drugs and other chemicals can be carried within microsphere pores to desired sites in the body. SEE ALSO Glass; Minerals; Semiconductors; Superconductors.

Loretta L. Jones

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Cerium

MELTING POINT: 798°C
BOILING POINT: 3,257°C
DENSITY: 6.773 g/cm^3
MOST COMMON IONS: Ce^{3+}, Ce^{4+}

58
Ce
CERIUM
140.12

In 1751 the Swedish chemist Axel F. Cronstedt found, near Bastnäs, Sweden, a mineral that was eventually named cerita (its name related to the planetoid Ceres). Independently, Martin Klaproth, Jöns J. Berzelius, and Wilhelm Hisinger, working with cerita, each isolated a product, ceria (in 1803), from which Carl G. Mosander obtained three different substances, as oxides: cerium, lanthanum, and a mixture of oxides known as didymia.

Cerium is the most abundant member of the **lanthanide**, or rare earth, elements. It has two stable **valence** states, Ce^{3+} (cerous) and Ce^{4+} (ceric). It is found as a **trace element** in several minerals, but only two, bastnasite, $LnFCO_3$, and monazite, $(Ln, Th)PO_4$ (where Ln = a lanthanide element, such as lanthanum, praseodymium, neodymium, or cerium), which are approximately 30 percent and 22 to 25 percent cerium, respectively, are the principal sources of this element.

lanthanides: a family of elements (atomic number 57 through 70) from lanthanum to lutetium having from 1 to 14 4f electrons

valence: combining capacity

trace element: element occurring only in a minute amount

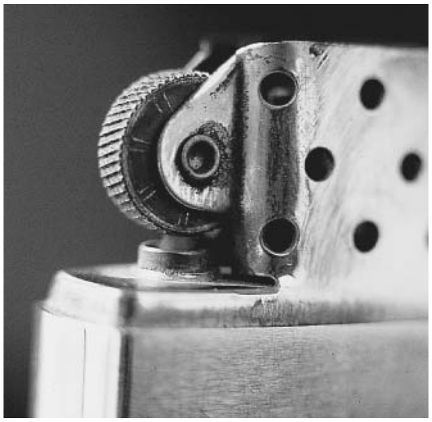
metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

To obtain cerium, a bastnasite concentrate is treated with sulfuric acid or hydrochloric acid, yielding the hydrated sulfate or the chloride of cerium. The sulfate is converted to the hydroxide or the carbonate, and then to the fluoride. A monozite concentrate is digested in an autoclave with an excess of caustic soda at 150°C (302°F).

$$LnTh(PO_4) + 3NaOH \rightarrow Na_3PO_4 + Ln(OH)_3 + Th(OH)_4$$

$Ln(OH)_3$ can be converted to the corresponding hydrated chloride or fluoride by treatment with the appropriate acids. These halide compounds are carefully dehydrated to yield the lanthanide anhydrous salts. Misch **metal** is a mixture of lanthanide elements (it is approximately 50% cerium), and is obtained via the electrolysis of the fused mixed lanthanide chlorides.

Of Ce(III) compounds: the nitrate, chloride, and bromide are water-soluble; the carbonate, fluoride, hydroxide, oxalate, and phosphate are water-insoluble; the acetate and sulfate are sparingly soluble. These compounds are usually prepared from a reactive precursor such as carbonate, basic carbonate, or oxide using the appropriate acids. They are practically colorless.



A cigarette lighter with a flint, which is made from cerium.

anion: negatively charged chemical unit, like Cl^-, CO_{32}^-, or NO_3^-

Ce(IV) compounds include soluble salts that are orange or red in color. Ceric sulfate crystals are orange, as are some complexes in which Ce(IV) is present in the **anion**. Diammonium hexanitrocerate $(NH_4)_2[Ce(NO_3)_6]$, for example, is strongly red.

There are practically no medical applications for cerium. Several metallurgical, glass, ceramic, and others applications exist, including:

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

catalysis: reaction induced by a substance that retains its own chemical identity

- lighter flints (misch metal)
- glass polishing (CeO_2 powders)
- glass decolorization (the **oxidation** of Fe^{2+} to Fe^{3+} by Ce^{4+})
- UV absorption (Ce^{4+} is opaque to near ultraviolet)
- enamels (CeO_2)
- luminescent applications
- **catalytic** (cracking crude oil to gasoline)
- vehicle emission control (CeO_2)

SEE ALSO BERZELIUS, JÖNS JAKOB; DYSPROSIUM; ERBIUM; EUROPIUM; GADOLINIUM; HOLMIUM; LANTHANUM; LUTETIUM; NEODYMIUM; PRASEODYMIUM; PROMETHIUM; SAMARIUM; TERBIUM; YTTERBIUM.

Lea B. Zinner
Geraldo Vicentini

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55
Cs
CESIUM
132.9054

Cesium

MELTING POINT: 28.5°C
BOILING POINT: 671°C
DENSITY: 1.873 g/cm^3
MOST COMMON IONS: Cs^+

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

fractional distillation: separation of liquid mixtures by collecting separately the distillates at certain temperatures

Cesium is an alkali **metal** that reacts explosively with water and melts just above room temperature. The word "cesium" is derived from *caesium* (Latin for "sky blue"). The name was chosen because of the blue lines observed by Robert Bunsen and Gustav Kirchhoff during their analysis of springwater with a spectroscope in 1860. Currently, cesium metal is generated via thermal decomposition of the azide, electrolysis of molten CsCN, or reduction of molten CsCl with calcium vapor followed by **fractional distillation**.

Like the other alkali metals, cesium is a soft, silvery metal, but it appears golden if it has been exposed to small amounts of oxygen. It is not found in its metallic state in nature; it is obtained as a byproduct of lithium processing of the mineral lepidolite. Its most significant ore is pollucite, and the world's largest pollucite deposit is found in Bernic Lake, Manitoba, Canada. Cesium's average crustal abundance is about 3 parts per million. Cesium is the most electropositive stable element and will ignite if exposed to air. Cesium burns blue in the flame test.

Both cesium and its compounds find practical uses. Cesium metal can be used as a getter to remove oxygen in phototubes. It is used in atomic clocks that are accurate to within five seconds per every three hundred years. (A second is defined as 9,192,631,770 oscillations of a Cs-133 atom.) CsI and CsF are used in scintillation counters to monitor ionizing radiation. CsCl is used to create density gradients for the separation and purification of **DNA** via ultracentrifugation. SEE ALSO Alkali Metals; Bunsen, Robert.

Nathan J. Barrows

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

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Chadwick, James

ENGLISH PHYSICIST
1891–1974

English physicist, Sir James Chadwick, recipient of the 1935 Nobel Prize in physics, "for the discovery of the neutron."

Sir James Chadwick was born of humble origins on October 20, 1891, to John Joseph and Anne Mary Chadwick in Clarke Lane just outside of Bollington, England. Primarily raised by his grandparents, he won a scholarship to nearby Victoria University in Manchester, where he entered the physics program by mistake. He had intended to enroll in the mathematics program, but waited in the wrong registration area so ended up being admitted to the physics department instead. Chadwick graduated in 1911 and then went to work in Ernest Rutherford's laboratory, beginning a long, productive relationship between the two men. Chadwick earned his M.S. in 1913; by the age of twenty-one he had already published five scientific papers. At that point, he won an 1851 Exhibition scholarship to study abroad for two years, whereupon he traveled to Germany to work with Hans Geiger.

During his period of study in Germany, Chadwick discovered that β-rays (electrons) are emitted in a continuous spectrum, at odds with other groups' results, and a finding that eventually led to the theory and discovery of the neutrino. While he was in Germany, World War I broke out, and Chadwick was rounded up with other English in the country and interned at Ruhleben.

After his release from Ruhleben in 1919, Chadwick followed Rutherford to the Cavendish Laboratory at Cambridge University, where he was named assistant director of research in 1923. Rutherford had been working on the disintegration of nitrogen nuclei under bombardment by **α-particles**, and Chadwick's first research upon his return to England involved the disintegration of different nuclei.

α-particle: subatomic particle with 2+ charge and mass of 4; an He nucleus

It was in the investigation of beryllium disintegration in 1932 that the neutron was discovered. Since the neutron has no charge, the typical electromagnetic methods of detection were useless. Chadwick bounced the mystery particle off atomic nuclei that were detectable, and, by the conservation of momentum and energy, he was able to determine that the neutron had a mass slightly greater than that of a proton.

fission: process of splitting a heavy atom into smaller pieces

With the discovery of the neutron as a fundamental particle, many paradoxes of physics and chemistry were finally resolved, and new areas of research evolved. Prior to the discovery of the neutron as a fundamental particle, scientists generally believed that the nucleus was comprised of protons and "nuclear electrons." However, one could not explain, for example, the spin of nuclei with that model. Now, at last, theory could predict the properties of the nucleus quite well. Also, since neutrons are not repelled by the charge on the atomic nucleus, they interact easily with nuclei. Neutron scattering enables the determination of crystal structures by probing the positions of nuclei in a sample. Neutrons can also catalyze **fission** reactions, for example, the fission of uranium nuclei that led to the creation of nuclear power plants and the atomic bomb.

Manhattan Project: government project dedicated to creation of an atomic weapon; directed by General Leslie Groves

Only three years after the discovery of the neutron, Chadwick was awarded the Nobel Prize in physics in 1935. He was lured away from Cambridge to accept the chair in physics at Liverpool University, where he oversaw the construction of the first cyclotron in England. As World War II broke out, Chadwick played a prominent role in the effort to create the atomic bomb, both in England, and, beginning in 1943, as the leader of the British effort on the **Manhattan Project**. Chadwick returned to his chair in Liverpool in 1946, but soon thereafter he accepted an offer from his alma mater, the College of Gonville and Caius at Cambridge, to serve as its master, a post he held until his retirement in 1958. He died in Cambridge on July 24, 1974. SEE ALSO Beryllium; Nuclear Chemistry; Radiation; Rutherford, Ernest.

Michael J. Fosmire

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Chalcogens

The chalcogens are the name for the Periodic Table group 16 (or V1). The group consists of the elements: oxygen, sulfur, selenium, tellurium, and polonium. The name of the group was proposed by Wilhelm Blitz and colleague Werner Fischer of the Institute of Inorganic Chemistry at the University of Hannover, Germany in 1932. The term "chalcogens" was derived from the Greek word *chalcos*, meaning "ore formers," since they all are be found in copper ores. Their compounds are referred to as "chalcogenides." These names became popular since they are analogous to the names of group 17(V11), halogens, meaning salt formers, and its compounds, halides. As an element oxygen is a gas while the other group members are solids. Both oxygen and sulfur can be found in pure form. All of the elements occur as ions in metal ores. The elements of this family have isotopes that vary in stability. Polonium is considered a radioactive element and to be handled with care.

The members of this group show increasing metal character as the atomic number increases. Both oxygen and sulfur are nonmetals, while selenium and tellurium are metalloids (both are semiconductors) and polonium is a metal. Bonding characteristics of these elements parallel their metal character. The smaller members of the group show a greater tendency to form covalent bonds than the larger members do. This is shown with the decrease of stability of H_2M compounds from H_2S to H_2Po.

Their electronegativities decrease with increasing atomic number (see table below). This trend explains the lessening of ionic character of the compounds of S - Po that are analogous to those of oxygen. It is for this reason, only oxygen can exhibit hydrogen bonding. This drastically changes the character of these compounds. If the boiling points of the H_2M compounds are compared, we find that the group shows this change in hydrogen bonding, since the smallest compound in weight has a boiling point almost 100° higher than any of the other group members.

Element	**O**	**S**	**Se**	**Te**	**Po**
Electronegativity	3.5	2.5	2.4	2.1	2.0
BP of H_2M	100.0°C	−59.55°C	−41.5°C	−2°C	

All of the elements can be found naturally as ions, most often as 2- ions (except for Po). Oxidation states of +2, +4, and +6 also can be found for members S - Po when combined with O, F, or Cl. The difference in oxidation states can be explained by the electronic structure of the elements. Oxygen is able to use only *s* and *p* orbitals for bonding. The larger members of the group use *d* orbitals in the hybridization and thus can participate in the use of an expanded octet. This is shown in compounds and complex ions such as: SOF_4, SF_4, $SeO_4{}^{2}-$, $TeF_8{}^{2}-$.

The elements and their compounds vary in their toxicity. It is interesting that oxygen and sulfur are essential to all life, while the compounds of selenium, tellurium, and polonium can be toxic. Selenium is an essential trace element even though at larger concentrations (above 5 ppm) it causes severe disorders. Tellurium compounds, while being toxic, have never been reported to cause a human fatality. Since polonium and its compounds are radioactive, they are considered extremely toxic in any concentration. SEE ALSO OXYGEN; POLONIUM; SELENIUM; SULFUR; TELLURIUM.

Catherine H. Banks

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Chappelle, Emmett

AMERICAN BIOCHEMIST
1925–

There are many ways that we could determine if there is life on other planets. The easiest method would be to look for aliens or any of the hallmarks

American biochemist Emmett W. Chappelle (l.), who used fluorescence in the detection of bacteria.

of civilization. But what if the life-form was microbial? Bacterial life may exist, but would we know it if we saw it?

Emmett Chappelle is a noted biochemist who has, among other accomplishments, devised a method for answering this question. Born on October 25, 1925, in Phoenix, Arizona, he received his B.S. in biochemistry from the University of California in 1950. From 1950 to 1953 he worked as an instructor in biochemistry at Meharry Medical College in Nashville, Tennessee. Chappelle received his M.S. in biochemistry in 1954 from the University of Washington and then returned to California, where he served as a research associate at Stanford University and as a scientist for the Research Institute of Advanced Studies at Stanford. In 1966 he began his work with the National Aeronautics and Space Administration (NASA) as an exobiologist and astrochemist. In 1977 Chappelle moved to the Goddard Space Flight Center as a remote sensing scientist.

adenosine triphosphate (ATP): molecule formed by the condensation of adenine, ribose, and triphosphoric acid, HOP(O)OH–O–(O)OH–OP(O)OH–OH; it is a key compound in the mediation of energy in both plants and animals

His research with Grace Picciolo led to his invention of a method for the detection of **adenosine triphosphate (ATP)**. The technique takes advantage of the naturally occurring luciferase enzyme and the chemical luciferin. Both are obtained from the lantern of a firefly; hence, this technique is sometimes referred to as a "firefly bioluminescent assay." In combination with ATP and magnesium ions, luciferin and luciferase fluoresce, generating a light intensity that is proportional to the amount of ATP present.

photon: a quantum of electromagnetic energy

The advantage of fluorescence is that a properly constructed photomultiplier, under dark conditions, can detect the emission of a single **photon**, so it is possible to monitor for very low concentrations of ATP. The patented invention outlines how this fluorescence can be used for the detection of bacteria, particularly in a urine sample, thereby speeding the diagnosis of a bacterial infection.

However, such a technique can be applied to any determination of ATP. If extraterrestrial life exists, then there is the possibility that it will employ either ATP or a similar energy molecule. If that energy molecule is introduced into a firefly bioluminescent assay, then light will be produced and it can be measured. The detection of ATP or a similar molecule would be good evidence for the presence of extraterrestrial life.

More recently, Chappelle has been involved in the use of laser-induced fluorescence as a method for determining the health of forest vegetation. The photosystem of green plants uses fluorescence as one way to lose excess energy from absorbed photons, accounting for between 2 and 6 percent of the total absorption. Measuring the amount of fluorescence over a forest allows researchers to monitor the amount of **photosynthesis** that is occurring. This technique has two significant advantages: First it is nonintrusive and can be used with living plants. Second, it can be performed from within a low-flying airplane, allowing researchers to monitor remote areas.

photosynthesis: process by which plants convert carbon dioxide and water to glucose

For his work investigating the biochemistry of life, Chappelle has won numerous awards including NASA's Exceptional Scientific Achievement Medal. SEE ALSO GLOBAL WARMING.

Todd W. Whitcombe

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Chardonnet, Hilaire

FRENCH CHEMIST
1839–1924

Louis-Marie-Hilaire Bernigaud, comte de Chardonnet, born in Besancon, France, is credited with having developed artificial silk, which came to be known as rayon. In the 1860s Chardonnet, originally trained as an engineer, assisted Louis Pasteur in an effort to save the French silk industry from an epidemic affecting silkworms.

In 1878, while working in a photographic darkroom, Chardonnet accidentally overturned a bottle of nitrocellulose. When he started to clean up the spill, he saw that the nitrocellulose had become viscous due to evaporation. As he wiped it, he noticed long, thin strands of fiber resembling those of silk.

Chardonnet began to experiment further with the nitrocellulose. He worked with the silkworm's food, mulberry leaves, turning them into a cellulose pulp with nitric and sulfuric acids, and stretched the resulting pulp into fibers. This fiber, cellulose nitrate, could be used in garments, but it was highly flammable. Some garments made of this early artificial silk reportedly burst into flame when a lit cigarette was nearby. Chardonnet solved this problem by denitrating these fibers with ammonium sulfide, which reduced the flammability of the material without sacrificing its strength.

French chemist Hilaire Chardonnet, who invented rayon.

Chardonnet received his first patent for artificial silk in 1884 and began manufacturing the material in 1891. In 1924 artificial silk came to be known as rayon. SEE ALSO CELLULOSE; FIBERS; PASTEUR, LOUIS; POLYMERS, SYNTHETIC.

Lydia S. Scratch

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Charles, Jacques

FRENCH MATHEMATICIAN AND PHYSICIST
1746–1823

Jacques-Alexandre-César Charles was a mathematician and physicist remembered for his pioneering work with gases and hydrogen balloon flights. Charles was born on November 12, 1746, in Beaugency, Loiret, France; his first occupation was as a clerk at the Ministry of Finance in Paris. However, his interests eventually turned to science.

In the late 1700s ballooning became a major preoccupation of France and other industrialized nations. In early June 1783 the Montgolfier brothers launched the first successful hot-air balloon in Paris. Charles, who was interested in aeronautics, understood the concept of buoyancy and also was aware of Henry Cavendish's discovery of hydrogen, an element some fourteen times lighter than air, seventeen years earlier. On August 27, 1783, Charles launched the first hydrogen-filled balloon using gas produced by the reaction of sulfuric acid on iron filings. Among the 50,000 witnesses of this event was Benjamin Franklin, then residing in Paris as the U.S. ambassador to France. When the balloon returned to Earth in the French countryside, it was reportedly attacked with axes and pitchforks by terrified peasants who believed it to be a monster from the skies. On November 21 of that same year the Montgolfier brothers launched the first hot-air balloon with humans aboard, managing an altitude of less than 30 meters (98 feet). Charles, with the aid of brothers Nicholas and Aine Jean Robert, became the first human to ascend in a hydrogen balloon just ten days later. A far greater height of almost 3,000 meters (9,843 feet) was attained thanks to the superior lift of the hydrogen balloon Charles had designed and helped build.

Charles is best known for his studies on how the volume of gases changes with temperature. The English scientist Robert Boyle had many years earlier determined the inverse relationship between the volume V and pressure P of a gas when temperature T is held constant. In 1662 he published the results that would later come to be known as Boyle's law ($V \alpha 1/P$ at constant T). During the winter of 1787 Charles studied oxygen, nitrogen, hydrogen, and carbon dioxide and found that the volume of all these gases increased identically with higher temperature when pressure was held constant ($V \alpha T$ at constant P). Charles did not publish the results of his work at the time, but another French scientist, Joseph-Louis Gay-Lussac, eventually learned of them. When Gay-Lussac did more extensive and precise experiments and published his similar findings in 1802 (as did the English scientist John Dalton), he acknowledged Charles's original work. Thus, the law governing the thermal expansion of gases, although sometimes called Gay-Lussac's law, is more commonly known as Charles's law.

While most of Charles's papers were on mathematics, he was ultimately an avid scientist and inventor. He duplicated a number of experiments that Franklin and others had completed on electricity and designed several instruments, including a new type of hydrometer for measuring densities and a reflecting goniometer for measuring the angles of crystals. Charles was elected to France's Academy of Sciences in 1785 and later became professor of physics at the Conservatoire des Arts et Métiers. He died in Paris on April 7, 1823. SEE ALSO BOYLE, ROBERT; CAVENDISH, HENRY; DALTON, JOHN; GAY-LUSSAC, JOSEPH-LOUIS.

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Chemical Engineering

Chemical engineers combine the science of chemistry with the discipline of engineering in order to manufacture materials and products essential to modern society. They are involved with the full scale of processes from the laboratory bench to the **pilot plant** and eventually at the manufacturing facility.

pilot plant: intermediate stage of testing for a chemical process to determine if it is industrially viable; between bench-top and production scale

How does chemical engineering differ from chemistry? Chemists discover the chemical reactions by which useful products may be made. Chemical engineers discover the processes and develop the equipment that allows the chemical reactions to work economically. The academic training of chemical engineers provides a strong background for a variety of areas, including:

- Process design
- Production engineering
- Research and development
- Safety
- Marketing/technical sales
- Environmental and waste management

Chemical engineering is particularly adaptable to solving the technological problems of modern society. Therefore, chemical engineers are often employed by the government and industrial firms. They make invaluable contributions to an improved quality of life by producing pharmaceutical products to cure diseases, fertilizers and pesticides to help feed a growing population, fabrics to clothe us, and petroleum products to warm our houses and move our cars. Chemical engineers also are deeply involved in preventing and treating pollution.

In addition to these key areas, chemical engineers are actively developing advanced materials used in the communications and space industries, food and beverage industries, and modern electronics.

The Laboratory versus a Plant Setting

It is instructive to examine some differences between chemical processes conducted in a laboratory setting compared to those larger-scale operations completed at either a pilot plant, where the process is conducted with intermediate-scale equipment used to optimze and scale up the process, or full-scale manufacturing facility. For example, the mixing of reactants in a small flask or beaker is easily accomplished using a magnetic stirrer or small mechanical stirrer. However, in an industrial process the phenomenon of uniform mixing is much more complicated, and specially designed agitators are required. Chemical engineers study the various mathematical models of mixing in order to design the most efficient mixing device.

Another example involves the heating of a reaction mixture. On a small scale, heating is accomplished using a hot plate or similar equipment, whereas on a large scale, heat exchangers are commonly used. The theory of heat transfer and the various designs of heat exchangers are topics studied by chemical engineers.

Another major difference occurring in a large-scale chemical plant is that fluids are being moved around from one unit to another. This requires special equipment such as pumps and valves and a knowledge of the fundamentals of transport phenomena and, in particular, fluid dynamics.

Chemical engineers are involved in a variety of different occupations within the general field of chemical engineering. The breakdown within the United States is as follows: process/production (30%); research and development (25%); sales/marketing (7%); education (4%); and other (13%).

A student interested in pursuing a career in chemical engineering should first of all be interested in mathematics and science, enjoy problem solving and troubleshooting, be decisive and innovative, and have excellent communication skills.

A Diverse Profession

In order to indicate the diverse nature of the chemical engineering profession, the typical work characteristics of different types of chemical engineers are examined.

First, let us consider chemical engineering research and development (R&D). The general objective in this area is to transform laboratory processes into commercial operations that are safe, efficient, and ecologically sound. Such engineers invariably work at the pilot plant level. They oversee the construction of the pilot plant, collect data, and decide whether the project should be taken to full scale. A research chemical engineer also collaborates with chemists in research laboratories. In addition to this, he or she works closely with the people who build the plants, namely, electricians, pipe fitters, boilermakers, and so forth. These chemical engineers also interact with specialists in industrial hygiene and safety, and waste disposal. The researcher spends a good deal of time analyzing and evaluating results, and transfers data to the process engineer and assists in the scale-up operations for commercial production.

Next, let us consider the chemical engineer in manufacturing (the so-called production engineer). This person is involved in producing a product in the required quality and quantity in a timely manner. This position requires exceptional leadership and interpersonal skills since one is interfacing with chemical operators on a routine basis. The production engineer (or plant manager) is also responsible for the safety of employees. In addition, a good deal of time is devoted to working with other departments, such as purchasing (raw materials), utilities (power), maintenance (repairs), marketing (production schedule), and research and process engineering (new and improved processes).

A third area involves the process engineer. This occupation concerns the scale-up of a process for commercial production. Here a chemical engineer will establish fundamental heat and material balances, develop working process flow sheets, and translate flow sheets into piping and instrument diagrams (PIDs). In addition, the process engineer has to specify the size of equipment and materials of construction. The types of equipment include reactors, distillation columns, heat exchangers, crystallizers, piping, and incinerators. This job involves close interactions with experts in chemistry, materials engineering, heat transfer, and computer simulation, to name a few. Also, the ability to work with mechanical, civil, and electrical engineers is very important. The process engineer assists as well with a plant startup.

Some chemical engineers choose to specialize in marketing and sales. These engineers are concerned with analyzing, developing, pricing, packaging, publicizing, and advertising. They must evaluate customer needs and also interact with production and R&D. In addition, it is vitally important that they understand all the details and properties of the product as well as its end uses. For this position one needs excellent people skills and a solid background in economics.

Current Trends

Prior to the 1970s, a large number of chemical engineers secured work in the booming petroleum industry and became involved in continuous processes. In more recent times, chemical engineers have entered many diverse fields—in particular, the pharmaceutical industry—working on the batch process level. Chemical engineers have also found employment with specialty chemical companies, as well as within the consumer and electronics industries.

Chemical engineers are actively involved in developing improved polymer processing and devices relevant to biomedical engineering. Another important research area is the physical and biological treatment of hazardous wastes. Computational methods are now used extensively in modeling studies, and computer simulation is routinely employed in plant design.

A further key area of interest involves separation techniques and technologies for solving separation problems in the chemical, environmental, food, pharmaceutical, and biotechnological industries.

Other exciting frontier areas of research in chemical engineering include molecular and nanoscale engineering, molecular simulation, surface modification, protein separation processes, supercritical fluid extraction, fluid particle systems, **catalysis** and reaction engineering, biochemical engineering, and computer-aided design. SEE ALSO CAREERS IN CHEMISTRY.

Reginald P. T. Tomkins

catalysis: the action or effect of a substance in increasing the rate of a reaction without itself being converted

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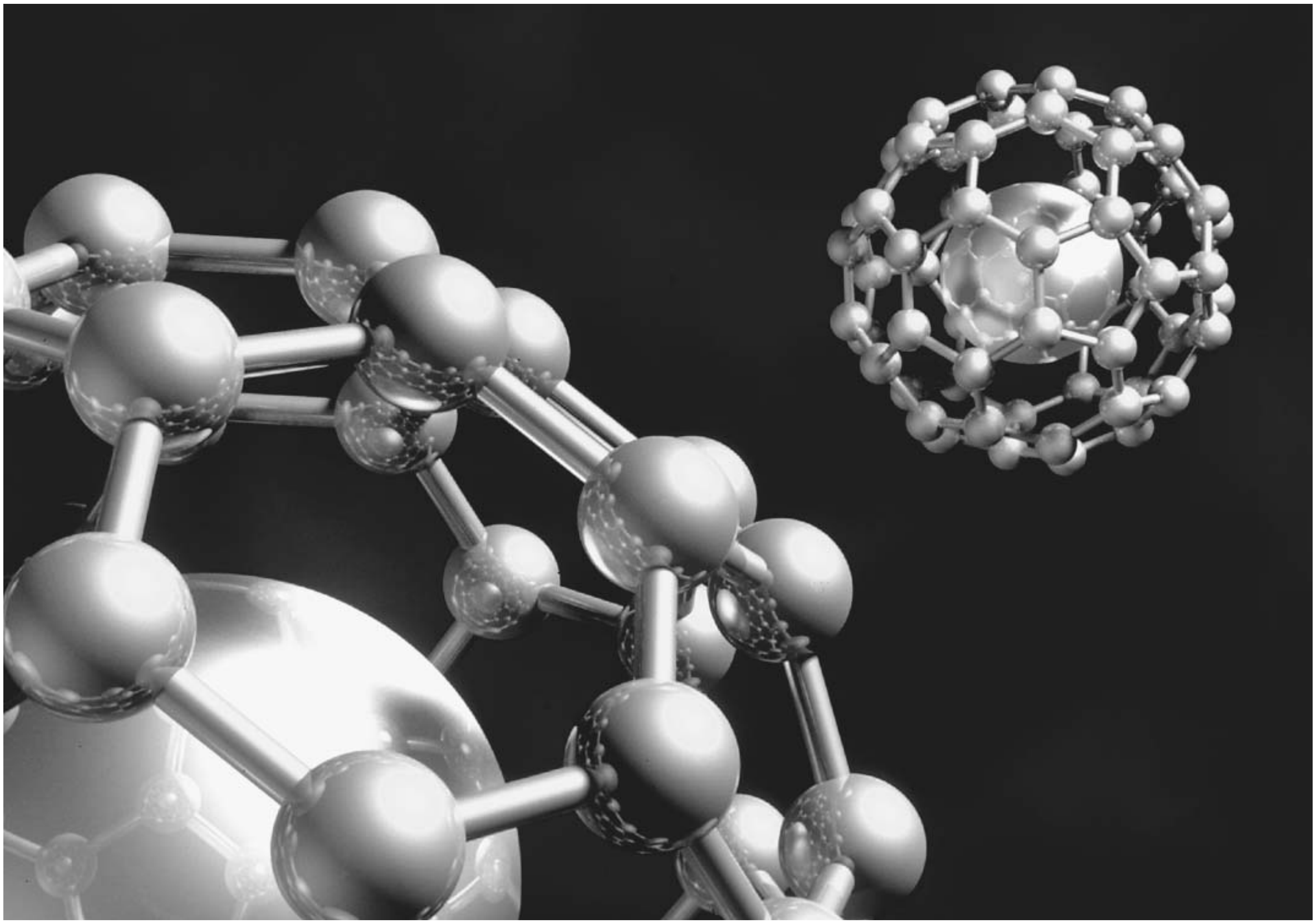
Chemical Informatics

As with many new disciplines, the field of chemical informatics has neither a precise name nor a clear definition. It is variously called cheminformatics, chemoinformatics, and molecular informatics, among other terms. Broadly defined, it encompasses the description, acquisition, visualization, management, and use of chemical information. A more narrow definition excludes the text-handling aspects of chemical information such as database searching and treats only the manipulation of two- and three-dimensional structural information. It is, however, generally agreed that cheminformatics (to use the currently most popular term) is indeed a legitimate new field in which chemistry and computer science intersect strongly. Those employed in this field develop new substances, materials, and processes by organizing, analyzing, and visualizing the information available to them. The present chief application of cheminformatics is in the field of drug discovery, but it is finding increasing acceptance and use in other applied areas of chemistry.

Although it derives its name and general focus from the slightly older field of bioinformatics, cheminformatics has its roots in a number of more established fields in chemistry, principally chemical information, chemometrics, and computational chemistry. The difference between cheminformatics and bioinformatics is mainly a matter of scale: bioinformatics is concerned mainly with data derived from the study of genes and large proteins, whereas cheminformatics focuses on small molecules. It emerged during the late 1990s from the convergence of two areas of chemistry that were earlier revolutionized by computer technology: the storage and retrieval of chemical data (generally referred to as chemical information), and the computational modeling of molecules and their behavior. An important aspect of this modeling had been the attempt to correlate structures of molecules with their biological activity, called qualitative structure-activity relationships (QSAR). More recently, the development of combinatorial chemical **synthesis** and high throughput screening (HTS) made possible the synthesis and testing of large numbers of compounds for drug testing—far more than could be handled by classical methods of analysis. The need to handle the resulting masses of data generated and the ability of modern computers to do so have hastened the development of cheminformatics in order to address the resulting glut of information. The most important current applications of cheminformatics are in the areas of molecular diversity analysis, the design of molecular libraries, and the virtual screening of potential drugs.

synthesis: combination of starting materials to form a desired product

Although the present focus of cheminformatics is mainly drug development, it has potential widespread applications in other areas, such as poly-



Computer-generated molecular structures.

mers, food science, and materials science. SEE ALSO Combinatorial Chemistry; Genome.

Bartow Culp

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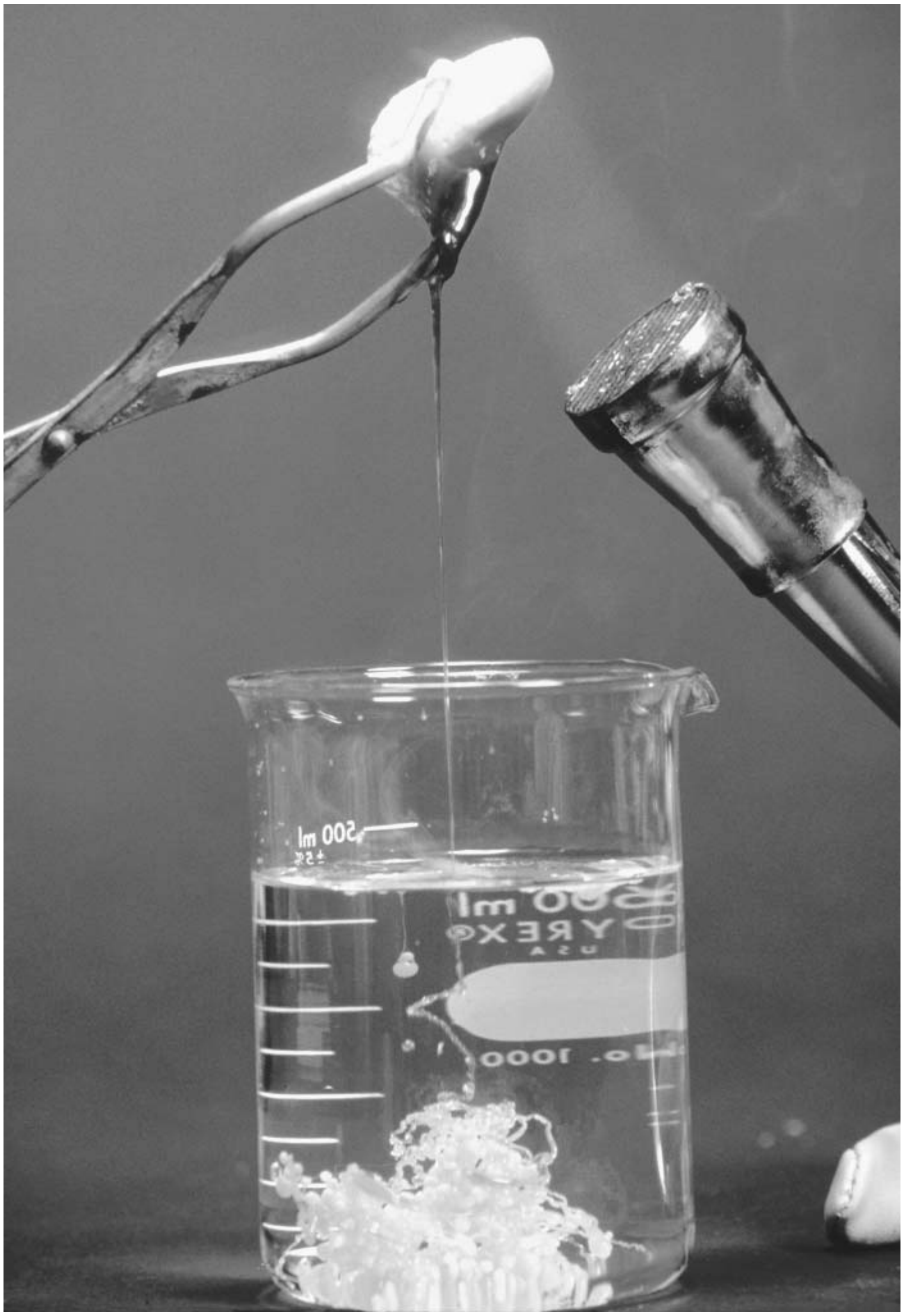
Chemical Reactions

A chemical reaction is a process in which one set of chemical substances (reactants) is converted into another (products). It involves making and breaking chemical bonds and the rearrangement of atoms. Chemical reactions are represented by balanced chemical equations, with chemical formulas symbolizing reactants and products. For specific chemical reactants, two questions may be posed about a possible chemical reaction. First, will a reaction occur? Second, what are the possible products if a reaction occurs? This



Sulfur reacting to heat.

entry will focus only on the second question. The most reliable answer is obtained by conducting an experiment—mixing the reactants and then isolating and identifying the products. We can also use periodicity, since elements within the same group in the Periodic Table undergo similar reactions. Finally, we can use rules to help predict the products of reactions, based on the classification of inorganic chemical reactions into four general categories: combination, decomposition, single-displacement, and double-displacement reactions.

Reactions may also be classified according to whether the **oxidation** number of one or more elements changes. Those reactions in which a change in oxidation number occurs are called **oxidation–reduction reactions**. One

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

oxidation–reduction reaction: reaction, sometimes called redox, that involves the movement of electrons between reactants to form products element increases its oxidation number (is oxidized), while the other decreases its oxidation number (is reduced).

Combination Reactions

In combination reactions, two substances, either elements or compounds, react to produce a single compound. One type of combination reaction involves two elements. Most **metals** react with most nonmetals to form ionic compounds. The products can be predicted from the charges expected for cations of the metal and **anions** of the nonmetal. For example, the product of the reaction between aluminum and bromine can be predicted from the following charges: 3+ for aluminum ion and 1− for bromide ion. Since there is a change in the oxidation numbers of the elements, this type of reaction is an oxidation–reduction reaction:

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

anion: negatively charged chemical unit, like Cl^-, CO_3^{2-}, or NO_3^-

$$2Al\ (s) + 3Br_2\ (g) \rightarrow 2AlBr_3\ (s)$$

Similarly, a nonmetal may react with a more reactive nonmetal to form a covalent compound. The composition of the product is predicted from the common oxidation numbers of the elements, positive for the less reactive and negative for the more reactive nonmetal (usually located closer to the upper right side of the Periodic Table). For example, sulfur reacts with oxygen gas to form gaseous sulfur dioxide:

$$S_8\ (s) + 8O_2\ (g) \rightarrow 8SO_2\ (g)$$

A compound and an element may unite to form another compound if in the original compound, the element with a positive oxidation number has an accessible higher oxidation number. Carbon monoxide, formed by the burning of hydrocarbons under conditions of oxygen deficiency, reacts with oxygen to form carbon dioxide:

$$2CO\ (g) + O_2\ (g) \rightarrow 2CO_2\ (g)$$

The oxidation number of carbon changes from +2 to +4 so this reaction is an oxidation–reduction reaction.

Two compounds may react to form a new compound. For example, calcium oxide (or lime) reacts with carbon dioxide to form calcium carbonate (limestone):

$$CaO\ (s) + CO_2\ (g) \rightarrow CaCO_3\ (s)$$

Decomposition Reactions

When a compound undergoes a decomposition reaction, usually when heated, it breaks down into its component elements or simpler compounds. The products of a decomposition reaction are determined largely by the identity of the anion in the compound. The ammonium ion also has characteristic decomposition reactions.

A few binary compounds decompose to their constituent elements upon heating. This is an oxidation–reduction reaction since the elements undergo a change in oxidation number. For example, the oxides and halides of noble metals (primarily Au, Pt, and Hg) decompose when heated. When red solid mercury(II) oxide is heated, it decomposes to liquid metallic mercury and oxygen gas:

$$2HgO\ (s) \rightarrow 2Hg\ (l) + O_2\ (g)$$

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

Some nonmetal oxides, such as the **halogen** oxides, also decompose upon heating:

$$2Cl_2O_5\ (g) \rightarrow 2Cl_2\ (g) + 5O_2\ (g)$$

Other nonmetal oxides, such as dinitrogen pentoxide, decompose to an element and a compound:

$$2N_2O_5\ (g) \rightarrow O_2\ (g) + 4NO_2\ (g)$$

Many metal salts containing oxoanions decompose upon heating. These salts either give off oxygen gas, forming a metal salt with a different nonmetal anion, or they give off a nonmetal oxide, forming a metal oxide. For example, metal nitrates containing Group 1A or 2A metals or aluminum decompose to metal nitrites and oxygen gas:

$$Mg(NO_3)_2\ (s) \rightarrow Mg(NO_2)_2\ (s) + O_2\ (g)$$

All other metal nitrates decompose to metal oxides, along with nitrogen dioxide and oxygen:

$$2Cu(NO_3)_2\ (s) \rightarrow 2CuO\ (s) + 4NO_2\ (g) + O_2\ (g)$$

Salts of the halogen oxoanions decompose to halides and oxygen upon heating:

$$2KBrO_3\ (s) \rightarrow 2KBr\ (s) + 3O_2\ (g)$$

Carbonates, except for those of the alkali metals, decompose to oxides and carbon dioxide.

$$CaCO_3\ (s) \rightarrow CaO\ (s) + CO_2\ (g)$$

A number of compounds—hydrates, hydroxides, and oxoacids—that contain water or its components lose water when heated. Hydrates, compounds that contain water molecules, lose water to form anhydrous compounds, free of molecular water.

$$CaSO_4 \cdot 2H_2O\ (s) \rightarrow CaSO_4\ (s) + 2H_2O\ (g)$$

Metal hydroxides are converted to metal oxides by heating:

$$2Fe(OH)_3\ (s) \rightarrow Fe_2O_3\ (s) + 3H_2O\ (g)$$

Most oxoacids lose water until no hydrogen remains, leaving a nonmetal oxide:

$$H_2SO_4\ (l) \rightarrow H_2O\ (g) + SO_3\ (g)$$

Oxoanion salts that contain hydrogen ions break down into the corresponding oxoanion salts and oxoacids:

$$Ca(HSO_4)_2\ (s) \rightarrow CaSO_4\ (s) + H_2SO_4\ (l)$$

Finally, some ammonium salts undergo an oxidation–reduction reaction when heated. Common salts of this type are ammonium dichromate, ammonium permanganate, ammonium nitrate, and ammonium nitrite. When these salts decompose, they give off nitrogen gas and water.

$$(NH_4)_2Cr_2O_7\ (s) \rightarrow Cr_2O_3\ (s) + 4H_2O\ (g) + N_2\ (g)$$

$$2NH_4NO_3\ (s) \rightarrow 2N_2\ (g) + 4H_2O\ (g) + O_2\ (g)$$

Ammonium salts, which do not contain an oxidizing agent, lose ammonia gas upon heating:

$$(NH_4)_2SO_4\ (s) \rightarrow 2NH_3\ (g) + H_2SO_4\ (l)$$

Single-Displacement Reactions

In a single-displacement reaction, a free element displaces another element from a compound to produce a different compound and a different free element. A more active element displaces a less active element from its compounds. These are all oxidation–reduction reactions. An example is the thermite reaction between aluminum and iron(III) oxide:

$$2Al\ (s) + Fe_2O_3\ (s) \rightarrow Al_2O_3\ (s) + 2Fe\ (l)$$

The element displaced from the compound is always the more metallic element—the one nearer the bottom left of the Periodic Table. The displaced element need not always be a metal, however. Consider a common type of single-displacement reaction, the displacement of hydrogen from water or from acids by metals.

The very active metals react with water. For example, calcium reacts with water to form calcium hydroxide and hydrogen gas. Calcium metal has an oxidation number of 0, whereas Ca^{2+} in $Ca(OH)_2$ has an oxidation number of +2, so calcium is oxidized. Hydrogen's oxidation number changes from +1 to 0, so it is reduced.

$$Ca\ (s) + 2H_2O\ (l) \rightarrow Ca(OH)_2\ (aq) + H_2\ (g)$$

Some metals, such as magnesium, do not react with cold water, but react slowly with steam:

$$Mg\ (s) + 2H_2O\ (g) \rightarrow Mg(OH)_2\ (aq) + H_2\ (g)$$

Still less active metals, such as iron, do not react with water at all, but react with acids.

$$Fe\ (s) + 2HCl\ (aq) \rightarrow FeCl_2\ (aq) + H_2\ (g)$$

Metals that are even less active, such as copper, generally do not react with acids.

To determine which metals react with water or with acids, we can use an activity series (see Figure 1), a list of metals in order of decreasing activity. Elements at the top of the series react with cold water. Elements above hydrogen in the series react with acids; elements below hydrogen do not react to release hydrogen gas.

The displacement of hydrogen from water or acids is just one type of single-displacement reaction. Other elements can also be displaced from their compounds. For example, copper metal reduces **aqueous solutions** of ionic silver compounds, such as silver nitrate, to deposit silver metal. The copper is oxidized.

aqueous solution: homogenous mixture in which water is the solvent (primary component)

$$Cu\ (s) + 2AgNO_3\ (aq) \rightarrow Cu(NO_3)_2\ (aq) + 2Ag\ (s)$$

The activity series can be used to predict which single-displacement reactions will take place. The elemental metal produced is always lower in the activity series than the displacing element. Thus, iron could be displaced from $FeCl_2$ by zinc metal but not by tin.

Figure 1. Activity series.

ACTIVITY SERIES

Li K Ba Ca Na	These metals will displace hydrogen gas from water
Mg Al Zn Fe Cd Ni Sn Pb	These metals will displace hydrogen gas from acids
H	
Cu Hg Ag Au	These metals will not displace hydrogen gas from water or acids

Double-Displacement Reactions

Aqueous barium chloride reacts with sulfuric acid to form solid barium sulfate and hydrochloric acid:

$$BaCl_2\ (aq) + H_2SO_4\ (aq) \rightarrow BaSO_4\ (s) + 2HCl\ (aq)$$

Sodium sulfide reacts with hydrochloric acid to form sodium chloride and hydrogen sulfide gas:

$$Na_2S\ (aq) + 2HCl\ (aq) \rightarrow 2NaCl\ (aq) + H_2S\ (g)$$

Potassium hydroxide reacts with nitric acid to form water and potassium nitrate:

$$KOH\ (aq) + HNO_3\ (aq) \rightarrow H_2O\ (l) + KNO_3\ (aq)$$

These double-displacement reactions have two major features in common. First, two compounds exchange ions or elements to form new compounds. Second, one of the products is either a compound that will separate from the reaction mixture in some way (commonly as a solid or gas) or a stable covalent compound, often water.

Double-displacement reactions can be further classified as precipitation, gas formation, and acid–base neutralization reactions.

Precipitation Reactions

Precipitation reactions are those in which the reactants exchange ions to form an insoluble salt—one which does not dissolve in water. Reaction occurs when two ions combine to form an insoluble solid or precipitate. We predict whether such a compound can be formed by consulting solubility rules (see Table 1). If a possible product is insoluble, a precipitation reaction should occur.

A mixture of aqueous solutions of barium chloride and sodium sulfate contains the following ions: $Ba^{2+}\ (aq)$, $Cl^{-}\ (aq)$, $Na^{+}\ (aq)$, and $SO_4^{2-}\ (aq)$. According to solubility rules, most sulfate, sodium, and chloride salts are soluble. However, barium sulfate is insoluble. Since a barium ion and sulfate ion could combine to form insoluble barium sulfate, a reaction occurs.

SOME SOLUBILITY RULES FOR INORGANIC SALTS IN WATER

Compound	Solubility
Na^+, K^+, NH_4^+	Most salts of sodium, potassium, and ammonium ions are soluble.
NO_3^-	All nitrates are soluble.
SO_4^{2-}	Most sulfates are soluble. Exceptions: $BaSO_4$, $SrSO_4$, $PbSO_4$, $CaSO_4$, Hg_2SO_4, and Ag_2SO_4.
Cl^-, Br^-, I^-,	Most chlorides, bromides, and iodides are soluble. Exceptions: AgX, Hg_2X_2, PbX_2, and HgI_2.
Ag^+	Silver salts, except $AgNO_3$, are insoluble.
O^{2-}, OH^-	Oxides and hydroxides are insoluble. Exceptions: NaOH, KOH, NH_4OH, $Ba(OH)_2$, and $Ca(OH)_2$ (somewhat soluble).
S^{2-}	Sulfides are insoluble. Exceptions: salts of Na^+, K^+, NH_4^+ and the alkaline earth metal ions.
CrO_4^{2-}	Most chromates are insoluble. Exceptions: salts of K^+, Na^+, NH_4^+, Mg^{2+}, Ca^{2+}, Al^{3+}, and Ni^{2+}.
CO_3^{2-}, $PO4^{3-}$, SO_3^{2-}, SiO_3^{2-}	Most carbonates, phosphates, sulfites, and silicates are insoluble. Exceptions: salts of K^+, Na^+, and NH_4^+.

Table 1.

$$BaCl_2\ (aq) + Na_2SO_4\ (aq) \rightarrow BaSO_4\ (s) + 2NaCl\ (aq)$$

Gas-Formation Reactions

A double-displacement reaction should also occur if an insoluble gas is formed. All gases are soluble in water to some extent, but only a few gases [HCl (*g*) and NH_3 (*g*)] are highly soluble. All other gases, generally binary covalent compounds, are sufficiently insoluble to provide a driving force if they are formed as a reaction product. For example, many sulfide salts will react with acids to form gaseous hydrogen sulfide:

$$ZnS\ (s) + 2HCl\ (aq) \rightarrow ZnCl_2\ (aq) + H_2S\ (g)$$

Insoluble gases are often formed by the breakdown of an unstable double-displacement reaction product. For example, carbonates react with acids to form carbonic acid (H_2CO_3), an unstable substance that readily decomposes into water and carbon dioxide. Calcium carbonate reacts with hydrochloric acid to form calcium chloride and carbonic acid:

$$CaCO_3\ (s) + 2HCl\ (aq) \rightarrow CaCl_2\ (aq) + H_2CO_3\ (aq)$$

Carbonic acid decomposes into water and carbon dioxide:

$$H_2CO_3\ (aq) \rightarrow H_2O\ (l) + CO_2\ (g)$$

The net reaction is:

$$CaCO_3\ (s) + 2HCl\ (\mathrm{aq}) \rightarrow CaCl_2\ (aq) + H_2O\ (l) + CO_2\ (g)$$

Sulfites react with acids in a similar manner to release sulfur dioxide.

Acid-Base Neutralization Reactions

A neutralization reaction is a double-displacement reaction of an acid and a base. Acids are compounds that can release hydrogen ions; bases are compounds that can neutralize acids by reacting with hydrogen ions. The most common bases are hydroxide and oxide compounds of the metals. Normally, an acid reacts with a base to form a salt and water. Neutralization reactions occur because of the formation of the very stable covalent water molecule, H_2O, from hydrogen and hydroxide ions.

$$HCl\ (aq) + NaOH\ (aq) \rightarrow NaCl\ (aq) + H_2O\ (l)$$

Recognizing the pattern of reactants (element or compound, and the number of each) allows us to assign a possible reaction to one of the described classes. Recognizing the class of reaction allows us to predict possible products with some reliability. SEE ALSO Acid-Base Chemistry; Solution Chemistry; Thermodynamics.

James P. Birk

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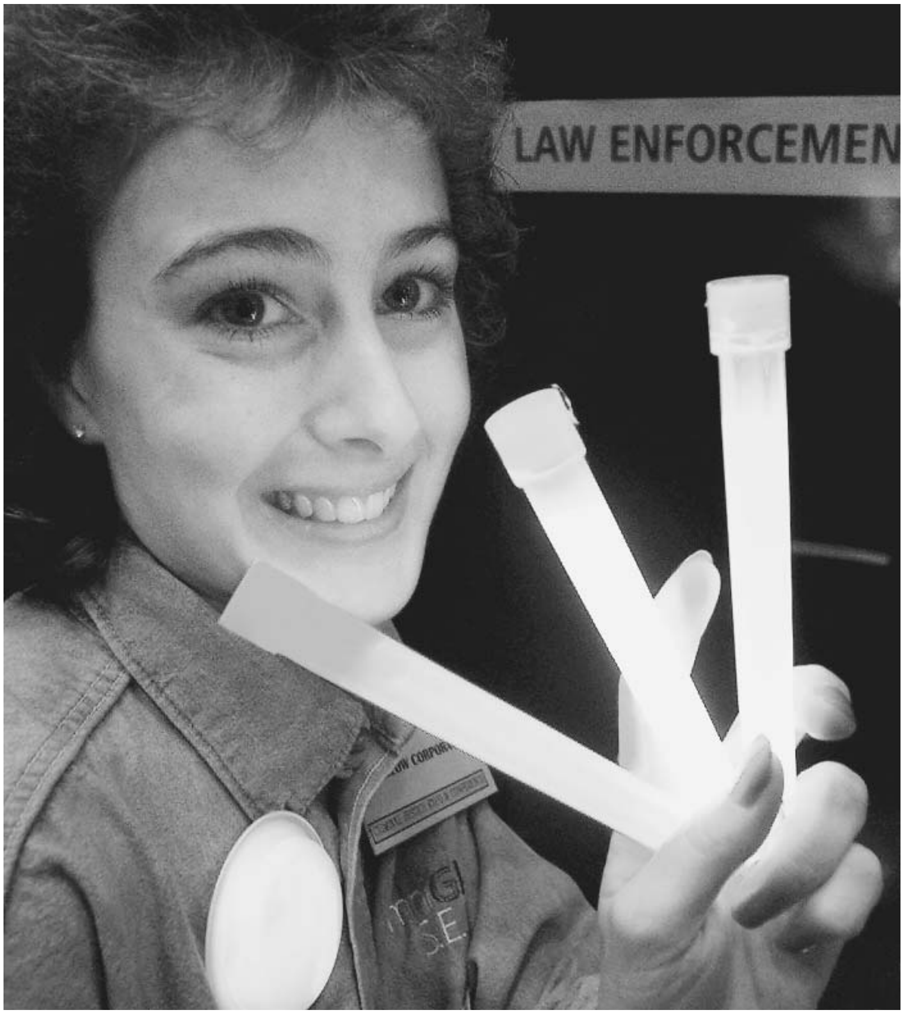
Chemiluminescence

When two molecules react chemically so that there is a release of energy (an exothermic reaction), that energy sometimes manifests itself not as heat but as light. This occurs because the energy excites the product molecules into which it has been funneled. A molecule in this excited state either relaxes to the ground state, with the direct emission of light, or transfers its energy to a second molecule, which becomes the light emitter. This process is referred to as chemiluminescence. The originally green, now multicolored, commercially made "light sticks" (often in the form of bracelets and necklaces) work in this way, utilizing the (exothermic) reaction of hydrogen peroxide with an oxalate **ester**. This **oxidation** reaction produces two molecules of carbon dioxide (CO_2), and the released energy is transferred to a fluorescent dye molecule, usually an anthracene derivative. Light sticks were developed by the U.S. Navy as an inconspicuous and easily shielded illumination tool for special operations forces dropped behind enemy lines. Besides their use as children's toys, they are also used extensively as a navigation aid by divers searching in muddy water.

ester: organic species containing a carbon atom attached to three moieties: an O via a double bond, an O attached to another carbon atom or chain, and an H atom or C chain; a compound with the general formula $RC(O)OR^1$

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)



These light sticks glow as a result of the energy released by a chemical reaction.

Chemiluminescence is also found in fireflies. The male firefly uses the reaction of a luciferin substrate and the enzyme luciferase with oxygen, with **adenosine triphosphate (ATP)** as an energy source, to create the illumination it uses to attract a mate. Because the detection of very minute amounts of light is possible, chemiluminescence and bioluminescence have become the basis of many sensitive analytical and bioanalytical techniques or assays used to quantify particular compounds in samples. Indeed, the use of these techniques is broad enough to justify the existence of a journal devoted to them, the *Journal of Bioluminescence and Chemiluminescence.*

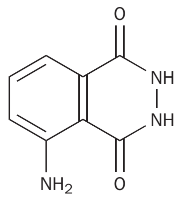
adenosine triphosphate (ATP): molecule formed by the condensation of adenine, ribose, and triphosphoric acid, HOP(O)OH–O–(O)OH–OP(O)OH–OH; it is a key compound in the mediation of energy in both plants and animals

In 1669 Hennig Brand, a German alchemist, was attempting to recover, by means of intense heat, the gold he hoped was lurking in human urine. The waxy white substance that he did retrieve, which glowed green when exposed to air, was in fact elemental phosphorus.

The emission of light observed by Brand was actually chemiluminescence. The light arises from PO_2 molecules in an excited state. This excited state of PO_2 is brought about by the reaction between PO and ozone, which are both **intermediates** in the fundamental reaction between oxygen in air and P_4 vapor evaporating from the solid white phosphorus. It is unfortunate that the chemiluminescent glow of phosphorus gave rise to the term

intermediate: molecule, often short-lived, that occurs while a chemical reaction progresses but is not present when the reaction is complete

"phosphorescence." Scientifically, phosphorescence is a process whereby absorbed photons are emitted at a later time, as exemplified by the glow of a watch face in the dark after its earlier exposure to light.



3-aminophthalhydrazide

Figure 1. Structure of Luminol, 3-aminophthalhydrazide.

Luminol (3-aminophthalhydrazide) is used in a commercially available portable device called the Luminox that measures minute concentrations (parts per billion) of the pollutant nitrogen dioxide in air. Luminol is also used frequently in laboratory demonstrations of the chemiluminescence phenomenon. Luminol-mediated chemiluminescence is the result of an oxidation reaction. The oxidation proceeds in two steps, which ultimately lead to the production of the aminophthalate **anion** in an excited state and the elimination of water and molecular nitrogen. The formation of the strong triple bond (N≡N) is a major factor in the release of energy in the form of light.

anion: negatively charged chemical unit, like Cl^-, CO_3^{2-}, or NO_3^-

nitric oxide: compound, NO, which is involved in many biological processes; the drug Viagra enhances NO-stimulation of pathways to counteract impotence; may be involved in killing tumors

Probably the simplest chemiluminescent reaction (and one that has been studied extensively) is the reaction between **nitric oxide**, NO, and ozone, O_3. The reaction (with about 10% efficiency) yields nitrogen dioxide in an excited state (NO_2*)

$$NO + O_3 = NO_2^* + O_2$$

$$NO_2^* = NO_2 + h\nu$$

The reaction was developed in the early 1970s as a specific and instantaneous method to detect nitric oxide in the exhaust of automobiles. This use of chemiluminescence rapidly led to application of the same phenomenon to monitor the presence of NO in the atmosphere. Both applications continue in use. Ozone can easily be produced by passing dry air or oxygen through an electric discharge. The ozone-containing stream and the sample to be evaluated are mixed in a dark chamber adjacent to a photomultiplier tube, and the chemiluminescence signal that is produced is amplified. These devices are capable of monitoring NO levels ranging from parts per trillion to thousands of parts per million; an individual instrument can sometimes measure concentrations extending across six orders of magnitude.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

The familiar yellow glow from a natural gas or wood-burning flame is not the result of chemiluminescence, but is due to bright, red-hot particles of carbon soot. The blue, green, and other colors produced when **metals** are put into flame can indeed be ascribed to chemiluminescence; in these instances the luminescence is accompanied by heat production.

According to information provided by the Harbor Branch Oceanographic Institution in Ft. Pierce, Florida, more than 90 percent of organisms living in the oceans at depths from 200 to 1,000 meters (656 to 3,281 feet) use chemiluminescence for activities such as attracting prey and avoiding predators. Light from the sky is quite weak at those depths; a fish that emits a dim glow from its lower parts could become invisible from below, while a fish without this capability would appear as a dark shadow. SEE ALSO BIOLUMINESCENCE; PHOSPHORUS; RADIATION.

Donald H. Stedman

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Chemistry and Energy

Energy is central to our understanding of chemistry, for atoms adopt arrangements that correspond to the lowest possible energy and electrons in atoms adopt the lowest possible energy distribution. The adoption of lowest energy arrangements of atoms is responsible for the characteristic shapes of molecules. For instance, the tetrahedral shape of the methane molecule (CH_4) corresponds to the lowest energy arrangement possible for one carbon atom and four hydrogen atoms. The characteristic bond lengths in a molecule are the distances between centers of atoms corresponding to the atoms' lowest energy arrangement. The distribution of electrons in molecules—whether they are present as forming single, double, or triple bonds, or whether they do not participate in bonding at all—corresponds to the arrangement of lowest energy for those electrons.

Energy considerations are central to determinations of whether a reaction will run in one direction or another, but great care must be exercised in this regard for although most reactions run in the direction of decreasing energy (e.g., the **combustion** of a fuel), some reactions run in the direction of increasing energy (e.g., the decomposition of pure ammonia maintained at a high temperature). To determine the spontaneous direction of a reaction, it is necessary to consider, not the quantity of energy absorbed or released but its quality as measured by the change in entropy. This is the domain of the second law of thermodynamics.

combustion: burning, the reaction with oxygen

Energy changes are also used to identify materials and to explore their detailed structures. This is the domain of **spectroscopy**, in which molecules are excited to higher energy states by the absorption of energy in the form of electromagnetic radiation. In some materials, the excess energy of an excited state is emitted as radiation: this is the origin of fluorescence and phosphorescence, in which high frequency radiation (such as **ultraviolet radiation**) is absorbed and emitted as lower energy visible radiation.

spectroscopy: use of electromagnetic radiation to analyze the chemical composition of materials

ultraviolet radiation: that portion of the electromagnetic spectrum with wavelengths shorter than visible but longer than x rays

When most people think of energy in connection with chemistry, however, they have in mind the production of energy for manufacturing, transportation, and the functioning of living organisms. The energy released by chemical reactions may be extracted as heat or as work. The ultimate source of the energy is the change in energy that accompanies the rearrangements of electrons and nuclei as atoms exchange partners. For instance, when a hydrocarbon fuel burns, the carbon–hydrogen and carbon–carbon bonds are replaced by the stronger carbon–oxygen and hydrogen–oxygen bonds of carbon dioxide and water, and the excess energy is released as heat. That is, at the high temperature of the reaction, the atoms are "loosened" from each other and allowed to adopt arrangements of lower energy.

The energy produced in a chemical reaction may also be extracted electrically. The device needed is called an electrochemical cell, which is a reaction vessel equipped with two electrodes. **Oxidation** (the loss of electrons) takes place at one electrode (the anode), and the electrons lost from the reactant are transferred to the electrode. They then travel through an external circuit, which might contain an electric motor, and re-enter the reaction vessel at the other electrode (the cathode), where they bring about reduction (the gain in electrons). In a primary cell, the reactants are sealed in at time of manufacture and the production of electricity continues until the

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

chemical reaction has reached **equilibrium**. In a secondary cell, an electric current is driven through the cell and reactants are formed at the electrodes. Once the cell is "charged," the newly formed reactants can be allowed to form products in the same way as in a primary cell. In a fuel cell, reactants are supplied continuously from the outside, and electricity is produced for as long as they are supplied.

equilibrium: condition in which two opposite reactions are occurring at the same speed, so that concentrations of products and reactants do not change

The production of energy by any chemical reaction has potential consequences for the environment. Of greatest concern is the generation of carbon dioxide (CO_2) by the combustion of hydrocarbon fuels (the so-called fossil fuels—natural gas, coal, and petroleum). Carbon dioxide is a potent greenhouse gas and its accumulation in the atmosphere appears to be furthering global warming, with dire consequences for humanity. Fuel cells that use hydrocarbons as **feedstock** are also sources of pollution, as they form carbon dioxide, but they are more efficient, and less carbon dioxide is produced for a given supply of energy. Fuel cells may also operate using hydrogen as feedstock, in which case they produce only water, which has no impact on the already wet environment. However, the most economical supply of hydrogen is the burning of hydrocarbons, which produces the unwanted carbon dioxide. There is hope that photochemical sources of hydrogen will become sufficiently economical and eliminate the covert pollution step, but it is unlikely that sufficient energy can be achieved diurnally: fossil fuels represent the accumulation of years of solar energy.

feedstock: the raw materials necessary to carry out chemical reactions

Nuclear energy, which is obtained when nucleons (protons and neutrons) are allowed to adopt lower energy arrangements and to release the excess energy as heat, does not contribute to the carbon dioxide load of the atmosphere, but it does present pollution problems of a different kind: radioactive waste. Optimists presume that this waste can be contained, in contrast to the burden of carbon dioxide, which spreads globally. Pessimists doubt that the waste can be contained—for thousands of years. Nuclear power depends directly on the discipline of chemistry in so far as chemical processes are used to extract and prepare the uranium fuel, to process spent fuel, and to encapsulate waste material in stable glass blocks prior to burial. Nuclear fusion, in contrast to nuclear **fission**, does not present such serious disposal-related problems, but it has not yet been carried out in an economic, controlled manner.

nuclear: having to do with the nucleus of an atom

fission: process of splitting an atom into smaller pieces

Chemistry contributes in many ways to the more efficient and cleaner utilization of fossil fuels. Chemists find ways of extracting fuels from ever scarcer supplies; of promoting cleaner, more efficient combustion; and of producing cleaner exhausts through the development of catalysts. They are involved in the development of electrode materials for more efficient fuel cells, and in the development of photovoltaic systems to be used for more effective solar power generation. SEE ALSO Energy; Thermodynamics.

Peter Atkins

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Chemotherapy

Chemotherapy is the controlled use of chemicals for a medicinal purpose. The term was coined by the German bacteriologist Paul Ehrlich, around 1900, when he examined aniline dyes and arsenicals as possible treatments for diseases such as trypanosomiasis and syphilis. He envisioned "magic bullets" that could target invading organisms and leave the host unscathed. This goal of providing therapeutic benefits with minimal side effects continues in all areas of drug development. Remarkable successes have been obtained in compounds that modulate normal biochemistry within the human body. These include **analgesics**, antihistamines, cardiac rhythm regulators, blood pressure modifiers, anesthetics, anti-inflammatory agents, sedatives, diuretics, and vasodilators. In the battle against the unwanted growth of invading organisms and mutated cells (cancer), the greatest successes have occurred in the bacterial antibiotics; in the twentieth century they have increased human longevity more than any other medication. Similar successes for drugs treating viral infections and cancer have been elusive.

analgesic: compound that relieves pain, e.g., aspirin

A young patient receiving a chemotherapy treatment.

In recent years chemotherapy has become a popular form of anticancer treatment. The goal of a magic bullet endures, but it is often difficult to attain because most of chemotherapy's useful agents are poisonous. This results from the similarities between cancerous cells and normal cells. Drugs that kill tumors are not specific enough to leave normal cells unharmed. Therefore, virtually all cancer chemotherapy is a delicate compromise between effectiveness and toxicity, resulting in significant side effects. Patients and physicians accept this because the alternatives are limited and the progression of the often fatal disease usually occurs more quickly without some intervening form of chemotherapy treatment.

The pursuit of chemical agents that can more effectively treat cancer has led to many decades of research by a multitude of chemists, biochemists, microbiologists, biologists, and research physicians. Thousands of chemicals have been synthesized and tested in tissue **cultures** and animal models. Only a modest number have proved to be useful in treating humans, but they have become the mainstay of the chemotherapeutic attack on cancer. In combination with early detection, surgery, radiation, and newly developing immunotherapies and targeted therapies, the judicious use of chemotherapy can kill tumors and limit their recurrence.

culture: living material developed in prepared nutrient media

Common Agents

The most active chemotherapeutic agents fall into a small number of broad categories depending on their mode of action: alkylating/cross-linking agents that interact with **DNA**; antibiotics that can kill mammalian cells instead of bacteria; antimetabolites/inhibitors that interfere with normal biochemistry; hormones that interact with **receptors** on tumor cells; and cytokines that can alter the balance of the intercellular communication system. Some commonly used agents, and their classifications, are listed in Table 1.

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

All these drugs, more generally, can be classified as either *reactive* or *interactive*. In the first case, biological activity depends on the chemical reaction of the drug with a target molecule. The resulting adduct interferes with normal cellular processes and may enhance cell death. Such reactive molecules are often indiscriminant, however, and are prone to powerful side effects. In the second case, biological activity depends only on the drug's structure, allowing it to interfere with cellular pathways that depend on lock-and-key recognition processes. These interactions can often be very specific, but may be limited in efficacy due to the existence of parallel pathways for most critical processes.

Reactions with DNA are prototypical of reactive anticancer chemicals. Alkylating and cross-linking agents such as nitrogen mustards, platinum compounds, alkane sulfonates, nitrosoureas, and methylating agents are believed to achieve their therapeutic effect by irreversibly binding to DNA and blocking its replication. This class of drugs is used routinely to treat most forms of cancer: sarcoma, carcinoma, teratoma, and leukemia.

Naturally occurring antibiotics (i.e., produced by other organisms) are complicated, multipurpose compounds. They often contain unsaturated polycyclic rings that can squeeze between DNA bases (intercalation) and interrupt DNA replication; quinone redox sites that can create free radicals

NAMES AND PROPERTIES OF ROUTINELY PRESCRIBED CHEMOTHERAPY AGENTS

Common Name	Primary Target	Mechanism	Similar Drugs
Alkylating Agents, Cross-linkers			
cyclophosphamide	DNA	nitrogen mustard (*reactive*)	ifosfamide melphalan
cisplatin	DNA	platinum coordination (*reactive*)	carboplatin
Antibiotics			
doxorubicin (adriamycin)	DNA	polycyclic rings allow intercalation (*interactive*), quinones allow redox reactions (*reactive*)	bleomycin mitomycin C daunorubicin
Antimetabolites, Inhibitors			
methotrexate	dihydrofolate reductase	mimics folate *interactive*)	trimetrexate
5-fluorouracil	thymdylate synthase, also incorporated into RNA and DNA	mimics deoxyuridine triphosphate (*reactive* and *interactive*)	5-azacytidine cytarabine 6-mercaptopurine
vincristine	microtubules	inhibits tubule assembly (*reactive*)	vinblastine
paclitaxel (taxol)	microtubules	inhibits tubule depolymerization (*reactive*)	docetaxel
etoposide	topoisomerase II	inhibits reconnection of DNA (*interactive*)	teniposide
topotecan	topoisomerase I	inhibits reconnection of DNA (*interactive*)	irinotecan
Hormones			
dexamethasone	glucocorticoid receptor	modify DNA transcription (*interactive*)	hydrocortisone prednisone cortisone
diethylstilbestrol	estrogen receptors	change hormonal balance (*interactive*)	estradiol modified estrogens
tamoxifen	estrogen receptors	blocks receptors in receptor-positive breast cancer (*interactive*)	torimenifene

SOURCE: Compiled from data contained in Perry, Michael C., ed. (2001). *The Chemotherapy Source Book,* 3rd edition. Philadelphia: Lippincott Williams & Wilkins.

Table 1. Names and properties of routinely prescribed chemotherapy agents.

in the cell; and electrophilic moieties that can alkylate the **guanine** of DNA. They are used routinely in the treatment of leukemia, germ cell tumors of the testis and ovary, lymphomas, and some childhood cancers.

Antimetabolites substitute for naturally occurring compounds in normal **metabolism** and **biosynthesis** reactions. They are designed to interfere with the normal biochemistry of a cell by deactivating or **retarding** enzyme action or by replacing normal nucleic acids in DNA and **RNA** with analogs that inhibit replication or repair. Special classes of **inhibitory** molecules include the microtubule-targeting drugs and topoisomerase inhibitors, which interfere with specific targets within a cell. They are used routinely in all forms of cancer, usually in combination with each other and with the alkylating/cross-linking agents.

Hormones and hormone receptor inhibitors can be administered because some tumors have hormone receptors. The response of the tumor to such therapy, however, is difficult to predict. It can be detrimental or beneficial depending on the hormone, the type of cancer, and even the individual. These drugs are used routinely to treat breast cancer patients with receptor-positive tumor types.

guanine: heterocyclic, purine, amine base found in DNA

metabolism: all of the biochemical processes that take place within living organisms; comprises processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those that break down complex food molecules, thus liberating energy (catabolism)

biosynthesis: formation of a chemical substance by a living organism

retardation: to slow down a chemical reaction

RNA: ribonucleic acid, a natural polymer used to translate genetic information in the nucleus into a template for the construction of proteins

inhibitory: relating to the prevention of an action that would normally occur

Cytokines, like hormones, are interactive molecules. They bind to receptors on either effector cells of the immune system or the tumor cells themselves. In doing so, they activate programs within the cells that may be useful at a particular time and location in killing the tumor or attracting immune killer cells. A special class of immune system cytokines, called interleukins, has been tested in melanoma and renal carcinoma with some encouraging results. Although cytokines are still largely experimental, their use is growing due to increased understanding of the complex signaling of the immune system.

Kinetics

excrete: to eliminate or discharge from a living entity

synthesis: combination of starting materials to form a desired product

To understand why chemical compounds are useful drugs in treating diseases like cancer, scientists study their complicated kinetics within the human body. The first concern is their rate of reaction or target binding affinities with other biological compounds. The second is their rate of distribution and **excretion**. Together, these are referred to as pharmacokinetics. This is part of a broader series of effects, referred to as pharmacodynamics, which include the positive and negative physiological changes induced by a drug. When a drug is administered (orally or by injection), it must reach the desired target in the organism before it is excreted or altered by detoxifying enzymes (usually located in the liver). Studies using radioactive forms of drugs have been used as tracers to follow both the chemical modifications and their distributions in various compartments of the body. Results have allowed the **synthesis** of new drugs with better chemistries, distributions, and toxicity profiles.

The most useful reactive drugs are those that have biologically relevant reaction rates. This means that they react slowly enough to reach their targets but fast enough to damage target cells before they are cleared. This appears to be a simple concept for drug design, but the immense number of reactions that can occur in a biological environment have made the discovery and development of such drugs a tedious procedure.

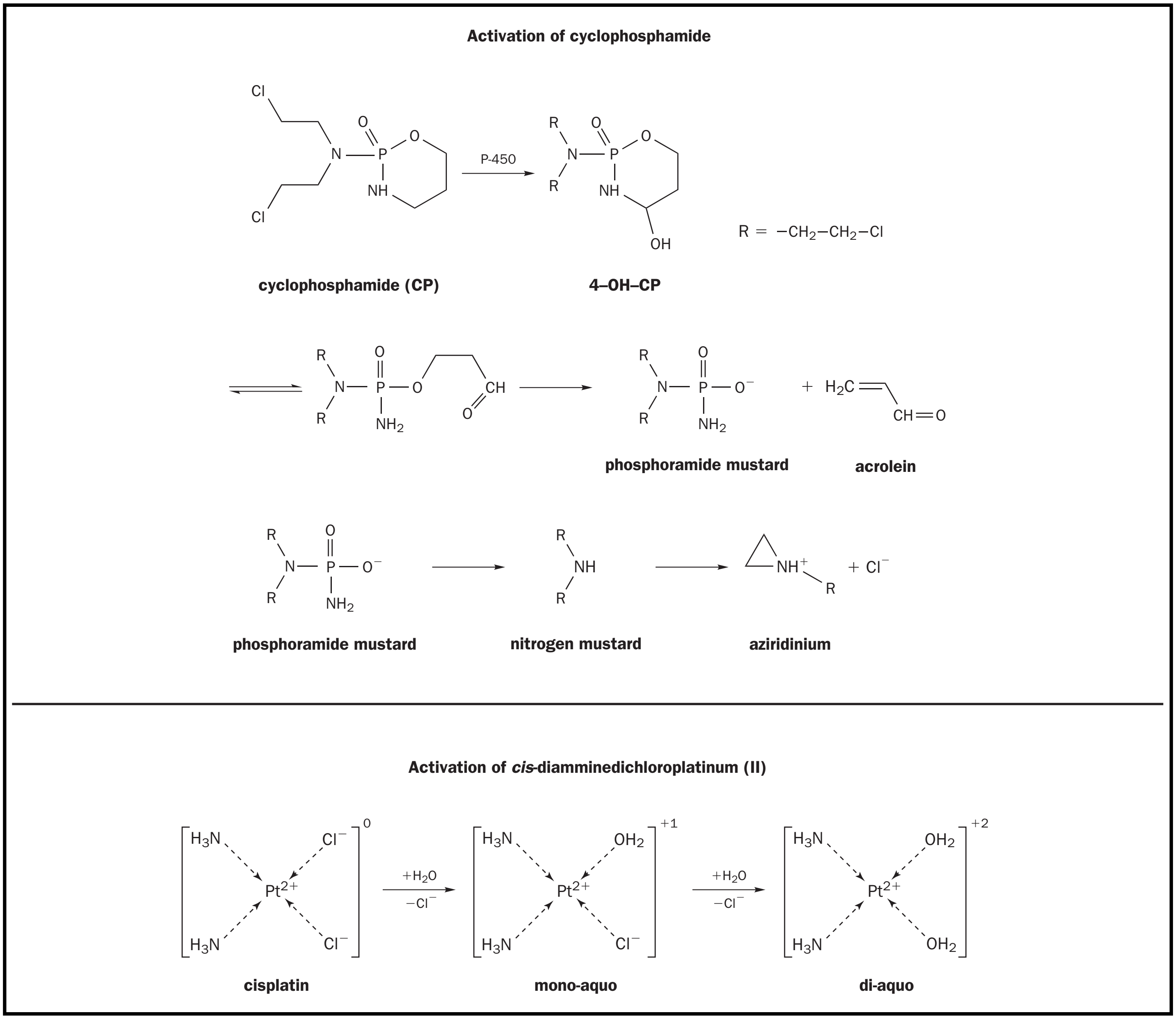
intermediate: molecule, often short-lived, that occurs while a chemical reaction progresses but is not present when the reaction is complete

A successful strategy for achieving this kinetic balance is to use a compound that has a long-lived **intermediate** form which keeps it near its target. Two widely used drugs, cyclophosphamide and cisplatin, are good examples of this, but for different reasons.

In cyclophosphamide, the nitrogen mustard moiety of the parent compound is unreactive because the electron-withdrawing property of the ring reduces the reactivity of the lone pair of nitrogen electrons. The result is a drug that is both nontoxic and nontherapeutic. As the drug circulates in the bloodstream, liver enzymes (cytochrome P450) oxidize the 4th position of the ring (see Figure 1). The 4-OH form undergoes nonenzymatic cleavage of the acyclic tautomer, forming a phosphoramide mustard. This last step occurs slowly enough for the 4-OH form to leave the liver and enter other cells. Once the charged product forms, it cannot escape the cells that it enters. The chloro-ethyl side groups then cyclize sequentially into highly reactive aziridinium forms, which attack and cross-link DNA, leading to cell death.

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

In cisplatin, the +2 **oxidation** state of the platinum atom forms four coordination bonds in a square plane. Each ammine supplies two electrons



Activation of cyclophosphamide

Activation of *cis*-diamminedichloroplatinum (II)

Figure 1. Activation reactions for the anticancer drugs cyclophosphamide and cisplatin.

from the filled orbital of nitrogen, while each chloride **anion** supplies two electrons and one negative charge that neutralizes the molecule. The result is a molecule stable to nucleophilic attack and able to cross cell membranes due to its charge neutrality. In the presence of low chloride, such as inside a cell, the chlorides begin to leave the platinum at a slow rate (a half-life of 5–6 hours). They are replaced by water molecules forming first mono-aquo and then di-aquo species, which are singly and doubly charged, respectively. These forms cannot penetrate the cell membrane and are confined inside the cell. Water makes a much better leaving group than Cl^-, resulting in rapid reactions with intracellular nucleophiles. With two sites of attack, the cross-linking of protein and DNA occurs readily.

anion: negatively charged chemical unit, like Cl^-, CO_3^{2-}, or NO_3^-

In the case of interactive drugs, the most useful are those that exhibit long-term biological stability which allows them to reach their targets before they are degraded. They also have very high affinities for their targets so they can block normal molecules from binding. Many of these have been extracted from fungi, bacteria, and plants. Years of evolution have fine-tuned these complex molecules into effective poisons that have been targeted against the predators of these organisms. In humans, many have shown remarkable antitumor properties with manageable toxicities. Others have been chemically modified to give them the necessary pharmacokinetic properties suitable for fighting cancer. It is believed that many more of these molecules remain to be discovered and that much will be learned by studying their mechanisms of action.

Specificity

Many successful drugs have shown specificity for certain tumors. The reason for this selectivity is usually not obvious, since the expected mechanisms of action often suggest that they would kill all cells equally well. In fact, many do harm normal cells, leading to the unpleasant side effects that most patients experience. Nonetheless, such drugs can be effective in reducing or eliminating large tumors while sparing the patient.

The specificity of a given drug for a particular tumor has largely been discovered by trial and error on patients enrolled in clinical trials. In many cases, the reasons for that specificity are still unknown but appear to result from the different biochemistries of tumor cells. In particular, the regulatory pathways in tumor cells are dramatically out of balance. This is often the result of several mutations in oncogenes and suppressor genes disabling the control elements of cell division and homeostasis. DNA replication accelerates and remains unwrapped longer, exposing it to more cross-linking. In some tumors, DNA repair enzymes are expressed at reduced levels, allowing damage to accumulate faster. There is also evidence that many active agents shift the unbalanced regulation of tumor cells into apoptosis (programmed cell death), causing the tumor to essentially commit suicide. These various lines of research show that although tumor cells are aggressive and uncontrolled, they are also vulnerable to the right kind of attack.

The continuing goal of mechanism-of-action and specificity research is to provide a better understanding of the interaction between drugs and tumor cells. This will allow the rational design of new drugs that are lower in toxicity and higher in effectiveness. As cellular targets are identified, as new proteins are characterized from the human genome project, as cell–cell communication pathways are elucidated, and as high-power computation is established, rational drug design will become more practical. Future chemotherapy will likely be targeted, individualized therapy, where patients will be fitted to therapies just as they would be to finely tailored clothes. SEE ALSO COORDINATION COMPOUNDS; EHRLICH, PAUL.

David A. Juckett

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Chevreul, Michel

FRENCH CHEMIST
1786–1889

French chemist Michel Chevreul, who established the melting point as a key criterion for the purity of a substance.

Michel-Eugène Chevreul was a chemist whose career spanned the greater part of the nineteenth century. He was born in Angers, France, on August 31, 1786, and died in Paris on April 9, 1889. Chevreul's father was a well-known physician. Raised in the midst of the terror of the French Revolution, Chevreul witnessed much violence and suffering. As a result, he maintained a lifelong aversion to politics and at an early age decided to devote his life to chemistry.

Chevreul's career as a scientist began at age seventeen when he became an assistant in the laboratory of Louis-Nicolas Vauquelin at the Muséum National d'Histoire Naturelle in Paris. While working in Vauquelin's laboratory, Chevreul began his study of organic chemistry with the investigation of the separation of natural coloring agents from their sources. At the age of twenty-four, he was named assistant naturalist at the museum. Chevreul then served as director of dyeing at the Manufacture Royale des Gobelins from 1824 to 1885. He became a member of the Academie des Sciences in 1826 and its president in 1839 and 1867. When Vauquelin retired, Chevreul attained the chair of chemistry at the museum, a position he held until his death in 1889.

Chevreul's career exemplifies the enormous strides made in the understanding of chemistry during the nineteenth century. He established the **melting point** as a key criterion for the purity of a substance. Even in the contemporary world, the melting point remains the first property determined to characterize a new solid. Chevreul excelled at the **elemental analysis** of organic substances and established the molecular formulas for many important chemical compounds. This procedure was considered very difficult in his time. His mentor, Vauquelin, had demonstrated that all foods are of four types: fats (**lipids**), proteins, starches, and sugars. In his continued studies of fats, Chevreul used the above procedures, along with various methods of purification for substances with animal origins, to identify several of the fatty acids as pure substances with consistent molecular formulas.

melting point: temperature at which a substance in the solid state undergoes a phase change to the liquid state

elemental analysis: determination of the percent of each kind of atom in a specific molecule

lipid: a nonpolar organic molecule; fatlike; one of a large variety of nonpolar hydrophobic (water-hating) molecules that are insoluble in water

Chevreul also contributed to the improvement of the ancient art of soap making. He identified soaps as the potassium salts of the fatty oleic and

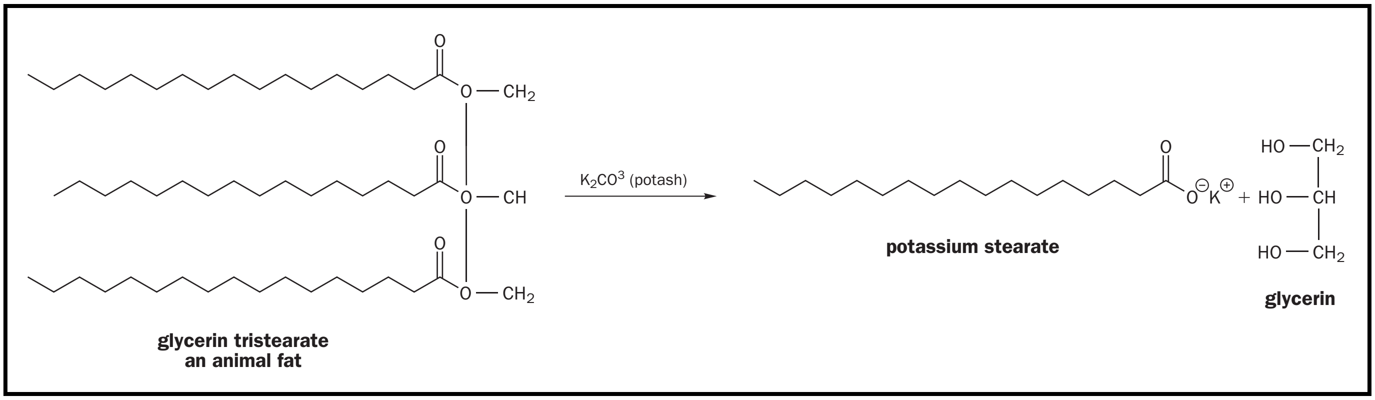

Figure 1. The saponification reaction.

stearic acids and animal fats from which soaps were derived as **esters** of the alcohol glycerol. This led to the replacement of potassium carbonate (**potash**) in soap manufacture with the cheaper and more reactive sodium hydroxide (lye), which became available commercially in the early 1800s. The reaction for the manufacture of soap, saponification, is shown in Figure 1. SEE ALSO Fats and Fatty Acids; Soap.

ester: organic species containing a carbon atom attached to three moieties: an O via a double bond, an O attached to another carbon atom or chain, and an H atom or C chain; a compound with the general formula RC(O)OR′

potash: the compound potassium oxide, K_2O

Lawrence H. Brannigan

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Chirality

The term "chiral" (from the Greek for "hand") is applied to molecular systems whose asymmetry results in handedness; that is, the existence of a pair of nonsuperimposable mirror-image shapes (as illustrated by the relationship between one's right and left hands). Lord Kelvin coined the term "chirality" in 1884, (Eliel, p. 4) but it did not come into common usage until the 1960s. Many macroscopic examples of handed systems exist, including any object that features an inherent spiral or twist that can exhibit a left- and right-handed form: scissors, spiral staircases, screw threads, gloves, and shoes. Some mineralogical materials exhibit handedness in the solid state. In 1801 the crystallographer René-Just Haüy (1743–1822) observed that there were right- and left-handed quartz crystals, a phenomenon known as hemihedrism. The term "enantiomorphous" ("in opposite shape") was created to describe the macroscopic relationships between nonsuperimposable, mirror-image crystalline forms.

Optical Activity

The concepts of three-dimensional isomerism, or stereochemistry, resulted from the proposition of molecular chirality. In 1812 Jean-Baptiste Biot

(1774–1862), a physicist and a crystallographer, observed optical activity in mineralogical samples such as quartz, in which an asymmetrical crystalline form was macroscopically observable. In 1815 Biot also observed optical activity in samples of certain liquids, such as turpentine, various essential oils, and solutions of substances such as sugar and camphor. Because both pure liquids and solutions of organic compounds exhibit optical activity, the property could not be attributed to a characteristic of the solid state but instead had to be attributed to the molecular structure. In 1848 Louis Pasteur (1822–1895) separated an optically inactive sample of a tartaric acid salt into **optically active** dextrorotatory and levorotatory components by physically segregating the enantiomorphous crystalline forms. He showed that what had been thought to be a pure substance (racemic acid) was a mixture of two compounds: the natural, dextrorotatory tartaric acid and a substance that, although identical to the first compound identified in all of its other chemical properties, was yet opposite in its solid state structure and in its observed rotation of polarized light. In 1860 Pasteur proposed that molecular structural asymmetry was the basis for these observations. Jacobus van't Hoff (1852–1911) and Joseph-Achille Le Bel (1847–1930) independently proposed, in 1874, that molecular asymmetry and its consequences on isomerization could be explained if the arrangement (configuration) of the groups on a tetravalent atom was tetrahedral. Macroscopically or microscopically, a tetrahedral array of four different things gives rise to two and only two different arrangements that have a nonsuperimposable mirror-image (enantiomorphic) relationship (see Figure 1). In the case of molecular structures, these two shapes would be examples of enantiomers.

optically active: capable of rotating the plane of plane-polarized light

Representing Chiral Geometry

Asymmetrical atomic centers giving rise to stereoisomers have been known as chiral centers, although the more general terms "stereocenter" and "stereogenic center" have come into common usage since the 1980s. Asymmetrical tetrahedral atoms are only one example of what is meant by a stereocenter because the definition of the term encompasses a larger territory of structural characteristics. Over the years, a variety of representations have been used to depict the three-dimensionality of stereocenters. The representations in Figure 2 all depict the same sense of chirality for one of the two mirror-image arrangements (enantiomers) of 2-bromobutane.

Molecular Chirality

Chirality is a term that can be applied to molecular mixtures as well as to individual molecular species. Mixtures of chiral molecules can range from having 100 percent of the sample representing the same sense of asymmetry

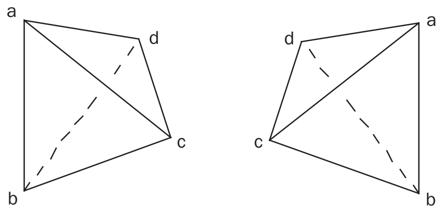


Figure 1. Nonsuperimposible mirror image arrangements for tetrahedra.

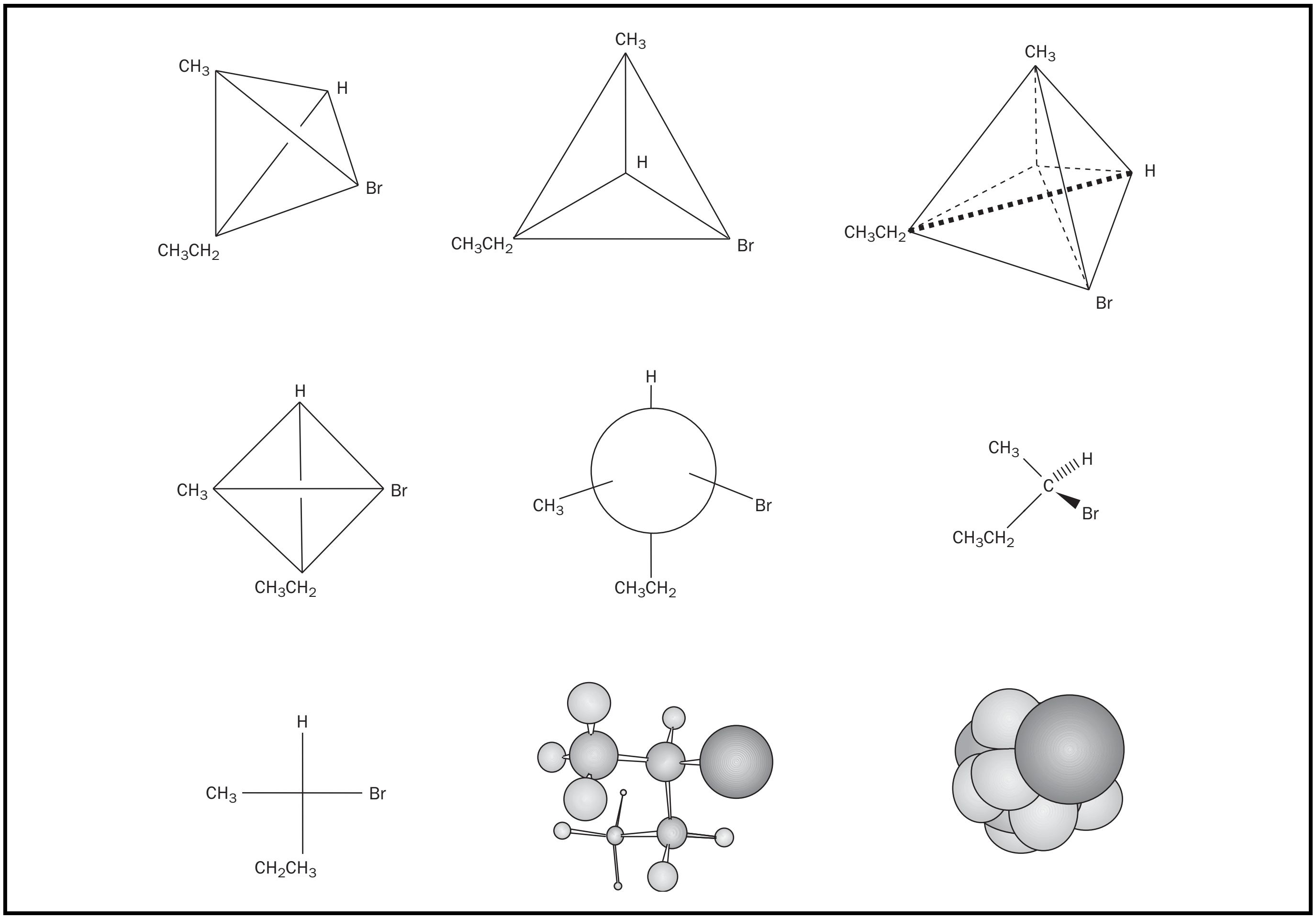


Figure 2. Representations for the three-dimensional geometry of a 2-bromobutane isomer.

(in which case the sample is a collection of homochiral molecules) to equal representation by molecules and their mirror-image isomers (in which case the sample is heterochiral or racemic), or any distribution inbetween (heterochiral and nonracemic). Extended tetrahedra (see bottom of Figure 3) are representative of molecules with an axis of chirality rather than a center of chirality. Molecular chirality results from one degree or another of twisting within a molecular structure, whereby a "turn to the left" can be distinguished from a "turn to the right." Even a simple stereocenter or an allene, when viewed from a certain perspective, presents a molecular twist that emerges as a common theme in the three-dimensional structure of chiral geometries (see Figure 3).

Restricted rotation in biphenyls (see Figure 4) creates another example of molecular chirality, which is called atropisomerism (literally "not turning," a reference to the restricted rotation). In other cases, the overall molecular architecture causes a twist of one sense or another to form. In helicenes, the simple interconversion realized by having one end of the molecule move past the other is restricted, and this results in isolatable chiral substances (see Figure 5). Different molecular geometries resulting from the bond rotations in butane, on the other hand, interconvert on a fast timescale at extremely low temperatures. The three staggered geometrical forms for rotation about the C2–C3 bond in butane are shown in Figure 6. Two of

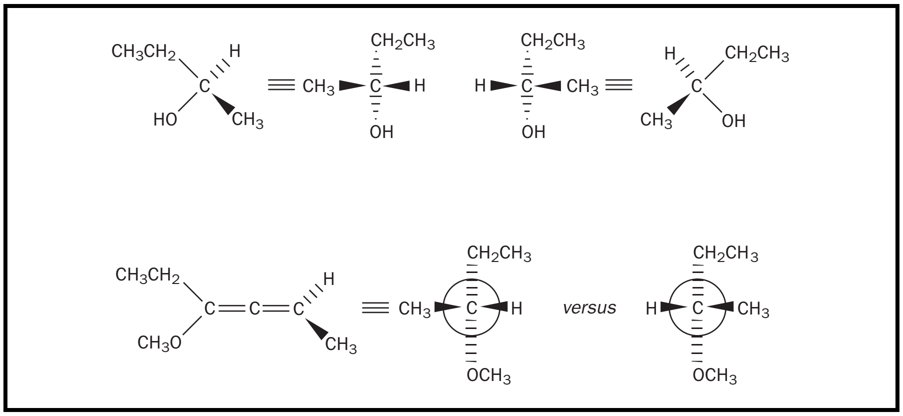


Figure 3. Examples of molecular twists present in chiral substances.

the conformational isomers of butane are chiral whereas the third is not. Molecular chirality can be examined by considering the definition. A molecular geometry that results in the possibility of a nonsuperimposable mirror image is chiral, but a superimposable mirror image renders the object achiral. The third conformational isomer shown in Figure 6 has a mirror plane of symmetry and a superimposable mirror image. It is achiral.

Stereoisomers: Enantiomers and Diastereomers

The two categories into which stereoisomers can be placed are absolutely distinctive in definition. Two stereoisomers that have a nonsuperimposable mirror-image relationship are called enantiomers. The only other category is defined negatively. Stereoisomers that are not enantiomers are called diastereomers (see Figure 7).

Molecules with a single stereocenter as the only source of configurational stereoisomerism can exist as one of two enantiomers; no configurational diastereomers are possible. Conformational stereoisomers, on the other hand, are most commonly diastereomeric. Molecules with two dissimilar stereocenters as the source of stereoisomerism can exist as one of

Figures 4, 5, and 6.

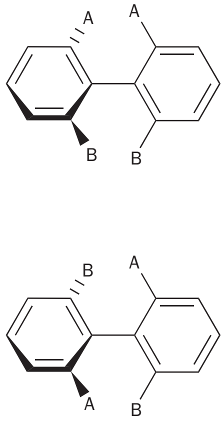


Figure 4. Biphenyl

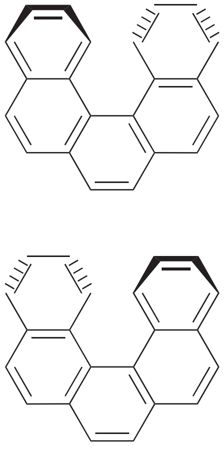


Figure 5. Helicene

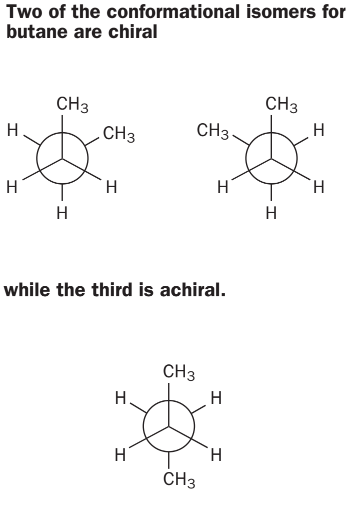


Figure 6. Butane

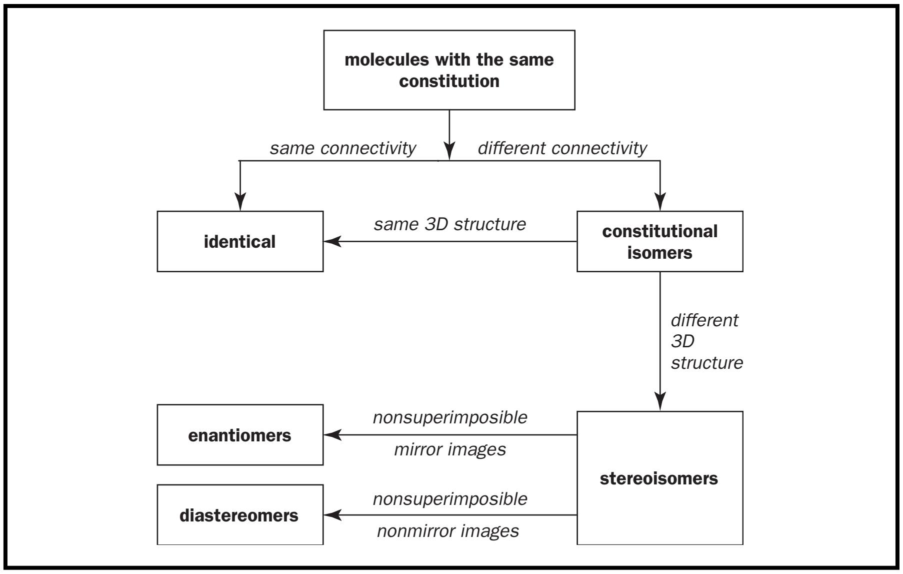
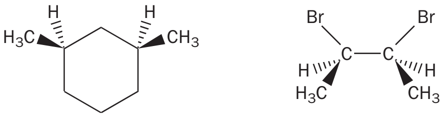


Figure 7. Schematic relationship between isomers.

four stereoisomers. Figure 8 outlines the relationships among these four stereoisomers.

As the number of stereocenters in a molecule increases, the number of possible diastereomers increases. A molecule with four dissimilar stereocenters, for example, can exist as one of sixteen stereoisomers. Of these sixteen stereoisomers there are four pairs of enantiomers, and the remaining four pairs are diastereomers. Molecules with configurational diastereomers also arise from many systems other than those with stereocenters. One of the most common examples is a double bond that is substituted in such a way that diastereomers exist. Any combination of two or more molecular features that give rise to stereoisomers will always produce diastereomers, whereas sources of chirality are needed to produce enantiomers. Because stereochemistry can have a high impact on molecular properties, diastereomers generally have easily discernable differences in their physical and chemical behaviors. Some molecules possess greater than or equal to two tetrahedral stereocenters and are nonetheless achiral. These are called meso stereoisomers. These occur when the internal symmetry of the molecule makes it superimposable on its mirror image.



Distinguishing Enantiomers

From 1874 to 1951 there was no experimental method that could be used to distinguish one enantiomeric form from the other. The physical property of optical activity formed the first basis on which labels were made. Naturally occurring (+)-glyceraldehyde [$HOCH_2CH(OH)CHO$] was usually used as the point of reference. Whatever its actual three-dimensional geometry, natural (+)-glyceraldehyde was assigned the designation (D), which stood for the configuration of dextrorotatory glyceraldehyde, and not for its optical rotation, which was designated as *d*- or (+). Optically active

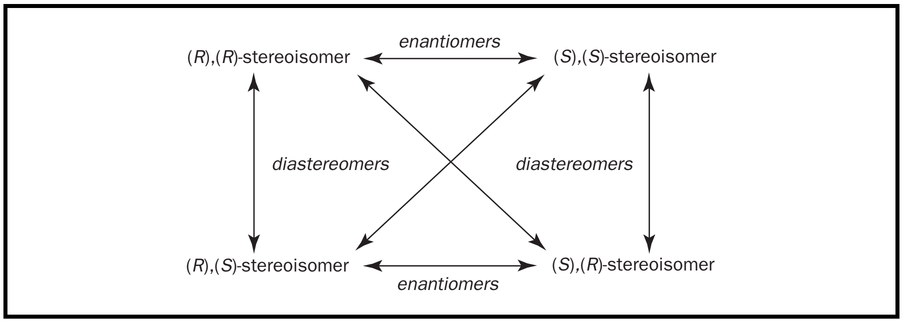


Figure 8. Schematic relationships for molecules with two different stereocenters.

molecules with single stereocenters of unknown configuration were, by precise chemical transformations, derived from or transformed into (D)-(+)-glyceraldehyde. In 1951 J. M. Bijvoet, A. F. Peerdeman, and A. J. van Bommel showed, using x-ray crystallography, that the absolute arrangement of atoms in space for sodium rubidium tartarate could be determined.

Enantiomers, and handed objects in general, can be distinguished only in a chiral environment. While a table-top (an achiral environment) interacts equally well with a left- or a right-handed glove, your own left hand (a chiral environment) can distinguish between these two chiral objects extremely easily. Plane-polarized light is comprised of equal intensities of right- and left-handed (hence, chiral) components. The interactions between these two components with inherently asymmetrical substances are unequal and give rise to the phenomenon of optical activity. In biochemical systems, enzymes represent a common chiral environment that can distinguish one enantiomeric form from another. Olfactory **receptor** sites and taste buds are also thought to be chiral because there are many examples of enantiomeric substances that can be distinguished by them. The two carvone enantiomers are the primary odor constituents of caraway and spearmint. Most of the naturally occurring amino acids are bitter tasting, whereas their enantiomers are sweet. In an achiral environment, the interactions and interactional energetics for enantiomers are identical and cannot be distinguished.

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

Separating Enantiomers

The majority of naturally occurring (plant and animal) substances for which stereoisomers are possible exist in nature as single enantiomers. The biochemical pathway used by one's body to synthesize cholesterol results in forming only a single stereoisomer, even though its connectivity represents a total of 128 possible stereoisomers. Because laboratory chemical reactions are not usually conducted in chiral environments, they will produce 1:1 (racemic) mixtures of enantiomers. Because only one enantiomer of a pharmaceutical (drug) is likely to be therapeutically active, chemists have devised strategies for preparing chemical compounds of only one enantiomer. These strategies are: (1) physical separation by temporarily converting the two enantiomers into two diastereomers (called resolution); (2) physical separation in a chiral **chromatographic** environment; (3) chemical discrimination in a chiral environment (using enzymes or other chiral platforms as chemical **reagents**); and (4) asymmetric **synthesis** of one enantiomer in preference to the other. Asymmetric chemical synthesis is extremely important because it allows chemists

chromatography: the separation of the components of a mixture in one phase (the mobile phase) by passing it through another phase (the stationary phase) making use of the extent to which the various components are absorbed by the stationary phase

reagent: chemical used to cause a specific chemical reaction

synthesis: combination of starting materials to form a desired product

to produce new chiral drug candidates, such as single enantiomers of non-naturally occurring amino acids. SEE ALSO Isomerism; Le Bel, Joseph-Achille; Pasteur, Louis; van't Hoff, Jacobus.

Brian P. Coppola

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17
Cl
CHLORINE
35.453

Chlorine

MELTING POINT: −101.5°C
BOILING POINT: −34°C
DENSITY: 3.214 g/cm^3 (liq. at 0°C)
MOST COMMON IONS: Cl^{1-}, Cl^{1+}, Cl^{3+}, Cl^{5+}, Cl^{7+}

Chlorine is one of the **halogen** family of elements and the first of that family to be discovered. Swedish chemist Carl Wilhelm Scheele produced chlorine in 1774 by the reaction of manganese dioxide (MnO_2) with a solution of hydrochloric acid (HCl). In 1810 English chemist Sir Humphry Davy determined chlorine to be an element and named it for the color of the gas (the Greek word *chloros* means "pale green").

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

Elemental chlorine is a diatomic molecule and is toxic. It has a high electronegativity that is about equal to that of oxygen. The most common **oxidation** numbers are 7, 5, 3, 1, and −1.

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

Chlorine is the most abundant of the halogens having a concentration of 19.87 parts per thousand (ppt) by weight in seawater and an average of 0.17 ppt in Earth's crust. It is produced commercially by electrolysis of seawater and brines. Sodium chloride (NaCl), or common table salt, can be obtained from seaside evaporation pools or mined from underground deposits.

Chlorine and its compounds have a large number of everyday uses. Chlorine is used in water purification as well in the production of safe plumbing components constructed of polyvinyl chloride (PVC). Chlorinated dyes, medicines, pesticides, disinfectants, and solvents have widespread applications. **Chlorofluorocarbon** compounds (CFCs) were once widely used as refrigerants, solvents, foaming agents, and spray-can propellants, but are now banned by international agreement due to the role of those compounds in the depletion of Earth's protective ozone layer. Chlorine was used during World War I (1914–1918) as a chemical warfare agent. SEE ALSO Bleaches; Davy, Humphry; Scheele, Carl.

chlorofluorocarbon (CFC): compound that contains carbon, chlorine, and fluorine atoms; it removes ozone in the upper atmosphere

John Michael Nicovich

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Cholecalciferol

Cholecalciferol is known as **vitamin** D_3. As early as 1870 people knew there was something in cod-liver oil that prevented rickets, a disease resulting in soft, deformed bones as a result of calcium deficiency. Sir Edward Mellanby contributed significantly to the understanding of the role of vitamin D: "It was in 1919/20," cites a University of California study, "that Sir Edward Mellanby, working with dogs raised exclusively indoors (in the absence of sunlight or ultraviolet light), devised a diet that allowed him to unequivocally establish that the bone disease rickets was caused by a deficiency of a trace component present in the diet." Mellanby is also credited with confirming that cod-liver oil could provide the missing vitamin. Calciferol was the second vitamin discovered that is soluble in fat; vitamin A was the first.

vitamins: molecules needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

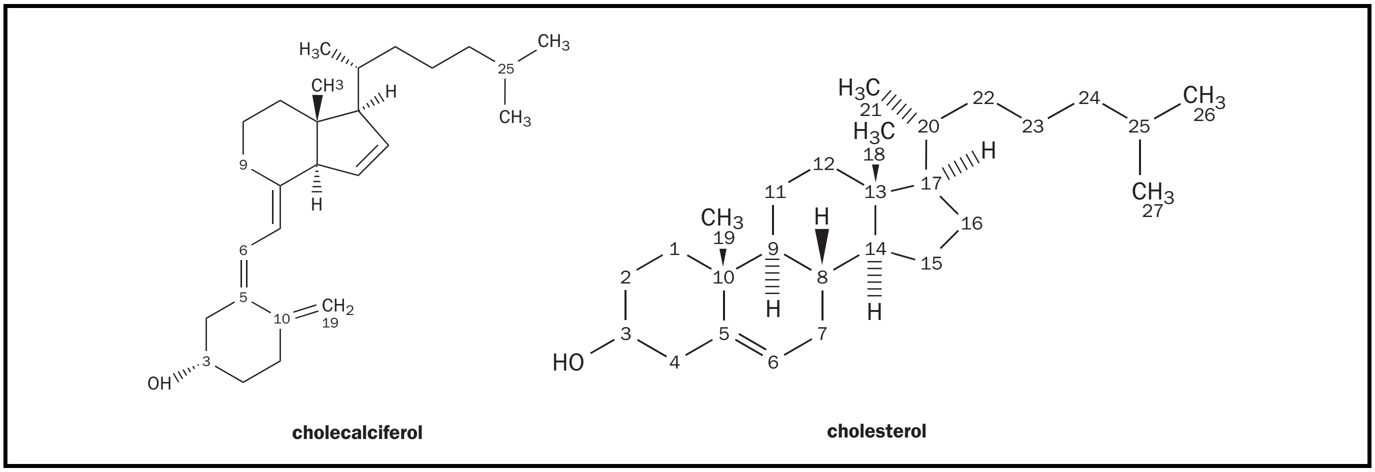
Normally, it would seem unusual to expose food to ultraviolet (UV) radiation before trying to isolate a nutrient, but starting in the 1890s reports indicated that once exposed to high levels of sunshine, humans were unlikely to develop rickets. Scientists now know that UV exposure is essential for the body to produce cholecalciferol from cholesterol. See Figure 1 for the structures of cholesterol and cholecalciferol. Cholesterol is the steroid **lipid** often associated with heart disease when too much is present; small amounts of cholesterol are needed to make cholecalciferol and a host of other steroid hormones. Since humans can manufacture all the cholecalciferol needed for good health from exposure to sunshine, vitamin D is commonly referred to as the sunshine vitamin.

lipid: a nonpolar organic molecule; fatlike; one of a large variety of nonpolar hydrophobic (water-hating) molecules that are insoluble in water

Vitamin D is involved in phosphorous and calcium **metabolism**. Cholecalciferol is converted into compounds that are directly involved in the absorption of calcium by the intestines. As with many steroid compounds, when cholecalciferol breaks down in the body, the resulting molecules are carried into the nucleus of certain cells and determine or change which genes are turned on or off. Recent reports suggest that the steroid hormone character of vitamin D may provide some anticancer activity.

metabolism: all of the biochemical processes that take place within living organisms; comprises processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those which break down complex food molecules, thus liberating energy (catabolism)

Figure 1. Structures of cholecalciferol and cholesterol.



To help prevent vitamin D deficiency, most milk is now enriched with it. Other good sources of the vitamin are meat, poultry, fish, peanut butter, eggs, margarine, and liver, especially cod-liver oil. These sources exist in addition to the vitamin D produced naturally from exposure to sunshine. Unlike water-soluble vitamins, such as vitamin C, fat-soluble vitamins are stored in the liver and fat tissue and can become highly toxic if taken in excess. For these reasons, most nutrition experts do not generally recommend additional dietary supplements for vitamin D. Some individuals taking special medication for cholesterol, or who have dark skin (which reduces the ability of sunshine to produce vitamin D), may require a diet rich in vitamin D or a supplement. SEE ALSO CALCIUM; CHOLESTEROL.

David Speckhard

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Cholesterol

Cholesterol is the most abundant sterol in animal tissues, making up as much as 25 percent of cell membranes. Cholesterol may be found free or as part of cholesteryl **esters**. It is a **precursor molecule** for many steroid hormones, including **glucocorticoids**, **androgens** and **estrogen**, aldosterone, and mineralocorticoids. A major component of lipoproteins, it is also the precursor for bile salts and bile acids, which are necessary for digestion. Gallstones contain large amounts of cholesterol.

Cholesterol is a seventeen-carbon polycyclic compound made up of three six-membered and one five-membered fused rings. The molecule is relatively **nonpolar** and **hydrophobic**, but is slightly polar due to the presence of an alcohol **functional group**.

Plants contain no cholesterol. In animals cholesterol **synthesis** occurs in many cells, but most cholesterol synthesis occurs in the liver. Food products from animals contain cholesterol, and the average adult consumes around 450 milligrams (0.016 ounces) per day. Dairy products and egg yolks are particularly rich in cholesterol. Diets low in fat content and high in vegetables, especially those containing polyunsaturated **lipids**, can help to lower plasma cholesterol levels. Many physicians recommend that their patients try to maintain cholesterol levels below 200 milligrams per deciliter.

Cholesterol in blood plasma is conjugated with other lipid molecules and with carrier proteins. These lipoprotein complexes may form droplets called chylomicrons, but cholesterol is usually transported as part of a number of larger lipoproteins, including low density lipoprotein (LDL), which carries cholesterol from the liver to muscle and other tissues, and high density lipoprotein (HDL), which carries cholesterol to the liver for conversion to bile acids. Physicians are especially concerned when patients have high levels of LDL (the so-called bad cholesterol) in blood; moderate exercise and

ester: organic species containing a carbon atom attached to three moieties: an O via a double bond, an O attached to another carbon atom or chain, and an H atom or C chain; a compound with the general formula RC(O)OR^1

precursor molecule: molecule that is the chosen starting point for the preparation of another molecule; a starting molecule in a chemical synthesis; a reactant molecule

glucocorticoid: class of hormones that promotes the breakdown of proteins to make amino acids available for gluconeogenesis; this elevates the blood sugar level and leads to glycogen synthesis in the liver

androgen: group of steroids that act as male sex hormones

estrogen: female sex hormone

nonpolar: molecule, or portion of a molecule, that does not have a permanent, electric dipole

hydrophobic: relating to a region of a molecule that will, in solution with water, tend to be in contact with few water molecules; if an entire molecule is hydrophobic, it will not dissolve in water

functional group: portion of a compound with characteristic atoms acting as a group

synthesis: combination of starting materials to form a desired product

lipid: a nonpolar organic molecule; fatlike; one of a large variety of nonpolar hydrophobic (water-hating) molecules that are insoluble in water low-cholesterol diets help to increase HDL (the so-called good cholesterol). Either high fat intake or problems with the transport of cholesterol to and from cells can lead to atherosclerosis (hardening of the arteries), which in turn can contribute to heart attack (myocardial infarction) or stroke.

Humans do not oxidize cholesterol for energy. Instead, cholesterol is converted to bile acids such as cholic acid and deoxycholic acid in liver tissue. Bile acids and salts are secreted into bile, which passes into the intestine and emulsifies fats for digestion. Although some bile acids may be reabsorbed in the intestine along with lipids, much cholesterol leaves the body in feces in the form of **metabolites** such as bile acids and salts.

metabolites: products of biological activity that are important in metabolism

Diets rich in oatmeal or other vegetable products are believed to help to lower plasma cholesterol levels. Soluble fibers from the vegetable materials absorb cholesterol and help to prevent absorption in the intestine. SEE ALSO LOW DENSITY LIPOPROTEIN; STEROIDS.

Dan M. Sullivan

Chromium

MELTING POINT: 1,860°C
BOILING POINT: 2,670°C
DENSITY: 7.19 g/cm^3
MOST COMMON IONS: Cr^{2+}, Cr^{3+}, CrO_4^{2-}, $Cr_2O_7^{2-}$

24
Cr
CHROMIUM
52.00

Chromium was first identified in 1797 by the French chemist Louis-Nicolas Vauquelin, who isolated it from crocoite, a mineral also called Siberian red lead. The name for chromium is taken from the Greek *chroma*, which means "color." This is a fitting name, because chromium compounds are often found in vividly colorful shades of green, red, or yellow. As such, chromium compounds historically have found extensive use as pigments for paints. In contrast, elemental chromium is a shiny, hard, yet brittle, steel-gray **metal**. Since chromium is not found naturally in its free elemental state, it is usually extracted from chromite, $FeCr_2O_4$.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Perhaps the best-known use of chromium is as a decorative, protective, shiny plating over other metals, with chrome-plated automobile parts being a familiar example. Chromium is also an important **alloy** component in stainless steel because it makes the steel stronger and more corrosion-resistant. Paint pigments account for more than one-third of all chromium usage each year.

alloy: metallic mixture of two or more elements, at least one of which is a metal

Overall, chromium is the twenty-first most abundant element in Earth's crust. It is usually found in the +2 (e.g., CrO), +3 (e.g., Cr_2O_3), or +6 (e.g., $K_2Cr_2O_7$) **oxidation** states, with chromic oxide, Cr_2O_3, being the ninth most abundant compound in Earth's crust. While chromium is considered a necessary micronutrient in human diets, many of its compounds are quite toxic. This is especially true of chromium in the +6 oxidation state, with compounds such as $K_2Cr_2O_7$ being identified as carcinogens. Thus chromium compounds should be handled carefully.

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

David A. Dobberpuhl

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Chromosome

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

eukaryotic: relating to organized cells of the type found in animals and plants

prokaryotic: relating to very simple cells of the type found in bacteria

A chromosome is a compactly folded complex of **DNA** and proteins containing many genes, found in the nuclei of **eukaryotic** organisms and in the nucleoids of **prokaryotic** organisms.

Each cell in an organism has a complete set of genetic information called a genome. Different organisms have different numbers of chromosomes in their genomes, ranging from a single chromosome in most bacteria to seventy-eight chromosomes in chickens. Humans cells have forty-six chromosomes, but these represent two sets of information as humans are diploid organisms; each cell has one information set inherited from the organism's mother and a second set inherited from its father. If an offspring inherits one X chromosome and one Y chromosome, he will be genetically male. If an offspring inherits X chromosomes from both parents, she will be genetically female.

code: mechanism to convey information on genes and genetic sequence

Chromosomes consist of two kinds of molecules, deoxyribonucleic acid (DNA) strands and proteins. Chromosomes from eukaryotic organisms have linear DNA strands containing approximately fifty genes per millimeter, compared to 2,500 genes per millimeter in bacteria. Some of the noncoding DNA (DNA that does not **code** for proteins) is found in special structures at the ends of the chromosomes called telomeres. Much of the noncoding DNA in eukaryotic chromosomes may be involved in compacting the DNA into the highly organized chromosome structure. Some of this DNA has highly repetitive sequences and has been useful in forensic analysis.

Proteins help to compact DNA: this is important because the DNA in a chromosome could not fit inside its cell if it were not compacted. Histones are positively charged proteins that neutralize negative DNA strands when they wrap around and form complexes with the DNA. This wrapped structure, called "beads on a string," represents the first level of compaction. The "beads" are condensed to form fibers, fibers fold into loops, loops combine with nuclear scaffold proteins to form rosettes, and rosettes condense to form coils. Finally, a chromatid with ten or more coils is formed. Nonhistone proteins within chromosomes are also important. These proteins have varied functions, including assisting in the unwinding of DNA and in the repairing of DNA.

Chromosomes from prokaryotic organisms have DNA strands that loop and form circles. The DNA in prokaryotic chromosomes forms complexes with histone like proteins that help to compact the DNA, link it to the cell membrane, and localize it in the nucleoid region of the cell. Some bacteria have extra chromosomal DNA—a mini-chromosome called a plasmid. Plasmids contain only a few genes but are rapidly exchanged among cells of a bacteria population. Plasmids have become useful tools in biotechnology and genetic engineering.

Recombination is a natural process of exchange of fragments of DNA strands between paired chromosomes, which happens occasionally during cell division. Genetic engineering techniques allow scientists to cut and paste DNA fragments from one source to another to produce recombinant chromosomes and transgenic organisms. SEE ALSO DNA REPLICATION; GENES; GENOME; PROTEINS.

David Speckhard

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Cleve, Per Theodor

SWEDISH CHEMIST
1840–1905

Per Theodor Cleve was a nineteenth-century expert in agricultural chemistry, inorganic and organic chemistries, geology, mineralogy, and oceanography.

Cleve's early schooling was in Stockholm, and after passing final examinations he went to Uppsala, Sweden, to study mineralogy and other sciences. Cleve earned a master's degree (M.Sc.) at the age of twenty-two years and completed his doctorate (Ph.D.) just one year later. During these years he received several travel grants that enabled him to visit laboratories in France, England, Italy, and Switzerland.

Some milestones of Cleve's teaching career at Uppsala University are: In 1860 the twenty-year-old student was appointed assistant professor in mineralogy; in 1863, at the age of twenty-three, he was named assistant professor in organic chemistry; and a year later he became professor of general chemistry and agricultural chemistry.

In Paris Cleve visited the research laboratory of chemist Charles-Adolphe Wurtz (1817–1884). The laboratory was unique in Europe in its attraction of young chemists, and here Cleve made many friends. Wurtz drew Cleve's attention to complex **metal** compounds. At age twenty-one Cleve published his first research paper on a complex chromium compound he had prepared and analyzed. In this paper he demonstrated that the compound was chromium trichloride-ammonia-water (in a 1:4:1 ratio). He later turned to the study of complex platinum compounds, of which he prepared hundreds. In 1872 Cleve, now thirty-two years old, published the results of this study in the *Transactions of the Royal Swedish Academy of Sciences.*

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Cleve studied the group of elements known as the **lanthanide** elements. In 1879 he discovered two new lanthanide elements: holmium and thulium. The following year he undertook a thorough investigation of the newly discovered element scandium and proved that it had the properties predicted

lanthanides: a family of elements (atomic number 57 through 70) from lanthanum to lutetium having from 1 to 14 4f electrons

by Dimitri Mendeleev years earlier with his discovery of the periodic law and his publication of *The Periodic Table*.

Cleve's most celebrated work in organic chemistry was the preparation and characterization of the isomeric aminonaphthalenesulfonic acids, today called Cleve's acids.

Royal Society: The U.K. National Academy of Science, founded in 1660

In 1894 Cleve was awarded the Davy Medal by the **Royal Society** in London. SEE ALSO HOLMIUM; LANTHANIDES; MENDELEEV, DIMITRI; SCANDIUM; THULIUM.

Ole Bostrup

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Clones

mitosis: process by which cells divide, particularly the division of the cell nucleus

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

A clone is an organism or cell derived asexually (through **mitosis**) from a single ancestor cell. The genetic content of the newer cell (or of any individual cell of the organism) is identical to that of the ancestor cell. In biochemistry a clone is a replica of all or part of a macromolecule, for example, deoxyribonucleic acid (**DNA**).

invertebrate: category of animal that has no internal skeleton

in vitro: Latin, meaning "in glass" and applied to experiments done under artificial conditions, that is, in a test tube

in vivo: Latin, meaning "in life" and applied to experiments conducted in a living cell or organism

nuclear: having to do with the nucleus of a cell

The word "clone" originated in 1903 when it was proposed by Herbert J. Webber of the U.S. Department of Agriculture as a term to designate the offspring of plants propagated artificially (and asexually) via methods such as "rooting cuttings." Most clones occur naturally, as most organisms reproduce asexually. Most animals reproduce sexually, but many of the less complex **invertebrates** reproduce asexually, giving rise to clones. Currently, the terms "clone" and "cloning" are used in association with recent animal reproduction procedures (having both **in vitro** and **in vivo** stages) and the ability of scientists to alter the genetic makeup of organisms toward the greater benefit of humans in such areas as medicine and agriculture.

Reproductive cloning in higher animals, such as mammals, requires **nuclear** transfer, in which the entire genetic content of a cell is transferred to an embryonic cell that has been emptied of its genetic material. (Only 1 to 2 percent of these transfers are successful.) The most notable animal clone, the sheep Dolly, was born in 1997. She was the first animal to be cloned from the mature cell of another animal. Dolly was proof that a single, mature (fully differentiated) cell contains workable versions of all the genes necessary to produce an entire organism. In 2001 it was announced that human embryos, at the six-cell stage, had been produced via nuclear transfer.

expressed: in biochemistry—copied

Therapeutic cloning can involve recombinant DNA technology or molecular cloning. A segment of DNA from one organism (a vector) is introduced into the DNA of a second organism, yielding a hybrid or recombinant DNA molecule. The hybrid DNA molecule is then introduced into a host organism, in which it can be rapidly replicated and **expressed** to produce proteins of commercial or medical importance. The first such protein to be marketed commercially was human insulin, which is a small protein, having fewer than 100 amino acids, and which was "manufactured" in *Escherichia*

Two calves cloned from cells in cow's milk, Japan.

coli bacteria (the host organism). The first agricultural protein made from recombinant DNA, bovine growth hormone, was approved for use in 1994 and is given to approximately 25 percent of cows in the United States (its use is banned in the European Union). Other recombinant DNA products used in medicine include tissue plasminogen activator (TPA), used as an **anticoagulant** in the treatment of heart attack and stroke victims; factor VIII, a blood coagulant deficient in hemophiliacs; human growth hormone; interferons, used in the treatment of cancer; interleukins; monoclonal **antibodies**; and vaccines, such as hepatitis B vaccine.

anticoagulant: molecule that helps prevent the clotting of blood cells

antibody: protein molecule that recognizes external agents in the body and binds to them as part of the immune response of the body

eukaryotic: relating to organized cells of the type found in animals and plants

Bacterial cells as host cells are not able to execute the read-out of many human genes and the genes of many other **eukaryotic** organisms, and eukaryotic host cells must be used. Animals that carry genetically engineered heritable genes are called transgenic. Transgenic animals have included lactating mammals such as sheep, goats, cows, and pigs. Most commonly an animal is engineered to produce a large quantity of a particular human protein in its milk. A widely used technique includes injecting a segment of DNA, human or animal, that contains the appropriate human gene (the DNA construct) into an embryo, and then implanting the embryo in a surrogate mother. If the technique is successful, the milk of the mature animal will contain active human protein in sufficient amounts to be of value. A herd of genetically engineered animals could then be produced using this technique, or possibly, eventually, via reproductive cloning.

Plant cells can also be used to mass-produce human proteins. Corn, soybean, and tobacco plants have been used in this way. The yield of protein from plants is generally higher than that from animals; however, human cells link carbohydrates to some antibodies, and these molecules cannot yet be produced in plants. Transgenic crops that are harvested for food are far more common than those used to produce human proteins.

Therapeutic cloning sometimes calls for the use of human stem cells. Stem cells are believed to be cells that have the potential to become any cell that exists in the mature organism; hence, it is felt that they might be used in the future to repair or even regenerate organs, such as the heart or pancreas, or portions of organs. Human stem cells were isolated in 1998. If a patient's stem cells were needed and were not available, cells from existing stem cell lines could be used, but in these cases, nuclear transfer would be required. This is presently legal in Britain but illegal in the United States. An alternative source would be generic stem cells combined with the administration to the patient of any necessary antirejection drugs. SEE ALSO GENES.

Vivienne A. Whitworth

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Coal

Coal, a naturally occurring combustible solid, is one of the world's most important and abundant energy sources. From its introduction 4,000 years ago as a fuel for heating and cooking, to its nineteenth- and twentieth-century use in generating electricity and as a chemical **feedstock**, coal, along with oil and natural gas, has remained an important source of energy. The United States alone has 1.7 trillion short tons of identified coal resources (natural deposits) and enough recoverable reserves (coal that can be developed for use) to meet its energy needs until the year 2225. Its demonstrated reserves include 274 billion short tons that existing technology can recover, representing 25 percent of the world's 1.08 trillion short tons of recoverable coal, and 508 billion short tons of coal that existing technology can potentially mine economically. Its recoverable reserves contain more than twice the energy of the Middle East's proven oil reserves. About 100 countries have recoverable reserves; 12 countries—among them Canada, the People's Republic of China, Russia, Poland, Australia, Great Britain, South Africa, Germany, India, Brazil, and Colombia—possess the largest reserves.

feedstock: raw materials necessary to carry out chemical reactions

Origin, Composition, and Structure of Coal

Geologists believe that underground coal deposits formed about 250–300 million years ago, when much of Earth was swamp covered with thick forest and plant growth. As the plants and trees died, they sank under Earth's wet surface, where insufficient oxygen slowed their decay and led to the formation of peat. New forests and plant life replaced the dead vegetation, and when the new forests and plants died, they also sank into the swampy ground. With the passage of time and accompanying heat buildup, underground lay-

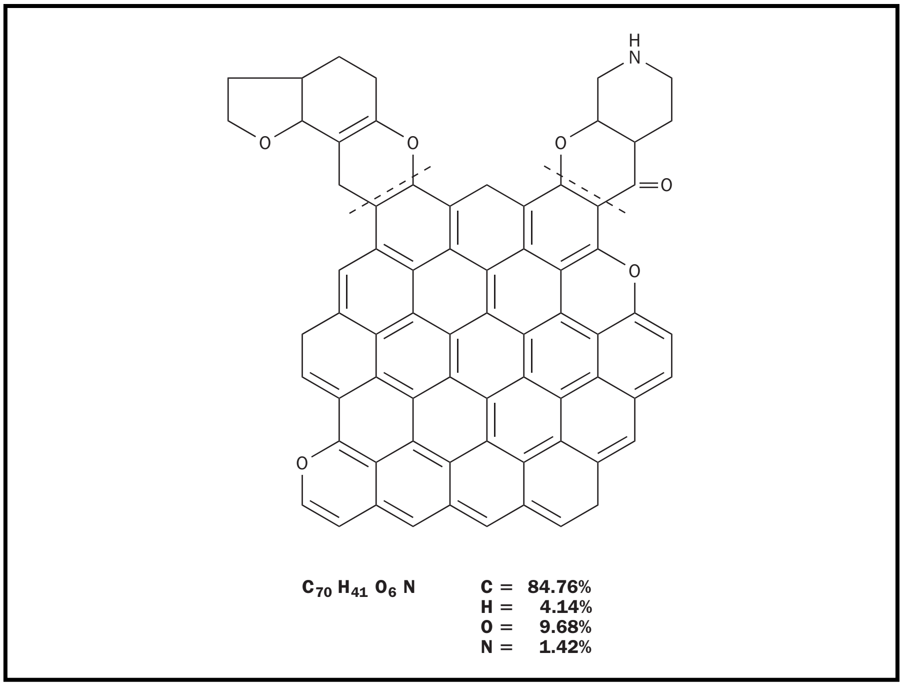

Figure 1. An example of the structure of coal.

ers of dead vegetation began to accumulate, becoming tightly packed and compressed, and gave rise to different kinds of coal, each with a different carbon concentration: anthracite, bituminous coal, subbituminous coal, and lignite. The English geologist William Hutton (1798–1860) reached this conclusion in 1833 when he found through microscopic examination that all varieties of coal contained plant cells and were of vegetable origin, differing only in the vegetation composing them. Because of its origin in ancient living matter, coal, like oil and gas, is known as a fossil fuel. It occurs in seams or veins in sedimentary rocks; formations vary in thickness, with those in underground mines 0.7–2.4 meters (2.5–8 feet) thick and those in surface mines, as in the western United States, sometimes 30.5 meters (100 feet) thick.

Until the twentieth century chemists knew very little about the composition and molecular structure of the different kinds of coal, and as late as the 1920s they still believed that coal consisted of carbon mixed with hydrogen-containing impurities. Their two methods of analyzing or separating coal into its components, destructive distillation (heating out of contact with air) and solvent extraction (reacting with different organic solvents such as tetralin), showed only that coal contained significant carbon, and smaller percentages of the elements hydrogen, oxygen, nitrogen, and sulfur. Inorganic compounds such as aluminum and silicon oxides constitute the ash. Distillation produced tar, water, and gases. Hydrogen was the chief component of the gases liberated, although ammonia, carbon monoxide and dioxide gases, benzene and other hydrocarbon vapors were present. (The composition of a bituminous coal by percentage is roughly: carbon [C], 75–90; hydrogen [H], 4.5–5.5; nitrogen [N], 1–1.5; sulfur [S], 1–2; oxygen [O], 5–20; ash, 2–10; and moisture, 1–10.) Beginning in 1910, research teams under the direction of Richard Wheeler at the Imperial College of Science and Technology in London, Friedrich Bergius (1884–1949) in Mannheim, and Franz Fischer (1877–1938) in Mülheim made important contributions that indicated the presence of benzenoid (benzenelike) compounds in coal. But confirmation of coal's benzenoid structure came only in 1925, as a result of the coal extraction and **oxidation** studies of William Bone (1890–1938) and his research team at Imperial College. The benzene tri-, tetra-, and other higher carboxylic acids they obtained as oxidation products indicated a preponderance of aromatic structures with three-, four-, and five-fused benzene rings, and other structures with a single benzene ring. The simplest structures consisted of eight or ten carbon atoms, the fused-ring structures contained fifteen or twenty carbon atoms.

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

Classification and Uses of Coal

European and American researchers in the nineteenth and early twentieth centuries proposed several coal classification systems. The earliest, published in Paris in 1837 by Henri-Victor Regnault (1810–1878), classifies types of coal according to their proximate analysis (determination of component substances, by percentage), that is, by their percentages of moisture, combustible matter, fixed carbon, and ash. It is still favored, in modified form, by many American coal scientists. Another widely adopted system, introduced in 1919 by the British scientist Marie Stopes (1880–1958), classifies types of coal according to their macroscopic constituents: clarain (ordinary bright coal), vitrain (glossy black coal), durain (dull rough coal), and fusain, also called mineral charcoal (soft powdery coal). Still another system is based on ultimate analysis (determination of component chemical elements, by percentage), classifying types of coal according to their percentages of fixed carbon, hydrogen, oxygen, and nitrogen, exclusive of dry ash and sulfur. (Regnault had also introduced ultimate analysis in his 1837 paper.) The British coal scientist Clarence A. Seyler developed this system in 1899–1900 and greatly expanded it to include large numbers of British and European coals. Finally, in 1929, with no universal classification system, a group of sixty American and Canadian coal scientists working under guidelines established by the American Standards Association (ASA) and the American Society for Testing Materials (ASTM) developed a classification that became the standard in 1936. It has remained unrevised since 1938.

The ASA–ASTM system established four coal classes or ranks—anthracite, bituminous, subbituminous, and lignite—based on fixed-carbon content and heating value measured in British thermal units per pound (Btu/lb). Anthracite, a hard black coal that burns with little flame and smoke, has the highest fixed-carbon content, 86–98 percent, and a heating value of 13,500–15,600 Btu/lb (equivalent to 14.2–16.5 million joules/lb [1 Btu=1,054.6 joules, the energy emitted by a burning wooden match]). It provides fuel for commercial and home heating, for electrical generation, and for the iron, steel, and other industries. Bituminous (low, medium, and high **volatile**) coal, a soft coal that produces smoke and ash when burned, has a 46–86 percent fixed-carbon content and a heating value of 11,000–15,000 Btu/lb (11.6–15.8 million joules/lb). It is the most abundant economically recoverable coal globally and the main fuel burned in steam turbine-powered electric generating plants. Some bituminous coals, known as metallurgical or coking coals, have properties that make them suitable for conversion to coke used in steelmaking. Subbituminous coal has a 46–60

volatile: low boiling, readily vaporized

Coal is one of the world's most abundant sources of energy.

percent fixed-carbon content and a heating value of 8,300–13,000 Btu/lb (8.8–13.7 million joules/lb). The fourth class, lignite, a soft brownish-black coal, also has a 46–60 percent fixed-carbon content, but the lowest heating value, 5,500–8,300 Btu/lb (5.8–8.8 million joules/lb). Electrical generation is the main use of both classes. In addition to producing heat and generating electricity, coal is an important source of raw materials for manufacturing. Its destructive distillation (carbonization) produces hydrocarbon gases and coal tar, from which chemists have synthesized drugs, dyes, plastics, solvents, and numerous other organic chemicals. High pressure coal hydrogenation or **liquefaction** and the indirect liquefaction of coal using Fischer–Tropsch syntheses are also potential sources of clean-burning liquid fuels and lubricants.

liquefaction: process of changing to a liquid form

Environmental Concerns

The major disadvantage of using coal as a fuel or raw material is its potential to pollute the environment in both production and consumption. This is the reason why many coal-producing countries, such as the United States, have long had laws that regulate coal mining and set minimum standards for both surface and underground mining. Coal production requires mining in either surface (strip) or underground mines. Surface mining leaves pits upon coal removal, and to prevent soil erosion and an unsightly environment, operators must reclaim the land, that is, fill in the pits and replant the soil. Acid mine water is the environmental problem associated with underground mining. Water that seeps into the mines, sometimes flooding them, and atmospheric oxygen react with pyrite (iron sulfide) in the coal, producing acid mine water. When pumped out of the mine and into nearby rivers, streams, or lakes, the mine water acidifies them. Neutralizing the mine water with lime and allowing it to settle, thus reducing the presence of iron pyrite before its release, controls the acid drainage.

combustion: burning, the reaction with oxygen

acid rain: precipitation that has a pH lower than 5.6; term coined by R. A. Smith during the 1870s

Coal **combustion** emits sulfur dioxide and nitrogen oxides, both of which cause **acid rain**. Several methods will remove or reduce the amount of sulfur present in many coals or prevent its release into the atmosphere. Washing the coal before combustion removes pyritic sulfur (sulfur combined with iron or other elements). Burning the coal in an advanced-design burner known as a fluidized bed combustor, in which limestone added to coal combines with sulfur in the combustion process, prevents sulfur dioxide from forming. Scrubbing the smoke released in the combustion removes the sulfur dioxide before it passes into the atmosphere. In a scrubber, spraying limestone and water into the smoke enables the limestone to absorb sulfur dioxide and remove it in the form of a wet sludge. Improved clean coal technologies inject dry limestone into the pipes leading from the plant's boiler and remove sulfur dioxide as a dry powder ($CaSO_3$) rather than a wet sludge. Scrubbing does not remove nitrogen oxides, but coal washing and fluidized bed combustors that operate at a lower temperature than older plant boilers reduce the amount of nitrogen oxides produced and hence the amount emitted.

chlorofluorocarbon (CFC): compound that contains carbon, chlorine, and fluorine atoms; it removes ozone in the upper atmosphere

Clean coal technologies and coal-to-liquid conversion processes have led to cleaner burning coals and synthetic liquid fuels, but acid rain remains a serious problem despite society's recognition of its damaging effects since 1852. Global warming resulting from the emission of the greenhouse gases, carbon dioxide, methane, and **chlorofluorocarbons**, is another coal combustion problem that industry and government have largely ignored since 1896, but it can no longer be avoided without serious long-term consequences.

Conclusion

Coal remains the world's most abundant fossil fuel, and along with petroleum and natural gas, it will continue to provide most of the world's energy. But all three are finite resources, and society should consume them wisely, not wastefully, in order to extend their lifetimes and reduce their harmful emissions. The conservation of fossil fuels and the development of alternative energies, such as solar and wind power, are pathways to a global society's cleaner energy future. SEE ALSO Fossil Fuels; Global Warming; Steel.

Anthony N. Stranges

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Cobalt

27
Co
COBALT
58.933

MELTING POINT: 1,495°C
BOILING POINT: 2,870°C
DENSITY: 8.9 g/cm^3
MOST COMMON IONS: Co^{2+}, Co^{3+}

The name "cobalt" derives from the German word *Kobold*, meaning "mischievous spirit." Cobalt was first applied by sixteenth-century copper miners in the Hartz mountains of central Europe to gray metallic ores; this not only failed to produce copper when roasted, but also emitted dangerous fumes. It was found that the ores, after elimination of sulphur and **arsenic** by roasting, could be fused with sand to produce a blue glass called smalt. The source of the blue color, however, was not established until 1742, when Swedish chemist Georg Brandt isolated the previously unidentified **metal** cobalt.

arsenic: toxic element of the phosphorus group

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Unlike its neighbors in the Periodic Table, iron, nickel, and copper, cobalt is not widespread in nature. It has an average abundance in Earth's crust of 25 parts per million (ppm); in ultrabasic rocks, where cobalt is most common, the average concentration is 110 ppm. Cobalt minerals may be concentrated by a range of geological processes to produce workable ores that typically contain 1,000–2,000 ppm.

Thirty-four cobalt minerals have been recognized, principally sulphides, selenides, arsenides, sulfarsenides, carbonates, sulfates, and arsenates. The main ore minerals are the sulfides linnaeite, carrolite, and cobaltiferous pyrite; the arsenides skutterudite and safflorite; the sulfosalt cobaltite; and the oxides asbolite (cobalt wad) and erythrite.

Cobalt has a wide range of industrial applications stemming from its variable **oxidation** states, color, and ability to form complexes. Its chief use, accounting for 45 percent of world demand, is in chemicals, particularly those used in catalysts, pigments, medical and agricultural agents, and nickel-cadmium (Ni-Cd) rechargeable batteries. Cobalt also has extensive metallurgical applications, including superalloys and other high temperature, erosion- and corrosion-resistant alloy steels. SEE ALSO MAGNETISM.

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

C. Graham Smith

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Codon

The genetic **code** (which includes the codon) serves as a basis for establishing how genes encoded in **DNA** are decoded into proteins. A critical interaction in protein **synthesis** is the interaction between the codon in messenger **RNA** (mRNA) and the anticodon in an aminoacyl-transfer RNA (aminoacyl-tRNA).

code: mechanism to convey information on genes and genetic sequence

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

synthesis: combination of starting materials to form a desired product

RNA: ribonucleic acid, a natural polymer used to translate genetic information in the nucleus into a template for the construction of proteins

A codon is a triplet of adjacent nucleotides in mRNA that specifies an amino acid to be incorporated in a protein. Because the codon can be made from three of the four possible ribonucleotides, there are 4^3 or 64 combinations, leading

The genetic information within a gene in DNA is encoded by a sequence of four nucleotides (A, T, G, and C). This must ultimately be translated into the twenty-letter (corresponding to amino acids) language of proteins. It is now known that this information is translated first into an **intermediate** message form called mRNA, and then converted into a specific protein. This latter process of converting from the "nucleotide alphabet" to the "protein alphabet" requires that specific segments on mRNA correspond to specific amino acids in the protein being manufactured. This connection is provided by the genetic code.

The translation process that occurs at the site of the **ribosomes** in the cytoplasm requires that the mRNA designate the codons that then specify the amino acid sequence for the protein. The codons on the mRNA must interact with the anticodons on the charged tRNA molecules, which bring to the site the specific amino acid residues. Watson-Crick complementary base pairing provides the specificity for this interaction.

intermediate: molecule, often short-lived, that occurs while a chemical reaction progresses but is not present when the reaction is complete

ribosome: large complex of proteins used to convert amino acids into proteins

amino acid sequence: twenty of the more than five hundred amino acids that are known to occur in nature are incorporated into a variety of proteins that are required for life processes; the sequence or order of the amino acids present determines the nature of the protein

to 64 different codons. The first letter of the codon is at the 5′-end, while the last letter is at the 3′-end. For example, 5′-AUG-3′.

The **amino acid sequence** of a protein will be specified by the sequence of contiguous codons in the mRNA template. The initial codon in the mRNA establishes the reading frame and defines the protein's initial amino acid.

There are three types of codons. There is an initiation codon, AUG, which signifies the initial amino acid (and also codes for methionine residues in internal positions) in the protein. There are 61 codons, including AUG, that designate individual amino acids. The remaining three codons (UAA, UAG, and UGA) are termination codons (also called stop codons or nonsense codons), which do not code for amino acids, but signal the end of the mRNA message and provide the "stop" signal for protein synthesis.

Two amino acid residues, tryptophan and methionine, have unique codons—UGG and AUG, respectively. All other amino acids may be coded for by more than one codon, such that the code is said to be degenerate. This degeneracy is not uniform, but varies according to the particular amino acids. For example, three amino acids (arginine, leucine, and serine) have six codons, five amino acids have four, isoleucine has three, and nine amino acids have two. The first two letters of each codon provide the primary determinant in the specificity. For example, the codons for amino acid valine are GUU, GUC, GUA, and GUG. The open reading frame of the mRNA, which extends from the AUG codon to the termination codon, establishes the protein that is to be synthesized.

nuclear: having to do with the nucleus of a cell

The correspondence between codons and the amino acids that they specify appears to be nearly, but not quite, universal among species. This genetic code is identical within **nuclear** genes in all species examined, including *Escherichia coli*, viruses, various plants, and humans, with the exceptions being those genes that are encoded in mitochondria and genes found in a small number of other organisms. This is cited as evidence that all life-forms have a common evolutionary ancestor, with the genetic code being preserved throughout evolution. SEE ALSO Protein Synthesis; Protein Translation; Ribonucleic Acid.

William M. Scovell

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Coenzyme

Coenzymes are small organic molecules that link to enzymes and whose presence is essential to the activity of those enzymes. Coenzymes belong to the larger group called cofactors, which also includes **metal** ions; **cofactor** is the more general term for small molecules required for the activity of their associated enzymes. The relationship between these two terms is as follows

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

cofactor: inorganic component that combines with an apoenzyme to form a complete functioning enzyme

I. Cofactors
  A. Essential ions
    1. Loosely bound (forming metal-activated enzymes)
    2. Tightly bound (forming **metalloenzymes**
  B. Coenzymes
    1. Tightly bound prosthetic groups
    2 Loosely bound cosubstrates

metalloenzyme: a protein enzyme that contains at least one metal atom, often in an active site of the protein

Many coenzymes are derived from **vitamins**. Table 1 lists vitamins, the coenzymes derived from them, the type of reactions in which they participate, and the class of coenzyme.

vitamins: molecules needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

Prosthetic groups are tightly bound to enzymes and participate in the **catalytic** cycles of enzymes. Like any **catalyst**, an enzyme–prosthetic group complex undergoes changes during the reaction, but before it can catalyze another reaction, it must return to its original state.

catalysis: the action or effect of a substance in increasing the rate of a reaction without itself being consumed

catalyst: substance that aids in a reaction while retaining its own chemical identity

Flavin **adenine** dinucleotide (FAD) is a prosthetic group that participates in several intracellular **oxidation**-reduction reactions. During the catalytic cycle of the enzyme succinate dehydrogenase, FAD accepts two electrons from succinate, yielding fumarate as a product. Because FAD is tightly bound to the enzyme, the reaction is sometimes shown this way

adenine: one of the purine bases found in nucleic acids, $C_5H_5N_5$

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

$$\text{succinate} + \text{E–FAD} \rightarrow \text{fumarate} + \text{E–FADH}_2$$

where E–FAD stands for the enzyme tightly bound to the FAD prosthetic group. In this reaction the coenzyme FAD is reduced to $FADH_2$ and remains tightly bound to the enzyme throughout. Before the enzyme can catalyze the oxidation of another succinate molecule, the two electrons now belonging to E–$FADH_2$ must be transferred to another electron acceptor, ubiquinone. The regenerated E–FAD complex can then oxidize another succinate molecule.

Cosubstrates are loosely bound coenzymes that are required in stoichiometric amounts by enzymes. The molecule nicotinamide adenine dinucleotide (NAD) acts as a cosubstrate in the oxidation-reduction reaction that is catalyzed by malate dehydrogenase, one of the enzymes of the citric acid cycle.

$$\text{malate} + \text{NAD}^+ \rightarrow \text{oxaloacetate} + \text{NADH}$$

Table 1. Vitamins, the coenzymes derived from them, the type of reactions in which they participate, and the type of coenzyme.

VITAMINS AND COENZYMES

Vitamin	Coenzyme	Reaction type	Coenzyme class
B_1 (Thiamine)	TPP	Oxidative decarboxylation	Prosthetic group
B_2 (Riboflavin)	FAD	Oxidation/Reduction	Prosthetic group
B_3 (Pantothenate)	CoA - Coenzyme A	Acyl group transfer	Cosubstrate
B_6 (Pyridoxine)	PLP	Transfer of groups to and from amino acids	Prosthetic group
B_{12} (Cobalamin)	5-deoxyadenosyl cobalamin	Intramolecular rearrangements	Prosthetic group
Niacin	NAD^+	Oxidation/Reduction	Cosubstrate
Folic acid	Tetrahydrofolate	One carbon group transfer	Prosthetic group
Biotin	Biotin	Carboxylation	Prosthetic group

SOURCE: Compiled from data contained in Horton, H. R., et al. (2002). *Principles of Biochemistry*, 3rd edition. Upper Saddle River, NJ: Prentice Hall.

In this reaction, malate and NAD^+ diffuse into the active site of malate dehydrogenase. Here NAD^+ accepts two electrons from malate; oxaloacetate and NADH then diffuse out of the active site. The reduced NADH must then be returned to its NAD^+ form. For each catalytic cycle, a "new" NAD^+ molecule is needed if the reaction is to occur; thus, stoichiometric quantities of the cosubstrate are needed. The reduced form of this coenzyme (NADH) is converted back to the oxidized form (NAD^+) via a number of simultaneously occurring processes in the cell, and the regenerated NAD^+ can then participate in another round of catalysis.

Coenzymes, then, are a type of cofactor. They are small organic molecules that bind tightly (prosthetic groups) or loosely (cosubstrates) to enzymes as they participate in catalysis. SEE ALSO ACTIVE SITE; COFACTOR; ENZYMES.

Paul A. Craig

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Cofactor

Enzymes are either proteins (polymers of amino acids) or ribozymes (polymers of ribonucleotides). Some protein-based enzymes require small molecules called cofactors to become fully functional. The relationship between enzymes and cofactors is shown by the equation

$$\textit{apoenzyme} + \textit{cofactor} = \textit{holoenzyme}$$

where **apoenzyme** refers to the nonfunctional protein and holoenzyme refers to the completely functional enzyme.

apoenzyme: the protein part of an enzyme that requires a covalently bound coenzyme (a low-molecular-weight organic compound) or a cofactor (such as a metal ion) for activity

There are two types of cofactors: metal ions and small organic molecules. The latter of the two are also called coenzymes. The relationship between cofactor and coenzyme and some further subclassification can be seen in the following simple outline.

I. Cofactors
  A. Essential ions
    1. Loosely bound (metal-activated enzymes)
    2. Tightly bound (**metalloenzymes**)
  B. Coenzymes
    1. Tightly bound prosthetic groups
    2. Loosely bound cosubstrates

metalloenzyme: a protein enzyme that contains at least one metal atom, often in an active site of the protein

Metal-activated enzymes may have an absolute requirement for the metal ion, or they may simply have enhanced activity in the presence of the metal ion. Phosphofructokinase is an example of a metal-activated enzyme, which catalyzes the reaction

fructose-6-phosphate + ATP → fructose-1,6-bisphosphate + ADP

A divalent metal ion (Mg^{2+}) is needed to coordinate the phosphate groups on the ATP molecule in order for phosphofructokinase to successfully catalyze this reaction. Mg^{2+}, Mn^{2+}, Ca^{2+}, and K^{+} often function as cofactors for metal-activated enzymes.

Metalloenzymes are enzymes that have a tightly bound metal ion. These metal ions are normally incorporated into the enzymes during enzyme **synthesis**, and removal of the metal ions often results in the complete denaturation of the enzyme. These metal ions may contribute either to the structure or the **catalytic** mechanism of a metalloenzyme. For example, horse liver alcohol dehydrogenase contains two tightly bound zinc ions (Zn^{2+}). The first zinc ion is structural: it is bound to four cysteine side chains and is essential to maintain the structural integrity of the enzyme. The second zinc ion is catalytic: it is bound to the side chains belonging to two cysteines and one histidine at the active site of the enzyme, and it participates in the catalytic cycle of the enzyme.

synthesis: combination of starting materials to form a desired product

catalysis: the action or effect of a substance in increasing the rate of a reaction without itself being consumed

A wide range of metal ions is present in metalloenzymes as cofactors. Copper zinc superoxide dismutase is a metalloenzyme that uses copper and zinc to help catalyze the conversion of superoxide **anion** to molecular oxygen and hydrogen peroxide. Thermolysin is a protease that uses a tightly bound zinc ion to activate a water atom, which then attacks a peptide bond. Aconitase is one of the enzymes of the citric acid cycle; it contains several iron atoms bound in the form of iron-sulfur clusters, which participate directly in the isomerization of citrate to isocitrate. Other metal ions found as cofactors in metalloenzymes include molybdenum (in nitrate reductase), selenium (in glutathione peroxidase), nickel (in urease), and vanadium (in fungal chloroperoxidase). SEE ALSO CATALYSIS AND CATALYSTS; COENZYMES; DENATURATION; ENZYMES; KREBS CYCLE.

anion: negatively charged chemical unit, like Cl^{-}, CO_3^{2-}, or NO_3^{-}

Paul A. Craig

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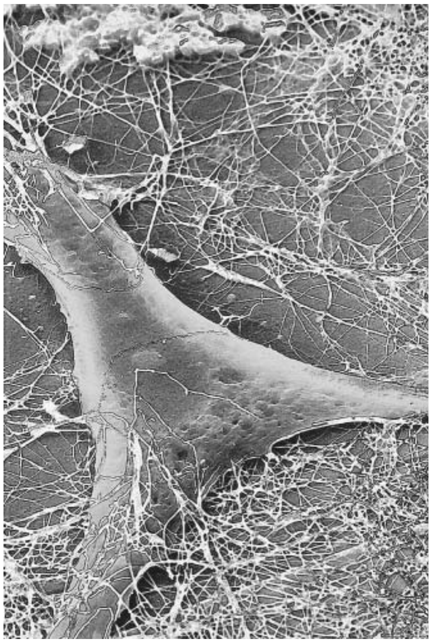
Coinage Metal ***See Copper, Gold, Nickel, Silver.***

Collagen

Collagen is a family of proteins; in animals these proteins play critical roles in tissue architecture, tissue strength, and cell to cell relationships. The major component of all connective tissue matrixes, collagen is found in tissues such as skin, blood vessels, bone, tendon, and ligament, and is characterized by tremendous strength.

The word "collagen" derives from the Greek word for "glue"; this derivation is based on the observation that insoluble collagen, when heated in water, becomes soluble, gummy gelatin that can be used in the manufacture of glues or as a thickener in foods. There are ten known forms of collagen that, because of differences in functional requirements and chemical environments, differ in some details of composition. All forms of collagen share the same basic structure: three **polypeptide** chains coiled together to form a triple **helix**. (These triple coils, in turn, become coiled together.) Collagen polypeptide chains generally contain around 1,000 amino acids.



A scanning electronic micrograph of a fibroblast and collages fibers. Collagen is a major component of connective tissue.

polypeptide: compound containing two or more amide units—C(O)NH—produced by the condensation of two or more amino acids

helix: form of a spiral or coil such as a corkscrew

vitamins: molecules needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

cofactor: inorganic component that combines with an apoenzyme to form a complete functioning enzyme

tropocollagen: fibers, or fibrils, consisting of three polypeptide sequences arranged in a helix

superhelix: helical-shaped molecule synthesized by another helical-shaped molecule

fibril: slender fiber or filament

covalent bond: bond formed between two atoms that mutually share a pair of electrons

biosynthesis: the synthesis of a substance in a living system

An individual collagen polypeptide chain has a large number of repeating amino acid sequences, most often glycine–X–Y, where X is often proline and Y is often hydroxyproline. Lysine, in its pure form or modified to hydroxylysine, is also found in collagen. Both hydroxyproline and hydroxylysine are formed via the enzyme-catalyzed oxidations of the proline and lysine amino acid side chains, which occur after the collagen polypeptide has been synthesized. These enzymatic reactions require ascorbic acid (**vitamin** C) as a **cofactor**.

Individual collagen polypeptides form an extended, left-handed triple helix, which is longer and less compact than the α-helixes often seen in proteins. Three of these helixes then form a molecule of **tropocollagen**, the basic building block of collagen, by coiling around a central axis in a right-handed, triple-helical arrangement. The side chain of every third amino acid is very close to the central axis of this **superhelix**. Glycine, with the smallest side chain of any amino acid, is more easily accommodated in these arrangements than the larger, bulkier amino acids.

Tropocollagen molecules associate in a staggered fashion to form collagen **fibrils**, which are stronger than steel wire of similar size. Collagen fibrils are strengthened and stabilized mainly by covalent cross-links, existing both within and between individual tropocollagen molecules. These crosslinks represent the enzyme-catalyzed formation of **covalent bonds** involving lysine and hydroxylysine side chains. The extent of cross-linking depends on the specific function of the collagen molecule involved and the age of the animal; older animals have more highly cross-linked and therefore more rigid collagen.

There are a number of collagen-related disorders that have been identified. Many of these are the result of derangements in the **biosynthesis** of collagen. Scurvy, characterized by bleeding gums, loose teeth, skin lesions, and weakened blood vessels, results from severe vitamin C deficiency, which makes it almost impossible for afflicted individuals to form hydroxyproline and hydroxylysine. The conditions, known collectively as the Ehlers–Danlo syndromes, result from defects in the processing of collagen polypeptides.

In addition to its importance in the production of animal glue, collagen is the basis for gelatin, which forms when collagen fibers are denatured as a result of heating and then get tangled up with each other. Collagen is also used for various biomedical applications. SEE ALSO DENATURATION; PEPTIDE BOND; PROTEINS.

Matthew A. Fisher

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Colligative Properties

Colligative properties are those properties of solutions that depend on the number of dissolved particles in solution, but not on the identities of the solutes. For example, the freezing point of salt water is lower than that of pure water, due to the presence of the salt dissolved in the water. To a good approximation, it does not matter whether the salt dissolved in water is sodium chloride or potassium nitrate; if the molar amounts of solute are the same and the number of ions are the same, the freezing points will be the same. For example, $AlCl_3$ and K_3PO_4 would exhibit essentially the same colligative properties, since each compound dissolves to produce four ions per formula unit. The four commonly studied colligative properties are freezing point depression, boiling point elevation, vapor pressure lowering, and osmotic pressure. Since these properties yield information on the number of solute particles in solution, one can use them to obtain the molecular weight of the solute.

Freezing Point Depression

The presence of a solute lowers the freezing point of a solution relative to that of the pure solvent. For example, pure water freezes at 0°C (32°F); if one dissolves 10 grams (0.35 ounces) of sodium chloride (table salt) in 100 grams (3.53 ounces) of water, the freezing point goes down to -5.9°C (21.4°F). If one uses sucrose (table sugar) instead of sodium chloride, 10 grams (0.35 ounces) in 100 grams (3.53 ounces) of water gives a solution with a freezing point of -0.56°C (31°F). The reason that the salt solution has a lower freezing point than the sugar solution is that there are more particles in 10 grams (0.35 ounces) of sodium chloride than in 10 grams (0.35 ounces) of sucrose. Since sucrose, $C_{12}H_{22}O_{11}$ has a molecular weight of 342.3 grams (12.1 ounces) per mole and sodium chloride has a molecular weight of 58.44 grams (2.06 ounces) per mole, 1 gram (0.035 ounces) of sodium chloride has almost six times as many sodium chloride units as there are sucrose units in a gram of sucrose. In addition, each sodium chloride unit comes apart into two ions (a sodium cation and a chloride **anion**) when

anion: negatively charged chemical unit, like Cl^-, CO_3^{2-}, or NO_3^-

The freezing point depression of a solution containing a dissolved substance, such as salt dissolved in water, is a colligative property.

dissolved in water. Sucrose is a nonelectrolyte, which means that the solution contains whole $C_{12}H_{22}O_{11}$ molecules. In predicting the expected freezing point of a solution, one must consider not only the number of formula units present, but also the number of ions that result from each formula unit, in the case of ionic compounds. One can calculate the change in freezing point (ΔT_f) relative to the pure solvent using the equation:

$$\Delta T_f = i\ K_f\, m$$

where K_f is the freezing point depression constant for the solvent (1.86°C·kg/mol for water), m is the number of moles of solute in solution per kilogram of solvent, and i is the number of ions present per formula unit (e.g., $i = 2$ for NaCl). This formula is approximate, but it works well for low solute concentrations.

Because the presence of a solute lowers the freezing point, many communities put salt on their roads after a snowfall, to keep the melted snow from refreezing. Also, the antifreeze used in automobile heating and cooling systems is a solution of water and ethylene glycol (or propylene glycol); this solution has a lower freezing point than either pure water or pure ethylene glycol.

Boiling Point Elevation

The boiling point of a solution is higher than that of the pure solvent. Accordingly, the use of a solution, rather than a pure liquid, in antifreeze serves to keep the mixture from boiling in a hot automobile engine. As with freezing point depression, the effect depends on the number of solute particles present in a given amount of solvent, but not the identity of those particles. If 10 grams (0.35 ounces) of sodium chloride are dissolved in 100 grams (3.5 ounces) of water, the boiling point of the solution is 101.7°C (215.1°F; which is 1.7°C (3.1°F) higher than the boiling point of pure water). The formula used to calculate the change in boiling point (ΔT_b) relative to the pure solvent is similar to that used for freezing point depression:

$$\Delta T_b = i\, K_b\, m,$$

where K_b is the boiling point elevation constant for the solvent (0.52°C·kg/mol for water), and *m* and *i* have the same meanings as in the freezing point depression formula. Note that ΔT_b represents an increase in the boiling point, whereas ΔT_f represents a decrease in the freezing point. As with the freezing point depression formula, this one is most accurate at low solute concentrations.

Vapor Pressure Lowering

The vapor pressure of a liquid is the **equilibrium** pressure of gas molecules from that liquid (i.e., the results of evaporation) above the liquid itself. A glass of water placed in an open room will evaporate completely (and thus never reach equilibrium); however, if a cover is placed on the glass, the space above the liquid will eventually contain a constant amount of water vapor. How much water vapor is present depends on the temperature, but not on the amount of liquid that is present at equilibrium (provided some liquid is present at equilibrium). (At room temperature, the vapor pressure of pure water is about 20 Torr, which is about one-fortieth of the total atmospheric pressure on a "normal" day at sea level.)

equilibrium: condition in which two opposite reactions are occurring at the same speed, so that concentrations of products and reactants do not change

If, instead of pure water, an **aqueous solution** is placed in the glass, the equilibrium pressure will be lower than it would be for pure water. Raoult's law states that the vapor pressure of the solvent over the solution is proportional to the fraction of solvent molecules in the solution; that is, if two-thirds of the molecules are solvent molecules, the vapor pressure due to the solvent is approximately two-thirds of what it would be for pure solvent at that temperature. If the solute has a vapor pressure of its own, then the total vapor pressure over the solution would be:

aqueous solution: solution in which water is the solvent (primary component)

$$\mathrm{P_{vap}} = \frac{2}{3}\,(\text{pure solvent vapor pressure}) + \frac{1}{3}\,(\text{pure solute vapor pressure})$$

Generally, one expects that solutes which are liquids in their pure form (such as ethyl alcohol) will have some vapor pressure of their own, whereas ionic compounds (such as sodium chloride) will not contribute to the total vapor pressure over the solution.

One consequence of this lowering in vapor pressure may be observed in a spilled can of soda. As the water evaporates, the soda becomes more sugar and less water, until the vapor pressure of the water is so low that it barely evaporates. As a result, the spilled soda remains sticky for a long time. Contrast this behavior with that of a water spill.

Osmotic Pressure

Osmosis is the process whereby a solvent passes through a semipermeable membrane from one solution to another (or from a pure solvent into a solution). A semipermeable membrane is a barrier through which some substances may pass (e.g., the solvent particles), and other species may not (e.g., the solute particles). Important examples of semipermeable membranes are the cell walls in cells of living things (plants and animals). Osmosis tends to drive solvent molecules through the semipermeable membrane from the low solute concentrations to the high solute concentrations; thus, a "complete"

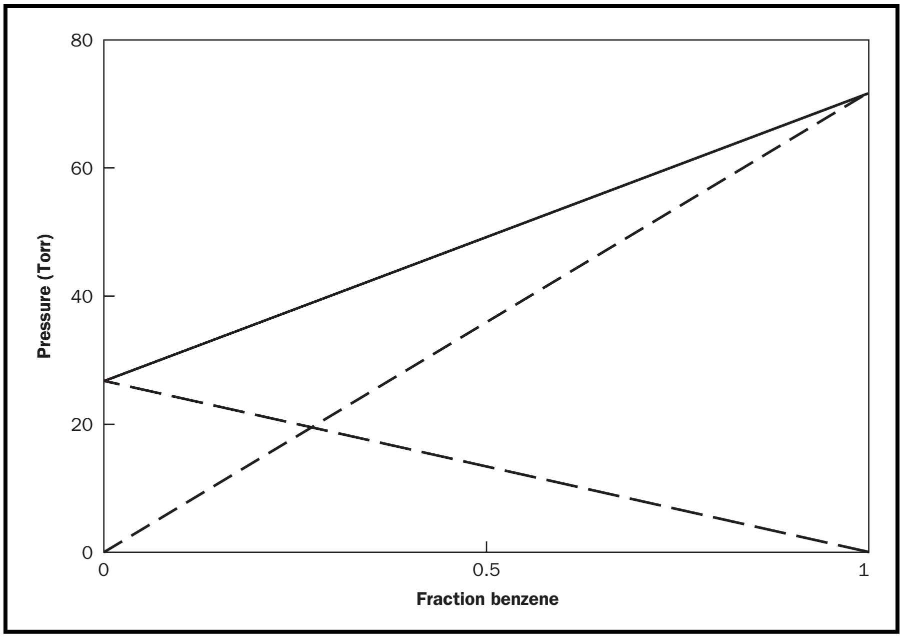

Figure 1. Vapor pressure over a benzene-toluene solution, plotted as a function of the fraction of benzene molecules in the solution. The solid curve is the total vapor pressure, while the short-dashed and long-dashed curves are the vapor pressures from the benzene and toluene, respectively. Note that the two dashed curves add up to the solid curve.

osmosis process would be one that ends with the solute concentrations being equal on both sides of the membrane. Osmotic pressure is the pressure that must be applied on the high concentration side to stop osmosis.

Osmosis is a very useful process. For example, meats can be preserved by turning them into jerky: The meat is soaked in a very concentrated salt solution, resulting in dehydration of the meat cells. Jerky does not spoil as quickly as fresh meat, since bacteria on the surface of the salty meat will fall victim to osmosis, and shrivel up and die. This process thus extends the life of the meat without the use of refrigeration.

There are times when one wishes to prevent osmosis when two solutions (or a pure solvent and a solution) are on opposite sides of a semipermeable membrane. Osmosis can be prevented by applying pressure to the more concentrated solution equal to the osmotic pressure on the less concentrated side. This can be accomplished either physically, by applying force to one side of the system, or chemically, by modifying a solute concentration so that the two solute concentrations are equal. (If one applies a pressure greater than the osmotic pressure to the higher concentration solution, one can force solvent molecules from the concentrated solution to the dilute solution, or pure solvent. This process, known as reverse osmosis, is often used to purify water.) A hospital patient receiving fluids intravenously receives an intravenous (IV) solution that is isotonic with (i.e., at the same solute concentration as) his or her cells. If the IV solution is too concentrated, osmosis will cause the cells to shrivel; too dilute a solution can cause the cells to burst. Similar problems would be experienced by freshwater fish swimming in salt water, or saltwater fish swimming in freshwater. The osmotic pressure, like other colligative properties, does not depend on the identity of the solute, but an electrolyte solute will contribute more particles per formula unit than a nonelectrolyte solute. **SEE ALSO** Solution Chemistry.

Wayne B. Bosma

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Colloids

Somewhere between the sizes of an atom and a grain of sand lies the realm of small particles called colloids. As will become evident, they are everywhere. The simplest colloidal materials, also generally known as suspensions or dispersions, consist of two mixed phases. The continuous or dispersing **phase** may be gas, liquid, or solid (or even plasma, the fourth phase of matter). Air, water, and plastics are common examples. The colloid particles make up the dispersed or suspended phase when uniformly distributed in the second, continuous phase. The dispersed matter may also be gas, liquid, or solid, and any combination in more complex suspensions. Colloidal dispersions are considered **homogeneous** mixtures even though they can be **heterogeneous** at or below the microscale.

phase: homogeneous state of matter consisting of gases, liquids, or solids

homogeneous: relating to a uniform mixture of substances

heterogenous: relating to a mixture of diverse substances

Colloids are typically defined as having at least one linear dimension approximately between 1 nanometer (3.94×10^{-8} inches) and 1 micrometer, or micron (3.94×10^{-5} inches). A length-scale restriction for colloids is straightforward but arbitrary and misleading; there are no absolute bounds. It is best to think of a colloid in terms of how the material behaves with respect to inertial or body forces, such as gravity and fluid flow. For example, particles that do not quickly settle out or float to the top of their dispersed phase are considered colloidal. Wood fibers used in paper-making behave as colloids in water even though they can be tens of microns in diameter and many millimeters in length; individual fibers would not be considered colloidal in air where they would settle in seconds.

Classification of Materials

Most kinds of colloidal suspensions maintain microscopic phase separation between two or more materials while having a uniform macroscopic distribution of each. Aerosols are fine liquid droplets or solid particulates that form in a gas phase. The inverse of an aerosol is a foam—gas bubbles or pockets trapped in a liquid or solid medium. Liquid foams often have neither a truly continuous phase nor a dispersed colloid in the usual sense. The bubbles are frequently very large with liquid films for separating them that are thin enough to exhibit colloidal characteristics. Soapsuds in a bathtub are a prime example of this phenomenon.

Aerosols of dust, smoke, mist, and fog are the most convenient colloids for observing light-scattering phenomena outside of the laboratory. This is demonstrated by the orange or red color of sunsets that results from dust and smoke blocking shorter wavelengths of light more than longer ones: violet, indigo, blue, and green over yellow, orange, and red. When the sun is higher, the light path through the atmosphere is much shorter with fewer dust particles to scatter it. Sunrise is not usually as red as sunset because

The scientific study of colloids began during the late 1800s with the continuing development of high-resolution microscopy and light-scattering theory (by Lord Rayleigh in 1871). Optical microscopy can view objects as small as approximately one-half the wavelength of light used, or roughly three-tenths of a micron for white light. Much smaller objects may still be located under the microscope by light scattering, but particle size becomes indistinguishable. Particle sizes can be measured to thousandths of a micron by carefully measuring the intensity of light scattered at different relative angles. Electron microscopy is capable of reproducing images at this scale, sometimes with atomic resolution.

A nanometer (nm) is one-billionth of a meter (10^{-9} m, or 3.94×10^{-8} inches), approximately six water molecules end-to-end. A micron (μm) is 1,000 nanometers or one-thousandth of a millimeter (10^{-6} m, or 3.94×10^{-5} inches); the thickness of one strand of hair is typically 50–100 microns ($1.97–3.93 \times 10^{-3}$ inches) in diameter. Fog and clouds contain water droplets of smaller diameters but still above 1 micron. Red blood cells are about 7 microns (2.76×10^{-4} inches), smoke particles under a micron to 10 nanometers (3.94×10^{-5} inches to 3.94×10^{-7} inches). Very large molecules called polymers (e.g., **DNA**, cellulose, nylon) are also colloids and may be as large as tens of nanometers, comparable to viruses.

larger particles entrained in hotter, daytime air currents settle out in the calmer and cooler night atmosphere. Light scattering also explains why yellow or amber fog lights actually improve visibility in fog and higher-intensity headlights do not. Increasing intensity yields increased scattering, whereas eliminating shorter wavelengths reduces the effect.

Liquid drops dispersed in a second liquid medium are called emulsions and may be the most important of all colloids, including blood and milk. Solid colloids suspended in liquid are called sols, or hydrosols, when waterborne. Solid suspensions include ice cream, sedimentary rock formations, colored plastics and ceramics filled with pigment particles (as opposed to dyes), and other synthetic composites. Composites are made from two solids to form a hybrid material with the desirable properties of each constituent: for example, a plastic continuous phase for its light weight with a **metal** or ceramic filler for strength.

Colloidal suspensions of polymers and **surfactants** present two distinct groups compared to other dispersed or dissolved materials and will be discussed in more detail below.

Interfaces and Interparticle Forces

Surface area is more important than size for defining colloids. They behave differently than classic objects, or macroscopic bodies, because of their high surface-to-volume ratio, or more accurately, surface-to-mass. The force due to gravity acts on the mass while **intermolecular forces** effectively act at particle surfaces. If these interparticle or surface forces are large enough to alter the effects of gravity on an object, then it has the characteristics of a colloid. For example, gold is more than nineteen times as dense as water and should sink in it. But a nanometer-sized gold sphere (a few hundred atoms) has so little mass that the forces of water molecules hitting it from all directions are enough to make it effectively buoyant. This effect of thermal energy in a dispersing fluid is called **Brownian motion**. The colloidal gold may remain stable for many years as long as it never collides with another interface, that is, the boundary between phases. The concept behind the adage "like dissolves like" is as important for colloids as it is for solutions.

Atomic and molecular interactions determine both chemical solubility and colloidal stability. Similar molecules attract each other more than dissimilar ones. This universal **attraction** between everything, called London dispersion, is the result of electron motion. Dispersion forces are partly re-

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

surfactants: surface-active agents that lower the surface tension of water; e.g., detergents, wetting agents

intermolecular force: force that arises between molecules, generally it is at least one order of magnitude weaker than the chemical bonding force

Brownian motion: random motion of small particles, such as dust or smoke particles, suspended in a gas or liquid; it is caused by collisions of the particle with gas or solvent molecules that transfer momentum to the particle and cause it to move

attraction: force that brings two bodies together, such as two oppositely charged bodies

The Scottish botanist Robert Brown (1773–1858), who also discovered the cell nucleus, first noticed small pollen particles wiggling and moving randomly under a microscope. Higher temperatures result in larger kinetic energies in the dispersant molecules, keeping even larger particles from sedimenting or floating. Thus, temperature is also a determining parameter in the definition of a colloid.

Light passing through a bottle containing sodium hydroxide (NaOH, left), and a bottle containing a colloidal mixture (right).

sponsible for keeping gold from dissolving in water since the two are not very similar. With this logic, a second gold particle in water would be attracted to the first and stick to it. This is called aggregation and cohesion; the aggregation of two unlike particles or interfaces is called adhesion.

More than London dispersion forces are often present. Even though a single molecule or atom has no **net charge**, it often has stable partial charges of equal positive and negative magnitudes, together called a dipole. Dipole interactions are attractive and often grouped with London dispersion under the collective label van der Waals interaction. Water is a highly polar molecule and gold is easily polarized, arguing for the even greater probability of aggregation. But as a metal, the gold interface with water easily builds up surface charge that repels other gold interfaces through the electrostatic or coulombic interaction. Nearly all materials acquire surface charge in water, more often negative than positive. Several other interparticle forces exist, but van der Waals and electrostatic forces usually determine colloidal behavior.

net charge: total overall charge

Surfactants, Adsorption, and Micelles

Molecules and surfaces are often qualitatively categorized as either **hydrophilic** (water-loving) or **hydrophobic** (water-fearing). Surface active agents or surfactants have both characteristics. One end of a simple surfactant is hydrophilic, the polar or ionic head group. The rest of the molecule is the hydrophobic tail, such as an oily hydrocarbon. Having very dissimilar parts in solution attracts the molecule to surfaces, as in detergency.

hydrophilic: a part of a molecule having an affinity for water

hydrophobic: a part of a molecule that repels water

Surfactants concentrate at interfaces by adsorption to remove lyophobic (solvent-fearing) parts from the solvent. This behavior lowers the liquid's surface tension; that is to say, it lessens the imbalance of intermolecular forces between the solvent and its surroundings. The surface tension of pure water causes it to bead up on hydrophobic surfaces, such as a water-proofed jacket or a rain-treated windshield. Liquids with lower surface tensions, such as oils and alcohols, bead up to lesser extents. Water can be made to wet hydrophobic material by adding surfactant; this is sometimes called "breaking" the surface tension.

vesicle: small compartment in a cell that contains a minimum of one lipid bilayer

At low concentrations, surfactants form traditional solutions. At higher concentrations, surfactant molecules may self-assemble into colloidal-scale structures in bulk solution referred to as micelles. They can be spheres, cylinders, **vesicles**, or bilayer sheets with nanometer to micron dimensions. Above the critical micelle concentration (CMC), micelles begin to grow by molecular association or aggregation. Hydrophobic tails escape water by sticking together in a core shielded by a shell of head groups. Surfactant solubility may sometimes be too low at room temperature for micellization; not enough molecules can dissolve to start associating.

Emulsions and Foams

emulsion: immiscible two-phase mixture in which one phase is dispersed (as small droplets) in the other phase

hydrogen bonding: intermolecular force between the H of an N–H, O–H, or F–H bond and a lone pair on O, N, or F

Oil in vinegar (mostly water) for salad dressing is a common **emulsion**. However, this is not a stable colloidal system. Usually, salad dressings must be shaken vigorously to redisperse the oil before pouring. The kinetic energy of shaking breaks up the oil into small droplets. But the oil quickly separates again, aggregating into a large, hydrophobic phase. This is called coalescence for droplets since they not only attach but also merge into a single, larger drop. The interfacial tension between oil and water is very high; in other words, they do not mix easily. The acetic acid in vinegar can act as a surfactant, but a much better one is needed to reduce the oil—water interfacial tension enough for stable emulsion formation.

One surfactant crucial to life occurs naturally in the lung, without which babies could never take their first breaths in air. Pulmonary surfactant decreases the surface tension of liquid (mostly water) in the lungs to almost zero so that tiny air sacs called alveoli can expand to get oxygen into the blood. Water has very high surface tension due to strong molecular attractions, including polar and **hydrogen bonding**. Molten salts, mercury, and other liquid metals have much higher surface tensions, but nearly all liquids at room temperature have lower surface tensions than water.

Mayonnaise, on the other hand, is a relatively stable emulsion due mostly to high viscosity (more precisely, viscoelasticity), though surfactants are also present. The oil and water in mayonnaise cannot separate into phases because the emulsion droplets do not have enough energy for much movement. In less viscous emulsions, surfactants are responsible for stability. They reduce interfacial tension for the formation of small particles that either repel or very weakly attract each other. Brownian motion must be able to counter the effects of interparticle attraction, sedimentation, or creaming, which is floatation. Micellar suspensions could also be considered microemulsions, although this is debatable.

Stable foams may be formed by surfactant solutions. Thin liquid films separate gas bubbles, which can be colloidal but are usually much larger. Once formed, gravity eventually drains the liquid until the films break. Viscous additives can slow drainage and increase bubble lifetime significantly. Solid emulsions and foams are less common, the dispersing phase being solid while a liquid or gas phase is dispersed.

Solid Dispersions, Gels, and Polymer Solutions

"Colloid" comes from the Greek word meaning "glue," which was traditionally a sol. Nearly all paints are sols. Particles of pigment, binder, and

The silica-based mineral opal may be considered a solid emulsion when enough water is trapped to have microscopic domains larger than the usual hydration layer. A solid foam coffee cup, thermos, or packing filler is made from polymer expanded with microscopic air pockets. Porous polymer and ceramic membranes could also be viewed as solid foams. Ice cream is a more complicated colloid and may be considered both solid foam and solid suspension. It has at least three phases: ice crystals, air bubbles, and frozen fatty cream. Higher-quality ice cream has more finely dispersed phases for a smoother taste.

filler create the color, strength, and substance of the solid coating after drying. Most paints must be shaken to disperse the particles evenly before application. Many polishing compounds are highly concentrated sols, perhaps even a paste. Rather than separating, these may set over time; the solid particles aggregate. If they pack loosely, the solid network can trap solvent to form a sol-gel. Stirring may redisperse the particles into a sol state again. Silica is known to form gels and gel layers in water.

Polymers, or macromolecules, in solution are lyophilic colloids, implying that they dissolve. However, polymer can still be separated from solvent by physical means, unlike traditional solutions. This is a further implication of its colloidal status. Larger molecules may be filtered or centrifuged from small ones, although some solvent inevitably remains. Even here the physical separation criterion for solutions is not absolute, since zeolites can filter dissolved molecules by size exclusion to tenths of nanometers and atomic **isotopes** may be separated by centrifugation.

isotope: form of an atom that differs by the number of neutrons in the nucleus

Polymers can also form gels, such as gelatin, as a solid suspension. Entangled polymer chains trap solvent. Some polymer mixtures form solid-in-solid solutions, such as poly(ethylene) and poly(propylene) blends in clothing fabrics. Polymers can also be surfactants, such as starch with hydrophilic and hydrophobic segments.

Colloids are extremely important to both commerce and life. The Information Age of the late twentieth century nurtured many advancements allowing more detailed investigation of colloidal materials. Lasers and computers, of course, have greatly affected all areas of science. In return, colloids play a major role in the semiconductor industry. Silica–alumina sols polish silicon wafers that go into diode lasers, memory chips, and microprocessors. Everyone takes advantage of colloidal suspensions, especially since the human body contains so many with its cells, proteins, and DNA. As society pushes to make so many things smaller, more functional, and more efficient, colloid science will become increasingly pertinent to technological developments. SEE ALSO Solution Chemistry.

D. Eric Aston

Nanotechnology is the interdisciplinary field that has evolved from the study of colloids and the techniques of integrated circuit fabrication. Biotechnology and the biological sciences are replete with numerous colloidal systems, including cells, cell membranes, viruses, bacteria, proteins, and DNA. Most of the hype in nanotechnology has centered on the future creation of microelectromechanical (MEM) devices and even nanobots. All endeavors in nanotechnology must deal with fundamental issues common to colloids, interparticle forces most directly. All areas of science are involved in nanotechnology, and it even began to have an impact on disciplines like business, economics, and law by the end of the twentieth century.

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Colorants *See Dyes, Pigments.*

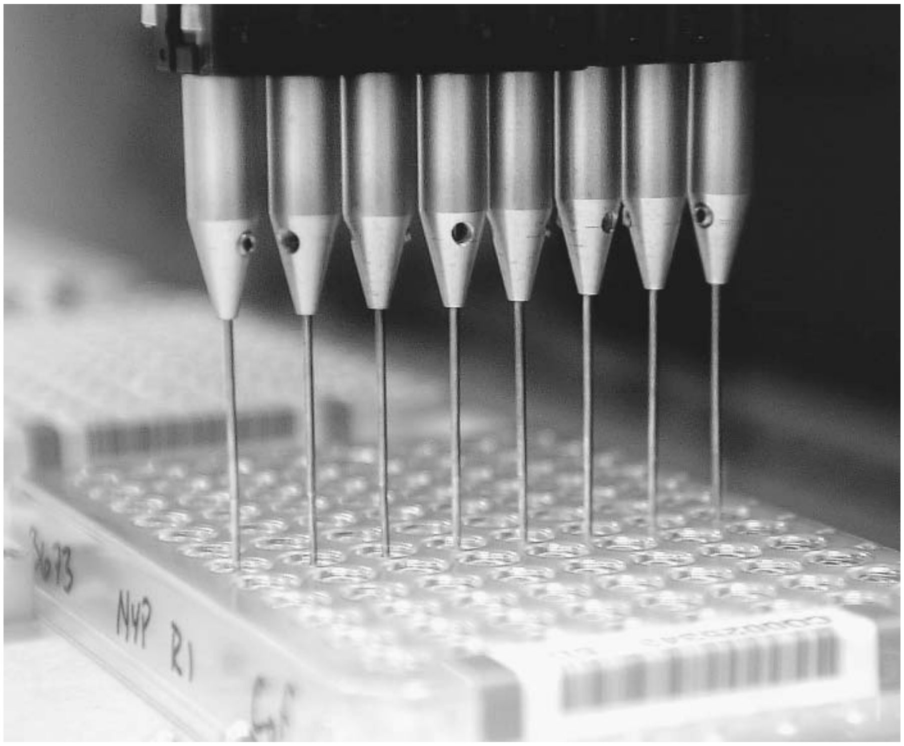
Combinatorial Chemistry

screen: process of comparing multiple reagents simultaneously to provide information on reaction of one reagent with another

polypeptide: compound containing two or more amino aryl—C(O)NH—units; produced by the condensation of two or more amino acids

Combinatorial chemistry is a sophisticated set of techniques used to synthesize, purify, analyze, and **screen** large numbers of chemical compounds, far faster and cheaper than was previously possible. The direct precursor of combinatorial chemistry was the solid-phase synthesis of **polypeptides** developed by American biochemist Robert Bruce Merrifield in the 1960s, followed by the advances in laboratory automation since then. Initial development of the field has been led by the pharmaceutical industry in the search for new drugs, but its applications are spreading into other fields of chemistry. Other terms associated with this field are *parallel array synthesis* and *high-throughput chemistry*.

Whereas classical synthetic chemistry involves the stepwise synthesis and purification of a single compound at a time, combinatorial chemistry makes it possible to synthesize thousands of different molecules in a relatively short amount of time, usually without the intermediate separation of compounds involved in the synthetic pathway, and with a high degree of automation. Such procedures result in the production of new compounds faster and in greater numbers than is possible with standard synthetic methods. The first and still the most common type of combinatorial synthesis involves attaching a molecular species onto a macroscopic substrate such as a plastic bead and performing one or several well-characterized chemical reactions on the species. After each reaction, the product mixture can be split among several reaction containers and then recombined after the reaction (a procedure called *mix and split*), or else carried out in parallel containers. The resulting mixture of compounds is referred to as a *molecular library* and can contain many thousands of individual compounds. The analysis, or *screening*, of these libraries to identify the compounds of interest, along with their subsequent isolation and identification, can be completed by a variety of methods. One example is *iterative deconvolution*; it involves the successive identification of each of the units backward along the chain of synthesized units. Another, called *positional scanning*, requires the multiple synthesis of a library, each time varying the location of a known unit along the chain and comparing the activities of the resulting libraries. More recent advances in library screening involve the "tagging" of a substrate with tiny radio frequency transmitters or unique two-dimensional barcodes. Another important recent advance by researchers allows combinatorial syntheses to be carried out in solution, which further extends the scope and utility of this field.



In a laboratory at Myriad Genetics, Salt Lake City, Utah, a robot adds solution to and stirs DNA samples from victims of the 2001 terrorist attack on New York City.

Although the initial applications of combinatorial and high-throughput chemistry have occurred in the pharmaceutical field, the same techniques are now being used successfully to aid in the discovery of new catalysts, polymers, and high temperature superconductors. SEE ALSO CHEMICAL INFORMATICS.

Bartow Culp

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Computational Chemistry

In 1929, shortly after the emergence of quantum mechanics, Paul Dirac made his famous statement that in principle the physical laws necessary to understand all of chemistry were at that point known—the only difficulty was that their application to chemical systems generally led to equations that were too difficult to solve. Consequently, at that time quantum principles could be rigorously applied only to simple atoms and molecules, such as H, He, H_2^+, and H_2.

During the 1930s the first approximate **quantum mechanical** methods for molecules were developed, leading to some success in modeling electronic behavior in many-electron molecules. For example, Eric Hückel developed a rudimentary molecular orbital model for the behavior of electrons in organic polyenes. During the late 1930s and early 1940s the first electronic digital computers were developed, and after World War II their use

quantum mechanical: theoretical model to describe atoms and molecules by wave functions significantly expanded the application of classical and quantum mechanical principles to chemical problems.

A measure of the progress that computer technology spawned was the awarding of the Nobel Prize in chemistry in 1966 to Robert Mulliken for his creation of molecular orbital theory and its use in the calculation of the electronic structure of molecules. In his acceptance speech Mulliken announced the emergence of computational chemistry as a recognized specialty within the field of chemistry: "In conclusion, I would like to emphasize strongly my belief that the era of computing chemists, when hundreds if not thousands of chemists will go to the computing machine instead of the laboratory for increasingly many facets of chemical information, is already at hand."

density-functional theory: quantum mechanical method to determine ground states

The 1998 Nobel Prize in chemistry, awarded to Walter Kohn (who developed the **density-functional theory**) and John Pople (who developed the use of computational methods in quantum chemistry) for their contributions to the advancement of computational chemistry, provided further evidence that the field had become a mature, reliable, and essential method of scientific inquiry. Today a vast literature exists, and computational chemistry has become an essential subject in the education of chemists at both the graduate and undergraduate levels.

transition metals: elements with valence electrons in d-sublevels; frequently characterized as metals having the ability to form more than one cation

heavy metal: by convention, a metal with a density greater than 5 g/cm^3; 70 elements are thus classified as heavy metals

The technical breadth of computational chemistry and the interdisciplinary character of its applications make the formulation of a concise definition challenging. Computational chemistry might be broadly defined as the attempt to model chemical and biochemical phenomena (structure, properties, reactivity, etc.) via computer-implementation of the theoretical principles of classical and quantum mechanical physics. Chemists and biochemists are interested in a wide array of molecules, including simple inorganic molecules, organic species of intermediate complexity, **transition metal** complexes with **heavy metal** ions, polymers, and biological macromolecules, such as proteins and nucleic acids. In their studies of these diverse species they have a wide range of computational tools at their command. Therefore, assessing the strengths and weaknesses of these tools, and choosing the most appropriate method for the task at hand is a serious challenge for the computational chemist.

Computational Quantum Chemistry

valence: combining capacity

At the most fundamental level chemical phenomena are determined by the behaviors of **valence** electrons, which in turn are governed by the laws of quantum mechanics. Thus, a "first principles" or *ab initio* approach to chemistry would require solving Schrödinger's equation for the chemical system under study. Unfortunately, Schrödinger's equation cannot be solved exactly for molecules or multielectron atoms, so it became necessary to develop a variety of mathematical methods that made approximate computer solutions of the equation possible.

nuclear: having to do with the nucleus of an atom

The Hartree–Fock (HF) approximation. The HF method is based on the Born–Oppenheimer and orbital approximations. Under the Born–Oppenheimer approximation the **nuclear** and electronic degrees of freedom of a molecule are decoupled, and the nuclei are held fixed while the electronic contribution to the energy is calculated. In the orbital approximation

British chemist John A. Pople, co-recipient of the 1998 Nobel Prize in chemistry, "for his development of computational methods in quantum chemistry."

the electrons occupy individual spin-orbitals, and as a consequence the *N*-electron Schrödinger equation is transformed into *N* one-electron equations. Both approximations facilitate computation, and the HF method proceeds by selecting a trial wave function (a molecular orbital formed as a linear combination of **atomic orbitals**, LCAO-MO) containing adjustable parameters, and subsequently solving a set of *N* coupled **integro-differential** equations through an iterative (self-consistent field) procedure.

Post-Hartree–Fock (PHF) methods. HF calculations for small to intermediate sized molecules generally yield reliable geometries, but fail to various degrees in predicting other important molecular properties. This is due to the **electron correlation error** introduced by the orbital approximation. PHF implementations introduce electron correlation into the calculation either by Møller–Plesset perturbation methods (MP2 and MP4), or by using wave functions based on many electron configurations (configuration interaction), rather than the **single Slater determinant** wave functions used in the HF method. These methods yield excellent results, but are computationally expensive (and good quantitative agreement with experiment comes at a price). As the level of theoretical rigor increases, the ability to interpret

atomic orbital: mathematical description of the probability of finding an electron around an atom

integro-differential: complex mathematical model used to calculate a phase transition

electron correlation error: quantum mechanical method for studying atoms, ions, or molecules

single Slater determinant: wave function used to describe atoms and molecules the results in terms of traditional chemical concepts decreases. For this reason, many chemists are willing to sacrifice quantitative agreement for qualitative, conceptual understanding.

size of the basis set: number of relatively simple mathematical functions (called the basis set) used to represent a more complicated mathematical function such as an atomic orbital

Semiempirical quantum mechanics. The computational effort in *ab initio* calculations increases as the fourth power of the **size of the basis set**, and, therefore, its application to large molecules is expensive in terms of time and computer resources. Consequently, semiempirical methods treating only the valence electrons, in which some integrals are ignored or replaced by empirically based parameters, have been developed. The various semiempirical parameterizations now in use (MNDO, AM1, PM3, etc.) have greatly increased the molecular size that is accessible to quantitative modeling methods and also the accuracy of the results.

Density functional theory (DFT). DFT is an alternative to the HF method, in which the fundamental role is played by the electron density ψ^2, rather than the wave function. The basis for this method is a proof by Pierre Hohenberg and Kohn that all physical properties of a molecule are completely determined by its electron density. The computational savings that DFT offers come from the fact that the wave function of an n-electron molecule depends on $3n$ spatial coordinates, whereas the electron density depends on just three spatial coordinates. Consequently, DFT calculations generally scale as the third power of the size of the basis set, rather than the fourth power of the HF methods.

Classical Computational Methods

Many chemical and biochemical systems of interest are too large for analysis with quantum mechanical methods, either *ab initio* or semiempirical. However, some of their properties may be modeled by classical or semiclassical methods. Classical computational methods do not provide electronic structure information.

Molecular mechanics (MM). MM is a nonquantum mechanical method of computing molecular structures and properties that treats a molecule as a flexible collection of atoms held together by chemical bonds. The method minimizes the molecular potential energy, which is generally calculated classically in terms of internal degrees of freedom such as bond lengths, bond angles, dihedral angles, and electrostatic and van der Waals nonbonding interactions. The MM minimization depends on an empirically-based parameterization scheme and is able to handle molecules with thousands of atoms. The MM method has been highly developed, especially by researchers in the pharmaceutical industry.

Molecular dynamics (MD). Within the MD method of computation, atomic and molecular trajectories are generated by the numerical integration of Newton's laws of motion. This requires specification of initial conditions and a knowledge of the forces acting on all constituents, which can be obtained either algebraically or numerically from a previously calculated potential energy surface. MD has important application in a variety of chemical disciplines, but is especially useful in biochemistry in the study of protein-folding, in probing alternative minimal energy states of macromolecules, and in other areas, such as enzyme-substrate docking.

Monte Carlo simulations (MC). MC computational methods are used to solve a wide variety of problems in mathematics and the natural sciences, including the evaluation of integrals, the solution of differential equations, and the modeling of physical phenomena. Unlike MD, which is **deterministic**, MC (as its name suggests) is based on the generation of random changes in the variables of a system, followed by reliance on some criterion for deciding whether the changes lead to a valid or significant new state of the system. For example, MC can be used to calculate bulk thermodynamic quantities by generating random changes in the positions of the atoms in an ensemble of molecules. The energy of the new arrangement is then calculated and its importance evaluated using the Boltzmann factor, ê(-E/kT). If this new arrangement passes the test, it is included (properly weighted, statistically) in the **manifold of ensemble states** that are used to calculate the average thermodynamic properties of the system being modeled.

deterministic: related to the assumption that all events are based on natural laws

manifold of ensemble states: a set of quantum states that meet the specific requirements (such as total energy) being considered in a calculation

Quantum mechanics/molecular mechanics hybrid method (QM/MM). MM is applicable to macromolecules such as enzymes, but cannot model the bond-breaking and bond-making that occurs within enzyme-substrate complexes at active sites. The solution is provided by a QM/MM hybrid approach, in which QM is used to model the active site and MM models are used for the rest of the enzyme structure.

Advances in computer technology and improved algorithm efficiency have greatly increased the size and range of chemical systems to which these computational methodologies can be applied. In addition, the increased availability of commercial software with efficient user interfaces for preparing input and analyzing output has made computational methods accessible to a rapidly growing number of chemists. SEE ALSO MOLECULAR ORBITAL THEORY; QUANTUM CHEMISTRY; THEORETICAL CHEMISTRY.

Frank Rioux

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Computer Chips ***See Semiconductors.***

Concentration Gradient

A concentration gradient occurs where the concentration of something changes over a certain distance. For example, a few drops of food dye in a glass of water diffuse along the concentration gradient, from where the dye exists in its highest concentration (for instance, the brightest blue or red) to where it occurs in its lowest concentration (the water is still clear). The diffusion will continue until the concentration of the dye becomes uniform in all directions of the water. Concentration gradients are the chemical driving force behind many processes that take place near cell membranes.

In general, two types of diffusion are found in living cells: passive and active. It is, however, very rare to encounter pure **passive diffusion**, where molecules or ions move freely across the cell membrane, following a concentration gradient. For example, water is free to move across a membrane in either direction. But if the solutes inside the cell are barred from moving across the membrane, the resulting phenomenon is called osmosis. The water passes across the membrane into a region of higher solute concentration attempting to reach the ideal **equilibrium**, where for each side of the membrane the water concentration is the same. This movement leads to the buildup of osmotic pressure, however, so the flow of water stops before the membrane bursts.

passive diffusion: mechanism of transporting chemical species across membranes

equilibrium: condition in which two opposite reactions are occurring at the same speed, so that concentrations of products and reactants do not change

Active diffusion occurs when membranes translocate or move molecules or ions from regions of low concentration to those of higher concentration. For example, many cells are able to increase the internal concentration of solutes until very high levels are reached and considerable concentration gradients are established. In this case, a process other than diffusion must be available to supply the energy. Generally, the energy comes from the hydrolysis of **adenosine triphosphate (ATP)**, an energy-rich molecule. Active transport is very important for tissues that are specialized, such as nerve and muscle tissues as well as secretory (or excretory) tissues like the kidneys of animals and the gills of marine life, so solutes may be absorbed against concentration gradients.

adenosine triphosphate (ATP): molecule formed by the condensation of adenine, ribose, and triphosphoric acid, HOP(O)OH–O–(O)OH–OP(O)OH–OH; it is a key compound in the mediation of energy in both plants and animals

In addition, ion concentration gradients existing between two sides of a membrane produce an electrical potential difference, ranging between 50 and 100 millivolts or mV (10^{-3} volt), the outside being positive with respect to the interior. This is the direct consequence of the distribution of cations, especially potassium and sodium ions. Any stimulation by electrical, mechanical, or chemical means at one point of the membrane will create a change in the potential membrane at that point. The altered potential, also called the active potential, will move as a wave over the membrane surface. This provides a means of rapid communication between different regions of a cell. In the case of an elongated nerve cell, this constitutes a nerve impulse.

It is interesting to note that this active potential is used by some fish, such as catfish and eel, to defend themselves as well as to stun their prey. The excitable membranes of the fish each develop a potential of 100 millivolts, but are stacked in such a manner that their potential differences add up to several hundred volts. SEE ALSO HYDROLYSIS; MEMBRANE; PROTEINS; TRANSMEMBRANE PROTEIN.

Joseph Bariyanga

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Coordination Compounds

Transition metals readily react with **halogens** to form binary compounds of various colors, for example: green-black **ferric** chloride ($FeCl_3$), deep blue cobalt chloride ($CoCl_2$), and golden yellow nickel bromide ($NiBr_2$). These compounds dissolve in water to give brightly colored solutions—but of *changed* colors: yellow solutions (containing Fe^{3+} ions), red solutions (Co^{2+} ions), and green solutions (Ni^{2+} ions). By evaporating the solutions, crystals of these new compounds can be obtained: yellow $FeCl_3 \cdot 6H_2O$, red $CoCl_2 \cdot 6H_2O$, and green $NiBr_2 \cdot 6H_2O$. Addition of ammonia to a green nickel solution changes its color to violet, and the compound $NiBr_2 \cdot 6NH_3$ can be crystallized. In all cases these beautiful color changes occur because a new chemical species has formed, and there have been changes in the bonding of the nonmetallic substance to the **metal** ion. Probably the best-known example of vivid color change is the dissolving of anhydrous white cupric sulfate ($CuSO_4$) in water to give a blue solution, containing $[Cu(H_2O)_4]^{2+}$. Addition of ammonia yields the deep blue $[Cu(NH_3)_4]^{2+}$, which forms crystals that have the formula $[Cu(NH_3)_4]SO_4 \cdot H_2O$.

transition metals: elements with valence electrons in d-sublevels; frequently characterized as metals having the ability to form more than one cation

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

ferric: older name for iron in the +3 oxidation state

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

anion: negatively charged chemical unit, like Cl^-, CO_3^{2-}, or NO_3^-

The neutral molecules NH_3 and H_2O bond directly to a metal atom by donating a lone pair of electrons to any empty orbital on the metal atom. **Anions** as well as neutral molecules can bond to a metal atom in this way. These neutral molecules or anions that bond to the metal are called **ligands**. Further examples of ligands are: Br^-, NO_2^-, CO, pyridine, $P(CH_3)_3$, and $O{=}As(C_2H_5)_3$. Some ligands can donate two pairs of electrons and are termed *bidentate*, for example, $H_2N–CH_2–CH_2–NH_2$ (ethylenediamine or en), and $O_2C–CO_2^{2-}$ (oxalate anion or ox).

ligand: molecule or ion capable of donating one or more electron pairs to a Lewis acid

A coordination compound (or coordination complex) consists of a **metal cation** or neutral atom to which neutral or negatively charged ligands have bonded. The number of ligand atoms to which the metal center is directly bonded is the metal cation's coordination number (c.n.), and this number is always greater than the regular **valence** or **oxidation** number (o.n.) of the metal. The coordination complex can be negatively charged, for example, $[AuCl_4]^-$, $[PtCl_6]^{2-}$, $[Co(NO_2)_6]^{3-}$, and $[Fe(CN)_6]^{3-}$; neutral, for example, $[Fe(CO)_5]$, $[Ni(PF_3)_4]$, and $[Rh(NH_3)_3Cl_3]$; or positively charged, for example, $[Cu(NH_3)_4]^{2+}$, $[Mn(H_2O)_6]^{2+}$, and $[Pt(NH_3)_5Cl]^{3+}$. $TiCl_4$ and UF_6 are neutral molecules (in which o.n. = c.n.), they are not coordination compounds; whereas $[AlCl_4]^-$ and $[FeF_6]^{3-}$ are coordination complexes in which the coordination number exceeds the oxidation number. The chromate anion, CrO_4, is not a coordination complex; the o.n. of the Cr atom is 6, but only four O atoms are bonded to it.

metal cation: positively charged ion resulting from the loss of one or more valence electrons

valence: combining capacity

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

Historical Development

By the mid-1870s Sophus Jørgensen in Denmark had systematized the synthetic methods for preparing the coordination compounds that were known at that time, especially those of cobalt(III). Only in 1893 was the mode of bonding in the complexes established, by Alfred Werner (who was awarded the Nobel Prize in 1913 for this work). Werner concluded that most coordination complexes were essentially **octahedral**, with six ligands bonded to a central metal ion (more or less, one above, one below, and four in the same plane as the metal ion). He deduced that Pd(II) and Pt(II) complexes were

octahedral: relating to a geometric arrangement of six ligands equally distributed around a Lewis acid; literally, eight faces

Table 1.

NAMING COORDINATION COMPOUNDS BASED ON COLOR

Color	Formula	Name
Yellow	$CoCl_3{\cdot}6NH_3$	Luteocobaltic chloride
Purple	$CoCl_3{\cdot}5NH_3$	Purpurocobaltic chloride
Green	$CoCl_3{\cdot}4NH_3$	Praseocobaltic chloride

square-planar, with four ligands bonded to the metal atom. He used the German word *Nebenvalenz* (meaning secondary valence) for coordination number, and *Hauptvalenz* (principal valence) for the oxidation number of the metal.

Nomenclature

Naming the compounds was originally based on color. The compound of empirical formula $[PtCl_2(NH_3)_2]$, now known to be $[Pt(NH_3)_4][PtCl_4]$, was named Magnus's green salt after its discoverer, Heinrich Gustav Magnus. The modern system, established by the International Union of Pure and Applied Chemistry (IUPAC), assigns names to compounds based on the identity of the metal, its oxidation state, the number and type of ligand (or ligands) attached to it, and the identities of the other cations and anions present. Some examples of IUPAC names are

$[Pt(NH_3)_2Cl_2]$	diamminedichloroplatinum(II)
$[Co(NH_3)_5Cl]Cl_2$	penta-amminecobalt(III) chloride
$K_4[Fe(CN)_6]$	potassium hexacyanoferrate(II)

The problem of nomenclature quickly becomes very great if, for example, a complex contains two different metal atoms linked by bridging groups.

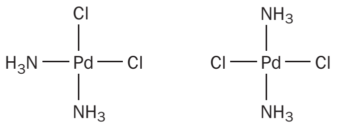
Stereoisomerism

As there is usually more than one way of arranging two or more ligands about a central metal ion, structural **isomers**, that is, two complexes of the same formula but different chemical and physical properties, are possible.

isomer: molecules with identical compositions but different structural formulas

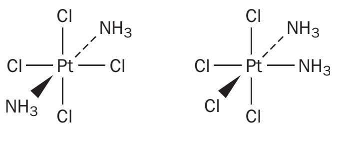
planar complex: arrangement of atoms in which all atoms lie within a common two-dimensional plane

Geometric isomers. Square-**planar complexes** [general formula MX_2B_2] and octahedral complexes [general formula MX_2B_4] can exist as geometric isomers, for example, *cis* and *trans* $[Pd(NH_3)_2Cl_2]$



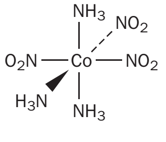
cis *trans*

and *cis* and *trans* $[Pt(NH_3)_2Cl_4]$.

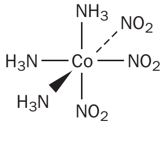


trans *cis*

In the case of octahedral complexes, [general formula MX_3B_3,] two isomers exist, *facial* (*fac*) and *meridional* (*mer*), for example, *fac* and *mer* $[Co(NH_3)_3(NO_2)_3]$.

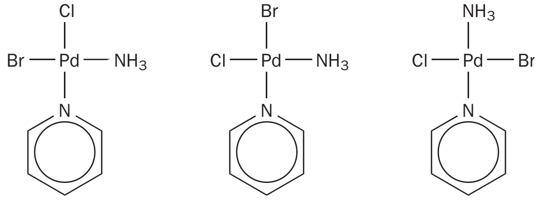


mer



fac

A square-planar complex of formula [MABXY] has three isomers. An example is $[PdClBrNH_3py]$, whose isomers were prepared by the Russian chemist I. Chernyaev in 1926.



Three isomers of $[PdClBrNH_3py]$

Polymerization isomers. In the case of octahedral complexes, formula $[MX_xB_b]_n$, polymerization isomers are often possible. The value of *n* is greater than or equal to 1. Several compounds of empirical formula $[Co(NH_3)_3(NO_2)_3]$ can be isolated.

$[Co(NH_3)_3(NO_2)_3]^\circ$ ($n=1$)

$[Co(NH_3)_4(NO_2)_2]^+[Co(NH_3)_2(NO_2)_4]^-$ ($n=2$)

$[Co(NH_3)_6]^{3+}[Co(NO_2)_6]^{3-}$ ($n=2$)

There are several more possibilities.

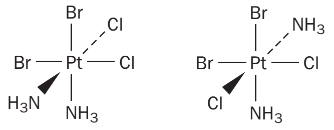
Hydration isomers. Hydration isomers exist for crystals of complexes containing water molecules, for example $CrCl_3z6H_2O$. This compound can exist in three different crystalline forms, in which the number of water molecules directly attached to the Cr^{3+} ion differs.

$[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$	dark green
$[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$	light green
$[Cr(H_2O)_6]Cl_3$	gray-blue

In each case, the coordination number of the chromium cation is 6.

Optical isomers. Optical isomers exist for octahedral complexes that do not possess a center of inversion or a mirror plane of symmetry. The complex and its mirror image are not superimposable. One isomer will rotate the plane of polarized light to the left, the other will rotate polarized light to the right. The complexes are said to be chiral and **optically active**. Some examples are $[Co(ox)_3]^{3-}$; *cis* $[Rh(en)_2Cl_2]^+$; and *cis*, *cis*, *cis* $[PtCl_2Br_2(NH_3)_2]$.

optically active: capable of rotating the plane of plane-polarized light



Chiral pairs

monodentate: capable of donating one electron pair; literally, one-toothed

Each of the isomers will react at the same rate with simple **monodentate** ligands such as water. They differ only in their reactivity toward other chiral compounds and toward polarized light.

Stereochemistry

In addition to the common octahedral and square-planar complexes, several other types of complexes (which can be classified according to coordination number) are observed.

heavy metal: by convention, a metal with a density greater than 5 g/cm^3; 70 elements are thus classified as heavy metals

Coordination number 2: collinear. Collinear complexes are common in the case of **heavy metal** cations of d^{10} electron configuration. Examples of collinear complexes are $[Au(CN)_2]^-$, formed during the extraction of gold from its ore, and $[Ag(NH_3)_2]^+$, formed when AgCl dissolves in ammonia solution.

Coordination number 3: trigonal planar. Trigonal-planar geometry is quite rare; these complexes are found in instances in which ligands are large and steric repulsions are dominant, for example, $[Pt\{P(\text{phenyl})_3\}_3]$.

Coordination number 4: tetrahedral. Tetrahedral complexes are common for d^{10} metal ion species such as Zn^{2+} and Ga^{3+}, and d^7 species, such as Co^{2+}. Examples of tetrahedral complexes are $[ZnCl_2(\text{pyridine})_2]$; $[GaCl_4]^-$; and $[CoCl_2(4\text{–methylpyridine})_2]$, which is deep blue.

Coordination number 5: trigonal-bipyramidal and square-pyramidal. Trigonal-bipyramidal and square-pyramidal geometries are common in the case of complexes of metal ions of coordination number 5. Examples of trigonal-bipyramidal complexes are $[CuCl_5]^{3-}$, $[Fe(CO)_3(PF_3)_2]$, and $[Mn(CO)_4NO]$. Examples of square-pyramidal complexes are $[Ni(CN)_5]^{3-}$ and $[CoCl(\text{dppe})_2]^+$.

Coordination numbers 7, 8, and 9: various. Further types of coordination geometry exist for large cations, especially those of the 31 lanthanide cations, for example, $[Ho(\text{acac})_3H_2O]$, $[NbF_7]^{2-}$, $[Mo(CN)_8]^{4-}$, and $[ReH_9]^{2-}$.

oxidation state zero: condition characterized by an atom having neither lost nor gained electrons

Carbonyls and Organometallic Compounds

Carbonyl compounds and organometallic compounds are two groups of coordination compounds in which carbon atoms are bonded to the metal center. In neutral carbonyls, carbon monoxide molecules are bonded to the metal atom, which is often in **oxidation state zero**. Examples of neutral carbonyl compounds are $[Ni(CO)_4]$ (tetrahedral); $[Fe(CO)_5]$ (trigonal-bipyramidal); and $[Mo(CO)_6]$ (octahedral).

dppe = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$; a bidentate neutral molecule that coordinates through the two phosphorus atoms.

Probably the most famous of the organometallic compounds is the exceedingly stable orange ferrocene, $[Fe(C_5H_5)_2]$. Its discovery in 1951 triggered an explosion in **coordination chemistry**, and the subsequent preparation of thousands of new organometallic compounds. Ferrocene consists of two planar, five-membered rings sandwiching an iron atom between them. Moreover, the bonding in organometallic compounds follows the same rules as the bonding in the carbonyls. The metal atom accepts electrons from the ligands until it achieves a valence electron count of 18 (the number of valence electrons in an atom of the nearest **inert** gas). This is called the Effective Atomic Number (EAN), or **eighteen-electron rule**, first stated by Nevil Sidgwick in 1927 for the metal carbonyls in which each CO group donates two electrons to the metal atom to form an M–C bond. Some examples of the rule are: $Ni(CO)_4$, **atomic number** of Ni = 28, atomic number of Kr = 36, 8 electrons are required, thus 4 CO groups are attached in a tetrahedral arrangement; $Re_2(CO)_{10}$, atomic number of Re = 75, atomic number of Rn = 86, 11 electrons are required for each Re atom. Five CO groups contribute ten electrons, the eleventh comes from sharing a pair of electrons in a Re–Re metal–metal *sigma* bond, giving octahedral geometry about the Re atom.

coordination chemistry: chemistry involving complexes of metal ions surrounded by covalently bonded ligands

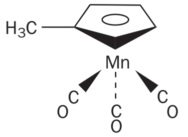
inert: incapable of reacting with another substance

Eighteen Electron Rule: rule noting that coordination complexes with eighteen electrons are stable; electrons from both metal species and ligand donor species are counted

atomic number: the number assigned to an atom of an element that indicates the number of protons in the nucleus of that atom

In ferrocene, each **cyclopentadienyl ring** is considered to donate five electrons to the iron atom, atomic number = 26, giving a total of 10 + 26 = 36 electrons, the atomic number of krypton. Similarly, bonding in the compound $[Mn(CO)_3(C_5H_4–CH_3)]$ obeys the EAN eighteen-electron rule.

cyclopentadienyl ring: five-membered carbon ring containing two C–C double bonds; formula C_5H_6



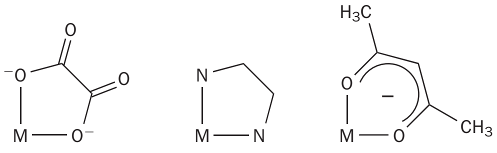
$[Mn(CO)_3\ (C_5H_4—CH_3)]$

The atomic number of Mn = 25; 25 + 5 + (3 × 2) = 36 electrons: the rule is satisfied. This mixed cyclopentadienyl carbonyl complex is of importance as an antiknock compound in gasoline.

Chelating Ligands

EDTA. The bidentate ligands ethylenediamine, oxalate anion, and acetylacetonate anion form **chelate** complexes of enhanced stability, due to the formation of inflexible five- or six-membered rings with the metal.

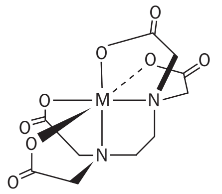
chelate: Greek for "claw"; compounds that have two or more ligand atoms that can attach to metal ions.



Bidentate ligands forming five- and six-membered rings

The compound ethylenediaminetetraacetic acid, on deprotonation, is the hexadentate tetraanion ligand EDTA, which forms remarkably stable complexes by simultaneously bonding through the two nitrogens and four oxygens, one each from the four acetate groups. EDTA is used in toilet soap as a water-softener, in bread as a preservative, and in underarm deodorants as a deodorizer. The magnesium derivative [MgH_2EDTA] is used to treat patients suffering from heavy metal poisoning. EDTA removes the active cation (M^{2+} or M^{3+}) by "engulfing" it to form a water-soluble octahedral complex, which is readily **excreted**.

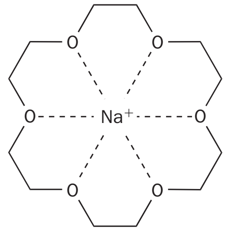
excrete: to eliminate or discharge from a living entity



Chiral complex [MEDTA]

The anion D2EHPA, derived from di(ethylhexyl) phosphoric acid, forms a strongly held four-membered {$M^{2+}O_2P$} ring.

Macrocyclic ligands. Cations of the group one metals form stable complexes with macrocyclic polyethers, for example, Na^+ and "18–crown–6," (–O–CH_2–CH_2–$)_6$.



Macrocylic complex [$Na^+ \cdot$18-crown-6]

The ultimate in encapsulation of a metal cation occurs by ligands termed *cryptands*, for example, $N(CH_2–CH_2–O–CH_2–CH_2–O–CH_2–CH_2)_3N$, which completely encapsulates the cation; the complex with the K^+ cation is 1,000 times more stable than the corresponding Na^+ complex. The preparation and study of these compounds, by Donald J. Cram, Jean-Marie Lehn, and Charles J. Pedersen, earned them the Nobel Prize in chemistry in 1987.

Bonding and Stability

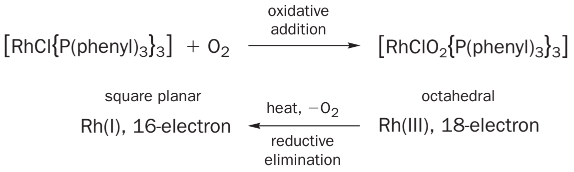
The strength of the metal–ligand bond ranges from the weak ion-dipole interaction between Mg^{2+} and the O atom of the water molecule in $[Mg(H_2O)_6]^{2+}$ (in Epsom salts), to the very strong bonding in the $[Fe(CN)_6]$ units in the pigment Turnbull's blue, to the metal–C **covalent bonds** in organometallic compounds. The colors and magnetic properties of transition metal complexes can be explained by crystal field theory, while the metal–ligand covalent bonding is described by the molecular orbital approach.

covalent bond: bond formed between two atoms that mutually share a pair of electrons

The metal atom in the square-planar complexes of Pd(II), Pt(II), Rh(I), Ir(I) has only sixteen electrons in its valence orbitals. These complexes are easily oxidized by the addition of oxygen or halogens to yield an octahedral complex that obeys the EAN (eighteen-electron) rule. When heated, the 18-electron complex loses the diatomic molecule and the metal is reduced to the 16-electron complex. This cycle is important in **homogeneous catalysis**.

homogeneous: relating to a mixture of the same materials

catalysis: the action or effect of a substance in increasing the rate of a reaction without itself being consumed



Homogeneous Catalysis

Coordination complexes serve as catalysts in several important industrial reactions. In the Oxo reaction, $Co_2(CO)_8$ reacts with H_2 to form $HCo(CO)_4$, which catalyzes the addition of H_2 and CO to olefins to give aldehydes. Wilkinson's **catalyst**, [RhCl{P(phenyl)$_3$}$_3$], is a catalyst used for the hydrogenation of alkenes, especially important in the manufacture of pharmaceuticals because it is very selective and is effective under mild ambient comditions. Polyethylene is produced from ethylene at low pressure by using $TiCl_4/Al(C_2H_5)_3$ as a catalyst; for developing this process, Karl Ziegler and Giulio Natta earned a Nobel Prize in 1963.

catalyst: substance that aids in a reaction while retaining its own chemical identity

Extractive Metallurgy

The extraction and purification of the valuable metals by hydrometallurgical processes are totally dependent on the formation of stable coordination compounds. A few examples are

palladium: *trans*$[Pd(NH_3)_2Cl_2]$

platinum: $[PtCl_6]^{2-}$

gold: $[Au(CN)_2]^-$ and $[AuCl_4]^-$

uranium: $[UO_2(SO_4)_3]^{4-}$

cobalt: $[Co(D2EHPA)_2]$

The neutral cobalt D2EHPA complex is unique in its being soluble in kerosene, a property that makes possible the industrial solvent extraction process.

Bioinorganic Systems

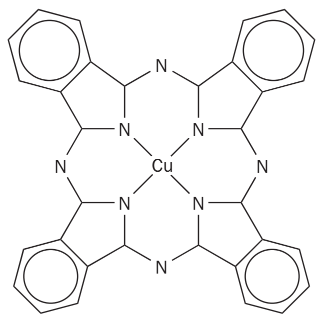
Coordination compounds play important roles in nature. **Chlorophyll**, which is involved in **photosynthesis** in plants, is a coordination complex of magnesium. Hemoglobin, the oxygen transporter in the human body, is a coordination complex of iron. **Vitamin** B_{12}, necessary for the prevention and cure of pernicious anemia, is a coordination complex of cobalt. In all three compounds, the metal ion is in an approximately octahedral environment, its coordination number is 6, and bonded to it are the four nitrogen atoms of a planar **porphyrin**-like ring. The basic planar ring structure is closely related to that of the extremely stable blue pigment, Cu(II)phthalocyanine.

chlorophyll: active molecules in plants undergoing photosynthesis

photosynthesis: process by which plants convert carbon dioxide and water to glucose

vitamins: molecules needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

porphyrin: common type of heterocyclic ligand that has four five-member rings with a nitrogen, all of which lie in a plane; nitrogen atom lone pairs are available for coordinate covalent bonds



Copper phthalocyanine complex

All metals will form coordination compounds. The stability of a coordination compound depends on the nature of the ligands and the atomic number and oxidation state of the metal. SEE ALSO BONDING; CHEMOTHERAPY; WERNER, ALFRED.

Michael Laing

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29
Cu
COPPER
65.34

Copper

MELTING POINT: **1,084.62°C**
BOILING POINT: **2,927°C**
DENSITY: **8.96 g/cm^3**
MOST COMMON IONS: **Cu^+, Cu^{2+}**

Copper was first used by humans more than 10,000 years ago. A copper pendant discovered in what is now northern Iraq has been dated to about 8700 B.C.E. For nearly five millennia copper was the only **metal** known to humans. Early copper artifacts—first decorative, then utilitarian—were undoubtedly hammered out from "native copper," pure copper found in con-

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

junction with copper-bearing ores in a few places around the world. By 5000 B.C.E., the dawn of **metallurgy** had arrived, as evidence exists of the **smelting** of simple copper oxide ores such as malachite and azurite.

metallurgy: the science and technology of metals

smelting: process by which ores are reduced in the production of metals

Known worldwide copper resources are estimated at nearly 2.6 trillion kilograms (5.8 trillion pounds), of which only about 12 percent (300 billion kilograms; 804 billion pounds) has been mined throughout history. Nearly all of this mined copper is still in circulation, as copper's recycling rate is higher than that of any other engineering metal.

As a molten liquid, copper may be poured to form cake or slabs from which plate, sheet, strip, and foil are rolled; billet or logs from which tube, rod, bar, and forgings are extruded; wire rod from which wire is drawn; and ingot or bricks from which copper may be alloyed with other metals or used by foundries for casting.

There are more than 450 copper **alloys**, including brasses, bronzes, copper-nickels, nickel-silvers, and other specialty alloys. Copper is naturally a salmon color and may oxidize or patinate to gradually become dark brown or a greenish blue. Its alloys may range from pink to brown to gold to silver in color.

alloy: mixture of two or more elements, at least one of which is a metal

Copper is used extensively for its high thermal and electrical conductivity and corrosion resistance. In the United States, the most predominant of thousands of copper and copper alloy applications include building construction (largely sheet, tube, building wire, and hardware), 45 percent; electrical and electronic products, 26 percent; transportation equipment, 9 percent; industrial machinery and equipment, 10 percent; and consumer products, 10 percent. SEE ALSO Electrochemistry.

Ken Geremia

Internet Resources

Copper in Your Home. Available from <http://www.copper.org/copperhome/homepage.html>.

The Copper Page. Available from <http://www.copper.org/>.

The Standards & Properties for Copper and Copper Alloys. Available from <http://properties.copper.org/>.

Cori, Carl and Gerty

AMERICAN BIOCHEMISTS
1896–1984 (CARL) 1896–1957 (GERTY)

Carl and Gerty Cori were a husband-and-wife team who worked closely together on research into carbohydrate metabolism.

Carl and Gerty were born in Prague, Czechoslovakia, and met as students at the German University of Prague where they both earned medical degrees in 1920. They were married that same year and migrated to the United States in 1923, both joining a research institute in Buffalo, New York. They became naturalized citizens of the United States in 1928.

In 1931 Carl accepted a position as professor of biochemistry at Washington University Medical School in St. Louis and Gerty was appointed as a research associate. She eventually achieved the rank of professor of biochemistry in 1947. The focus of their research was carbohydrate (sugar) metabolism and the influence of various hormones on these metabolic pathways.

American biochemists Gerty Therese Radnitz Cori and Carl Ferdinand Cori, corecipients of the 1947 Nobel Prize in physiology or medicine, "for their discovery of the course of the catalytic conversion of glycogen."

In 1936 they discovered the previously unknown metabolic intermediate glucose-1-phosphate, known as the "Cori ester." (See Figure 1).

Research into the formation of this ester demonstrated that it was formed from glycogen, a polymer of glucose employed by many living system as way to store energy. Over the next few years the Coris demonstrated the existence of a new enzyme, polysaccharide phosphorylase, which catalyzes both the formation of glucose-1-phosphate from glycogen and the reverse reaction in which glucose-1-phosphate is incorporated into glycogen; they also succeeded in purifying the enzyme. Since many enzyme-catalyzed reactions are reversible, demonstration of the pathways required ingenious use of selective enzyme inhibitors that permitted the Coris to demonstrate distinct reactions and isolate the enzymes carrying out the reactions. They eventually linked the formation of glucose-1-phosphate from glycogen in the liver to the transport of glucose to muscle cells where, under anaerobic conditions, glucose can be used as an energy source resulting in the formation of lactic acid. The lactic acid can then be transported back to the liver and, through a series of reactions, be used to reform glycogen. This pathway is known as the Cori cycle. The importance of the Coris's work was recognized when they received the Nobel Prize for physiology or medicine in 1947.

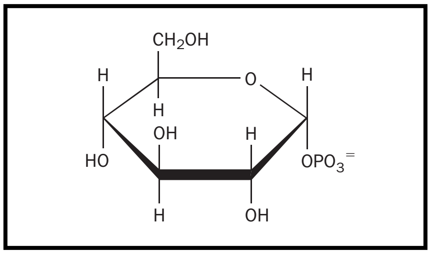

Figure 1. Structure of the Cori ester.

The Coris were also noted for their work investigating the influence of various hormones on carbohydrate metabolism. For example, they demonstrated that epinephrine, a hormone released by the adrenal gland, stimulates the formation of an enzyme that forms glucose from glycogen. They also discovered that insulin stimulates the enzyme hexokinase, which promotes the formation of glycogen from glucose and that a hormone released by the pituitary inhibits the activity of this enzyme. For this and other work the Coris received the Squibb Award in Endocrinology; Gerty was awarded the Garvan Medal of the American Chemical Society as well as a number of other awards and prizes.

After Gerty's death in 1957, Carl continued his work on the mechanism of enzymes involved in carbohydrate metabolism and remarried in 1960. He continued to publish the results of his research into the early 1980s until shortly before his death in 1984. SEE ALSO Enzymes; Krebs Cycle.

Robert K. Griffith

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Corrosion

Corrosion is the deterioration a material undergoes as a result of its interaction with its surroundings. Although this definition is applicable to any type of material, it is usually reserved for metallic **alloys**. Of the 105 known chemical elements, approximately eighty are **metals**, and about half of these can be alloyed with other metals, giving rise to more than 40,000 different alloys. Each of the alloys will have different physical, chemical, and mechanical properties, but all of them can corrode to some extent, and in different ways.

alloy: mixture of two or more elements, at least one of which is a metal

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Corrosion is a natural phenomenon. When newly made steel is first exposed to the air, its originally shiny surface will be covered with rust in a few hours. The tendency of metals to corrode is related to the low stability of the metallic state. Metals occur either in the pure metallic state, the zero **oxidation** state, or in the form of compounds with other elements (they acquire positive states of oxidation). In the natural world, most metals are found as compounds with other elements, indicating the greater stability of their oxidized forms. For this reason, to obtain the pure metal from one of its compounds, it is necessary to put in energy. The reverse is true when a metal is exposed to its environment: it tends to release this stored energy through the processes of corrosion. This is rather analogous to what happens when an object is suspended at a point above the ground (equivalent to the metallic state). When allowed to fall or reach a stable state, it returns to a position of minimum energy on the ground (equivalent to the metal's oxidized state).

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

The chemical reactions that take place in corrosion processes are reduction-oxidation (redox) reactions. Such reactions require a species of material that is oxidized (the metal), and another that is reduced (the oxidizing agent). Thus the complete reaction can be divided into two partial reactions: one, oxidation; the other, reduction. In oxidation, the metal loses electrons. The zone in which this happens is known as the anode. In the reduction reaction, the oxidizing agent gains the electrons that have been shed by the metal, and the zone in which this happens is the cathode.

This metal bolt is rusted, a result of the oxidation of the iron metal of which it is composed.

galvanic: relating to direct current electricity especially when produced chemically

Corrosion processes not only influence the chemical properties of a metal but also generate changes in its physical properties and its mechanical behavior. This is why the effects of corrosion are manifested in a variety of forms. The most common form is uniform corrosion, whereby there is a generalized, overall "attack" of the entire exposed surface of the metal, leading to a more or less uniform reduction in the thickness of the affected metal. In contrast, there is the process of localized corrosion, in which an intense attack takes place only in and around particular zones of the metal, leaving the rest of the metal unaffected; an example is pitting corrosion. Some other forms of corrosion are stress corrosion cracking, **galvanic** corrosion, selective alloy breakdown, intergranular corrosion, fatigue, friction, erosion, cavitation, hydrogen enbrittlement, biocorrosion, and high temperature oxidation.

It is easy to find everyday objects that show signs of corrosion. A used automobile consists essentially of different metals, plastics, paints, metallic coatings, and so forth, which have been exposed to a variety of aggressive conditions. These materials are exposed to the action of atmospheric agents under conditions of high temperature, are incorporated in closed water circuits, or are subject to mechanical wear. As a result, we see many signs of corrosion in cars, chiefly on the bodywork and in the exhaust system, and especially after years of use.

Traffic signs, streetlamp standards, metal barriers and fences, and many other items seen along roads are usually manufactured in galvanized steel (normal mild steel with a zinc coating). On such items it is common to see "white" corrosion (zinc oxide), characteristic of the oxidation of a zinc coating, often with spots of red rust also appearing that indicate that the steel base is being corroded.

The sea and the salty atmosphere are saline media that are highly aggressive to metals. Marine structures such as ships, bridges, and drilling rigs and platforms usually show signs of severe corrosion unless they have been properly protected. Cars kept near oceans show signs of corrosion.

Alloys of copper used in the casting of sculptures, and used externally on some buildings, usually show a greenish coloring that corresponds to a layer of corrosion product known as copper patina that gives some protection against further corrosion.

The degradation of reinforced concrete in buildings is commonly caused by the corrosion of the steel reinforcing bars within the concrete, rather than by the loss of the mechanical properties of concrete.

Corrosion processes affect many areas of human activity in which metal products are used. In general, as levels of economic development increase, so do costs incurred as a result of corrosion. It is estimated that the costs attributable to the corrosion of metallic materials amount to 4 percent of the gross domestic product of the developed countries. And this cost, representing a loss of resources, would be even higher if methods of protection against corrosion were not so widely applied. It is estimated that because of this protection, populations are able to reduce these potential losses by a factor of about 30 percent.

Many methods for preventing or reducing corrosion exist, most of them orientated in one way or another toward slowing rates of corrosion. A series of methods that are based on depositing a layer of a second material on the surface of a metal structure to impede the structure's contact with an aggressive medium have been developed. The most prevalent of these is painting, and a wide range of protective paints is now available. As a general estimate, for every 100 m^2 of exposed metal surface, paint is applied to 90 m^2. Included among these surface covering methods are metallic surface treatments, such as chrome, nickel, and galvanized coatings, and inorganic treatments, such as chromates, anodizing coatings, and phosphate coatings.

Another method of protection uses inhibitors, which are substances added to the liquid medium, again to reduce rates of corrosion. Antifreeze liquids utilized in the cooling circuits of vehicle engines have inhibitor agents incorporated into their formulations in order to reduce corrosion problems.

Cathodic protection is an anticorrosion technique widely used in ships and in buried or submerged pipe work. This method seeks to reduce the rate of corrosion of the structure to be protected by joining it to "sacrificial" anodes. In other words, the structure is joined to another metal (an anode) that corrodes more readily, effectively diverting the tendency to corrode away from the structure.

As an alternative to using metals that must be protected by one or other of the methods described, engineers often have an option to use an alloy selected for having a greater resistance to corrosion caused by its surroundings. But better corrosion resistance usually comes at a higher materials and/or manufacturing cost. Engineers must take into account that the corrosion resistance of any alloy depends on both the medium and the working conditions. Hence, alloys with good resistance in one environment may have poor resistance in another, and their resistance is also likely to vary according to differences in exposure conditions, such as temperature or stress. SEE ALSO Oxygen.

F. Javier Botana

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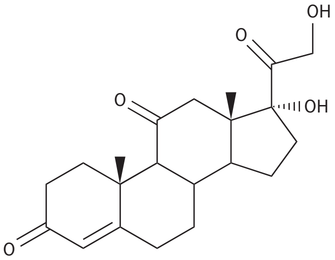
Cortisone

Cortisone is a steroid produced in the adrenal glands of the human body. The isolation of cortisone from the mixture of molecules produced in these glands was carried out by American biochemist Edward Kendall and coworkers. Kendall shared the Nobel Prize in physiology or medicine for this work in which he also helped establish the usefulness of cortisone in the treatment of arthritis.

The isolation of cortisone from adrenal glands is a laborious process, so its widespread utility as a medicine awaited the development of synthetic pathways to its production. Percy Julian was the first scientist to accomplish a commercially viable **synthesis** using protein from soybeans, and since his work an increasing number of applications have been found.



The structure of cortisone is shown above. Like other steroids, the molecule contains four fused rings. It is an example of an anti-inflammatory compound—one that reduces swelling. In many cases, swelling causes pain so the ability to reduce inflammation can be important for pain management, including the case of arthritis. In addition to arthritis, cortisone can be used to treat asthma, dermatological diseases, and tuberculosis and to fight the rejection of organ transplants by the body's immune system. SEE ALSO JULIAN, PERCY; STEROIDS.

Thomas A. Holme

EDWARD KENDALL (1886–1972)

Edward Kendall recognized that symptoms of one type of arthritis decrease in females during pregnancy. He worked to isolate and identify hormones that could be responsible for this occurrence. It was during this search that cortisone was discovered in adrenyl glands. For this scientific breakthrough, Kendall was awarded the Nobel Prize in 1950.

—Valerie Borek

synthesis: combination of starting materials to form a desired product

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Cosmetic Chemistry

The global market for skincare and color cosmetics exceeded 53 billion dollars in 2002. The number of new products brought to market continues to expand exponentially. Cosmetic chemists are always looking for interesting and exotic ingredients that improve skin's appearance and health. A vast array of compounds is required to supply these products. The latest edition of the Cosmetics Toiletries and Fragrance Association (CTFA) Dictionary lists more than 10,000 raw materials. Every year hundreds of new ingredients are added to the list of those that have been used for centuries. Some materials used today can be traced to 11,000 B.C.E. in the animal drawings from the caves of Altimira.

History

The appearance of skin care formulation dates to around 3000 B.C.E. in ancient Egypt. Most concoctions were prepared from natural materials. Cleopatra is said to have bathed in donkeys' milk to keep her skin smooth and supple. One naturally occurring material used by the ancients was red ochre, or iron oxide. Lumps of red ore were formed when iron oxidized or rusted. The red iron oxide was found in burial tombs in ceremonial lip tints and rouge preparations. It was also used to draw the ancient cave pictures of animals, as seen in Altimira, and is still used in many makeup formula-

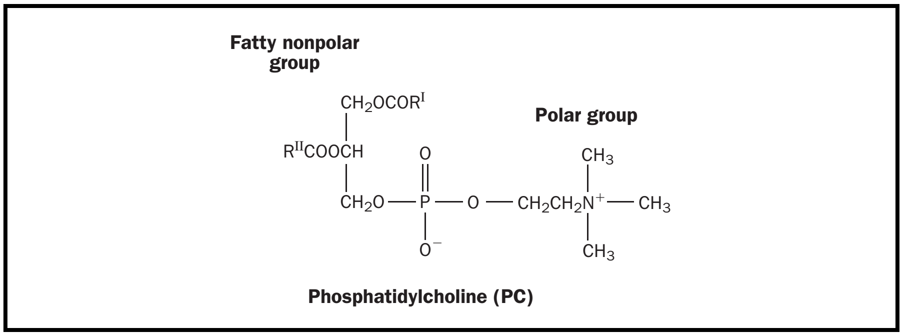


Figure 1. Phosphatidylcholine (PC).

tions today. Eye paints have also been found at ancient gravesites. These paints consisted primarily of a copper-based green ore called malachite that was mined from nearby quarries. Animal fat was combined with fragrant substances such as frankincense and myrrh to produce early skin ointments. More sophisticated creams and lotions were fine tuned through trial and error and passed down over many generations.

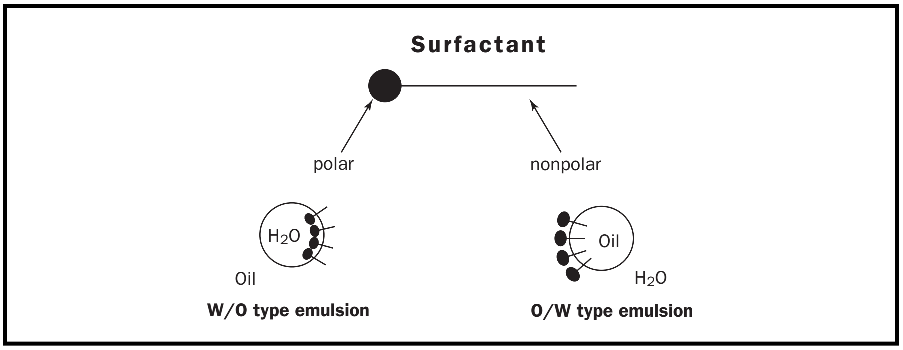
Emulsions

The majority of creams and lotions are emulsions. An emulsion can be defined simply as two immiscible fluids in which one liquid is dispersed as fine droplets in the other. Homogenized milk is an example of a typical oil-in-water (o/w) emulsion. Milk fat (oil) is dispersed in water as fine droplets by the homogenization process. The reason the fat does not float to the top immediately is due to the presence of emulsifiers; in this case, a milk protein called sodium caseinate as well as several phopholipids. In the case of water-in-oil (w/o) emulsions, water is dispersed as droplets and suspended in the oil phase. The nondispersed liquid or external suspending phase is also called the continuous phase. Mayonnaise, vinegar water dispersed as fine droplets in a continuous phase of soybean oil, is an example of a water-in-oil emulsion. Lecithin from eggs stabilizes the mayonnaise emulsion.

Surfactants

Most emulsifiers can be considered surfactants or surface-active agents. These materials are able to reduce the surface tension of water. What makes an emulsifier surface active is related to its HLB, or hydrophile-lipophile balance. HLB is determined by the size of the *hydrophilic* (water-loving or polar) portion of a molecule as compared to the size of the *lipophilic* (oil-loving or nonpolar) portion. The HLB system was created to rank the relative polarity of materials. The most polar, water soluble, materials are at the top of the twenty-point scale with more non-polar, oil soluble, materials closer to zero. The HLB of sodium caseinate is assigned a value of around fourteen because of it's high solubility in water. Lecithin, being poorly soluble in water, has an HLB value of about six. Both have polar groups. The polar group in the milk protein is sodium. Lecithin's surface-active component is a molecule called phosphotidylcholine or PC (See Figure 1). The polar, or water soluble part of PC is the phosphate functional group. The emulsifiers' polar groups orient toward the polar water phase. Their lipophilic, nonpolar groups oriented toward the oil phase to form micelles (see Figure 2). These spherical structures provide stability to the emulsion through Hydrogen bonding and weak electrical forces.

Figure 2. Surfactant.



solvated: dissolved

Skin-care emulsifiers can be divided into two groups based on ionic charge (See Figure 3). Materials that can dissociate into charged species are considered ionic while those that do not are called nonionic. Ionic emulsifiers can be further classified by type of charge. Anionics are negatively charged when **solvated** as in sodium stearate or soap.

When fatty acids are reacted with alkali they form soaps. The process of soap formation is called saponification. The negatively charged stearic acid group is the main emulsifying unit of the soap, giving it the anionic classification. Positively charged emulsifiers are called cationic. Quarternium24's emulsifying unit dissociates into the positively charged ammonium group. Amphoterics are compounds that express both negative and positive charges.

humectant: moisture retaining

ester: organic species containing a carbon atom attached to three moieties: an O via a double bond, an O attached to another carbon atom or chain, and an H atom or C chain; a compound with the general formula RC(O)OR′

Nonionic emulsifiers are often used in skin-care emulsion for their safety and low reactivity. They are generally classified by chemical similarity. Glycerin, commonly added to cosmetic emulsions for its **humectant** properties, is the backbone of a class of emulsifiers called Glyceryl **esters**. Glyceryl monostearate, or GMS, is called a monoester because of its sole ester linkage (see Figure 4). The diester is prepared by esterifying two molecules of stearic acid for every molecule of glycerin. Glyceryl mono- and diesters are very effective emulsifiers because they contain both polar hydroxyl (OH) groups as well as non-polar fatty acids. If all three of Glycerin's hydroxyl groups are reacted, the resulting triester will have little emulsifying capability.

Stearic acid is called C18 fatty acid. The fatty acids, present in fats and oils, are classified according to their carbon-chain lengths. Because stearic acid is a major component of many of the fats and oils used in beauty treatments, stearate-based emulsifiers are particularly useful. Fatty acids are key components of many cosmetic emulsifiers due their miscibility in a variety of natural and synthetic oils.

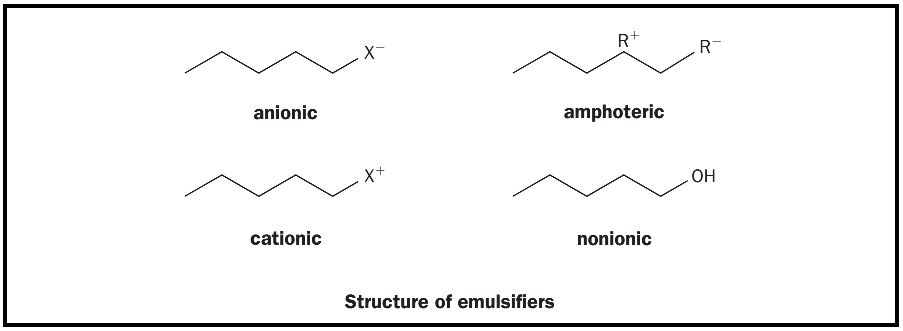


Figure 3. Structures of emulsifiers.

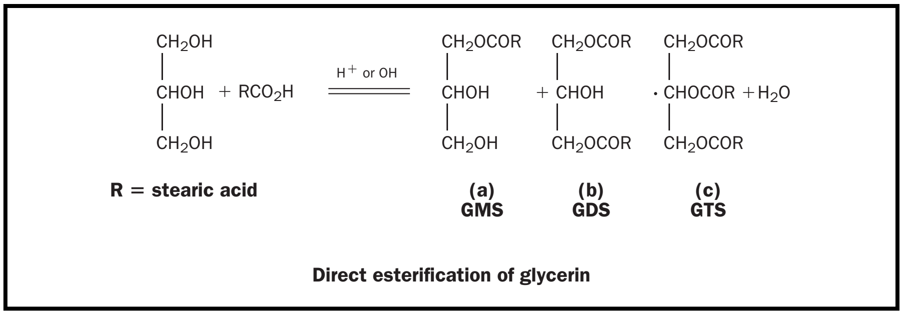


Figure 4. Direct esterification of glycerine.

Esters polyethylene glycol or ethylene glycol are called PEG esters. A PEG ester's solubility is determined by the number of PEG molecules reacted per molecule of acid. PEG 6 oleate for instance has six molecules of PEG reacted with one molecule of oleic acid. As the number of polar, PEG molecules per acid molecule increases the water solubility/HLB is increased; PEG 8 oleate is more soluble than PEG 6 oleate. The cosmetic chemist will often use blends of glyceryl esters and a PEG ester with high and low HLB values to determine the required polarity to emulsify various fats and oils. The many types of emulsifiers are too numerous to list here, however *McCutcheon's Emulsifiers and Detergents* is an excellent source for a more complete listing.

Emollients

The majority of emollients used in personal care and beauty items are fats and oils, also called lipids. Animal fat or tallow is composed primarily of stearic and palmitic acids with carbon chains lengths of 18 and 16 respectively. Many of the major cosmetic companies are moving away from animal-based materials like tallow to renewable vegetable-based materials. Coconut oil and palm kernel oil are often used. Some of the key characteristics required in good emollients are good spreading properties, low toxicity/skin irritation and good oxidative stability. Oleic acid, a major constituent of olive oil has poor oxidative stability due to the presence of its double bond. Fats and oils are considered saturated if they do not have double bonds. Unsaturated oils like olive oil have double bonds that can react with oxygen, especially when heated. The oxidation process can produce off colors and odors in lipids causing them to go rancid and unusable.

Petroleum-based emollients such as petroleum jelly and mineral oil are found in many formulations because they do not contain double bonds or reactive functional groups. Silicone oils such as cyclomethicone, dimethicone are often added to increase slip and emolliency (See Figure 5).

Oils that contain high levels of essential fatty acids, EFAs, are prized for their ability to replenish lipids (oils) that are found naturally within the skin layers. Linoleic acid is an example of an EFA. Long-chain alcohols, also called fatty alcohols, are useful as emollients and emulsion stabilizers. Their polar hydroxyl groups orient to the water phase with their fatty chains oriented towards the oil phase. Esters of fatty alcohols and fatty acids make excellent emollients because of their low reactivity and good stability.

Lanolin, derived from sheep's wool, is often called wool grease. Lanolin has been used for centuries due to it's unique composition of complex sterols, fatty alcohols, and fatty acids. Cholesterol, a cyclic molecule called

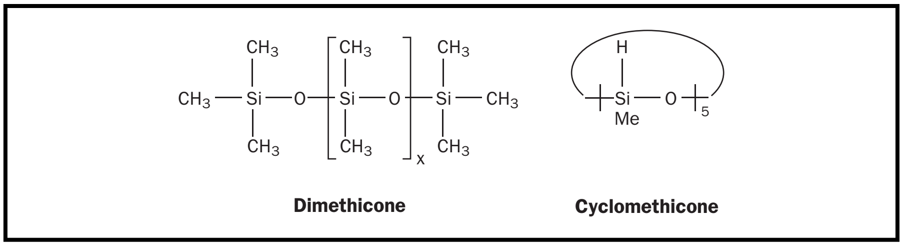


Figure 5. Dimethicone and cyclomethicone.

a sterol, is a major component. The polar hydroxyl groups of sterols and alcohols enable the grease to absorb and hold water. Skin is primarily composed of water, countless oils and emollients are used to nourish and protect it.

Moisturizers

hygroscopic: readily absorb and retain moisture

transepidermal: through the outermost layer of skin

The main distinction between moisturizers and emollients is their solubility in water. Healthy skin requires moisture. Moisturizers are generally polar materials that are **hygroscopic** in nature; they hold onto water. An important tool to assess the efficiency of moisturizers is the high scope. It measures **transepidermal** water loss or TEWL. After a moisturizer is applied to the skin, the moisture level is recorded. After several minutes the moisture level will be reduced due to the natural tendency of the skin to release moisture over time. Ingredients that can maintain a high level of moisture in the upper layers of the skin for several hours can reduce the rate at which water is lost. Glycerin is a very cost-effective ingredient used to help reduce TEWL. Sorbitol, sucrose, glucose, and other sugars are also commonly used to hydrate the skin. Aloe, which contains a mixture of polysaccharides, carbohydrates, and minerals, is an excellent moisturizer. As skin becomes drier in the winter months, it may be necessary to incorporate materials that better seal the moisture in the skin.

Waxes

turbidity: fluidity

Waxes are composed primarily of long-chain esters that are solid at room temperature. Anyone who has ever dipped a finger in molten wax has experienced its sealing properties. Some common waxes used in cosmetics are beeswax, candelilla, carnauba, polyethylene, and paraffin. The melting points of waxes vary widely depending on their unique composition and chain lengths. Commonly used in lip balms and sticks, waxes function as structuring agents, giving the stick enough rigidity to stand up on its own, as well as barrier properties. By combining waxes with different properties such as high shine, flexibility, and brittleness, optimal cosmetic performance can be achieved. Often waxes are combined with compatible oils to achieve the desired softness. Compatibility is generally determined by gauging the **turbidity** and degree of separation of two materials mixed together above their melt points. Waxes are particularly useful in hand creams and mascara emulsions for their thickening and waterproofing properties.

Thickeners

By incorporating enough wax into a thin lotion, a thick cream can be formed. Many thickeners are polymers. Cellulose, a fine powder polymer of repeat-

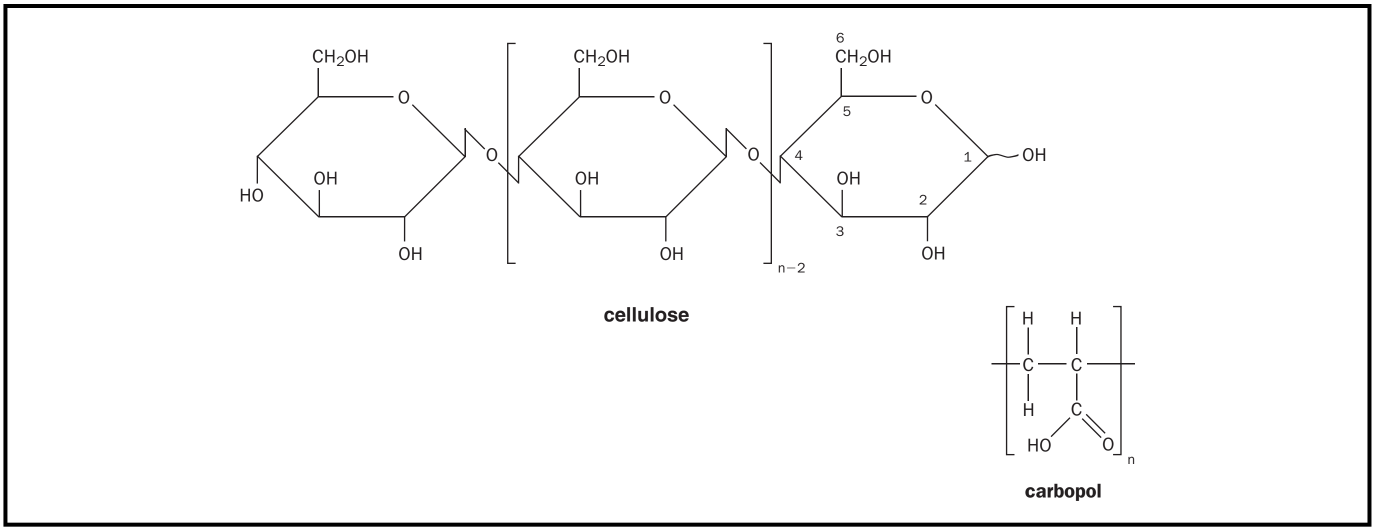


Figure 6. Cellulose and carbopol.

ing D-glucose units, swells in hot water creating a gel network. Carbopol, a polyacrylic acid, swells when neutralized (See Figure 6). Bentone clays swell when their structure, resembling a stack of cards, is opened up through mechanical shear. Carrageenan, pectin, and locust bean gum are all examples of cosmetic thickeners that are also used in some of our favorite foods such as jellies, salad dressings, and pie fillings.

Active Ingredients

Materials that work physiologically within the skin or aid in protecting the skin from insult are also called active ingredients. The term "cosmeceuticals" coined by famed dermatologist Dr. Albert Kligman, refers to a product that is in-between a cosmetic and a drug. Although a cosmetic, by legal definition, can only serve to beautify and protect the surface of the skin, many cosmetic products can be shown to penetrate the dermal layers of the skin to exact a physiological change.

Fruit acids are an example of an active material. Also called alpha hydroxyacids or AHAs, they have the ability to penetrate the skin, where they can increase the production of collagen, elastin, and intracellular substances thus improving the appearance of the skin. Thousands of cosmetic actives are used to affect the skin in a variety of ways. They are used to lighten, tighten, and firm the skin. They can be used to suppress perspiration as in the case of aluminum chlorohydrate. Salicylic acid and benzoyl peroxide are important ingredients because of their anti-acne activity (See Figure 7). Some active materials are added to skin treatments to protect the skin from the environment. Dimethicone and petrolatum are examples of skin protectants.

Sunscreens

Sunscreens are a class of compounds that protect the skin from ultraviolet radiation. Wavelengths between 290nm and 400nm are particularly damaging to the skin. Sunscreens' ability to absorb or reflect these damaging wavelengths are rated by their SPF or sun-protection factor. For instance a person protected with a factor-15 sunscreen will be able to stay in the sun

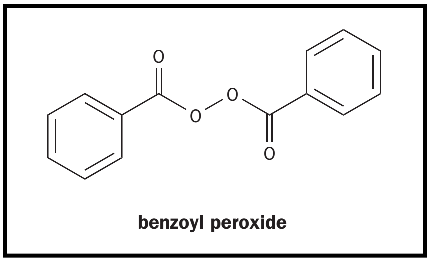


Figure 7. Structure of Benzoyl peroxide.

fifteen times longer than if unprotected. Octyl methoxycinnamate, octyl salycilate, titanium dioxide, and avobenzone are some important topical sunscreens. They can be classified as either UVA or UVB sunscreens depending the wavelengths they absorb. Benzophenone 4, a water-soluble UV filter, is commonly used to protect the color of cosmetic products.

Color

Pigments and dyes are used in products to impart a color. Titanium dioxide (TiO_2) is a white pigment that is mined. In combination with natural mined and synthetic iron oxides, which range in color from red, yellow, black and brown, depending upon the degree of oxidation and hydration, a range of color can be produced that will be suitable for almost every skin tone. Face powders are produced by blending inorganic oxides and fillers. Fillers are inert, generally inexpensive materials such as kaolin, talc, silica, and mica that are used to extend and fully develop colors. Pressed powders like eyeshadows and blushers are prepared by blending additional binding ingredients such as oils and zinc stearate and pressing the mixture into pans.

Eyeshadows and lipsticks often contain pearlescent pigments commonly called pearls. Pearls sparkle and reflect light to produce a multitude of colors. They are prepared by precipitating a thin layer of color on thin platelets of mica. Varying the thickness of the color deposited changes the angle of light refracted though the composite, creating different colors.

Organic pigments are used to color lipsticks and eyeshadows. When organics are precipitated on a substrate they are called lake pigments. The term lake refers to the laking or precipitating of the organic salt onto a metal substrate such as aluminum, calcium, or barium. They are called D&C (drug and cosmetic) and FD&C (food, drug and cosmetic) colors. Some examples are D&C Red#7 calcium lake and FD&C Yellow #5 aluminum lake. Dyes such as FD&C Blue#1 and D&C Yellow #10 are readily soluble as opposed to pigments, which are insoluble. Dyes are useful in providing tints for lotions, oils, and shampoos.

Preservatives

Most cosmetic products require the addition of preservative to prevent microbial contamination and rancidity. Parabens and ester of parabenzoic acid are by far the most commonly used because of their effectiveness against gram-positive bacteria. Phenoxyethanol is used to protect against gram-negative strains. The cosmetic chemist will generally employ a mixture of preservatives to protect against different bacterial strains as well as yeasts and molds. Antioxidants such as tocopherol (vitamin E) and BHT are also added to prevent oxidation of sensitive ingredients as well as protect the skin from free-radical damage.

Conclusion

As long as society continues to puts great emphasis on looking young and beautiful cosmetic chemistry will continue to flourish. A good understanding of the fundamentals of emulsion chemistry and skin physiology are prerequisites, when formulating personal care products. A good cosmetic chemist must be able to combine science and art to create products with the feel and look that consumers desire.

John Castro

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Cottrell, Frederick

AMERICAN CHEMIST
1877–1948

Frederick Cottrell invented the "electrostatic precipitator," which removes pollutants from smoke. Cottrell was born on January 10, 1877, in Oakland, California, the son of Henry and Cynthia Cottrell. His ingenuity and interest in the applied sciences were demonstrated early on. At the age of thirteen, he ran his own printing business with a handpress in the basement of his home, publishing, among other works, a four-page technical magazine, *Boy's Workshop*. He also earned money from odd jobs as an electrician and landscape photographer.

After graduating from Oakland High School, Cottrell attended the University of California at Berkeley. He graduated at the age of nineteen in 1896 with a B.S. in chemistry. He taught high school chemistry for four years and then traveled to Germany, where he earned a doctorate in physical chemistry at the University of Leipzig in 1902. He returned to a teaching appointment at Berkeley, but resigned in 1906 to do independent research on industrial pollution.

A local form of air pollution, the acidic mists from the chimney of a nearby sulfuric acid factory, had triggered Cottrell's interest in this field. Recognizing that fine droplets and solid particles in smoke are held in suspension by the repulsion of electrical charges on their surfaces, Cottrell decided to build a device that could neutralize these charges. The result was a set of probes with a charge of opposite sign that neutralized the charges on the suspended material and caused it to precipitate. The first patent for the electrostatic precipitator was issued on August 11, 1908.

The precipitator was soon at work, removing the acid mist from the stack gases of the sulfuric acid plant. A modification of the original design then removed **arsenic** dust, as well as lead particles, from the emissions of a lead smelter. A further modification precipitated the dust from the emissions of a cement plant.

arsenic: toxic element of the phosphorus group

Cottrell had struggled to finance the experiments that led to the development of the electrostatic precipitator. Although the profits from the eventual manufacture of his precipitator could have made him a wealthy man, he decided that a portion of these monies should go to the support of scientific research. In 1912 he founded the Research Corporation, which is still the recipient of fees from the original patents and distributes them as research grants.

In 1911 Cottrell was appointed chief physical chemist at the U.S. Bureau of Mines, where he rose to the position of director in 1919. He joined the National Research Council (NRC) in 1921, and in 1922 became director of the Department of Agriculture's Fixed Nitrogen Laboratory. He retired in 1930 and devoted the remainder of his life to the Research Corporation. Cottrell died on November 16, 1948, while attending a scientific meeting in Berkeley, California.

Cottrell precipitators continue to benefit the environment by removing particulates from the gases routinely emitted by factory chimneys. Companies that install them find that the devices soon pay for themselves in terms of the value of the materials that are recovered from the precipitated solids.

The Research Corporation continues to benefit the advancement of science through its grants. The organization tends to favor young scientists in need of funds to support their first major projects. As Cottrell himself remarked, "Bet on the youngsters. They are long shots, but many will pay off" (Barker, p.17). Among the recipients of Research Corporation grants were Ernest Lawrence, who developed the cyclotron, for which he received a Nobel Prize in physics, and contributed to the development of atomic energy, and Robert Goddard, pioneer rocket scientist. SEE ALSO LAWRENCE, ERNEST.

Lyman R. Caswell

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FRENCH ENGINEER AND PHYSICIST
1736–1806

Charles-Augustin de Coulomb was born to affluent parents in Angoulême, France. His father's family was prominent in the legal profession and involved in the administration of the Languedoc region of France. His mother's family was quite wealthy. After being raised in Angoulême, Charles moved with his family to Paris, where he entered the Collège Mazarin and pursued a classical education.

After a brief stay in Montpellier, Coulomb returned to Paris to study at the École du Génie at Mézières. This was one of the first schools of engineering; it specifically focused on military engineering. Coulomb graduated in 1761 with a degree in engineering and the rank of lieutenant in the Corps du Génie. Over the next twenty years, he was posted to a variety of locations where he became involved in the structural design of forts and fortifications, and soil mechanics.

In 1777 his work on torsion balances (among other subjects) won Coulomb a share of the Grand Prix of the Académie des Sciences. Historically, all measurements of weight had been obtained by using a two-pan balance, which is simply a bar centered on a **fulcrum**. Coulomb's **torsion balance** replaced the fulcrum with a fine silk thread or hair, and rather than the up-and-down motion of the pan balance, he used a twist or torsion around this thread. He was able to show that the amount of torsion is proportional to the amount of force; thus he devised a method for measuring very small interactions.

fulcrum: prop or support to an item like a lever

torsion balance: instrument used to measure small forces (weights), based upon the resistance of a wire to be twisted

With his very fine torsion balance, Coulomb was able to demonstrate that the **repulsive force** between two small spheres electrified with the same type of electricity is inversely proportional to the square of the distance between the centers of the two spheres. At the time, the electron had not yet been discovered, so the underlying reason for this remained a mystery but Coulomb was able to demonstrate that both repulsion and **attraction** followed this principle. He was not able to make the quantitative step to show that the force was also directly proportional to the product of the charges, but he did complete some experiments exploring this relationship. As a consequence, the law governing one of the four fundamental forces of nature is named Coulomb's law:

repulsive force: force that repels two bodies; charges of the same sign repel each other

attraction: force that brings two bodies together, such as two oppositely charged bodies

$$F = kq_1q_2/r^2$$

For his work in setting physics on a course of discovery, the fundamental unit of charge was named the "coulomb" in his honor. SEE ALSO Bonding.

Todd W. Whitcombe

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Cryogenics

Cryogenics is the science that addresses the production and effects of very low temperatures. The word originates from the Greek words *kryos* meaning "frost" and *genic* meaning "to produce." Under such a definition, it could be used to include all temperatures below the freezing point of water (0°C). However, Professor Heike Kamerlingh Onnes of the University of Leiden in the Netherlands first used the word in 1894 to describe the art and science of producing much lower temperatures. He used the word in reference to the **liquefaction** of permanent gases such as oxygen, nitrogen, hydrogen,

liquefaction: process of changing to a liquid form

and helium. Oxygen had been liquefied at −183°C a few years earlier (in 1887), and a race was in progress to liquefy the remaining permanent gases at even lower temperatures. The techniques employed in producing such low temperatures were quite different from those used somewhat earlier in the production of artificial ice. In particular, efficient heat exchangers are required to reach very low temperatures. Over the years the term "cryogenics" has generally been used to refer to temperatures below approximately −150°C.

According to the laws of thermodynamics, there exists a limit to the lowest temperature that can be achieved, which is known as absolute zero. Molecules are in their lowest, but finite, energy state at absolute zero. Such a temperature is impossible to reach because the input power required approaches infinity. However, temperatures within a few billionths of a degree above absolute zero have been achieved. Absolute zero is the zero of the absolute or thermodynamic temperature scale. It is equal to −273.15°C or −459.67°F. The metric or SI (International System) absolute scale is known as the Kelvin scale whose unit is the kelvin (not Kelvin), which has the same magnitude as the degree Celsius. The symbol for the Kelvin scale is K, as adopted by the Thirteenth General Council on Weights and Measures (CGPM) in 1968, and not °K. Thus, 0°C equals 273.15 K. The English absolute scale, known as the Rankine scale, uses the symbol °R and has an increment the same as that of the Fahrenheit scale. In terms of the Kelvin scale, the cryogenic region is often considered to be that below approximately 120 K (−153°C). The common permanent gases referred to earlier change from gas to liquid at atmospheric pressure at the temperatures shown in Table 1, called the normal boiling point (NBP). Such liquids are known as cryogenic liquids or cryogens. When liquid helium is cooled further to 2.17 K or below, it becomes a superfluid with very unusual properties associated with being in the **quantum mechanical** ground state. For example, it has zero viscosity and produces a film that can creep up and over the walls of an open container, such as a beaker, and drip off the bottom as long as the temperature of the container remains below 2.17 K.

quantum mechanical: theoretical model to describe atoms and molecules by wave functions

The measurement of cryogenic temperatures requires methods that may not be so familiar to the general public. Normal mercury or alcohol thermometers freeze at such low temperatures and become useless. The platinum resistance thermometer has a well-defined behavior of electrical resistance versus temperature and is commonly used to measure temperatures accurately, including cryogenic temperatures down to about 20 K. Certain semiconducting materials, such as **doped** germanium, are also useful as electrical resistance thermometers for temperatures down to 1 K and below, as long as they are calibrated over the range they are to be used. Such

dope: to add a controlled amount of an impurity to a very pure sample of a substance, which can radically change the properties of a substance

NORMAL BOILING POINTS OF COMMON CRYOGENIC FLUIDS

Cryogen	(K)	(°C)	(°R)	(°F)
Methane	111.7	−161.5	201.1	−258.6
Oxygen	90.2	−183.0	162.4	−297.3
Nitrogen	77.4	−195.8	139.3	−320.4
Hydrogen	20.3	−252.9	36.5	−423.2
Helium	4.2	−269.0	7.6	−452.1
Absolute zero	0	−273.15	0	−459.67

Table 1. Normal boiling points of common cryogenic fluids

secondary thermometers are calibrated against primary thermometers that utilize fundamental laws of physics in which a physical variable changes in a well-known theoretical way with temperature.

The production of cryogenic temperatures almost always utilizes the compression and expansion of gases. In a typical air liquefaction process the air is compressed, causing it to heat, and allowed to cool back to room temperature while still pressurized. The compressed air is further cooled in a heat exchanger before it is allowed to expand back to atmospheric pressure. The expansion causes the air to cool and a portion of it to liquefy. The remaining cooled gaseous portion is returned through the other side of the heat exchanger where it precools the incoming high-pressure air before returning to the compressor. The liquid portion is usually distilled to produce liquid oxygen, liquid nitrogen, and liquid argon. Other gases, such as helium, are used in a similar process to produce even lower temperatures, but several stages of expansion are necessary.

A multicelled human embryo, $2\frac{1}{2}$ days after its removal from a womb. It was cryogenically stored at the Bourn Hall Fertility Clinic, Cambridgeshire, England.

Cryogenics has many applications. Cryogenic liquids like oxygen, nitrogen, and argon are often used in industrial and medical applications. The electrical resistance of most **metals** decreases as temperature decreases. Certain metals lose all electrical resistance below some transition temperature and become superconductors. An electromagnet wound with a wire of such a metal can produce extremely high magnetic fields with no generation of heat and no consumption of electric power once the field is established and the metal remains cold. These metals, typically niobium **alloys** cooled to 4.2 K, are used for the magnets of magnetic resonance imaging (MRI) systems in most hospitals. Superconductivity in some metals was first discovered in 1911 by Kamerlingh Onnes, but since 1986, another class of materials, known as high temperature superconductors, have been found to be superconducting at much higher temperatures, currently up to about 145 K. They are a type of ceramic, and because of their brittle nature, they are more difficult to fabricate into wires for magnets.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

alloy: mixture of two or more elements, at least one of which is a metal

Other applications of cryogenics include fast freezing of some foods and the preservation of some biological materials such as livestock semen as well as human blood, tissue, and embryos. The practice of freezing an entire human body after death in the hope of later restoring life is known as cryonics, but it is not an accepted scientific application of cryogenics. The freezing of portions of the body to destroy unwanted or malfunctioning tissue is known as cryosurgery. It is used to treat cancers and abnormalities of the skin, cervix, uterus, prostate gland, and liver. SEE ALSO SUPERCONDUCTORS; TEMPERATURE; THERMODYNAMICS.

Ray Radebaugh

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CT Scans

A computed axial tomograph is an axial (cross sectional) view computed from a large set of values, each corresponding to the attenuation of an x-ray beam passed transversely (i.e. in the plane of the desired image) through the subject. In medical applications the subject is a patient; however, applications are not limited to medicine. Computed tomography (fr Greek tomos and graphikos for section or slice and drawing, respectively) has applications in areas as diverse as material sciences, archeology, manufacturing, and facility security.

A CAT Scanner is a machine designed to collect and process the x ray transmission data required to construct and display a computed axial tomograph. "CT scanner" is nearly synonymous with CAT scanner, but recognizes that computed views are not limited to axial views.

Basic physics

photons: a quantum of electromagnetic energy

X rays (comprised of photons) diminish exponentially in intensity as they pass through a material of thickness Δx according to the relationship:

(1) $I_{out} = I_{in}\ e^{-a^{*}\Delta x}$. Where "I" is the intensity, "e" is the Naperian constant, "a" is the attenuation coefficient of the material, and "Δx" is the distance traveled. When "n" adjacent materials are transversed, the formula can be applied repeatedly to yield

(2) $I_{out} = I_{in} * e^{-a_{0*}{}^{\Delta x}} * e^{-a_{1*}{}^{\Delta x}} * e^{-a_{2*}{}^{\Delta x}} \ldots e^{-a_{n*}{}^{\Delta x}}$. Which is equivalent to

(3) $I_{out} = I_{in} * e^{-a_{0*}{}^{\Delta}x_0 - a_{1*}{}^{\Delta}x_1 - a_{2*}{}^{\Delta}x_2 \ldots - a_{n*}{}^{\Delta}x_n}$, which yields

(4) $^{-}\ln(I_{out}/I_{in}) = a0\Delta x0 + a1\Delta x1 + a2\Delta x2 \ldots an\Delta xn$

Thus the logarithm of the attenuation along any ray is a linear function of the distances traveled through the materials encountered and their respective attenuation coefficients.

Scope of computation

The fundamental computational problem of axial tomography is to solve a group of equations for the attenuation coefficients of each voxel. A voxel —is a volume element, in particular the smallest volume element the system can manage—similar concept to *pixel.* The solution grid is chosen from the points where rays from different rotation angles intersect. After the attenuation coefficients have been determined for the solution grid, averaging and interpolation are used to superimpose a display grid of cubical voxels. For useful resolution, voxels must be small, consequently the system of equa-


A patient is having a CAT scan.

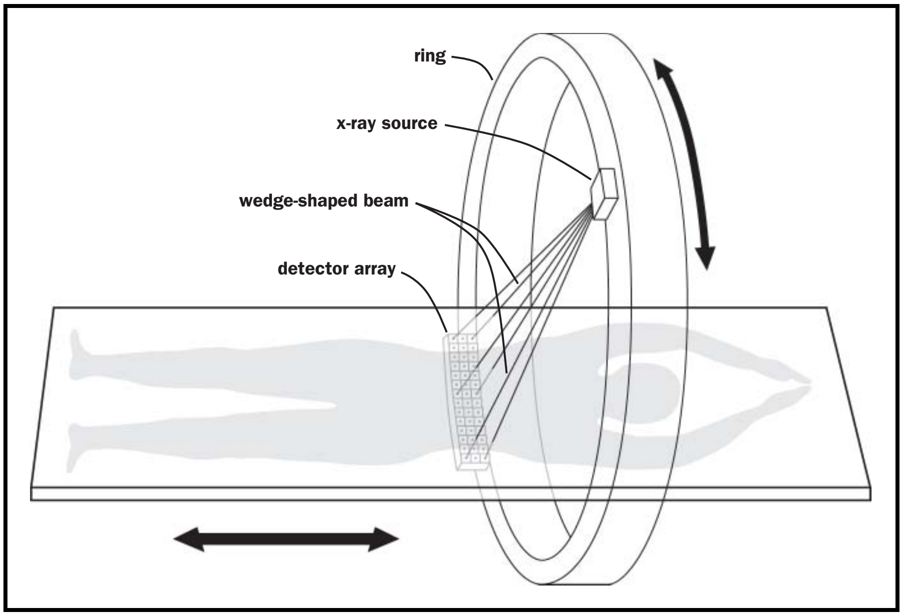
tions becomes very large, i.e., for a resolution of 2mm x 2mm across a body 500mm (19.7 inches) in diameter the minimum number of equations for a solution will be on the order of 64,000 for each transverse slice or "cut." If the detector arc contains 256 detectorsper slice, recordings from about 250 positions around the axis are required. Scanning a region 10 cm long with a corresponding resolution (2mm/cut) will require 50 cuts and the total number of equations becomes 3,200,000. Fortunately mathematicians and computer scientists have been pursuing efficient computational methods for similar problems for decades. A profound improvement was made in 1965 when J. W. Cooley and J. W. Tukey introduced the fast Fourier transform. Present methods require working knowledge of linear algebra, calculus, differential equations, matrices, vector calculus, Fourier transforms, and some programming experience to be appreciated.

By 2002, scans of the resolution and extent mentioned above could be acquired and solved within a few seconds. Consequently the radiation exposure of the patient was limited to safe levels despite the amount of information obtained.

Practical Scanners

A realistic scanner (Figure 1) has a point as the source of x rays. This point produces a wedge-shaped beam aimed at an arc of detectors (possibly more than one layer thick, to acquire data for adjacent cuts simultaneously). The source and detectors have a constant geometric relationship because they are fixed to a rigid ring (gantry). The ring is rotated about the axis of the subject lying on an x ray–transparent table that moves along the ring axis. Exposures are made at many angular positions to acquire sufficient data to compute the voxel values for the cut(s). For the resulting attenuation dataset to be useful it must be recorded with precise values for the corresponding angular position of the beam and the linear position of the table. If slip rings (or telemetry) connect the power, control, and data cables between the

Figure 1. Diagram of a CAT scanner.



ring and the frame, the ring can rotate continuously without reversing between cuts. Continuous rotation with continuous linear table motion of one detector-array-width per ring-revolution produces an aptly named helical scan (loosely called a "spiral" scan). If the detectors and processing electronics are fast enough, rotation, exposure, and detection can also be continuous. The fastest systems can complete a scan of a beating heart so rapidly that there is negligible motion artifact in the computed image—similar to stop action photography with fast shutter speeds and fast film.

History

Austrian mathematician Johann Radon (1887–1956) suspected that images might be created from rays traveling in the plane of a subject and in 1917 presented a proof that this was at least theoretically possible. Decades later, his work proved fundamental in developing methods for computing axial tomographs. CAT scanners could not be built until the late 1960s, as even a rudimentary CAT scanner requires the confluence of imagination and several technologies (just as da Vinci's helicopter had to wait for the invention of the internal combustion engine and light metal alloys).

CAT scanners require affordable computational power, reliable micro-sized solid state detectors, materials dimensionally stable with respect to time and temperature, high power x ray–source tubes with precisely shaped anodes, and considerable sophistication in computational methods. Similarly, the burgeoning field of computational chemistry would be nonexistent without computational power unattainable until very the end of the twentieth century.

British engineer Sir Godfrey Newbold Hounsfield invented the CAT scanner as soon as it was practical to do so. Beginning in the late 1960s he conceived demonstration conceptual laboratory models that took hours to acquire and analyze data for a single low-resolution slice. Hounsfield was assisted in implementing his ideas by radiologists James Ambrose and

A CAT scan of a human brain with Parkinson's Disease, with visible atrophy.

Louis Kreel. Hounsfield obtained a British patent in 1972 and a US patent in 1976and shared the 1979 Nobel Prize for medicine and physiology, with Allan MacLeod Cormack, a physicist at Yale who had independently developed mathematical methods required to solve the inverse problem of axial tomography.

Refinements

Such a vast quantity of information is collected by high-resolution scanners that additional refinements are needed to help physicians quickly absorb the information. The principal aids are computed color contrasts and images computed from selected viewpoints.

Contrast and Color. The attenuation differences of similar tissues can be enhanced by the administration (intravenously or by mouth) of contrast agents (sometimes called "dyes") that will collect preferentially in one tissue type before eventual elimination by the body. These agents contain salts of heavy atoms, such as iodine, that attenuate x rays more rapidly than living tissue. Even if the attenuation coefficient change might be inapparent to a human viewing a simple gray-level presentation of the data, differences detectable to the imaging system (with or without contrast) permit attenuation coefficients within different ranges to be displayed as different colors:

such as red for blood, pink for muscle, silver for tendon, ivory for bone, and yellow for nervous tissue.

Computed Views. By convention, medical CAT views are oriented with the viewer looking from the feet toward the head with the patient supine. However once the grids of multiple slices have been solved for the attenuation coefficient of each voxel, there are no restrictions except imagination and computation costs on how that information can be presented. Such constructed views actually contain no more information than a series-of-slices presentation, but they can present the information in a way that emphasizes clinically important details. Imagine a rash on the inside of the thorax, this would be very difficult to perceive by mentally integrating the subtle chest wall changes from dozens of slice views. In contrast a computed view looking toward the chest wall from inside the thorax might make the rash obvious. However, only a careful medical history and examination would prompt the physician to request that view from the infinite number of possible computed views.

New applications

Very high resolution systems (voxel diameters of 1 mm or less) may replace exploratory procedures such as endoscopy. The scan data can be processed interactively to give the physician views corresponding to a "virtual" endoscopic examination under his control. However, parallel studies in which hundreds of patients receive literal or virtual visualization procedures with comparison of diagnostic accuracy, and long term outcome will be necessary before virtual examinations can be accepted as the standard of medical care. SEE ALSO NUCLEAR MAGNETIC RESONANCE; SPECTROSCOPY.

endoscopy: a procedure in which an endoscope, comprised of a flexible fiber optic bundle and light source, is passed into the esophagus to examine the wall of the esophagus and the lining of the stomach

J. Carver Hill

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Curie, Marie Sklodowska

POLISH/FRENCH PHYSICIST
1867–1934

Physicist-chemist Marie Sklodowska Curie, sometimes referred to as the "mother of atomic physics," is perhaps the best-known woman scientist of all time—a legend of twentieth-century science. Cowinner of the Nobel Prize in physics in 1903, she was the first person to be awarded a second Nobel Prize, this time in chemistry, in 1911.

French chemist Marie Sklodowska Curie, co-recipient, with Pierre Curie, of the 1903 Nobel Prize in physics and recipient of the 1911 Nobel Prize in chemistry.

Marya Sklodowska was born in Warsaw, Poland, on November 7, 1867. Educated in government schools, she worked for several years in Poland as a governess before going to Paris in 1891 for further study. By dint of considerable effort she completed the physics course at the Sorbonne in 1893, and the course in mathematics the following year. She married physicist Pierre Curie in 1895.

Although her first research focused on the magnetic properties of steel, for her doctoral work she moved to the new field of "radioactivity," as it came to be called. Her studies, a continuation of the work of her teacher, physicist Henri Becquerel, developed directly from Becquerel's 1895 observation that uranium minerals emit rays that pass through opaque materials and fog a photographic plate (as well as discharge an electroscope by making the surrounding air conductive). Marie Curie, with the collaboration of her husband, undertook a systematic investigation of the Becquerel radiation to try to discover its source. Their starting material was the residue left after the extraction of uranium from pitchblende, a uranium ore. The fact that this residue was more radioactive than purified uranium oxide suggested it as a likely source for some unknown material more radioactive than uranium.

Her work at this time was done in minimal facilities that had been secured for her by Pierre Curie at the Paris École Municipale de Physique et de Chimie Industrielle, the industrial college at which he was teaching. With the collaboration, initially, of Gustav Bémont, head of the chemistry section of the École Municipale, she took on the laborious task of isolating the postulated unknown material by chemical methods (group separation and fractional **crystallization**). Pierre Curie established the electrical properties of the rays emitted by the fractions. In June 1898, following their isolation of a fraction 400 times more radioactive than uranium, the Curies reported the presence in the fraction of what was probably a new element. That element, named polonium by Marie Curie, was the first element discovered via its property of radioactivity. Six months later, working with a different fraction, the Curies discovered a second new element. It was given the name radium. In spite of its still impure state, it had an activity a million times that of uranium.

crystallization: process of producing crystals of a substance when a saturated solution in an appropriate solvent is cooled or some solvent is removed by evaporation

In 1902 Marie Curie succeeded in isolating one-tenth of a gram (0.0035 ounces) of pure radium chloride from eight tons of pitchblende residue, a task that required an enormous amount of physical labor. The **atomic weight** of radium she determined to be 225. These results aroused immediate interest. She received her doctoral degree in 1903, her radioactivity investigations forming the major part of her thesis. It was undoubtedly one of the most remarkable doctoral theses ever written. Her Nobel Prize in

atomic weight: weight of a single atom of an element in atomic mass units (AMU) physics, shared that same year with Henri Becquerel and Pierre Curie, received unprecedented press coverage. Pierre Curie was appointed to a professorship in physics at the Sorbonne in 1904. He died suddenly in 1906.

From 1900 until 1904 Marie Curie taught physics at a college for women teachers in the Paris suburb of Sèvres. In 1906, after her husband's death, she succeeded to his professorship in physics, becoming the first woman to hold a teaching post at the Sorbonne. Her scientific research continued, and the tremendous world interest in the new field of radioactivity, coupled with her own international prestige, attracted many students and research workers to her laboratory in the period leading up to World War I. To a notable extent, however, she stepped aside from the increasingly competitive field of atomic physics (which she had in part created) after 1906, and left to others, for example, Ernest Rutherford and his colleagues, the further theoretical development of modern **atomic theory**. Her own work after 1906 tended more toward radiochemistry, and consisted, primarily, of investigations of the radioactive elements (including the substances that came to be called **isotopes**) and their disintegration processes and products. A number of her students and coworkers made notable contributions to both radiochemistry and physics that included: the development of instrumentation for the detection of subatomic particles; characterizations of the range (distance traveled from source) and energy of **α-particles**; descriptions of the effects of α-particles on chemical processes; investigation of β-rays; and the disintegration products in the thorium series. Marie Curie's Nobel Prize in chemistry (1911) was awarded for her discoveries of radium and polonium, and the isolation of radium and the study of its properties.

PIERRE CURIE

Electromagnetic rays emitted by radioactive materials are classifiable into three distinct groups: alpha (α), beta (β), and gamma (γ). Seminal studies by Pierre Curie, the Curie team's major investigator of these rays, include his study of α-rays, his demonstration that β-rays are negatively charged, and his observation (with Marie Curie) that radium causes induced radioactivity.

atomic theory: physical concept that asserts that matter is composed of tiny particles called atoms, the specific characteristics of which determine the type and form of the matter

isotope: form of an atom that differs by the number of neutrons in the nucleus

α-particle: subatomic particle with 2+ charge and mass of 4; an He nucleus

The applications of radiation as a diagnostic tool in medicine were quickly recognized. With the coming of World War I, Curie became director of the Red Cross Radiological Service and worked with her daughter Irène to provide radiology stations for the French army. In 1918 she began work at the new Paris Institute of Radium. She continued to lecture at the Sorbonne until 1934, but gradually turned over the leadership of her laboratory at the Institute of Radium to her daughter and her son-in-law, Frédéric Joliot. By the 1920s she was in poor health. The high doses of radiation to which she had been exposed over the years had taken their toll. Despite failing health, to raise funds for the support of the institute, she made several speaking tours in Europe and the United States. Although never accepted into the Paris Academy of Sciences, she was the first woman elected to the French Academy of Medicine. She died on July 4, 1934, of leukemia, misdiagnosed as tuberculosis, in a nursing home in the Département of Haute-Savoie region of France. SEE ALSO BECQUEREL, ANTOINE-HENRI; POLONIUM; RADIOACTIVITY; RADIUM; RUTHERFORD, ERNEST; THORIUM; URANIUM.

Mary R. S. Creese

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Curium

96
Cm
CURIUM
247

MELTING POINT: 1,340°C
BOILING POINT: 3,110°C
DENSITY: 13.5 g/cm^3
MOST COMMON IONS: Cm^{3+}

The element curium was discovered in 1944 by Glenn T. Seaborg, Ralph A. James, and Albert Ghiorso at the University of California at Berkeley. Its discovery was a result of the bombardment of plutonium-239 (^{239}Pu) with helium ions. Curium was named after the Nobel laureates Pierre and Marie Curie, who were pioneers in the discovery of radioactivity. Although curium is synthetic, minute traces of this element may exist in natural uranium deposits. Curium has ten known **isotopes**, all of which are radioactive. The longest-lived is ^{247}Cm, which has a half-life of 16 million years. Although curium has little use outside of research, ^{242}Cm (half-life 163 days) has been used in isotopic power generators, as it produces about 3 watts of heat energy per gram due to its **radioactive decay**. Curium-245 (^{245}Cm, half-life 8,500 years) is **fissionable**, and can be used as **nuclear** reactor fuel enrichment. Curium was also the **α-particle** source for the Alpha Proton X-ray Spectometer. The physical properties of curium include a boiling point of 1,340°C (2,444°F), and a melting point of 3,110°C (5,630°F). Its density is 13.5 g/cm^3. Curium is very reactive with oxygen, steam, and acids (but not with bases). Several oxides and halides of this element have been prepared. Curium has no known biological uses. If ingested, it tends to accumulate in bone marrow, where it is highly dangerous because its high intensity of radioactivity destroys red blood cells. SEE ALSO Actinides; Actinium; Americium; Berkelium; Californium; Curie, Marie Sklodowska; Einsteinium; Fermium; Mendelevium; Neptunium; Nobelium; Plutonium; Protactinium; Thorium; Uranium.

isotope: form of an atom that differs by the number of neutrons in the nucleus

radioactive decay: process involving emission of subatomic particles from the nucleus, typically accompanied by emission of very short wavelength electromagnetic radiation

fissionable: of or pertaining to unstable nuclei that decay to produce smaller nuclei

nuclear: having to do with the nucleus of an atom

α-particle: subatomic particle with 2+ charge and mass of 4; an He nucleus

Carolyn J. Anderson

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Cytosine *See Nucleotide.*

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Volume 1

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p. 253: Robot adds solution and stirs DNA samples from New York Terrorism victims, photograph by Douglas C. Pizac. AP/Wide World Photos. Reproduced by permission; p. 255: Pople, John, Sugar Land, Texas, 1998, photograph Brett Coomer. AP/Wide World Photos. Reproduced by permission; p. 268: Cori, Carl F. and Gerty T. Cori, photograph. The Library of Congress; p. 270: Rust, oxidation of ferrous metal bolt, photograph by Matt Meadows. Peter Arnold, Inc. Reproduced by permission; p. 283: Multi-celled human embryo 2.5 days after it was removed from the womb and stored cryogenically at the Bourn Hall Fertility Clinic, Cambridgeshire, England, photograph. AP/Wide World Photos. Reproduced by permission; p. 285: CAT scan, photograph. © 1990 Terry Qing/FPG International Corp. Reproduced by permission; p. 287: Human brain with Parkinson's Disease showing atrophy, Computerized Axial Tomography, CAT, scan. © GJLP/CNRI/Phototake. Reproduced by permission; p. 289: Curie, Marie, photograph. AP/Wide World Photos. Reproduced by permission.

Volume 2

p. 2: Dalton, John, engraving. The Library of Congress, Prints and Photographs Division; p. 3: Davy, Sir Humphrey, portrait. Corbis-Bettmann. Reproduced with permission; p. 6: Broken egg, photograph by Arthur Beck. Corbis. Reproduced by permission; p. 7: Sunny side up egg, photograph by Japack Company/Corbis. Reproduced by permission; p. 12: Dewar, Sir James, portrait. The Library of Congress; p. 14: A female patient undergoing a cerebral angiography, photograph by Laurent. Photo Researchers. Reproduced by permission; p. 18: Baby wearing a disposable diaper, photograph by Elizabeth Thomason. Copyright © 2003 Elizabeth Thomason. Reproduced by permission; p. 23: DNA, computer graphics, photograph by Clive Freeman. Photo Researchers, Inc. Reproduced by permission; p. 25: Dupont, Eleuthere Irenee, engraving. Archive Photos, Inc. Reproduced by permission; p. 27: Textiles, fabric dyes, photograph by Randy Duchaine. Stock Market. Reproduced by permission; p. 31: Ehrlich, Paul, in laboratory, 1908, photograph. Liaison Agency/Hulton Getty. Reproduced by permission; p. 32: Einstein, Albert, photograph. Archive Photos. Reproduced by permission; p. 40: Hitchings, George, Gertrude Elion, photograph. AP/Wide World. Reproduced by permission; p. 43: Wheelchair racers participating in a marathon in Washington, D.C., photograph by Joe Sohm. Chromosohm/Stock Connection/PictureQuest. Reproduced by permission; p. 45: Electronic display (concentric octagons) of energies from subatomic particles, photograph. Newman Laboratory of Nuclear Science, Cornell University, National Audubon Society Collection/Photo Researchers, Inc. Reproduced by permission; p. 51: Leachate from the Dowelanco plant in Lafayette, Indiana, photograph by Sandra Marquardt. Greenpeace. Reproduced by permission; p. 52: Chemicals being sprayed on agricultural land on the Everglades Park border, Florida, photograph. Earth Scenes/© Arthur Gloor. Reproduced by permission; p. 55: Enzyme, lock-and-key model of interaction, drawing by Hans & Cassidy. Gale Research; p. 58: Chemical reaction, nitric acid, photograph. © LevyYoav/Phototake NYC. Reproduced by permission; p. 69: Reed, Ken and Peter Mckay, taking part in a demonstration against embryonic stem cell research outside of George Washington University Hospital, photograph by Kamenko Pajic. AP/Wide World Photos. Reproduced by permission; p. 70: Harman, Jane, holding up a support sign of stem cell research, at a press conference, outside the Capitol building, in Washington D.C., photograph by Shawn Thew. Getty Images. Reproduced by permission; p. 75: Nuclear explosion at sea, photograph by PHOTRI. Stock Market. Reproduced by permission; p. 78: Engraving of Professor Faraday delivering a lecture at the Royal Institution, London, photograph. © Corbis. Reproduced by permission; p. 86: Fermi, Enrico, photograph. © Bettmann/Corbis. Reproduced by Corbis Corporation; p. 88: Truck applying fertilizer in rice field, photograph by Thomas Del Brase. Stock

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Volume 3

p. 1: Kekule, Friedrich, photograph. Photo Researchers, Inc. Reproduced by permission; p. 3: Kelsey, Frances Oldham, photograph. The Library of Congress; p. 5: Khorana, Har Gobind, photograph. AP/Wide World Photos. Reproduced by permission; p. 8: Acid dehydration of sugar, photograph by David Taylor. Science Photo Library, National Audubon Society Collection/Photo Researchers, Inc. Reproduced by permission; p. 10: Krebs, Hans Adolf, photograph. The Library of Congress; p. 16: Lavoisier, Antoine-Laurent, photograph. The Library of Congress; p. 17: Instruments from Lavoisier's lab, portrait. The Library of Congress; p. 18: Lawrence, Ernest (with atom smasher), photograph. Corbis-Bettmann. Reproduced by permission; p. 23: Le Bel, Joseph Achille, photograph. Photo Researchers, Inc. Reproduced by permission; p. 24: Leblanc, Nicholas, photograph. Bettmann/Corbis. Reproduced by permission; p. 28: Leloir, Luis F., photograph. UPI/Corbis-Bettmann. Reproduced by permission; p. 29: Lewis, Gilbert N., photograph. Corbis-Bettmann. Reproduced by permission; p. 34: Liebig, Justes von, portrait. The Library of Congress; p. 40: Transmission electron micrograph of lipid droplets in a rat fat cell, magnified x 90,000, photograph by David M. Phillips, The Population Council/Photo Researchers, Inc. Reproduced by permission; p. 41: Woman holding a digital fishfinder, photograph. © AFP/Corbis. Reproduced by permission; p. 45: Waterstrider bug, photograph. © Hermann Eisenbeiss, National Audubon Society Collection/Photo Researchers, Inc. Reproduced by permission; p. 46: Liquids, viscosity, photograph. © Yoav Levy/Phototake NYC. Reproduced by permission; p. 48: Lister, Joseph, photograph. © Bettmann/Corbis. Reproduced by permission; p. 50: Lonsdale, Kathleen, photograph. AP/Wide World Photos. Reproduced by permission; p. 52: False-color angiogram showing stenosis in the carotid artery, photograph by Alfred Pasteka. © CNRI/ Science Photo Library, National Audubon Society Collection/Photo Researchers, Inc. Reproduced by permission. p. 56: Bar magnet with iron filings showing field of force (bright blue background), photograph. Grantpix/Photo Researchers, Inc. Reproduced by permission; p. 60: Oppenheimer, J. Robert, 1946, photograph. © Bettmann/Corbis. Reproduced by permission; p. 62: Martin, Archer, photograph by Nick Sinclair. Photo Researchers, Inc. Reproduced by permission; p. 63: Red sports car, photograph. © Royalty Free/Corbis. Reproduced by permission; p. 67: Maxwell, James Clerk, engraving. The Library of Congress; p. 69: Post-mounted sundial in a Bolivian town, photograph. © John Slater/Corbis. Reproduced by permission; p. 72: Teenage girl being weighed on large scale, photograph by Robert J. Huffman. Field Mark Publications. Reproduced by permission; p. 74: Hahn, Otto, standing with Lise Meitner, photograph. Photo Researchers, Inc. Reproduced by permission; p. 77: Mendeleev, Dmitri Ivanovich, in the chemical factory of the University of St. Petersburg, photograph. © Bettmann/Corbis. Reproduced by permission; p. 82: Landfill with aluminum drum for mercury waste, photograph. Recio/Greenpeace. Reproduced by permission; p. 83: Ritalin tablets, photograph. © Photo Researchers, Inc. Reproduced by permission; p. 85: Lothar von Meyer, Julius, photograph. Photo Researchers, Inc. Reproduced by permission; p. 86: Millikan, Robert A., photograph. The Library of Congress; p. 88: Stratas of banded liassic limestone and shale on a seacliff by

Chinch Gryniewicz. Ecoscene/Corbis. Reproduced by permission; p. 89: Matrix of diamond, photograph. U. S. National Aeronautics and Space Administration (NASA); p. 104: Chaney, Michael wearing special 3-D glasses to view a computer model of Fluoxetine, or Prozac. Lilly Research Labs, Indianapolis, February 22, 1994, photograph. Corbis. Reproduced by permission; p. 115: Three-dimensional computer model of a protein molecule of matrix porin found in the E. Coli bacteria, photograph. © Corbis. Reproduced by permission; p. 118: Two models which represent the arrangement of atoms in a chemical molecule, illustration. Tek Image/Science Photo Library. Photo Researcher, Inc. Reproduced by permission; p. 122: Moseley, Henry, photograph. Photo Researchers, Inc. Reproduced by permission; p. 124: Six-legged frog, photograph. JLM Visuals. Reproduced by permission; p. 130: Coffee shop sign at the Pike Place Public Market, Seattle, Washington, ca. 1990, photograph by Stuart Westmorland. CORBIS/Stuart Westmorland. Reproduced by permission; p. 132: Professor Walther Nernst of Berlin University, Nobel Prize winner for physics, in his laboratory, photograph. © Bettmann/Corbis. Reproduced by permission; p. 137: Diagram showing transmitting and receiving neurons and the role of serotonin in communication between one neuron and the next, illustration by Frank Forney; p. 143: Photovoltaic cell powered desalination system, Saudi Arabia, photograph. Mobil Solar Energy Corporation/Phototake NYC. Reproduced by permission; p. 144: Newton, Sir Isaac (oval frame, allegorical elements surrounding), engraving. The Library of Congress; p. 153: Hand pouring liquid nitrogen into beaker, photograph. © David Taylor/Photo Researchers. Reproduced by permission; p. 155: Nobel, Alfred (wearing suit, checked bow tie), drawing. The Library of Congress; p. 158: Scientist from University of California—Berkley studying helium gas being released from a hot spring in Yellowstone National Park, photograph. © James L. Amos/Corbis. Reproduced by permission; p. 168: Lasers focus on a small pellet of fuel in attempt to create nuclear fusion reaction, photograph. © Roger Ressmeyer/Corbis. Reproduced by permission; p. 169: Seaborg, Glenn, photograph by Lawrence Berkeley. Photo Researchers, Inc. Reproduced by permission; p. 172: Nuclear reactors, interior of the containment building, photograph by Mark Marten. Photo Researchers, Inc. Reproduced by permission; p. 174: Nuclear fusion, computer simulation, photograph by Jens Konopka and Henning Weber. Photo Researchers, Inc. Reproduced by permission; p. 178: Magnetic Resonance Imaging System (room with equipment and viewing machine), photograph by Mason Morfit. FPG International Corp. Reproduced by permission; p. 181: Colored positron emission tomography (PET) scans comparing the brain of a depressed person (top) with the brain of a healthy person, illustration. © Photo Researchers, Inc. Reproduced by permission; p. 192: Oppenheimer, Dr. J. Robert, atomic physicist and head of the Manhattan Project, photograph. National Archives and Records Administration; p. 209: Ostwald, Friedrich Wilhelm, portrait. The Library of Congress; p. 211: Doctor communicating with a patient lying in a pressure chamber and undergoing hyperbaric oxygen therapy, photograph by James King-Holmes/Science Photo Library. Reproduced by permission; p. 214: Woodcut from “Works”, of Paracelsus ca. 1580 edition, of Mercury in its alchemical form as Azoth, photograph. Fortean Picture Library. Reproduced by permission; p. 218: © Kevin Fleming/Corbis. Reproduced by permission; p. 220: Pasteur, Louis, photograph. Hulton-Deutsch Collection/Corbis. Reproduced by permission; p. 222: Pauli, Wolfgang, photograph by Zurich Bettina. Courtesy of CERN-European Organization for Nuclear Research. Reproduced by permission; p. 223: Pauling, Linus, proponent of heavy vitamin C use, tossing an orange, photograph. © Roger Ressmeyer/Corbis. Reproduced by permission; p. 225: Penicillin, photograph by Andrew McClenaghan, photograph. Photo Researchers, Inc. Reproduced by permission; p. 229: Early Periodic Table, portrait. The Library of Congress; p. 234: Worker in

protective photograph by Ed Young. Corbis. Reproduced by permission; p. 238: Smith, Billy, Drilling Foreman, seated at Drake Well, photograph. AP/Wide World. Reproduced by permission; p. 241: Man in red hardhat standing on bluish oil refinery equipment, yellow flames from burning natural gas at top right, photograph. © Lowell Georgia/Corbis. Reproduced by permission; p. 249: The first known photograph of a courtyard outside Niepce's room, photograph. The Bettmann Archive/Corbis. Reproduced by permission; p. 256: Hot water vaporizing as it is thrown into air during minus 35-degree Fahrenheit temperature, Boundary Waters Canoe Area Wilderness, Minnesota, USA, photograph © Layne Kennedy/Corbis. Reproduced by permission; p. 258: X-ray diffraction crystallography, photograph by James King-Holmes. OCMS/Science Photo Library/ Photo Researchers, Inc. Reproduced by permission; p. 259: Several open cans of paint in an assortment of colors, photograph by Matthias Kulka. Corbis. Reproduced by permission; p. 262: Planck, Max, photograph. © Bettmann/Corbis. Reproduced by permission.

Volume 4

p. 5: Travolta, John, with Karen Lynn Gorney in a scene from "Saturday Night Fever," photograph. The Kobal Collection. Reproduced by permission; p. 12: Ghost crab walking among a sandy shoreline, photograph. Sapelo Island National Estuarine Research Reserve. Reproduced by permission; p. 30: Priestley, Joseph, engraving. International Portrait Gallery; p. 38: Scientist adjusts equipment used in fast protein liquid chromatography, photograph. Photo Researchers, Inc. Reproduced by permission; p. 50: Spectrum of electromagnetic radiation, (chart) illustrations by Robert L. Wolke. Reproduced by permission; p. 52: Radioactive emission of alpha particles from radium, yellow sunburst, dark blue background, photograph. Photo Researchers, Inc. Reproduced by permission; p. 58: International mobile radiological radiologists measuring soil radioactivity levels near Ukraine's Chernobyl Nuclear Plant, wearing protective clothing, from International Mobile Radiological Laboratories, near Chernobyl, Ukraine, photograph. © Reuters NewsMedia Inc./Corbis. Reproduced by permission; p. 60: Radon test kit and carbon monoxide detector, photograph by Robert J. Huffman.
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Reproduced by permission; p. 227: Man, writing, being flanked by two other men watching. AP/Wide World Photos. Reproduced by permission; p. 228: Army medic, taking an x-ray of a fellow soldier simulating an injury, photograph. © Bettmann/Corbis. Reproduced by permission; p. 236: Stanford Linear Accelerator Center, photograph by David Parler. National Audubon Society Collection/Photo Researchers Inc. Reproduced by permission; p. 241: Alchemist (seated left wearing eyeglasses) and his assistants, engraving. The Granger Collection, New York. Reproduced by permission; p. 244: Computer generated graphic of a molecule of hemoglobin-carrier of oxygen in the blood, photograph. © Science Photo Library. Photo Researchers. Reproduced by permission; p. 249: Urey, Harold, photograph. The Library of Congress; p. 253: Van Der Waals, Johannes Diderik, photograph. Science Photo Library. Photo Researchers, Inc. Reproduced by permission; p. 255: Helmont, Jan (Baptise) Van (standing), print; p. 256: Hoff, Jacobus Henricus vant, photograph. Photo Researchers, Inc. Reproduced by permission; p. 258: Banded gila monster, photograph by Renee Lynn. The National Audubon Society Collection/Photo Researchers, Inc. Reproduced by permission; p. 261: Allesandro Volta, standing, body turned slightly to his left, painting. UPI/Corbis-Bettmann. Reproduced by permission; p. 263: Waksman, Selman A.(in laboratory), photograph. The Library of Congress.; p. 265: Molecular graphic of water molecules evaporating from a solution, photograph. © K. Eward/Photo Researchers. Reproduced by permission; p. 270: Dead fish, killed from water pollution, photograph. © U.S. Fish & Wildlife Service; p. 273: Newly treated water in the Orange County Water Treatment Works, Florida, photograph by Alan Towse. © Ecoscene/CORBIS. Reproduced by permission; p. 275: Watson, Dr. James Dewey, with DNA model, 1962, photograph. UPI/Corbis-Bettmann. Reproduced by permission; p. 277: Werner, Alfred, portrait. The Library of Congress; p. 279: Willstatter, Richard, photograph. Photo Researchers, Inc. Reproduced by permission; p. 280: Wohler, Friedrich, portrait. The Library of Congress; p. 282: Woodward, Robert Burns (standing with unknown man, viewing book), photograph. The Library of Congress; p. 284: Cylindrical map of the eastern half of the surface of Venus, as viewed from the spacecraft Magellan, photograph. NASA/JPL/CALTECH. Reproduced by permission; p. 285: Yalow, Rosalyn, 1978, photograph. Corbis-Bettmann. Reproduced by permission; p. 288: Yukawa, Hideki (holding chalk, pointing to writing on board), photograph. The Library of Congress; p. 293: Kangaroo on the beach in Australia, photograph. © Australian Picture Library/Corbis. Reproduced by permission; p. 294: Zsigmondy, Richard, portrait. The Library of Congress.

Glossary

acetylcholine: neurotransmitter with the chemical formula $C_7H_{17}NO_3$; it assists in communication between nerve cells in the brain and central nervous system

acid rain: precipitation that has a pH lower than 5.6; term coined by R. A. Smith during the 1870s

activation analysis: technique that identifies elements present in a sample by inducing radioactivity through absorbtion of neutrons

adenine: one of the purine bases found in nucleic acids, $C_5H_5N_5$

adenosine triphosphate (ATP): molecule formed by the condensation of adenine, ribose, and triphosphoric acid, HOP(O)OH–O–(O)OH–OP(O)OH–OH; it is a key compound in the mediation of energy in both plants and animals

adrenalin: chemical secreted in the body in response to stress

alchemy: medieval chemical philosophy having among its asserted aims the transmutation of base metals into gold

aldehyde: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the RC(O)H functional group

aliphatic: having carbon atoms in an open chain structure (as an alkane)

aliquot: specific volume of a liquid used in analysis

alkaloid: alkaline nitrogen-based compound extracted from plants

alloy: mixture of two or more elements, at least one of which is a metal

α subunit: subunit that exists in proteins that are composed of several chains of amino acids, the first unit in the "counting" of the units

α-particle: subatomic particle with 2+ charge and mass of 4; a He nucleus

amalgam: metallic alloy of mercury and one or more metals

amine functional group: group in which nitrogen is bound to carbon in an organic molecule in which two other groups or hydrogen atoms are bound to nitrogen; major component of amino acids

amino acid residue: in a protein, which is a polymer composed of many amino acids, that portion of the amino acid that remains to become part of the protein

amino acid sequence: twenty of the more than five hundred amino acids that are known to occur in nature are incorporated into a variety of proteins that are required for life processes; the sequence or order of the amino acids present determines the nature of the protein

amphetamine: class of compounds used to stimulate the central nervous system

anabolism: metabolic process involving building of complex substances from simpler ones, using energy

analgesic: compound that relieves pain, e.g., aspirin

androgen: group of steroids that act as male sex hormones

angiotensin: chemical that causes a narrowing of blood vessels

anhydrous compound: compound with no water associated with it

anion: negatively charged chemical unit, like $Cl-$, $CO_{32}-$, or NO_3-

anthcyanin: antioxidant flavanoid that makes raspberries red and blueberries blue

antibody: protein molecule that recognizes external agents in the body and binds to them as part of the immune response of the body

anticoagulant: molecule that helps prevent the clotting of blood cells

antiscorbutic: substance that has an effect on scurvy

apoenzyme: the protein part of an enzyme that requires a covalently bound coenzyme (a low molecular weight organic compound) or a cofactor (such as a metal ion) for activity

aqueous solution: homogenous mixture in which water is the solvent (primary component)

aromatic: having a double-bonded carbon ring (typified by benzene)

asparagine residue: amino acid asparagine unit as it occurs in a polypeptide chain

atomic mass units: unit used to measure atomic mass; 1/12 of the mass of a carbon-12 atom

atomic number: the number of protons in an atomic nucleus, expressed in terms of electric charge; it is usually denoted by the symbol Z

atomic orbital: mathematical description of the probability of finding an electron around an atom

atomic spectrum: electromagnetic array resulting from excitement of a gaseous atom

atomic theory: concept that asserts that matter is composed of tiny particles called atoms

atomic weight: weight of a single atom of an element in atomic mass units (amu)

attraction: force that brings two bodies together, such as two oppositely charged bodies

axial bond: covalent bond pointing along a molecular axis

azo dye: synthetic organic dye containing a –N=N– group

bacteriophage multiplication: process by which immune system cells responsible for battling bacterial infections reproduce

basal metabolism: the process by which the energy to carry out involuntary, life-sustaining processes is generated.

β subunit: subunit that exists when two or more polypeptide chains associate to form a complex functional protein, the chains are referred to as "subunits"; these subunits are often identified as α, β, etc.

biological stain: dye used to provide contrast among and between cellular moieties

biomass: collection of living matter

biosynthesis: formation of a chemical substance by a living organism

boat conformation: the arrangement of carbon atoms in cyclohexane, C_6H_{12}. In which the spatial placement of the carbon atoms resembles a boat with a bow and a stern

brine: water containing a large amount of salts, especially sodium chloride (NaCl)

Brownian motion: random motion of small particles, such as dust or smoke particles, suspended in a gas or liquid; it is caused by collisions of the particle with gas or solvent molecules which transfer momentum to the particle and cause it to move

calc: calcium carbonate

calcine: to heat or roast to produce an oxide (e.g., CaO from calcite)

capacitor plate: one of several conducting plates, or foils, in a capacitor, separated by thin layers of dielectric constant, an insulating material

carboxylate: structure incorporating the –COO– group

carboxyl group: an organic functional group, –C(O), found in aldehydes, ketones, and carboxyl acids.

carboxylic acid: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the $-CO_2H$ functional group

catabolism: metabolic process involving breakdown of a molecule into smaller ones resulting in a release of energy

catalysis: the action or effect of a substance in increasing the rate of a reaction without itself being converted

catalyst: substance that aids in a reaction while retaining its own chemical identity

catalytic conversion: catalytic oxidation of carbon monoxide and hydrocarbons in automotive exhaust gas to carbon dioxide and water

cell culture: artificially maintained population of cells, grown in a nutrient medium and reproducing by asexual division

cephalosporin C: family of antibiotics obtained from a fungus acting in a manner similar to penicillin

chain of custody: sequence of possession through which evidentiary materials are processed

chair conformation: arrangement of atoms in a cycle structure (usually a six-membered ring) that appears to be arranged like a chair (as opposed to the other conformation which is described as a "boat")

chemical-gated: of a membrane protein whose action to open a pore in the membrane occurs only after a substrate has been binded to the protein or a cofactor

chlorofluorocarbon (CFC): compound containing carbon, chlorine, and fluorine atoms that remove ozone in the upper atmosphere

chlorophyll: active molecules in plants undergoing photosynthesis

chromatography: the separation of the components of a mixture in one phase (the mobile phase) by passing in through another phase (the stationary phase) making use of the extent to which the components are absorbed by the stationary phase

chromophore: part of the molecule that yields characteristic colors

cladding: protective material surrounding a second material, which is frequently tubes filled with uranium dioxide pellets in a nuclear reactor

cleave: split

cobrotoxin: polypeptide toxin containing sixty-two residues that is found in the venom of cobras

code: mechanism to convey information on genes and genetic sequence

cofactor: inorganic component that combines with an apoenzyme to form a complete functioning enzyme

coherent mass: mass of particles that stick together

color fastness: condition characterized by retention of colored moieties from a base material

combustion: burning, the reaction with oxygen

competitive inhibitor: species or substance that slows or stops a chemical reaction

complementarity: basis for copying the genetic information, where each nucleotide base has a complementary partner with which it forms a base-pair

congener: an element or compound belonging to the same class

constitutional isomer: form of a substance that differs by the arrangement of atoms along a molecular backbone

contact activity: process involving the touching of different surfaces

contraction: the shortening of a normal trend of a quantity

coordinate covalent bond: covalent bond in which both of the shared electrons originate on only one of the bonding atoms

coordination chemistry: chemistry involving complexes of metal ions surrounded by covalently bonded ligands

corrosive gas: gas that causes chemical deterioration

covalent bond: bond formed between two atoms that mutually share a pair of electrons

crystal lattice: three-dimensional structure of a crystaline solid

crystallization: process of producing crystals of a substance when a saturated solution in an appropriate solvent is either cooled or some solvent removed by evaporation

culture: living material developed in prepared nutrient media

cyanobacterium: eubacterium sometimes called “the blue-green alga”; it contains chlorophyll (the pigment most abundant in plants), has very strong cell walls, and is capable of photosynthesis

cyclopentadienyl ring: five-membered carbon ring containing two C–C double bonds; formula C_5H_6

cysteine residue: sulfhydryl-containing cysteine unit in a protein molecule

cytosine: heterocyclic, pyrimidine, amine base found in DNA

dedifferentiation: the opposite of the biological process of differentiation by which a relatively unspecialized cell undergoes a progressive change to a more specialized form or function

degradative: relating to or tending to cause decomposition

degrade: to decompose or reduce the complexity of a chemical

delocalized: of a type of electron that can be shared by more than one orbital or atom

denitrification: process of removing nitrogen

density-functional theory: quantum mechanical method to determine ground states

depolarization: process of decreasing the separation of charge in nerve cells; the opposite of hyperpolarization

deterministic: related to the assumption that all events are based on natural laws

deuteron: nucleus containing one proton and one neutron, as is found in the isotope deuterium

dialcohol: organic molecule containing two covalently-bonded –OH groups

diamagnetic: property of a substance that causes it to be repelled by a magnetic field

diamine: compound, the molecules of which incorporate two amino groups (–NH_2) in their structure, such as 1,2 diamino ethane (sometimes called ethylenediamine) and the three diamine benzene compounds

dibasic acid: acidic substance that incorporates two or more acidic hydrogen atoms in one molecule, such as sulfuric (H_2SO_4) and phosphoric (H_3PO_4) acids

dihydroxy compound: compound with molecules that incorporate two hydroxyl groups (–OH) in their structure, such as 1,2 dihydroxy ethane (sometimes called glycol) and the three dihydroxy benzene compounds

directing effect: ability of a functional group to influence the site of chemical reaction, such as substitution, for a molecule

discharge display tube: glass tube containing gas at low pressure through which a beam of electrons is passed

disperse system: two-phase system in which one phase, the disperse phase, is distributed in the second phase, the dispersion medium

disulfide bond: bond in a complex substance that involves two bonding sulfur atoms, –S–S–

disulfide bridge: covalent –S–S– linkage that provides cross-links in protein molecules

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

dope: to add a controlled amount of an impurity to a very pure sample of a substance, which can radically change the properties of a substance

drug resistance: ability to prevent the action of a particular chemical substance

ductile: property of a substance that permits it to be drawn into wires

Eighteen Electron Rule: rule noting that coordination complexes with eighteen electrons are stable; electrons from both metal species and ligand donor species are counted

electrolyte solution: a liquid mixture containing dissolved ions

electron correlation error: quantum mechanical method for studying atoms, ions, or molecules

electronegative: capable of attracting electrons

electrophoresis: migration of charged particles under the influence of an electric field, usually in solution; cations, the positively charged species, will move toward the negative pole and anions, the negatively charged species, will move toward the positive pole

electrostatic interaction: force that arises between electrically charged particles or regions of particles

elemental analysis: determination of the percent of each atom in a specific molecule

emulsifier: substance that stabilizes the formation of an emulsion—normally it contains molecules with both polar and non-polar functional groups

emulsion: immiscible two-phase mixture in which one phase is dispersed (as small droplets) in the other phase

enantiomorphic shape: mixture of molecules with the same molecular formulas but different optical characteristics

endohedral: descriptive term for a point within a three-dimensional figure

endoplasmic reticulum: internal membrane system that forms a net-like array of channels and interconnections of organelles within the cytoplasm of eukaryotic cells

Equation of State for Ideal Gases: mathematical statement relating conditions of pressure, volume, absolute temperature, and amount of substance; $PV = nRT$

equatorial bond: covalent bond perpendicular to a molecular axis

equilibrium: condition in which two opposite reactions are occurring at the same speed, so that concentrations of products and reactants do not change

erythromycin: antibiotic used to treat infections

ester: organic species containing a carbon atom attached to three moieties: an O via a double bond, an O attached to another carbon atom or chain, and an H atom or C chain; the $R(C{=}O)OR$ functional group

esterification: chemical reaction in which esters (RCO_2R_1) are formed from alcohols (R_1OH) and carboxylic acids (RCO_2R')

estrogen: female sex hormone

eukaryotic cell: cell characterized by membrane-bound organelles, most notably the nucleus, and that possesses chromosomes whose DNA is associated with proteins

excitatory: phenomenon causing cells to become active

excitatory neurotransmitter: molecule that stimulates postsynaptic neurons to transmit impulses

exclusion principle: principle that states that no two electrons can have the same four quantum numbers

excrete: to eliminate or discharge from a living entity

expressed: made to appear; in biochemistry—copied

extracellular matrix: entity surrounding mammalian tissue cells, also called connective tissue; composed of structural proteins, specialized proteins, and proteoglycans

face centered cubic structure: close-packed crystal structure having a cubic unit cell with atoms at the center of each of its six faces

feedstock: mixture of raw materials necessary to carry out chemical reactions

Fermi conduction level: vacant or partially occupied electronic energy level resulting from an array of a large number of atoms in which electrons can freely move

ferric: older name for iron in the +3 oxidation state

ferrous: older name for iron in the +2 oxidation state

fibril: slender fiber or filament

fission: process of splitting of an atom into smaller pieces

fissionable: of or pertaining to unstable nuclei that decay to produce smaller nuclei

5′ end: situation in nucleic acids in which the phosphate group is attached at the fifth carbon atom from where the base is attached

folic acid: pteroylglutamic acid; one of the B complex vitamins

formaldehyde: name given to the simplest aldehyde HC(O)H, incorporating the –C(O)H functional group

fractional distillation: separation of liquid mixtures by collecting separately the distillates at certain temperatures

fulcrum: prop or support to an item as in a lever

functional group: portion of a compound with characteristic atoms acting as a group

galactose: six-carbon sugar

galvanic: relating to direct current electricity, especially when produced chemically

galvanometer: instrument used to detect and measure the strength of an electric current

gas density: weight in grams of a liter of gas

glucocorticoid: class of hormones that promotes the breakdown of proteins to make amino acids available for gluconeogenesis; this elevates the blood sugar level and leads to glycogen synthesis in the liver

glucose: common hexose monosaccharide; monomer of starch and cellulose; also called grape sugar, blood sugar, or dextrose

golgi apparatus: collection of flattened stacks of membranes in the cytoplasm of eukaryotic cells that function in the collection, packaging, and distribution of molecules synthesized in the cell

gram negative: bacteria that do not retain their color when exposed to basic dyes such as crystal violet and then exposed to organic solvents; named after Danish bacteriologist Hans Christian Joachim Gram

gram positive: bacteria that retain their color when exposed to basic dyes such as crystal violet and then exposed to organic solvents; named after Danish bacteriologist Hans Christian Joachim Gram

Gray: unit of radiation dose per second; 1 Gray = 1 J/kg

greenhouse effect: presence of carbon dioxide in the atmosphere prevents heat from escaping, thereby raising Earth's temperature

Griess reagent: solution of sulfanilic acid and a-naphthylamine in acetic acid; reagent for nitrites

guanine: heterocyclic, purine, amine base found in DNA

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

heavy metal: by convention, a metal with a density greater than 5 g/cm^3; 70 elements are thus classified as heavy metals

helix: in the shape of a spiral or coil, such as a corkscrew

heme group: functional group formed by an iron atom interacting with a heterocyclic ligand called a porphyrin

hemiacetal: relating to organic compounds formed from an alcohol and a carbonyl-containing molecule

hemlock: poisonous herb of the genus Conium

Hippocrates: Greek physician of fifth century B.C.E. known as the "father of medicine"

homogeneous: relating to a mixture of the same materials

homogeneous solution: mixture of molecules that forms a single phase (solid, liquid, or gas)

hormonal signaling: collective processes by which hormones circulate in the blood stream to their target organs and trigger the desired responses

hydrogen bonding: intermolecular force between the H of an N–H, O–H or F–H bond and a lone pair on O, N or F of an adjacent molecule

hydrolyze: to react with water

hydrophilic: having an affinity with water

hydrophobic: water repelling

hyperbolic relationship: a geometric system in which two or more lines can be drawn through any point in a plane and not intersect a given line in that plane

hyperpolarization: process of causing an increase in charge separation in nerve cells; opposite of depolarization

hypertension: condition in which blood pressure is abnormally high

Ibn Sina: given name of an Islamic scientist known in the West as Avicenna (979–1037); reputed to be the author of more than 100 books that were Europe's most important medical texts from the 12th century until the 16th century

inert: incapable of reacting with another substance

inhibitory: preventing an action that would normally occur

integro-differential: complex mathematical model used to calculate a phase transition

interface tension: contractile force at the junction of two liquids

intermediate: molecule, often short-lived, that occurs while a chemical reaction progresses but is not present when the reaction is complete

intermolecular force: force that arises between molecules, generally it is at least one order of magnitude weaker than the chemical bonding force

internuclear: distance between two nuclei

intestinal epithelium: layer of cells in the intestines that allows the passage of water and solutes

intramolecular force: force that arises within molecules—essentially the force associated with chemical bonds

invertebrate: category of animal that has no internal skeleton

in vitro: Latin, meaning "in glass" and applied to experiments done under artificial conditions, that is, in a test tube

in vivo: Latin, meaning "in life" and applied to experiments conducted in a living cell or organism

ion exchange chromatography: form of liquid-solid chromatography based on the reversible formation of bonds between the fixed ions bound to an insoluble matrix of an ion exchanger and mobile counter ions present in the liquid phase passing over the insoluble matrix

ionization: dissociation of a molecule into ions carrying + or − charges

isolate: part of a reaction mixture that is separated and contains the material of interest

isomer: molecules with identical compositions but different structural formulas

isoprene: common name for 2-methyl-1,3butadiene, the monomer of the natural rubber polymer

isostructural: relating to an arrangement of atomic constituents that is geometrically the same although different atoms are present

isotope: form of an atom that differs by the number of neutrons in the nucleus

ketone: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the RC(O)R functional group

kinetic theory: theory of molecular motion

Kohlrausch drum: rotating cylinder used to mount a variable resistance slide wire for a polarograph

lanthanides: a family of elements (atomic number 57 through 70) from lanthanum to lutetium having from 1 to 14 4f electrons

lattice: systematic geometrical arrangement of atomic-sized units that describe the structure of a solid

ligand: molecule or ion capable of donating one or more electron pairs to a Lewis acid

lipid: a nonpolar organic molecule; fatlike; one of a large variety of nonpolar hydrophobic (water-hating) molecules that are insoluble in water

lipophilic: a molecule that tends to congregate in solution with lipids—it will be a nonpolar molecule or the nonpolar portion of a molecule

liposome: sac formed from one or more lipid layers that can be used for drug transport to cells in the body

liquefaction: process of changing to a liquid form

locomotor: able to move from place to place

Lucretius: Roman poet of first century B.C.E., also known as Titus Carus; author of *De Rerum Natura*

lysergic acid: one of the Ergot series of alkaloids, which constrict blood vessels so that the victim develops burning sensations in the limbs, gangrene, and, ultimately, convulsions; the diethylamide of this substance (LSD) induces visual perception disorders, delusion

lysis: breakdown of cells; also the favorable termination of a disease

macrolide: substance with a large ring lactone structure

macronutrient: one of a number of substances, needed in relatively large amounts, that provide nourishment for living organisms

macroscopic phenomena: events observed with human vision unassisted by instrumentation

mammalian toxicity: poisonous effect on humans and other mammals

Manhattan Project: government project dedicated to creation of an atomic weapon; directed by General Leslie Groves

manifold of ensemble states: a set of quantum states that meet the specific requirements (such as total energy) being considered in a calculation

mechanical energy: energy of an object due to its position or motion

mediate: to act as an intermediary agent

melting point: temperature at which a substance in the solid state undergoes a phase change to the liquid state

mentorship: the process by which a wise and trusted teacher guides a novice in the development of his/her abilities

metabolism: the complete range of biochemical processes that take place within living organisms; comprises processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those that break down complex food molecules, thus liberating energy (catabolism)

metabolites: products of biological activity that are important in metabolism

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

metal cation: positively charged ion resulting from the loss of one or more valence electrons

metalloenzyme: a protein enzyme that contains at least one metal atom, often in an active site of the protein

metalloid: elements that exhibit properties that are between those of metals and nonmetals; generally considered to include boron, silicon, germanium, arsensic, antimony, tellurium, and polonium

metallothionein: class of low molecular weight proteins and polypeptides with very high metal and sulfur content; thought to play a role in concentration and flow of essential elements, e.g., Cu and Zn, and in ameliorating the influence of toxic elements, e.g., Hg and Cd, in the body

metallurgy: the science and technology of metals

microchemistry: chemical investigation carried out on a microscopic level

microcrystalline: relating to the structure of crystals of very small size, typically a micron (μm) in dimension

micromolar: relating to a solution of a substance that is in the concentration range of micromoles per liter, or 10^{-6} moles per liter

mitochondrial matrix: soluble phase inside the inner mitochondrial membrane containing most of its enzymes

mitosis: process by which cells divide, particularly the division of the cell nucleus

molecular identity: “fingerprint” of a molecule describing the structure

monoclinic: one of several arrangements of atoms found in crystalline solids; characterized by a unit cell of three axes each of a differing length; two axes are mutually perpendicular while the third is at an oblique angle

monodentate: capable of donating one electron pair; literally, one-toothed

monosaccharide: one class of the natural products called carbohydrates with the general formula $C_x(H_2O)_y$; monosaccharides have a weak sweet taste, are readily soluble in water, and are called sugars

mordant dye: dye substance containing an acidic moiety, e.g., a carboxyl group, which binds metallic compounds, forming insoluble colored compounds

natural philosophy: study of nature and the physical universe

nesosilicate: any silicate in which the SiO_4 tetrahedra are not interlinked

net charge: total overall charge

neurologic: of or pertaining to the nervous system

neuropathy: degenerative state of the nerves or nervous system

neuropeptide: neurotransmitter released into the blood stream via nerve cells

neutron activation analysis: method for detecting traces of elements by bombardment with high-flux neutrons and then measuring the decay rate of the radioactive products

Newtonian: based on the physics of Isaac Newton

nicotine adenine dinucleotide (NAD): one compound of a group of coenzymes found in hydrogen-transferring enzymes

nitric oxide: compound, NO, which is involved in many biological processes; the drug Viagra enhances NO-stimulation of pathways to counteract impotence; may be involved in killing tumors

nitrotoluic acid: benzoic acid molecule with methyl and nitro groups attached

noble gas: element characterized by inert nature; located in the rightmost column in the Periodic Table

noncovalent: having a structure in which atoms are not held together by sharing pairs of electrons

noncovalent aggregation: non-specific interaction leading to the association of molecules

nonpolar: molecule, or portion of a molecule, that does not have a permanent, electric dipole

nuclear: (a) having to do with the nucleus of an atom; (b) having to do with the nucleus of a cell

nucleosynthesis: creation of heavier elements from lighter elements via fusion reactions in stars

octahedral: relating to a geometric arrangement of six ligands equally distributed around a Lewis acid; literally, eight faces

odd chain fatty acid: long chain carboxylic acid with an odd number of carbon atoms

oligomeric chain: chain that contains a few repeating units of a growing polymeric species

opioid: naturally produced opium-like substance found in the brain

optically active: capable of rotating the plane of plane-polarized light

organoleptic: effect of a substance on the five senses

organometallic compound: compound containing both a metal (transition) and one or more organic moieties

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

oxidation state zero: condition characterized by an atom having neither lost nor gained electrons

oxidation–reduction reaction: reaction, sometimes called redox, that involves the movement of electrons between reactants to form products

oxide ion conductor: series of oxides of various compounds in perovskite structure—especially of interest in high-temperature fuel cells

parabolic curve: planar curve each point of which is equidistant from a straight line (axis)

paraffin: saturated aliphatic hydrocarbon (alkane), or hydrocarbon wax

partial pressure: portion of a total pressure of a gas mixture contributed by a single type of gas in the sample

passive diffusion: mechanism of transporting solutes across membranes

pasteurization: process of heating foods such as milk to destroy bacteria

peerage: a body of peers; dignitaries of equal standing

perpendicular: condition in which two lines (or linear entities like chemical bonds) intersect at a 90-degree angle

pH effect: effect caused by a change in the concentration of hydrogen ions

phase: homogenous state of matter

phenol: common name for hydroxybenzene (C_6H_5OH)

phosphorylation: the addition of phosphates into biological molecules

photodiode assembly: grouping of electronic devices which includes a photodiode—a photodetector; useful in medical diagnostics, bar code readers, and guidance systems

photon: a quantum of electromagnetic energy

photosynthesis: process by which plants convert carbon dioxide and water to glucose

physostigmine: alkaloid derived from the leaves of the Calabar bean, formula $C_{15}H_{12}N_3O_2$; salts used for anticholinesterase activity

pilot plant: intermediate stage of testing for chemical process, between bench-top and production scale

planar complex: arrangement of atoms in which all atoms lie within a common two-dimensional plane

plane polorized light: electromagnetic radiation (light) in which the electric (or magnetic) vectors are all vibrating in the same plane

platelet: smallest noncellular component of human blood

pneumatic chemist: early chemist who studied primarily the properties of gases

polynucleotide synthesis: formation of DNA or RNA

polypeptide: compound containing two or more amide units—C(O)NH—produced by the condensation of two or more amino acids

porphyrin: common type of heterocyclic ligand that has four five-member rings with a nitrogen, all of which lie in a plane; nitrogen atom lone pairs are available for coordinate covelent bonds

postsynaptic neuron: receptor nerve cell

potash: the compound potassium oxide, K_2O

precipitation: process of separating a solid substance out of a solution

precursor molecule: molecule that is the chosen starting point for the preparation of another molecule; a starting molecule in a chemical synthesis; a reactant molecule

primary electrochemical cell: voltaic cell based on an irreversible chemical reaction

principal oxidation state: oxidation state that is most important

prism: triangular-shaped material made from quartz or glass used to diffract light

prodrug: precursor of a drug that is converted into an active form by a metabolic process

progesterone: steroid found in the female reproductive system; formula $C_{21}H_{30}O_2$

prokaryotic: relating to very simple cells of the type found in bacteria

propagating: reproducing; disseminating; increasing; extending

protecting group: substance added to a functional group of a molecule preventing further reaction until the substance is removed by subsequent reactions

proximate percent: nearest percent of a population (e.g. people, substances)

purine base: one of two types of nitrogen bases found in nucleic acids

putative: commonly believed or hypothesized

pyramidal: relating to a geometric arrangement of four electron-donating groups at the four vertices of a pyramid

pyrimidine base: one of two types of nitrogen bases found in nucleic acids

pyruvate: anion of pyruvic acid produced by the reaction of oxygen with lactic acid after strenuous exercise

quantum: smallest amount of a physical quantity that can exist independently, especially a discrete amount of electromagnetic energy

quantum mechanical: theoretical model to describe atoms and molecules by wave functions

quantum physics: physics based on the fact that the energy of an electron is equal to its frequency times Planck's constant

radioactive decay: process involving emission of subatomic particles from a nucleus, typically accompanied by emission of very short wavelength electromagnetic radiation

radioelement: a radioactive element; one in which the nucleus spontaneously decomposes (decays) producing α (alpha) and β (beta) particles and γ (gamma) rays

rare earth elements: older name for the lanthanide series of elements, from lanthanum to lutetium

rate-limiting step: slowest step in a complex reaction; it determines the rate of the overall reaction; sometimes called the rate-determining step

reagent: chemical used to cause a specific chemical reaction

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

reducing agent: substance that causes reduction, a process during which electrons are lost (or hydrogen atoms gained)

reducing potential: stored energy capable of making a chemical reduction occur

relativistic calculation: quantum mechanical model that includes the effects of relativity, particularly for core electrons

repulsive force: force that repels two bodies; charges of the same sign repel each other

reserpine: one of a group of alkaloids found naturally in the shrub *Rarewolfia serpentina*; has been used for centuries to treat hypertension, insomnia, and mental disorders; more recently it has been used to reduce blood pressure

retardation: to slow down a chemical reaction

retrosynthetic analysis: method of analyzing chemical reactions that starts with the product and works backward to determine the initial reactants

reverberator furnace: furnace or kiln used in smelting that heats material indirectly by deflecting a nearby flame downward from the roof

ribosome: large complex of proteins used to convert amino acids into proteins

RNA: ribonucleic acid, a natural polymer used to translate genetic information in the nucleus into a template for the construction of proteins

RNA polymerase: enzyme used to make RNA using DNA as a template

rough endoplasmic reticulum: regions of endoplasmic reticulum the outer surfaces of which are heavily studded with ribosomes, which make proteins for activities within membrane-bounded organelles

Royal Society: The U.K. National Academy of Science, founded in 1660

rutile: common name of TiO_2; also a common structural type for compounds with the general composition AB_2

saltpeter: potassium nitrate; chile saltpeter is sodium nitrate

screen: process of comparing multiple reagents simultaneously to provide information on reaction of one reagent with another

seed germination: beginning of the process by which a seed produces a new plant

selenium toxicity: condition created by intake of excess selenium (Se) from plants or seleniferous water; acute and chronic toxicity are known

semisynthetic: produced by synthesis from natural starting materials

serology: the study of serum and reactions taking place within it

sigma plus pi bonding: formation of a double bond within a molecule or ion

single Slater determinant: wave function used to describe atoms and molecules

size of the basis set: number of relatively simple mathematical functions (called the basis set) used to represent a more complicated mathematical function such as an atomic orbital

smelting: process by which ores are reduced in the production of metals

Socrates: Greek philosopher, c.470–399 B.C.E.

somatic cell: cells of the body with the exception of germ cells

spectral line: line in a spectrum representing radiation of a single wavelength

spectroscopy: use of electromagnetic radiation to analyze the chemical composition of materials

spinel: name given to a group of minerals that are double oxides of divalent and trivalent metals, for example, $MgO \cdot Al_2O_3$ or $MgAl_2O_4$; this mineral is called spinel; also a structural type

stacking interactions: one type of interaction that affects conformation of double-stranded DNA; caused by van der Waals forces

stereospecific: yielding one product when reacted with a given compound but the opposite product when reacted with its stereoisomer

steric repulsion: repulsive force that exists when two atoms or groups get too close together

sterol: steroid containing an alcohol group; derived from plants or animals; e.g., cholesterol

stigmasterol: sterol found in soybeans, $C_{29}H_{48}O$

stratosphere: layer of the atmosphere where ozone is found; starts about 6.2 mi (10 km) above ground

streptomycin: antibiotic produced by soil bacteria of genus *Streptomyces*

subcritical: mass of nuclear materials below the amount necessary to cause a chain reaction

subshell: electron energy sublevel, of which there are four: *s*, *p*, *d*, and *f*

sulfonamides: first of a series of drugs used for the prevention and cure of bacterial infections in humans; sulfanomides are amides of sulfuric acids and contain the $-SO_2NRR_1$ group

super-heavy elements: elements of atomic number greater than 103

superhelix: helical-shaped molecule synthesized by another helical-shaped molecule

surfactants: surface-active agents that lower the surface tension of water; e.g., detergents, wetting agents

synaptic cleft: tiny space between the terminal button of one neuron and the dendrite or soma of another

synthesis: combination of starting materials to form a desired product

synthon: in retrosynthesis, molecules are broken into characteristic sections called synthons

tetrachloride: term that implies a molecule has four chlorine atoms present

tetravalent oxidation state: bonding state of an atom that can form four bonds

theoretical physics: branch of physics dealing with the theories and concepts of matter, especially at the atomic and subatomic levels

3′ end: situation in nucleic acids in which the phosphate group is attached at the third carbon atom from where the base is attached

thykaloid membrane: part of a plant that absorbs light and passes the energy on to where it is needed

thymine: one of the four bases that make up a DNA molecule

toluic acids: methylbenzoic acids

torsion balance: instrument used to measure small forces (weights), based upon the resistance of a wire to be twisted

toxicology: division of pharmacology dealing with poisons, their identification, detection, effects on the body, and remedies

toxin: poisonous substance produced during bacterial growth

trace element: element occurring only in a minute amount

transcription: enzyme-catalyzed assembly of an RNA molecule complementary to a strand of DNA

transition metal complex: species formed when a transition metal reacts with ions or molecules, including water

transition metals: elements with valence electrons in d-sublevels; frequently characterized as metals having the ability to form more than one cation

translational process: transfer of information from codon on mRNA to anticodon on tRNA; used in protein synthesis

trigonal bipyramidal: geometric arrangement of five ligands around a central Lewis acid, with ligands occupying the vertices of two trigonal pyramids that share a common face; three ligands share an equatorial plane with the central atom, two ligands occupy an axial position

tropocollagen: fibers, or fibrils, consisting of three polypeptide sequences arranged in a helix

tyrosine: one of the common amino acids

ultraviolet radiation: portion of the electromagnetic spectrum with wavelengths shorter than visible but longer than x rays

uracil: heterocyclic, pyrimidine, amine base found in RNA

valence: combining capacity

vertabrates: animals that have a skeleton

vesicle: small compartment in a cell that contains a minimum of one lipid bilayer

vitamins: organic molecules needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

vitriol: sulfate of a metal; there are blue (Cu), white (Zn), green (Fe), and rose (Co) vitriols

volatile: low boiling, readily vaporized

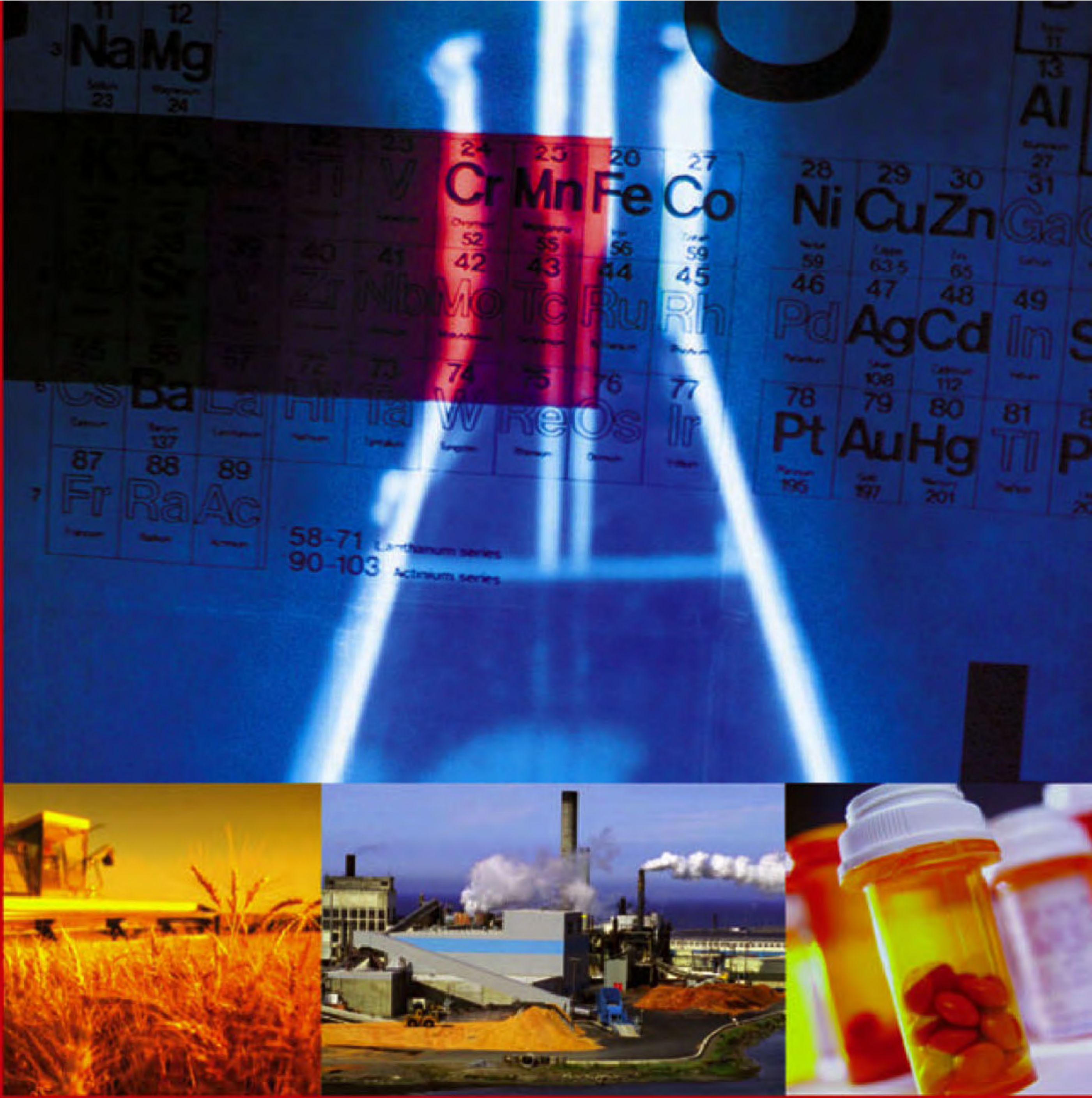
voltage: potential difference expressed in volts

vulcanized rubber: chemical process of mixing rubber with other materials like sulfur; it strengthens rubber so it can be used under hot or cold conditions; discovered by Charles Goodyear

wetting agent: molecule that, when added to a liquid, facillitates the spread of the liquid across a surface

zoology: branch of biology concerned with the animal kingdom

zwitterion: molecule that simultaneously contains a positive and a negative charge



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D-J 2

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D–J 2

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Chemistry: Foundations and Applications

J. J. Lagowski, Editor in Chief

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10 9 8 7 6 5 4 3 2 1

Table of Contents

Volume 1

Volume 2

Volume 3

Volume 4

Preface

Chemistry. The word conjures up mystery—perhaps magic—smoke, fireworks, explosions, unpleasant odors. But it could evoke “smokeless burning,” which would be invisible, fluorescent lights, “neon” signs, the quiet crumbling of rocks under the pressure of freezing water, the slow and quiet formation of caves in limestone, and the delightful scents of perfumes or fruit aromas. There is no magic, only knowledge and understanding. We offer this *Encyclopedia* as a contribution to help readers gain knowledge and understanding of chemistry.

Chemistry was manifested as an art at the beginnings of civilization. The early decorative chemical arts included the preparation of pigments such as the Egyptian blue applied to King Tutankhamen’s golden death mask; the various bronze alloys that were used to make vases in the ancient world of the Middle East as well as in China; and the glass objects that have been found in Mesopotamia (now known as Iraq). Those chemical arts became a science in the eighteenth century when Antoine Laurent Lavoisier (1743–1794) led what has been called “the chemical revolution.” Using accurate measurements of primarily mass, early chemists began to make order out of the myriad of substances that are found in the natural world. This order was eventually expressed in a number of chemical concepts that include the laws of chemical composition (constant composition, mass conservation, multiple proportions), periodicity, the nature of atoms, chemical bonding, and a variety of concepts involving chemical structures. The early symbiosis of chemistry with civilization remains. Chemistry is still a useful science in the advancement of civilization. Chemists have developed and refined the core concepts of chemistry to the point where they have become powerful tools to assist humankind in the acquisition of materials of practical use to extend and preserve civilization. Humans now have available a broader array of substances with a remarkable spectrum of properties than was available before chemistry became a science. Light emitting diodes (LEDs) produce more light than the individual torches, candles, and oil lamps of the distant past—indeed, than the incandescent light bulbs of the immediate past—more efficiently and with less pollution. Polymeric materials or composites can be produced with virtually any property desired—from stretching clingy Saran Wrap to Kevlar used in bullet proof vests; from nonstick Teflon to optical fibers; from rubber objects that are impervious to oil and gasoline to tires that can be used for 100,000 miles before needing replacement; from fibers that compete with (in some cases surpass) natural materials to plastics that have more desirable optical properties than glass. In a word, chemistry is *everywhere.*

There is no magic, only knowledge and understanding.

These volumes are a contribution to assist readers in their understanding of chemistry and chemical ideas and concepts. The 509 articles have been carefully chosen to provide basic information on a broad range of topics. For those readers who desire to expand their knowledge of a topic, we have included bibliographic references to readily accessible sources.

The continual evolution of the discipline of chemistry is reflected in our treatment of the elements. The careful reader will note that we have included articles for the first 104 elements; the remainder of the elements are "recently" discovered or exist only as short-lived species and, accordingly, are not readily available for the usual chemical studies that reveal, for example, their bulk properties or reactivity and much of the "standard chemistry" that is of interest. Much of what little we know about the elements beyond 104 permits us to place these elements in their appropriate places in the periodic table, which nevertheless still turns out to be quite insightful from a chemical point of view.

Entries in the *Encyclopedia* are in alphabetic sequence. Cross-references appear in small capitals at the ends of the articles to help readers locate related discussions. Articles range from brief, but concise, definitions to extensive overviews that treat key concepts in larger contexts. A list of common abbreviations and symbols, and a list of the known elements, as well as a modern version of the periodic table are included in the For Your Reference section at the beginning of each volume. A glossary and a comprehensive index appear at the end of each volume. Contributors are listed alphabetically, together with their academic and professional affiliations, at the beginning of each volume.

Following this preface, we offer a topical arrangement of the articles in the *Encyclopedia.* This outline provides a general overview of the principal parts of the subject of chemistry and is arranged in alphabetical order.

Many individuals have contributed greatly and in many ways to this *Encyclopedia.* The associate editors—Alton J. Banks, Thomas Holme, Doris Kolb, and Herbert Silber—carried the major responsibility in shaping the intellectual content of the *Encyclopedia.* The authors of the articles executed that plan admirably and we thank them for that effort.

The staff at Macmillan Reference USA—Marie-Claire Antoine, Hélène Potter, Ray Abruzzi, Gloria Lam, and Christine Slovey—have been outstanding in their dedication and contributions to bring this *Encyclopedia* from its initial concept to the current reality. Without their considerable input, insightful guidance, and effort this *Encyclopedia* would never have seen the light of day. I take this opportunity to thank them personally and publicly. I am particularly grateful to Rita Wilkinson, my administrative assistant for her persistent and careful attention to details that kept the editorial office and my office connected for the smooth transmission of numerous critical details. I am especially grateful to Christine Slovey who, through her determined efforts and dedication, made a potentially difficult and tedious task far less onerous and, indeed, enjoyable.

J. J. Lagowski

Topical Outline

Analytical Chemistry Applications

Adhesives
Agricultural Chemistry
Analytical Chemistry
Bleaches
Ceramics
Chemical Engineering
Chemical Informatics
Coal
Cosmetics
Cryogenics
Detergents
Disposable Diapers
Dyes
Explosions
Fertilizer
Fibers
Food Preservatives
Forensic Chemistry
Formulation Chemistry
Freons
Gardening
Gasoline
Gemstones
Genetic Engineering
Glass
Hair Dyes and Hair Treatments
Herbicides
Industrial Chemistry, Inorganic
Industrial Chemistry, Organic
Insecticides
Irradiated Foods
Materials Science
Nanochemistry
Nylon
Pesticides
Pigments
Polymers, Synthetic
Recycling
Rocketry
Superconductors
Zeolites

Aqueous Chemistry

Acid-Base Chemistry
Bases
Bleaches
Chemical Reactions
Colloids
Corrosion
Equilibrium
Solution Chemistry
Water

Astrochemistry

Astrochemistry

Biochemistry

Acetylcholine
Active Site
Allosteric Enzymes
Amino Acid
Antibiotics
Artificial Sweeteners
Base Pairing
Bioluminescence
Caffeine
Carbohydrates
Cellulose
Chemiluminescence
Cholecalciferol
Cholesterol
Chromosome
Clones
Codon
Coenzyme
Cofactor
Collagen
Cortisone
Denaturation
Deoxyribonucleic Acid
Disaccharides
DNA Replication
Dopamine
Double Helix
Endorphins
Enzymes
Epinephrine
Estrogen
Fats and Fatty Acids
Fibrous Protein
Genes
Genetic Engineering
Genome
Globular Protein
Glycolysis
Glycoprotein
Hemoglobin
Hydrolase
Hydrolysis
Ion Channels
Kinase
Krebs Cycle
Lipid Bilayers
Lipids
Low Density Lipoprotein (LDL)
Membrane
Methylphenidate
Mutagen
Mutation
Neurochemistry
Neurotoxins
Neurotransmitters
Nicotinamide
Nicotinamide Adenine Dinucleotide (NAD)
Nicotine
Norepinephrine
Nucleic Acids
Nucleotide
Peptide Bond
Phospholipids

Photosynthesis
Polymerase Chain Reaction (PCR)
Polymers, Natural
Polysaccharides
Proteins
Primary Structure
Protein Solubility
Protein Synthesis
Protein Translation
Quaternary Structure
Residue
Restriction Enzymes
Retinol
Rhodium
Ribonucleic Acid
RNA Synthesis
Secondary Structure
Starch
Steroids
Stimulants
Storage Protein
Substrate
Taste Receptors
Teratogen
Tertiary Structure
Testosterone
Thiamin
Toxicity
Transmembrane Protein
Transport Protein
Triglycerides
Venom
Zwitterion

Biographies

Al Razi, Abu Bakr Muhammed ibn Zakariya
Anfinsen, Christian
Arrhenius, Svante
Avery, Oswald
Avogadro, Amedeo
Baekeland, Leo
Balmer, Johann Jakob
Bardeen, John
Becquerel, Antoine-Henri
Berg, Paul
Berthollet, Claude-Louis
Berzelius, Jöns Jakob
Black, Joseph
Bohr, Niels
Boltzmann, Ludwig
Boyle, Robert
Bragg, William Henry
Bragg, William Lawrence
Brønsted, Johannes Nicolaus
Bunsen, Robert
Caldwell, Mary
Calvin, Melvin
Cannizzaro, Stanislao
Carnot, Sadi
Carothers, Wallace
Carver, George Washington
Cavendish, Henry
Chadwick, James
Chappelle, Emmett
Chardonnet, Hilaire
Charles, Jacques
Chevreul, Michel
Cleve, Per Theodor
Cori, Carl and Gerty
Cottrell, Frederick
Coulomb, Charles
Curie, Marie Sklodowska
Dalton, John
Davy, Humphry
de Broglie, Louis
Dewar, James
du Pont, Éleuthère Irénée
Ehrlich, Paul
Einstein, Albert
Elion, Gertrude Belle
Fahrenheit, Gabriel
Faraday, Michael
Fermi, Enrico
Fischer, Emil Hermann
Fleming, Alexander
Franklin, Rosalind
Gadolin, Johan
Gay-Lussac, Joseph-Louis
Gibbs, Josiah Willard
Goodyear, Charles
Haber, Fritz
Hall, Charles
Heisenberg, Werner
Hess, Germain Henri
Heyrovsky, Jaroslav
Hodgkin, Dorothy
Julian, Percy
Kekulé, Friedrich August
Kelsey, Frances Kathleen Oldham
Khorana, Har Gobind
Krebs, Hans Adolf
Lavoisier, Antoine
Lawrence, Ernest
Le Bel, Joseph-Achille
Leblanc, Nicolas
LeChâtelier, Henri
Leclanché, Georges
Leloir, Luis
Lewis, Gilbert N.
Liebig, Justus von
Lister, Joseph
Lonsdale, Kathleen
Lucretius
Marsden, Ernest
Martin, Archer John Porter
Maxwell, James Clerk
Meitner, Lise
Mendeleev, Dimitri
Menten, Maud
Meyer, Lothar
Millikan, Robert
Morgan, Agnes Fay
Moseley, Henry
Nernst, Walther Hermann
Newton, Isaac
Nobel, Alfred Bernhard
Northrop, John
Oppenheimer, Robert
Ostwald, Friedrich Wilhelm
Paracelsus
Pasteur, Louis
Pauli, Wolfgang
Pauling, Linus
Perkin, William Henry
Planck, Max
Priestley, Joseph
Raman, Chandrasekhara
Ramsay, William
Remsen, Ira
Robinson, Robert
Röntgen, Wilhelm
Rutherford, Ernest
Rydberg, Johannes
Sanger, Frederick
Scheele, Carl
Schrödinger, Erwin
Seaborg, Glenn Theodore
Seibert, Florence
Soddy, Frederick
Stanley, Wendell
Staudinger, Hermann
Strutt, John (Lord Rayleigh)
Sumner, James
Svedberg, Theodor
Synge, Richard Laurence Millington
Szent-Györgyi, Albert
Thomson, Joseph John
Todd, Alexander
Travers, Morris
Urey, Harold
van der Waals, Johannes
Van Helmont, Johann Baptista
Van't Hoff, Jacobus Hendricus
Volta, Alessandro
Waksman, Selman
Watson, James Dewey
Weizmann, Chaim

Werner, Alfred
Willstätter, Richard
Wöhler, Friedrich
Woodward, Robert
Yalow, Rosalyn
Yukawa, Hideki
Zsigmondy, Richard

Chemical Substances

Coordination Compounds
Materials Science
Minerals
Nanochemistry
Nylon
Plastics
Rubber
Rydberg, Johannes
Silicone
Soap
Starch
Steel
Water

Computing

Chemical Informatics
Computational Chemistry
Digital X Ray
Molecular Modeling

Elements

Actinides
Actinium
Alkali Metals
Alkaline Earth Metals
Allotropes
Aluminum
Americium
Antimony
Argon
Arsenic
Astatine
Barium
Berkelium
Beryllium
Bismuth
Boron
Bromine
Cadmium
Calcium
Californium
Carbon
Cerium
Cesium
Chalcogens
Chlorine
Chromium
Cobalt
Copper
Curium
Dysprosium
Einsteinium
Erbium
Europium
Fermium
Fluorine
Francium
Fullerenes
Gadolinium
Germanium
Gold
Hafnium
Halogens
Helium
Holmium
Hydrogen
Indium
Iodine
Iridium
Iron
Lanthanides
Lanthanum
Lawrencium
Lead
Lithium
Lutetium
Magnesium
Manganese
Mendelevium
Mercury
Molybdenum
Neodymium
Neon
Neptunium
Nickel
Niobium
Nitrogen
Nobelium
Noble Gases
Osmium
Oxygen
Ozone
Palladium
Platinum
Plutonium
Polonium
Potassium
Praseodymium
Promethium
Protactinium
Radium
Radon
Rhenium
Rhodium
Rubidium
Ruthenium
Rutherfordium
Samarium
Scandium
Selenium
Silicon
Silver
Sodium
Sulfur
Tantalum
Technetium
Tellurium
Terbium
Thallium
Thorium
Thulium
Tin
Titanium
Transactinides
Tungsten
Uranium
Vanadium
Xenon
Ytterbium
Yttrium
Zinc
Zirconium

Energy

Chemistry and Energy
Energy
Energy Sources and Production
Explosions
Fire, Fuels, Power Plants
Fossil Fuels
Heat
Manhattan Project
New Battery Technology
Nuclear Fission
Nuclear Fusion
Petroleum
Solar Cells
Solid-State Devices
Storage Protein
Sustainable Energy Use
Temperature
Thermochemistry
Thermodynamics

Environmental Chemistry

Air Pollution
Atmospheric Chemistry
Environmental Pollution
Fertilizer

Freons
Global Warming
Green Chemistry
Herbicides
Insecticides
Pesticides
Recycling
Water Pollution
Water Quality

History

Alchemy

Inorganic Chemistry

Ceramics
Gemstones
Industrial Chemistry, Inorganic
Materials Science
Minerals
Nomenclature of Inorganic Chemistry

Medicine

Acetaminophen
Acetylsalicylic Acid
Acne Medication
Antibiotics
Ascorbic Acid
Carcinogen
Chemotherapy
CT Scans
Heavy Metal Toxins
Ibuprofen
Insulin
Interferon
Irradiated Foods
Neurotoxins
Neurotransmitters
Nuclear Medicine
Penicillin
Pharmaceutical Chemistry
Sulfa Drugs
Teratogen
Toxicity
Venom

Organic Chemistry

Aromaticity
Freons
Industrial Chemistry, Organic
Nylon
Organic Chemistry
Organic Halogen Compounds
Organometallic Compounds
Pesticides
Petroleum
Polyesters
Polymers, Synthetic
Rubber
Terpenes
Zwitterion

Physical Chemistry

Catalysis and Catalysts
Colloids
Concentration Gradient
Corrosion
Electrochemistry
International System of Units
Kinetics
Measurement
Nuclear Magnetic Resonance
Physical Chemistry
Quantum Chemistry
Spectroscopy
Surface Chemistry
Theoretical Chemistry

Radiation

Digital X Ray
Radiation
Radiation Exposure
Radioactivity

Reactions

Chemical Reactions
Combinatorial Chemistry
Equations, Chemical
Equilibrium
Inhibitors
Recombinant DNA
Synthesis, Chemical

States of Matter

Gases
Liquid Crystals
Liquids
Solid State

Structure

Chirality
Isomerism
Lewis Structures
Magnetism
Molecular Geometry
Molecular Modeling
Molecular Structure
Molecules
Periodic Table
Primary Structure
Quaternary Structure
Secondary Structure
Stoichiometry
Tertiary Structure

For Your Reference

TABLE 1. SELECTED METRIC CONVERSIONS

WHEN YOU KNOW	MULTIPLY BY	TO FIND
Temperature		
Celsius (°C)	1.8 (°C) +32	Fahrenheit (°F)
Celsius (°C)	°C +273.15	Kelvin (K)
degree change (Celsius)	1.8	degree change (Fahrenheit)
Fahrenheit (°F)	[(°F) −32] / 1.8	Celsius (°C)
Fahrenheit (°F)	[(°F −32) / 1.8] +273.15	Kelvin (K)
Kelvin (K)	K −273.15	Celsius (°C)
Kelvin (K)	1.8(K −273.15) +32	Fahrenheit (°F)

WHEN YOU KNOW	MULTIPLY BY	TO FIND
Distance/Length		
centimeters	0.3937	inches
kilometers	0.6214	miles
meters	3.281	feet
meters	39.37	inches
meters	0.0006214	miles
microns	0.000001	meters
millimeters	0.03937	inches

WHEN YOU KNOW	MULTIPLY BY	TO FIND
Capacity/Volume		
cubic kilometers	0.2399	cubic miles
cubic meters	35.31	cubic feet
cubic meters	1.308	cubic yards
cubic meters	8.107×10^{-4}	acre-feet
liters	0.2642	gallons
liters	33.81	fluid ounces

WHEN YOU KNOW	MULTIPLY BY	TO FIND
Area		
hectares (10,000 square meters)	2.471	acres
hectares (10,000 square meters)	107,600	square feet
square meters	10.76	square feet
square kilometers	247.1	acres
square kilometers	0.3861	square miles

WHEN YOU KNOW	MULTIPLY BY	TO FIND
Weight/Mass		
kilograms	2.205	pounds
metric tons	2205	pounds
micrograms (μg)	10^{-6}	grams
milligrams (mg)	10^{-3}	grams
nanograms (ng)	10^{-9}	grams

TABLE 2. ALPHABETIC TABLE OF THE ELEMENTS

Symbol	Element	Atomic Number	Atomic Mass*	Symbol	Element	Atomic Number	Atomic Mass*
Ac	Actinium	89	(227)	Mt	Meitnerium	109	(266)
Al	Aluminum	13	26.982	Md	Mendelevium	101	(258)
Am	Americium	95	(243)	Hg	Mercury	80	200.59
Sb	Antimony	51	121.75	Mo	Molybdenum	42	95.94
Ar	Argon	18	39.948	Nd	Neodymium	60	144.24
As	Arsenic	33	74.922	Ne	Neon	10	20.180
At	Astatine	85	(210)	Np	Neptunium	93	237.048
Ba	Barium	56	137.33	Ni	Nickel	28	58.69
Bk	Berkelium	97	(247)	Nb	Niobium	41	92.908
Be	Beryllium	4	9.012	N	Nitrogen	7	14.007
Bi	Bismuth	83	208.980	No	Nobelium	102	(259)
Bh	Bohrium	107	(262)	Os	Osmium	76	190.2
B	Boron	5	10.811	O	Oxygen	8	15.999
Br	Bromine	35	79.904	Pd	Palladium	46	106.42
Cd	Cadmium	48	112.411	P	Phosphorus	15	30.974
Ca	Calcium	20	40.08	Pt	Platinum	78	195.08
Cf	Californium	98	(251)	Pu	Plutonium	94	(244)
C	Carbon	6	12.011	Po	Polonium	84	(209)
Ce	Cerium	58	140.115	K	Potassium	19	39.1
Cs	Cesium	55	132.90	Pr	Praseodymium	59	140.908
Cl	Chlorine	17	35.453	Pm	Promethium	61	(145)
Cr	Chromium	24	51.996	Pa	Protactinium	91	231.036
Co	Cobalt	27	58.933	Ra	Radium	88	226.025
Cu	Copper	29	63.546	Rn	Radon	86	(222)
Cm	Curium	96	(247)	Re	Rhenium	75	186.207
Ds	Darmastadtium	110	(269)	Rh	Rhodium	45	102.906
Db	Dubnium	105	(262)	Rb	Rubidium	37	85.47
Dy	Dysprosium	66	162.50	Ru	Ruthenium	44	101.07
Es	Einsteinium	99	(252)	Rf	Rutherfordium	104	(261)
Er	Erbium	68	167.26	Sm	Samarium	62	150.36
Eu	Europium	63	151.965	Sc	Scandium	21	44.966
Fm	Fermium	100	(257)	Sg	Seaborgium	106	(263)
F	Fluorine	9	18.998	Se	Selenium	34	78.96
Fr	Francium	87	(223)	Si	Silicon	14	28.086
Gd	Gadolinium	64	157.25	Ag	Silver	47	107.868
Ga	Gallium	31	69.723	Na	Sodium	11	22.990
Ge	Germanium	32	72.61	Sr	Strontium	38	87.62
Au	Gold	79	196.967	S	Sulfur	16	32.066
Hf	Hafnium	72	178.49	Ta	Tantalum	73	180.948
Hs	Hassium	108	(265)	Tc	Technetium	43	(98)
He	Helium	2	4.003	Te	Tellurium	52	127.60
Ho	Holmium	67	164.93	Tb	Terbium	65	158.925
H	Hydrogen	1	1.008	Tl	Thallium	81	204.383
In	Indium	49	114.82	Th	Thorium	90	232.038
I	Iodine	53	126.905	Tm	Thulium	69	168.934
Ir	Iridium	77	192.22	Sn	Tin	50	118.71
Fe	Iron	26	55.847	Ti	Titanium	22	47.88
Kr	Krypton	36	83.80	W	Tungsten	74	183.85
La	Lanthanum	57	138.906	U	Uranium	92	238.029
Lr	Lawrencium	103	(260)	V	Vanadium	23	50.942
Pb	Lead	82	207.2	Xe	Xenon	54	131.29
Li	Lithium	3	6.941	Yb	Ytterbium	70	173.04
Lu	Lutetium	71	174.967	Y	Yttrium	39	88.906
Mg	Magnesium	12	24.305	Zn	Zinc	30	65.38
Mn	Manganese	25	54.938	Zr	Zirconium	40	91.224

*Atomic masses are based on the relative atomic mass of ^{12}C=12. These values apply to the elements as they exist in materials of terrestrial origin and to certain artificial elements. Values in parenthesis are the mass number of the isotope of the longest half-life.

TABLE 3. COMMON ABBREVIATIONS, SYMBOLS, AND ACRONYMS

′	minute (of arc); single prime
″	second (of arc); double prime
+	plus
$^+$	positive charge
−	minus
$^-$	negative charge
±	plus-or-minus
∓	minus-or-plus
×	multiplied by
·	multiplied by
÷	divided by
=	equals
≠	not equal to
∽	about, approximately
≅	congruent to; approximately equal to
≈	approximately equal to
≡	identical to; equivalent to
<	less than
≤	less than or equal to
>	greater than
≥	greater than or equal to
%	percent
°	degree (temperature; angle of arc)
@	at
—	single bond
═	double bond
: :	double bond
≡	triple bond
: : :	triple bond
∞	infinity
∝	variation
∂	partial derivative or differential
α	proportional to, alpha
√	square root
Δ	delta; increment of a variable
ϵ_0	dielectric constant; permittivity
θ	plane angle
λ	wavelength
μ	magnetic moment; micro
μA	microampere
μC	microcoulomb
μF	microfarad
μg	microgram
μg/ml	microgram per milliliter
μK	microkelvin
μm	micrometer (also called micron)
μmol;	micromole
μs, μsec	microsecond
ν	frequency
υ	velocity
π or pi	ratio of the circumference of a circle to its diameter; double as in double bond
σ	single as in single bond; Stefan-Boltzmann constant
Σ	summation
ϕ	null set
ψ	amplitude of a wave (as in *wave,* or *psi, function)*
→	reaction to right
←	reaction to left
↔	connecting resonance forms
⇆	equilibrium reaction beginning at right
⇄	equilibrium reaction beginning at left
⇌	reversible reaction beginning at left
⇋	reversible reaction beginning at right
↑	elimination
⇓	absorption
a	acceleration
A	area
a_o	Bohr Unit
AAS	atomic absorption spectroscopy
ABS	alkylbenzene sulfate
ACS	American Chemical Society
ADH	alcohol dehydrogenase
ADP	adenosine diphosphate
AEC	Atomic Energy Commission
AES	atomic emission spectroscopy
AFM	atomic force microscope; atomic force microscopy
AFS	atomic fluorescence spectroscopy
ALDH	aldehyde dehydronase
amp	ampere
AMS	accelerator mass spectrometry
AMU	atomic mass unit
atm.	standard atmosphere (unit of pressure)
ATP	adenosine triphosphate
β	beta
b.p.	boiling point
Btu	British thermal unit
c	centi-; speed of light
C	carbon; Celsius; centigrade; coulomb
C	heat capacity; electric capacitance

TABLE 3. COMMON ABBREVIATIONS, SYMBOLS, AND ACRONYMS [continued]

Ci	Curies
cm	centimeter
CT	computed tomography
d	d-orbital
D	dipole moment
DC	direct current
deg	degree
dr	diastereomer ratio
e	elementary charge
E	electric field strength; energy
E_a	activation energy
E_g	bandgap energy
EA	electron affinity
er	enantiomer ratio
eV	electron volts
f	f-orbital
F	Fahrenheit; Faraday's constant; fluorine
F	force
g	gram
g	g-orbital; gas
h	hour
h	Planck's constant
Hz	hertz
i	i-orbital
IUPAC	International Union of Pure and Applied Chemistry
J	joule
J	electric current density
k	k-orbital
K	degrees Kelvin; Kelvin; potassium
K_a	acidity constant for the dissociation of weak acid (the weaker the acid, the lower the K_a value
k_B	Boltzmann's constant
Kg	kilogram
kHz	kilohertz
kJ	kilojoule
kJ mol	kilojoule mole
km	kilometer
K_m	Michaelis constant
l	length; liquid
L	lambert; liter
L	length; Avogadro's constant
LD	lethal dose
L/mole	liters per mole
ln	natural logarithm
log	logarithm
m	meter; milli-; molal (concentration)
m	mass
M	molar (concentration)
m_e	electron mass
mA	milliamperes
mg	milligram
mg/L	milligrams per liter
MHz	megahertz
min	minute
ml	milliliter
MO	molecular orbital
p	p-orbital
ω	omega
ppb	parts per billion
ppm	parts per million
ppt	parts per trillion
psi	per square inch; English for ψ
q	quantity
REM	Roentgen Equivalent Man (radiation-dose unit of measure)
s	solid; s-orbital
S	entropy
sec	second; secant
SEM	scanning electron microscope
SI	Système Internationale (International System of Measurements)
SPM	scanning probe microscope
STM	scanning tunneling microscope
STP	standard temperature and pressue (˚C, 1 atm)
Sv	sievert unit (1 Sv = 100 REM; used to measure radiation dose)
t	time
T	moment of force, thermodynamic temperature (in degrees Kelvin); torque
T_c	critical temperature
TEM	transmission electron microscope
u	unified atomic mass unit
U	electric potential
V	electric potential; vanadium; volume
V	volt
vap.	vaporization
VB	valence bond
vel.	velocity
VSEPR	valence shell electron pair repulsion
Z	atomic number

PERIODIC TABLE OF THE ELEMENTS*†

	I	II
5	3 LITHIUM **Li** 6.941	4 BERYLLIUM **Be** 9.012
	11 SODIUM **Na** 22.990	12 MAGNESIUM **Mg** 24.305
	19 POTASSIUM **K** 39.1	20 CALCIUM **Ca** 40.08
	37 RUBIDIUM **Rb** 85.47	38 STRONTIUM **Sr** 87.62
	55 CESIUM **Cs** 132.90	56 BARIUM **Ba** 137.33
	87 FRANCIUM **Fr** (223)	88 RADIUM **Ra** 226.025

1 HYDROGEN **H** 1.008

d	21 SCANDIUM **Sc** 44.966	22 TITANIUM **Ti** 47.88	23 VANADIUM **V** 50.942	24 CHROMIUM **Cr** 51.996	25 MANGANESE **Mn** 54.938	26 IRON **Fe** 55.847	27 COBALT **Co** 58.933	28 NICKEL **Ni** 58.69	29 COPPER **Cu** 63.546	30 ZINC **Zn** 65.38
	39 YTTRIUM **Y** 88.906	40 ZIRCONIUM **Zr** 91.224	41 NIOBIUM **Nb** 92.908	42 MOLYBDENIUM **Mo** 95.94	43 TECHNETIUM **Tc** (98)	44 RUTHENIUM **Ru** 101.07	45 RHODIUM **Rh** 102.906	46 PALLADIUM **Pd** 106.42	47 SILVER **Ag** 107.868	48 CADMIUM **Cd** 112.411
	71 LUTETIUM **Lu** 174.967	72 HAFNIUM **Hf** 178.49	73 TANTALUM **Ta** 180.948	74 TUNGSTEN **W** 183.85	75 RHENIUM **Re** 186.207	76 OSMIUM **Os** 190.2	77 IRIDIUM **Ir** 192.22	78 PLATINUM **Pt** 195.08	79 GOLD **Au** 196.967	80 MERCURY **Hg** 200.59
	103 LAWRENCIUM **Lr** (260)	104 RUTHERFORDIUM **Rf** (261)	105 DUBNIUM **Db** (262)	106 SEABORGIUM **Sg** (263)	107 BOHRIUM **Bh** (262)	108 HASSIUM **Hs** (265)	109 MEITNERIUM **Mt** (266)	110 DARMASTADTIUM **Ds** (269)	111 UNUNUNIUM **Uuu** (272)	112 (?)

	III	IV	V	VI	VII	VIII
						2 HELIUM **He** 4.003
p	5 BORON **B** 10.811	6 CARBOM **C** 12.011	7 NITROGEN **N** 14.007	8 OXYGEN **O** 15.999	9 FLUORINE **F** 18.998	10 NEON **Ne** 20.180
	13 ALUMINUM **Al** 26.982	14 SILICON **Si** 28.086	15 PHOSPHORIUS **P** 30.974	16 SULFUR **S** 32.066	17 CHLORINE **Cl** 35.453	18 ARGON **Ar** 39.948
	31 GALLIUM **Ga** 69.73	32 GERMANIUM **Ge** 72.61	33 ARSENIC **As** 74.922	34 SELENIUM **Se** 78.96	35 BROMINE **Br** 79.904	36 KRYPTON **Kr** 83.80
	49 INDIUM **In** 114.82	50 TIN **Sn** 118.71	51 ANTIMONY **Sb** 121.75	52 TELLURIUM **Te** 127.60	53 IODINE **I** 126.905	54 XENON **Xe** 131.29
	81 THALLIUM **Tl** 204.383	82 LEAD **Pb** 207.2	83 BISMUTH **Bi** 208.980	84 POLONIUM **Po** (209)	85 ASTATINE **At** (210)	86 RADON **Rn** (222)

f	57 LANTHANUM **La** 138.906	58 CERIUM **Ce** 140.15	59 PRAESEODYMIUM **Pr** 140.908	60 NEODYMIUM **Nd** 144.24	61 NEODYMIUM **Pm** (145)	62 SAMARIUM **Sm** 150.36	63 EUROPIUM **Eu** 151.965	64 GADOLINIUM **Gd** 157.25	65 TERBIUM **Tb** 158.925	66 DYSPROSIUM **Dy** 162.50	67 HOLMIUM **Ho** 164.93	68 ERBIUM **Er** 167.26	69 THULIUM **Tm** 168.934	70 YTTERBIUM **Yb** 173.04
	89 ACTINIUM **Ac** 227.03	90 THORIUM **Th** 232.038	91 PROTACTINIUM **Pa** 231.036	92 URANIUM **U** 238.029	93 NEPTUNIUM **Np** 237.048	94 PLUTONIUM **Pu** (244)	95 AMERICIUM **Am** (243)	96 CURIUM **Cm** (247)	97 BERKELIUM **Bk** (247)	98 CALIFORNIUM **Cf** (251)	99 EINSTEINIUM **Es** (252)	100 FERMIUM **Fm** (257)	101 MENDELEVIUM **Md** (258)	102 NOBELIUM **No** (259)

*Each element in the table is listed with (from top to bottom) its atomic number, its name, its symbol, and its atomic mass. Atomic mass numbers in parentheses are the mass numbers of the longest-lived isotope. Other atomic mass numbers are the average mass number of the naturally occurring isotopes.

†The names and labels for elements beyond number 103 are controversial. IUPAC initially ruled in favor of Latin names based on atomic number, but in 1994 a set of specific names and symbols was suggested. After considerable debate, a revised final list of names for elements 104-109 was issued on August 30, 1997. Temporary names were also assigned for elements 110 and 111. Various groups have suggested alternatives names for some of these elements. Additional elements continue to be synthesized, though with increasing difficulty, with no definite upper atomic-number limit yet established.

Contributors

Catalina Achim
Carnegie Mellon University
Pittsburgh, Pennsylvania

David T. Allen
University of Texas at Austin
Austin, Texas

Carolyn J. Anderson
Washington University School of Medicine
St. Louis, Missouri

Ronald D. Archer
Professor Emeritus
University of Massachusetts, Amherst
Amherst, Massachusetts

D. Eric Aston
University of Idaho
Moscow, Idaho

Peter Atkins
University of Oxford
Oxford, United Kingdom

Cynthia Atterholt
Western Carolina University
Cullowhee, North Carolina

Michèle Auger
Laval University
Quebec, Quebec, Canada

Karl W. Böer
Professor Emeritus
University of Delaware
Newark, Delaware

Catherine H. Banks
Peace College
Raleigh, North Carolina

Joseph Bariyanga
University of Wisconsin
Milwaukee, Wisconsin

Nathan J. Barrows
University of Northern Colorado
Greeley, Colorado

David A. Bassett
Brockton, Massachusetts

James D. Batteas
CUNY - College of Staten Island
Staten Island, New York

Bruce Beaver
Duquesne University
Pittsburgh, Pennsylvania

C. Larry Bering
Clarion University
Clarion, Pennsylvania

Bill Bertoldi
Kingsford, Michigan

W. E. Billups
Rice University
Houston, Texas

Koen Binnemans
Catholic University of Leuven
Leuven, Belgium

James P. Birk
Arizona State University
Tempe, Arizona

Jeffrey R. Bloomquist
Virginia Polytechnic Institute and State University
Blacksburg, VA

John E. Bloor
University of Tennessee
Knoxville, Tennessee

George Bodner
Purdue University
West Lafayette, Indiana

Paul W. Bohn
University of Illinois
Urbana, Illinois

Valerie Borek
Boothwyn, Pennsylvania

Erwin Boschmann
Indiana University
Indianapolis, Indiana

Wayne B. Bosma
Bradley University
Peoria, Illinois

Ole Bostrup
The Danish Society of The History of Chemistry
Fredensborg, Denmark

F. Javier Botana
University of Cadiz
Cadiz, Spain

Lawrence H. Brannigan
Southwestern Illinois College
Bellville, Illinois

Ronald Brecher
GlobalTox International Consultants Inc.
Guelph, Ontario, Canada

Jeffrey C. Bryan
University of Wisconsin-La Crosse
La Crosse, Wisconsin

Robert A. Bulman
National Radiological Protection Board
Oxfordshire, England

Jean-Claude Bunzli
Swiss Federal Institute of Technology
Lausanne, Switzerland

Douglas Cameron
Montana Tech of the University of Montana
Butte, Montana

Michael C. Cann
University of Scranton
Scranton, Pennsylvania

Charles E. Carraher Jr.
Florida Atlantic University
Boca Raton, Florida

Henry A. Carter
Augustana University College
Camrose, Alberta, Canada

John Castro
Huntington Station, New York

Lyman R. Caswell
Texas Woman's University
Denton, Texas

Raymond Chang
Williams College
Williamstown, Massachusetts

Philip J. Chenier
University of Wisconsin
Eau Claire, Wisconsin

Peter E. Childs
University of Limerick
Limerick, Ireland

Gregory R. Choppin
Florida State University
Tallahassee, Florida

Abraham Clearfield
Texas A&M University
College Station, Texas

Brian P. Coppola
University of Michigan
Ann Arbor, Michigan

Eugene C. Cordero
San José State University
San José, California

Paul A. Craig
Rochester Institute of Technology
Rochester, New York

M. J. Crawford
Ludwig-Maximilians-Universtät-München
Munich, Germany

Mary R. S. Creese
University of Kansas
Lawrence, Kansas
(retired)

Bartow Culp
Purdue University
West Lafayette, Indiana

Carlos Eduardo da Silva Cortes
Universidade Federal Fluminense
Rio de Janeiro, Brazil

G. Brent Dawson
University of North Carolina at Greensboro
Greensboro, North Carolina

Stephanie E. Dew
Centre College
Danville, Kentucky

Anthony Diaz
Central Washington University
Ellensburg, Washington

Diego J. Diaz
University of Illinois at Urbana-Champaign
Urbana, Illinois

James S. Dickson
Iowa State University
Ames, Iowa

David A. Dobberpuhl
Creighton University
Omaha, Nebraska

Daryl J. Doyle
Kettering University
Flint, Michigan

Michael Eastman
Northern Arizona University
Flagstaff, Arizona

Andrew Ede
University of Alberta
Edmonton, Canada

Edward M. Eyring
University of Utah
Salt Lake City, Utah

Scott E. Feller
Wabash College
Crawfordsville, Indiana

Kurt W. Field
Bradley University
Peoria, Illinois

Matthew A. Fisher
St. Vincent College
Latrobe, Pennsylvania

George Fleck
Smith College
Northampton, Massachusetts

Michael J. Fosmire
Purdue University
West Lafayette, Indiana

Mark Freilich
The University of Memphis
Memphis, Tennessee

Ken Geremia
Copper Development Association, Inc.
New York, New York

Gregory S. Girolami
University of Illinois, Champaign-Urbana
Urbana, Illinois

Carmen Giunta
Le Moyne College
Syracuse, New York

Harold Goldwhite
California State University, Los Angeles
Los Angeles, California

Barbara E. Goodman
University of South Dakota
Vermillion, South Dakota

Gordon W. Gribble
Dartmouth College
Hanover, New Hampshire

Robert K. Griffith
West Virginia University
Morgantown, West Virginia

Neena Grover
Colorado College
Colorado Springs, Colorado

William G. Gutheil
University of Missouri-Kansas City
Kansas City, Missouri

David G. Haase
North Carolina State University
Raleigh, North Carolina

Arthur M. Halpern
Indiana State University
Terre Haute, Indiana

R. Adron Harris
The University of Texas at Austin
Austin, Texas

John Harwood
Tennessee Technological University
Cookeville, Tennessee

Ian S. Haworth
University of Southern California
Los Angeles, California

James M. Helt
CUNY- College of Staten Island
Staten Island, New York

J. Carver Hill
Cary, North Carolina

Darleane C. Hoffman
Lawrence Berkeley National Laboratory, University of California
Berkeley, California

Thomas A. Holme
University of Wisconsin-Milwaukee
Milwaukee, Wisconsin

Chaim T. Horovitz
Emeritus Professor
Rehovot , Israel

John D. Hostettler
San José State University
San José, California

Brian R. James
University of British Columbia
Vancouver, British Columbia, Canada

Frank A. J. L. James
The Royal Institution
London, England

Mark Jensen
Argonne National Laboratory
Argonne, Illinois

Melvin D. Joesten
Vanderbilt University
Nashville, Tennessee

W. L. Jolly
University of California, Berkeley
Berkeley, California

Loretta L. Jones
University of Northern Colorado
Greeley, Colorado

David A. Juckett
Michigan State University
Lansing, Michigan
Barros Research Institute
Holt, Michigan

Paul J. Karol
Carnegie Mellon University
Pittsburgh, Pennsylvania

Vladimir Karpenko
Charles University
Prague, Czech Republic

George B. Kauffman
California State University, Fresno
Fresno, California

W. Frank Kinard
College of Charleston
Charleston, SC

Thomas M. Klapotke
Ludwig-Maximillians-Universität München
Munich, Germany

Kyle Knight
University of Tennessee at Chattanooga
Chattanooga, Tennessee

Paul E. Koch
Penn State, Behrend College
Erie, Pennsylvania

Doris K. Kolb
Bradley University
Peoria, Illinois

Kenneth E. Kolb
Bradley University
Peoria, Illinois

Daniel P. Kramer
Kramer & Asscociates, Ltd.
Centerville, Ohio

Ágúst Kvaran
University of Iceland
Reykjavik, Iceland

J. J. Lagowski
The University of Texas
Austin, Texas

Michael Laing
Professor Emeritus
University of Natal
Durban, South Africa

Rattan Lal
The Ohio State University
Columbus, Ohio

Thomas H. Lane
Dow Corning Coporation
Midland, Michigan

Alan B. G. Lansdown
Imperial College School of Medicine
London, United Kingdom

Amanda Lawrence
University of Illinois, Champaign-Urbana
Urbana, Illinois

Peter B. Leavens
University of Delaware
Newark, Delaware

G. J. Leigh
University of Sussex
Brighton, United Kingdom

H. Eugene LeMay, Jr.
University of Nevada
Reno, Nevada

Kenneth B. Lipkowitz
North Dakota State University
Fargo, North Dakota

Ingrid A. Lobo
University of Texas at Austin
Austin, Texas

Walter Loveland
Oregon State University
Corvallis, Oregon

Phyllis A. Lyday
U.S. Geological Survey
Reston, Virginia

Paul A. Maggard Jr.
North Carolina State University
Raleigh, North Carolina

Michael E. Maguire
Case Western Reserve University
Cleveland, Ohio

Keith L. Manchester
University of the Witwatersrand, Johannesburg
South Africa

Dean F. Martin
University of South Florida
Tampa, Florida

Barbara B. Martin
University of South Florida
Tampa, Florida

James D. Martin
North Carolina State University
Raleigh, North Carolina

Anthony F. Masters
University of Sydney
New South Wales, Australia

Seymour Mauskopf
Duke University
Durham, North Carolina

Sean McMaughan
Texas A&M University
College Station, Texas

Paul F. McMillan
University College London, Christopher Ingold Laboratories
London, United Kingdom

Edward A. Meighen
McGill University
Montreal, Canada

Louis Messerle
University of Iowa
Iowa City, Iowa

Donald E. Moreland
Professor Emeritus
North Carolina State University
Raleigh, North Carolina

Matthew J. Morra
University of Idaho, Soil & Land Resources Division
Moscow, Idaho

Richard Mowat
North Carolina State University
Raleigh, North Carolina

Frank Mucciardi
McGill University
Montreal, Quebec, Canada

Kathleen L. Neeley
University of Kansas
Lawrence, Kansas

John Michael Nicovich
Georgia Institute of Technology
Atlanta, Georgia

Robert Noiva
University of South Dakota School of Medicine
Vermillion, South Dakota

Charles E. Ophardt
Elmhurst College
Elmhurst, Illinois

Richard Pagni
University of Tennessee
Knoxville, Tennessee

Gus J. Palenik
University of Florida
Gainsville, Florida

Robert P. Patterson
North Carolina State University, Crop Science Department
Raleigh, North Carolina

Harry E. Pence
State University of New York, College at Oneonta
Oneonta, New York

Mark A. Pichaj
Biola University
La Marada, California

John Pickering
San José State University
Nuclear Science Facility
San José, California

Tanja Pietraß
New Mexico Tech
Socorro, New Mexico

A. G. Pinkus
Baylor University
Waco, Texas

Jennifer L. Powers
Kennesaw State University
Kennesaw, Georgia

Suzanne T. Purrington
North Carolina State University
Raleigh, North Carolina

Ray Radebaugh
National Institute of Standards and Technology, Cryogenics Technologies Group
Boulder, Colorado

Thomas B. Rauchfuss
University of Illinois, Champaign-Urbana
Urbana, Illinois

Geoffrey W. Rayner-Canham
Sir Wilfred Grenfell College

Corner Brook, Newfoundland, Canada

Marelene Rayner-Canham
Sir Wilfred Grenfell College
Corner Brook, Newfoundland, Canada

Jeffrey C. Reid
North Carolina Geological Survey
Raleigh, North Carolina

Richard E. Rice
Florence, Montana

D. Paul Rillema
Wichita State University
Wichita, Kansas

Frank Rioux
St. John's University
College of St. Benedict
St. Joseph, Minnesota

Robert Rittenhouse
Walla Walla College
College Place, Washington

Elizabeth S. Roberts-Kirchhoff
University of Detroit Mercy
Detroit, Michigan

Brett Robinson
Horticultural and Food Research Institute of New Zealand
Palmerston North, New Zealand

Herbert W. Roesky
University of Göttingen
Göttingen, Germany

Hiranya S. Roychowdhury
New Mexico State University
Las Cruces, New Mexico

Gordon Rutter
Royal Botanic Garden Edinburgh
Edinburgh, United Kingdom

Martin D. Saltzman
Providence College
Providence, Rhode Island

Jerry L. Sarquis
Miami University
Oxford, Ohio

Nancy N. Sauer
Los Alamos National Laboratory
Los Alamos, New Mexico

Wolf-Dieter Schubert
Vienna University of Technology
Vienna, Austria

Joachim Schummer
University of South Carolina
Columbia, South Carolina

Alan Schwabacher
University of Wisconsin-Milwaukee
Milwaukee, Wisconsin

A. Truman Schwartz
Macalester College
Saint Paul, Minnesota

William M. Scovell
Bowling Green State University
Bowling Green, Ohio

Lydia S. Scratch
Ottawa, Ontario, Canada

Peter Rudolf Seidl
Universidade Federal do Rio de Janeiro
Rio de Janeiro, Brazil

N. M. Senozan
California State University
Long Beach, California

James F. Shackelford
University of California at Davis
Davis, California

Stephanie Dionne Sherk
Westland, Michigan

Ben Shoulders
The University of Texas at Austin
Austin, Texas

David B. Sicilia
University of Maryland
College Park, Maryland

Herbert B. Silber
San José State University
San José, California

Robert J. Silva
Lawrence Berkeley National Laboratory, University of California
Berkeley, California

Sharron W. Smith
Hood College
Frederick, Maryland

C. Graham Smith
Penicuik, United Kingdom

Mary L. Sohn
Florida Institute of Technology
Melbourne, Florida

David Speckhard
Loras College
Dubuque, Iowa

Jonathan N. Stack
North Dakota State University
Fargo, North Dakota

Conrad L. Stanitski
University of Central Arkansas
Conway, Arkansas

Donald H. Stedman
University of Denver
Denver, Colorado

Anthony N. Stranges
Texas A&M University
College Station, Texas

Dan M. Sullivan
University of Nebraska at Omaha
Omaha, Nebraska

Tammy P. Taylor
Los Alamos National Laboratory
Los Alamos, New Mexico

Ann T. S. Taylor
Wabash College
Crawfordsville, Indiana

Sidney Toby
Rutgers University
Piscataway, New Jersey

Reginald P. T. Tomkins
New Jersey Institute of Technology
Newark, New Jersey

Anthony S. Travis
The Hebrew University
Jerusalem, Israel

Donald G. Truhlar
University of Minnesota
Minneapolis, Minnesota

Georgios Tsaparlis
University of Ioannina
Ioannina, Greece

Dennis G. Tuck
University of Windsor
Windsor, Ontario, Canada
(deceased)

Geraldo Vicentini
Instituto de Quimíca, *University of São Paulo*
São Paulo, Brazil

Nanette M. Wachter
Hofstra University
Hempstead, New York

George H. Wahl Jr.
North Carolina State University
Raleigh, North Carolina

Helen R. Webb
Monash University
Clayton, Victoria, Australia

Laurence E. Welch
Knox College
Galesburg, Illinois

J. Reed Welker
University of Arkansas
Fayetteville, Arkansas
(retired)

Guang Wen
Tottori University
Tottori, Japan

Todd W. Whitcombe
University of Northern British Columbia
Prince George, British Columbia, Canada

Vivienne A. Whitworth
Ryerson University
Toronto, Ontario, Canada

David A. Williams
University College London
London, United Kingdom

Robert K. Wismer
Millersville University
Millersville, Pennsylvania

Ronni Wolf
Kaplan Medical Center
Rechovot, Israel

Adele J. Wolfson
Wellesley College
Wellesley, Massachusetts

Burghard Zeiler
Wolfram Bergbau und Hüttenges m.b.H.
Austria, Germany

Lea B. Zinner
Departamento de Química
São Paulo, Brazil

Cynthia G. Zoski
Georgia State University
Atlanta, Georgia

Thomas M. Zydowsky
FMC Corporation
Princeton, New York

D, Vitamin *See Cholecalciferol.*

Dalton, John

ENGLISH CHEMIST
1766–1844

The fundamental idea of modern chemistry is that matter is made up of atoms of various sorts, which can be combined and rearranged to produce different, and often novel, materials. The person responsible for “this master-concept of our age” (Greenaway, p. 227) was John Dalton. He applied Newton’s idea of small, indivisible atoms to the study of gases in the atmosphere and used it to advance a quantitative explanation of chemical composition. If French chemist Antoine Lavoisier started the chemical revolution, then it was Dalton who put it on a firm foundation. His contemporary, the Swedish chemist Jöns J. Berzelius, said: “If one takes away from Dalton everything but the atomic idea, that will make his name immortal.”

John Dalton was born on or about September 6, 1766, to Quaker parents, in Eaglesfield, a remote village in the north of England. He was largely self-educated, and learned most of his mathematics and science by teaching others. He studied mathematics in a local school until the age of 11, started his own school at the age of 12, and at 15 joined his brother Jonathan in teaching at, and later running, a Quaker school in Kendal. The Quakers were a small dissenting (from the established Church of England) sect, and Dalton was thus a nonconformist, like the scientists Joseph Priestley and Michael Faraday. Dalton was taught and influenced by fellow Quakers Elihu Robinson, a wealthy instrument maker, and John Gough, a blind polymath. In Kendal Gough taught the young Dalton Latin, Greek, French, mathematics, and science, and in return Dalton read to him from books and newspapers. Gough encouraged Dalton to study natural phenomena and to keep a meteorological journal, which Dalton began on March 24, 1787. Dalton maintained this journal methodically for the rest of his life, making his last meteorological observations on his deathbed. He made over 200,000 measurements over a period of fifty-seven years, and a neighbor in Manchester is supposed to have said that she was able to set her clock by Dalton’s daily appearance to take the temperature. Dalton’s meteorological observations launched his scientific career and provided the material for his first book, *Meteorological Observations and Essays* (1793).

British chemist and physicist John Dalton, who drew up the first list of atomic weights.

In 1793 Dalton moved to Manchester, becoming professor of mathematics and **natural philosophy** at New College. He stayed there until 1799, at which time he resigned in order to devote more time to research. He continued to teach private pupils in order to earn a living. According to legend, a visiting French scientist once traveled to Manchester to meet the famous Dalton. He had difficulty in finding him, finally locating him in a small house in an obscure street. He then had to wait while Dalton finished teaching a lesson in mathematics to a small boy.

Dalton stayed in Manchester for the rest of his life, and it was there that he did most of his important work, the results of which were published in the *Memoirs* of the Manchester Literary and Philosophical Society (MLPS). His first scientific paper, published by the MLPS in 1798, described his red-green color blindness. Dalton is said to have purchased for his mother a pair of what he thought were dull-colored stockings—Quakers did not wear bright colors—which she could not wear because they were scarlet. This misadventure motivated Dalton to investigate his color recognition deficiency. He was the first to describe red-green color blindness, sometimes known as Daltonism.

natural philosophy: study of nature and the physical universe

partial pressure: portion of a total pressure of a gas mixture contributed by a single type of gas in the sample

Dalton's study of the atmosphere, prompted by his weather measurements, led him in 1803 to his law of **partial pressures** (in a mixture of gases, each gas acts as an independent entity), and subsequently to the study of the combining of elements. He compared marsh gas (methane, CH_4) with olefiant gas (ethane, C_2H_4), and found that ethane contained exactly double the mass of carbon to the same mass of hydrogen. It is this relationship between the two gases that guided him to his law of multiple proportions. He imagined a chemical atomic model, whereby one atom of an element could combine only with one, two, or three atoms (and so on) of a second element, the combinations forming distinct compounds. He visualized atoms as small hard balls and constructed small wooden models to illustrate how they combined. He invented symbols that enabled him (and others) to notate chemical formulas ✷. Dalton drew up the first list of atomic weights. Dalton's ideas about atoms and their combinations were first aired in 1803 at meetings of the MLPS, mentioned in Thomas Thomson's *System of Chemistry* (1807), and finally published by Dalton in his most important book, *New System of Chemical Philosophy* (1808).

✷See an image of Dalton's symbols in the Atoms article.

Dalton's most significant work was done between 1795 and 1805, but fame came later—when the importance of his **atomic theory** was realized. He became a member of the **Royal Society** in 1822, received its first Royal Medal in 1826, and was honored with a state pension in 1833, among other honors. He died on July 27, 1844, and 40,000 people attended his funeral. SEE ALSO Berzelius, Jöns Jakob; Faraday, Michael; Lavoisier, Antoine; Priestley, Joseph.

atomic theory: concept that asserts that matter is composed of tiny particles called atoms, the particular characteristics of which determine the type and form of the matter

Royal Society: The U.K. National Academy of Science, founded in 1660

Peter E. Childs

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Databases *See Chemical Informatics.*

Davy, Humphry

ENGLISH CHEMIST
1778–1829

English chemist Sir Humphry Davy, who developed the first coherent theory of electrochemical action.

Sir Humphry Davy, the son of woodcarver, was born on December 17, 1778, in Penzance, Cornwall, then a highly industrialized area in the far west of England. In 1798 he moved to Bristol to work at the Pneumatic Institution under Thomas Beddoes, a physician who used gases for medicinal purposes. There he discovered the physiological properties of nitrous oxide (laughing) gas, which established his reputation as a chemist. In Bristol he became friends with the poets Samuel Taylor Coleridge and Robert Southey. No mean poet himself, Davy, at the suggestion of his friends, saw the second edition of William Wordsworth's *Lyrical Ballads*—that seminal text of English Romanticism—through to publication.

In 1801, at the age of twenty-two, Davy was appointed assistant professor and director of the laboratory at the newly founded Royal Institution (1799), and the following year he became professor of chemistry. In the eleven years that he was there, Davy firmly established the Royal Institution's reputation for excellent lectures on science and other areas of culture (he even influenced Coleridge to lecture there). In addition, he was a strong supporter of the utilitarian function of the Royal Institution, particularly in its application of chemical knowledge to the improvement of agriculture and industrial processes, in both of which Davy played a major role. But Davy also transformed the Royal Institution into a setting where in-depth scientific research would be carried out, something that its founders had not planned. But because of its commitment to providing spectacular lectures, the Royal Institution quickly came to have one of the best equipped laboratories in Europe, where research could be conducted.

During the first decade of the nineteenth century, Davy undertook fundamental work on electrochemistry following Alessandro Volta's invention of the electric battery at the end of the eighteenth century. Davy developed the first coherent theory of electrochemical action, whereby he argued that electrochemical decomposition took place at the **metal** poles through which electricity passed into a compound. Indeed, Davy posited that electrical force was the basis of all chemistry. During the course of his work, he discovered sodium and potassium, and later magnesium, calcium, strontium, and barium. Using the same electrochemical techniques, Davy eventually showed that chlorine and iodine were chemical elements rather than compounds, contrary to what French chemists had believed.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

In 1812 he was knighted by the prince regent for his contributions to electrochemistry, married a wealthy widow Jane Apreece, and was thus able to retire from the Royal Institution at the age of thirty-four, although he remained the director of its laboratory. It was in this capacity that he appointed Michael Faraday as an assistant in the laboratory early in 1813. Later that year with his wife, her maid, and Faraday as an assistant, amanuensis (scribe), and reluctant valet, Davy embarked on an eighteen-month tour of the European continent, visiting many laboratories and sites of natural and cultural interest. On their return, Davy invented, with Faraday's assistance, the miners' safety lamp, which reinforced his reputation in applied science. With a confidence that was shared by all romantics of the time, Davy believed that nothing was beyond his reach, and in 1820 he was elected president of the **Royal Society**. This was a position he was ill-equipped to undertake after the forty-two-year presidency of Joseph Banks. Banks had been an autocratic president, and Davy had neither the ability to continue to lead in that mode, nor the power to take the society in a different direction. Davy sought to keep the peace between various factions within the society, but without success. His hostile attitude toward Faraday at this time was largely governed by the politics of the Royal Society. Davy's frustrations were compounded in the mid-1820s when his attempts to develop an electrochemical method for protecting the copper sheeting of the Royal Navy's ships failed. This resulted in strained relations between the government and the Royal Society, which culminated in the government abolishing the Board of Longitude, the only body then channeling state money into science. Davy suffered a stroke and resigned the presidency in 1827; he subsequently traveled abroad, where he died in Geneva, Switzerland, on May 29, 1829. Despite the ups and down of his career, during the nineteenth century Davy came to be regarded as a towering figure and a comparison with him was an enormous compliment. SEE ALSO Barium; Calcium; Faraday, Michael; Magnesium; Potassium; Sodium; Strontium; Volta, Alessandro.

Royal Society: The U.K. National Academy of Science, founded in 1660

Frank A. J. L. James

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de Broglie, Louis

FRENCH PHYSICIST
1892–1987

Louis-Victor-Pierre-Raymond de Broglie was born into a noble French family. He initially studied history at the Sorbonne in Paris, intending to enter the diplomatic service. His elder brother Maurice had chosen to forgo a diplomatic career for one in physics, despite opposition from his family. Louis also became interested in science and decided to pursue a degree in **theoretical physics**. His plans, however, were interrupted by World War I, during which time he served in a wireless telegraphy unit stationed at the Eiffel Tower.

theoretical physics: branch of physics dealing with the theories and concepts of matter, especially at the atomic and subatomic levels

In 1920 de Broglie returned to his studies; later he stated that his attraction "to theoretical physics was . . . the mystery in which the structure of matter and of radiation was becoming more and more enveloped as the strange concept of the quantum, introduced by Max Planck in 1900 in his researches into black-body radiation, daily penetrated further into the whole of physics" (quoted by Heathcote, pp. 289–290).

During this same period de Broglie's brother Maurice was studying experimental physics, and he was particularly interested in x rays. The brothers frequently discussed x rays, and their dual nature (both wavelike and particle-like behavior) suggested to Louis that this same particle-wave duality might also apply to particles such as electrons.

In his doctoral dissertation in 1924, Louis de Broglie developed the equation $\lambda = h/mv$, which predicts that the wavelength λ of a particle is inversely proportional to its mass m and velocity v, where h is Planck's constant.✷ The wavelength associated with a submicroscopic object—an electron, for example—is large relative to the size of the object and is therefore significant in describing its behavior, whereas the wavelength associated with a macroscopic object—a basketball, for example—is negligibly small relative to its size, and therefore the wavelike behavior of such an object is unnoticeable.

✷See Max Planck article for more about Planck's constant.

The dual nature of electrons proposed by de Broglie, together with the dual nature of electromagnetic radiation proposed by Max Planck, led to the development of **quantum mechanics** by the Austrian physicist Erwin Schrödinger in 1926. The following year American physicists Charles J. Davisson and Lester H. Germer and others demonstrated experimentally that electrons can be diffracted just like light. That is, as electrons pass through a narrow slit, they spread out in a wavelike pattern similar to that of diffracted light.

quantum mechanics: theoretical model to describe atoms and molecules by wave functions

De Broglie accomplished his most important work in physics while still a young man, receiving the Nobel Prize in physics in 1929. After obtaining his doctorate in 1924, he taught at the Sorbonne, and in 1928 he was named professor of theoretical physics at the Henri Poincaré Institute in Paris. In 1932 he also became professor of theoretical physics at the Sorbonne, retiring from that post in 1962.

Throughout his long life, de Broglie remained active in the development and interpretation of quantum mechanics and wrote more than twenty-five books on various topics related to this field of study. As a member of the French Commission on Atomic Energy, he was a long-time advocate for the peaceful use of atomic power. De Broglie also wrote a number of popular books to help promote public understanding of modern physics, and in recognition of these efforts, the United Nations Educational, Scientific, and Cultural Organization (UNESCO) awarded him the Kalinga Prize in 1952. He was the recipient of many awards and honors for his work in quantum mechanics.

As a young scientist de Broglie had believed that the statistical nature of modern physics masks our ignorance of the underlying reality of the physical world, but for much of his life he also believed that this statistical nature is all that we can know. Toward the end of his life, however, de Broglie turned back toward the views of his youth, favoring causal relationships in place of the accepted probabilistic picture associated with quantum mechanics. SEE ALSO PLANCK, MAX; SCHRÖDINGER, ERWIN

Richard E. Rice

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Denaturation

Protein molecules carry out many important tasks in living systems. Most important, the majority of proteins are quite specific about which task they perform. Protein structure is what dictates this specificity, and the three-dimensional (tertiary) structure is particularly important. When this specific three-dimensional structure is disrupted, the protein loses its functionality and is said to have undergone denaturation.

hydrogen bonding: intermolecular force between the H of an N–H, O–H, or F–H bond and a lone pair on O, N, or F of an adjacent molecule

The interactions, such as **hydrogen bonding**, that dictate the tertiary structure of proteins are not as strong as covalent chemical bonds. Because these interactions are rather weak, they can be disrupted with relatively modest stresses.

If a solution containing a protein is heated, it will reach a temperature at which properties such as viscosity or the absorption of ultraviolet (UV) light will change abruptly. This temperature is called the melting temperature of the protein (because the measurement is analogous to that made for the melting of a solid). The melting temperature varies for different proteins, but temperatures above 41°C (105.8°F) will break the interactions in many proteins and denature them. This temperature is not that much higher than normal body temperature (37°C or 98.6°F), so this fact demonstrates how dangerous a high fever can be.

An egg white before the denaturation of the albumin protein causes the transucent substance to change in color and viscosity.

A familiar example of heat-caused denaturation are the changes observed in the albumin protein of egg whites when they are cooked. When an egg is first cracked open, the "whites" are translucent and runny (they flow like a liquid), but upon heating they harden and turn white. The change in viscosity and color is an indication that the proteins have been denatured.

Factors other than heat can also denature proteins. Changes in pH affect the chemistry of amino acid residues and can lead to denaturation. Hydrogen bonding often involves these side changes. Protonation of the amino acid residues (when an acidic proton H^+ attaches to a lone pair of electrons on a nitrogen) changes whether or not they participate in hydrogen bonding, so a change in the pH can denature a protein.

Changes in salt concentration may also denature proteins, but these effects depend on several factors including the identity of the salt. Some salts, such as ammonium sulfate, tend to stabilize protein structures and increase the melting temperature. Others, such as calcium chloride, destabilize proteins and lower the melting temperature and are called chaotropic. Salts in this category can also be used in the laboratory to help purify proteins that are being studied, by lowering their solubility and causing them to "salt out." SEE ALSO HEAVY METAL TOXINS; PROTEINS.

Thomas A. Holme

The heat-caused denaturation in albumin protein in egg whites causes the once translucent, runny substance into one that is white and firm.

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Deoxyribonucleic Acid (DNA)

Deoxyribonucleic acid (DNA) is the genetic material of most living organisms. One of its main functions is to produce ribonucleic acid (RNA), which then makes proteins. Thus, information within DNA allows a cell to make most of the molecules it needs to function.

DNA and RNA are nucleic acids that are composed of sugars, phosphates, and nitrogenous bases (or a base). The four bases found in DNA are **guanine** (G), **cytosine** (C), thymidine (T), and **adenine** (A). Each sugar attached to a base and phosphate is called a nucleotide. Hence, DNA is a collection of nucleotides.

Bases from two different strands interact to form a double-helical structure. Guanine forms three **hydrogen bonds** with cytosine, whereas adenine forms two hydrogen bonds with thymidine. **Stacking interactions** between the planar bases also stabilize the DNA structure. Phosphates and sugars form the backbone of DNA.

The DNA sequence is represented by writing the base sequence from the **5′ end** to the **3′ end** of one strand, for example, 5′-GATTACA-3′ represents:

5′-GATTACA-3′
3′-CTAATGT-5′

The sugars and phosphates are omitted in this notation. A comparison of DNA sequences comparison allows one to determine the relationship between different organisms and is also used to find small differences in humans (so-called DNA fingerprinting). SEE ALSO NUCLEIC ACIDS; NUCLEOTIDE; RIBONUCLEIC ACID.

Neena Grover

guanine: heterocyclic, purine, amine base found in DNA

cytosine: heterocyclic, pyrimidine, amine base found in DNA

adenine: one of the purine bases found in nucleic acids, $C_5H_5N_5$

hydrogen bond: interaction between H atoms on one molecule and lone pair electrons on another molecule that constitutes hydrogen bonding

stacking interactions: one type of interaction that affects conformation of double-stranded DNA; caused by van der Waals forces

5′ end: situation in nucleic acids in which the phosphate group is attached at the fifth carbon atom from where the base is attached

3′ end: situation in nucleic acids in which the phosphate group is attached at the third carbon atom from where the base is attached

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Detergents

Soap and cleanliness are inseparable, and cleansing, be it personal hygiene or laundering, is part of human history. Stringent guidelines with regard to the cleanliness of holy sites are a part of all the major religions, and the sanctification of the state of cleanliness as well as its signification of purity of body and soul are recurrent themes in their liturgies.

The origins of the word "soap" and of the first use of soap are obscure. According to one Roman legend, soap was discovered serendipitously near Mount Sapo, an ancient location for animal sacrifice not far from Rome. Animal fat mixed with wood ashes (the ancient source of alkali) and rainwater created an excellent soap mixture. Roman housewives noticed that the strange yellow substance in the water of the Tiber River (flowing near Mount Sapo) made their clothes cleaner and brighter than ordinary water.

Soapmaking became an art among the Phoenicians (fl. ca. 600 B.C.E.) and underwent significant advances in Mediterranean countries in which local olive oil was boiled with alkali ashes (as part of soapmaking) at around the same time.

Ascribing value to cleanliness seems to have been a part of the civilizing of humankind. After the fall of Rome (in 467 C.E.), a decline in attention paid to personal cleanliness and the maintenance of sanitation contributed to the great plague of the Middle Ages, and made especially grim contributions to the Black Death plague epidemic of the fourteenth century. Cleanliness and regular bathing became unremarkable in much of Europe not until 300 years later.

ester: organic species containing a carbon atom attached to three moieties: an O via a double bond, an O attached to another carbon atom or chain, and an H atom or C chain; the R(C═O)OR functional group

For several centuries in Europe, soapmaking was limited to small-scale production that often used plant ashes containing carbonate (**esters** of carbonic acid) dispersed in water, which were then mixed with animal fat and boiled until the water evaporated. The reaction of fatty acid with the alkali carbonate of the plant ashes formed a soap and glycerol.

The real breakthrough in soap production was made in 1780 by a French chemist and physician, Nicolas Leblanc, who invented the process of obtaining soda (sodium carbonate, Na_2CO_3) from common salt (the Leblanc process), and increased the availability of this alkali at a reasonable cost. With the development of power to operate factories, soapmaking grew from a "cottage industry" into a commercial venture and became one of the fastest-growing industries of the modern era. Body soap, which had been a luxury item affordable by royalty and the very rich, became a household item of ordinary folks as well.

etiology: causes and origins of a disease

Throughout the nineteenth century, physicians were realizing the value of soap as a medicinal agent. A well-known protagonist of soap was scientist and educator Ignaz Phillipp Semmelweis, who in 1847 discovered the infectious **etiology** of puerperal fever and therefore required medical students to wash their hands before they examined patients. Semmelweis encouraged

INGREDIENTS OF SOAP, SHAMPOO, AND DETERGENT

Ingredients	Percent of Total by Weight
Surfactants	30-70
Plasticizers and binders	20-50
Lather enhancers	0-5
Fillers and binders	5-30
Water	5-12
Fragrance	0-3.0
Opacifying agents	0-0.3
Dyes and pigments	<1

Table 1. Ingredients of soaps and detergents.

his colleagues to adopt his antiseptic methods, telling them, "while we talk, talk, talk, gentlemen, women are dying. I am not asking anything world-shaking. I am asking you only to wash. . . . For God's sake, wash your hands." In a circular handed out in Budapest during the summer of 1865, he implored new mothers: "Unless everything that touches you is washed with soap and water and then chlorine solution, you will die and your child with you!"

The chemistry of soap manufacturing stayed essentially unchanged until World War II, at which time synthetic detergents (syndets) became available. There had been a search for cleansing agents that would foam and clean when added to seawater in response to the need of sailors who spent months at sea under severe freshwater restrictions.

The Chemistry of Soaps, Shampoos, and Laundry Detergents

Soaps, shampoos, and laundry detergents are mixtures of ingredients (see Table 1). The **surfactants** are the essential cleaning substances and they determine the cleansing and lathering characteristics of the soap, as well as its texture, plasticity, abrasiveness, and other features. Surfactants are compounds that have a dual affinity: They are both **lipophilic** and **hydrophilic**. A surfactant molecule consists of a lipophilic tail group, which links to greasy soil, and a hydrophilic and polar head group, which renders the molecule water-soluble; this arrangement helps to disperse and rinse away greasy soil. Variations in the balance between **hydrophobic** and hydrophilic features determine the use of the surfactant as a detergent, **wetting agent**, or **emulsifier**.

surfactants: surface-active agents that lower the surface tension of water; e.g., detergents, wetting agents

lipophilic: a molecule that tends to associate in solution with lipids—it will be a nonpolar molecule or the nonpolar portion of a molecule

hydrophilic: having an affinity for water

hydrophobic: repelling water

wetting agent: molecule that, when added to a liquid, facillitates the spread of that liquid across a surface

emulsifier: substance that stabilizes the formation of an emulsion—normally it contains molecules with both polar and nonpolar functional groups

Surfactants are classified according to the nature of the hydrophilic head. There are four main classes: anionic, cationic, amphoteric, and nonionic. The first three refer to charged surfactant molecules. An anionic surfactant possesses a negative charge and needs to be neutralized with an alkaline or basic material in order for its full detergent capacity to be realized, whereas a cationic surfactant is positively charged and needs to be neutralized by an acid. Amphoterics include both acidic (negative) and basic (positive) groups, and nonionics contain no ionic constituents. "Natural" soap contains an anionic surfactant. The majority of surfactants that are used in personal cleansing bars and shampoos have anionic head groups.

It is noteworthy that almost all anionic surfactants are sodium or potassium salts of the negatively charged head groups; thus the advertising slogans “alkali free” and “soapless soap” are incorrect. Most soaps and shampoos contain a mixture of two to four surfactants (out of the thousands of synthetic surfactants that are currently available). In addition, there are innumerable plasticizers, binders, moisturizers, and fillers that are also used to formulate these soaps and shampoos. Creation of the formula of a soap is a complicated enterprise and it requires, in addition to a knowledge of chemistry and even engineering, both imagination and inspiration. The contemporary formulation of soaps is the result of research and development, as well as trial and error, carried out over a course of many years by research teams. It is as much art as it is science, and it requires a long learning experience.

The Process of Washing

The most obvious target of cleansing is the outermost layer of the skin, the keratinizing epithelium. It is a cornified (hardened) cell envelope and it has an extremely tough protein/**lipid** polymer structure. This hard and lipophilic layer of the epidermis and the surface hairs would not easily retain dirt if it were not for a hydrolipid film that covers the outermost layer of skin and that picks up particles of soil. This natural outer film of lipid entraps and glues environmental dust, pollutants, smoke, keratinous debris, organic and inorganic compounds in sweat, cosmetics, and other substances that come in contact with it. The hair of the scalp (corresponding to a surface area of about 8 square meters, or 86 square feet, for an average female head) is cleansed regularly. The scalp gets coated with sebum, the product of the sebaceous appendages that flows into hair follicles and a natural lubricating oil that contributes luster to the hair, on the one hand, but entraps dirt, on the other.

lipid: a nonpolar organic molecule; fatlike; one of a large variety of nonpolar hydrophobic (water-hating) molecules that are insoluble in water

Washing the skin consists of the removal of the outer layer of grease (lipid) in which the soil (no matter what kind) is embedded. It is a complex physicochemical process that includes the following:

1. A weakening of the binding forces between the keratinized epithelium and the layer of grease via the reduction of the surface tension between the water and the water-resistant oil/grease. Because of this reduced surface tension, water (and surfactant molecules) can penetrate into the finest wrinkles of the skin. In this way, more and more interface is occupied by surfactant, and the adhesiveness of the soil-containing layer is further weakened, a process facilitated by mechanical rubbing.
2. Transfer of portions of the layer of oil to the aqueous vehicle. It is facilitated by the action of the micelles created when the soil was emulsified. The micelles have negatively charged surfaces and are repulsed by the overall negative charge of the keratin of the skin epithelium.
3. Dispersion/suspension of the oil and dirt particles in the soap foam, preventing these particles from being redeposited on the surface.

The Interaction of Soaps with the Skin

Surgeons need to scrub. Health-care providers and employees of food services must take a range of precautions against the dissemination of microorganisms. Very often, the simple act of washing one’s hands is not fateful but nevertheless wise. Most experts in infection control and epidemiology maintain that hand washing remains the most powerful defense against infections. Germs are all around us, and can linger anywhere: the office phone, door handles, shopping baskets, money, even the button you push when you call for an elevator. You can unknowingly come into contact with germs. One simple rub of the eye or bite of a sandwich using unwashed hands can introduce any number of illnesses into your body. Hand washing reduces the risk. At the same time, most contemporary dermatologists agree that the comfortable classes have become preoccupied with cleanliness. Less, not more, washing is better for the skin. However, the irritant, toxic, and harmful effects of soaps have been exaggerated by some advertisers. (After all, what better way to promote their "mild," "nonallergenic," and "soapless" products?)

Washing with soap makes no discretely identifiable contribution to health. Its value lies more in the feeling it engenders in the user. People derive great enjoyment from washing: It gives them a tremendous sense of well-being. SEE ALSO BLEACHES; HAIR DYES AND HAIR TREATMENTS; LEBLANC, NICOLAS.

Ronni Wolf

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Dewar, James

BRITISH CHEMIST AND PHYSICIST
1842–1923

Sir James Dewar was born in Kincardine, Scotland, on September 20, 1842, the son of an innkeeper. He attended local schools until he was ten when he suffered a serious case of rheumatic fever lasting two years. During this period he built a violin, and music remained a lifelong interest of his. In 1858 he entered the University of Edinburgh. There he studied physics and chemistry. Dewar, in an early display of his dexterity, developed a mechanical model of Alexander Crum Brown's graphic notation for organic compounds. This was sent to Friedrich Kekulé in Ghent who then invited Dewar to spend some time in his laboratory.

After holding a number of chemical posts in Scotland, Dewar was appointed Jacksonian Professor of **Natural Philosophy** at the University of Cambridge in 1873, and four years later he was appointed Fullerian Professor of Chemistry at the Royal Institution. He held both chairs concurrently, but spent most of his time in London. At Cambridge he collaborated with George Downing Liveing on an extensive **spectroscopic** study linking spectra with atomic and molecular states. This led to a very public disagreement with Norman Lockyer about the dissociation of matter in the Sun and stars. One of Dewar's chief characteristics was his ability to engage, at times, in quite vitriolic arguments with other scientists; Robert John Strutt, the fourth Lord Rayleigh wrote that to argue with Dewar was akin to being a fly in molasses.

natural philosophy: study of nature and the physical universe

spectroscopy: use of electromagnetic radiation to analyze the chemical composition of materials

Scottish chemist and physicist Sir James Dewar, the first person to liquefy hydrogen.

Joule–Thomson effect: the change in temperature of a gas when it is compressed or allowed to expand through a small opening

At the Royal Institution, Dewar found himself at the intersection of major scientific networks involving the government and industry. He thus collaborated in the late 1880s with Frederick Abel on the invention of the explosive cordite. Nevertheless, at the Royal Institution Dewar focused almost entirely on cryogenics. In 1877 oxygen had been liquefied in France, and the following year Dewar demonstrated this for the first time in England at a lecture at the Royal Institution. New methods for obtaining low temperatures were developed in the 1880s, but Dewar's ability to take advantage of these methods was restricted by his not being fully in charge of the Royal Institution. However, after forcing John Tyndall's retirement in 1887, Dewar became the director of its laboratory. He improved low-temperature methods, especially by the application of the **Joule–Thomson effect** that produced much lower temperatures. Dewar had now turned his attention to hydrogen, which he could not liquefy even at the low temperatures obtainable.

In the mid-1890s Dewar was responsible for one of the most important developments in the history of the Royal Institution: the establishment and endowment of the Davy–Faraday Research Laboratory of the Royal Institution. This not only entailed the acquisition of a new building, but also the direct support of Dewar's cryogenic research. Success came in 1898 when he finally liquefied hydrogen. However, in the race with Heike Kamerlingh Onnes at the University of Leiden to liquefy helium, Dewar lost and the Nobel Prize went to Kamerlingh Onnes. Although Dewar was nominated several times, he never won the coveted prize.

One of the consequences of Dewar's work was his invention of the vacuum flask to minimize heat loss. It was expensive and time-consuming to liquefy gases; hence, Dewar designed a container where, once liquefied, gases could be kept for as long as possible. Still known as the Dewar flask among chemists, it is more widely known as the Thermos, named after the company that obtained the patent for the flask and to whom Dewar lost an ensuing court case.

Dewar's later work involved investigating the chemical and physical properties of substances at low temperatures, including low-temperature calorimetry. With the outbreak of the Great War (or World War I, 1914–1918), the laboratory at the Royal Institution lost most of its staff and Dewar turned his attention to soap bubbles. By the end of the war Dewar, now in his late seventies, did not have the energy to restart the laboratory, nor would he retire. He died on March 27, 1923, and his funeral service was held in the director's flat at the Royal Institution. SEE ALSO KEKULÉ, FRIEDRICH AUGUST.

Frank A. J. L. James

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Digital X Ray

X-ray technology provides physicians and technicians with a noninvasive method for seeing inside objects. In the case of a patient's body, this may allow diagnosis of disease or injury without surgery. Both conventional and digital x-ray methods employ high **voltage** electronic tubes such as synchrotons that emit very short wavelength, high energy electromagnetic radiation in the range of 10^{-11}–10^{-8} meters (3.28×10^{-10}–3.94×10^{-6} feet) (a frequency of about 3×10^{19} Hz to 3×10^{16} Hz). One Hz (Hertz) is equal to 1 cps (cycle per second).

voltage: potential difference expressed in volts

Unlike longer-wavelength, lower-frequency visible light, x-ray radiation consists of waves so small that they can pass through solid materials with little effect. As the radiation moves through materials of different densities (bone and tissue, for example), some waves are blocked and produce shadows that result in light-and-dark images. Some materials, such as bone or metal, are opaque and appear as light areas, while other materials such as air in body cavities allow most of the x-ray waves to pass through, producing dark areas in the image.

Conventional x-ray images are captured by special photographic film, sensitized with silver salts that are converted by developing processes to dark and light images. Photons striking a photographic **emulsion** convert some silver ions to tiny particles of silver that grow large enough during the process of developing to form tiny grains in the photographic negative. Digital x-ray processes use individual crystal **photodiode assemblies** (each photodiode acts as a very small light-sensitive transistor, using the light energy from individual photons to modulate an electrical current flowing through the diode) containing compounds such as cadmium tungstate or bismuth germanate to capture light energy as electrical pulses that are then converted from analog to digital signals, stored in computer memory, and processed to form visual images on computer screens. Because electronic sensors may be more sensitive than film, digital x-ray processes may use as little as 10 percent of the energy needed for conventional x rays (and may thus require less massive shielding).

emulsion: immiscible two-phase mixture in which one phase is dispersed (as small droplets) in the other phase

photodiode assembly: grouping of electronic devices that includes a photodiode—a photodetector; useful in medical diagnostics, bar code readers, and guidance systems

Although different types of x-ray technology may be ideally suited to different applications, the use of electronic sensors and digital technology offer several advantages over conventional x rays. The capture of an image by a photosensitive electronic device is rapid and allows the image to be enlarged, colored, or adjusted in density. In addition, the use of electronically captured images may be less expensive, allowing computer-assisted data processing and storage. Conventional x-ray film must be developed, washed, fixed, and dried, requiring chemical substances that may be harmful to the environment, and the resulting images on film may require massive storage facilities.

Digital x rays can be modified electronically to increase contrast, display certain structures in color or three dimensions, or subtract areas that interfere, allowing clearer pictures of structures such as veins and arteries. Very small differences in density may be amplified for even clearer viewing. This may be important in cases in which a contrast medium is injected into veins or arteries; enhancing small differences allows the use of smaller amounts of the contrast medium, lessening the danger to patients.

This patient is undergoing cerebral angiography. Digital x rays use electronic signals to form visual images, rather than the photographic method of the conventional x ray.

After digital x-ray images have been obtained, they may be easily copied, displayed, stored electronically, shared with patients, or sent to remote locations for examination by highly trained technicians. The images may be conveniently linked to other equipment or processes such as CAT (computer axial tomography) scans or three-dimensional displays. Digital technology may also be employed in security applications for the remote scanning of packages and luggage. SEE ALSO Selenium.

Dan M. Sullivan

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Disaccharides

Sucrose, or table sugar, is the most common disaccharide. Although the term "sugar" is commonly used to refer to sucrose, sucrose is only one of a large group of sugars. Disaccharides are carbohydrates containing two **monosaccharides** linked by a glycosidic bond. Glycosidic bonds form when the anomeric carbon of one sugar reacts with a hydroxyl group belonging to a second sugar. Sugars with free anomeric carbons can reduce **ferric** (Fe^{3+}) and cupric (Cu^{2+}) ions, and are called reducing sugars. Anomeric carbons

monosaccharide: one class of the natural products called carbohydrates with the general formula $C_x(H_2O)_y$; monosaccharides have a weak sweet taste, are readily soluble in water, and are called sugars

ferric: older name for iron in the +3 oxidation state involved in glycosidic bonds are nonreducing. In general, disaccharides and polysaccharides contain both reducing and nonreducing sugars. These carbohydrates are represented and their formulas are written from nonreducing end to reducing end.

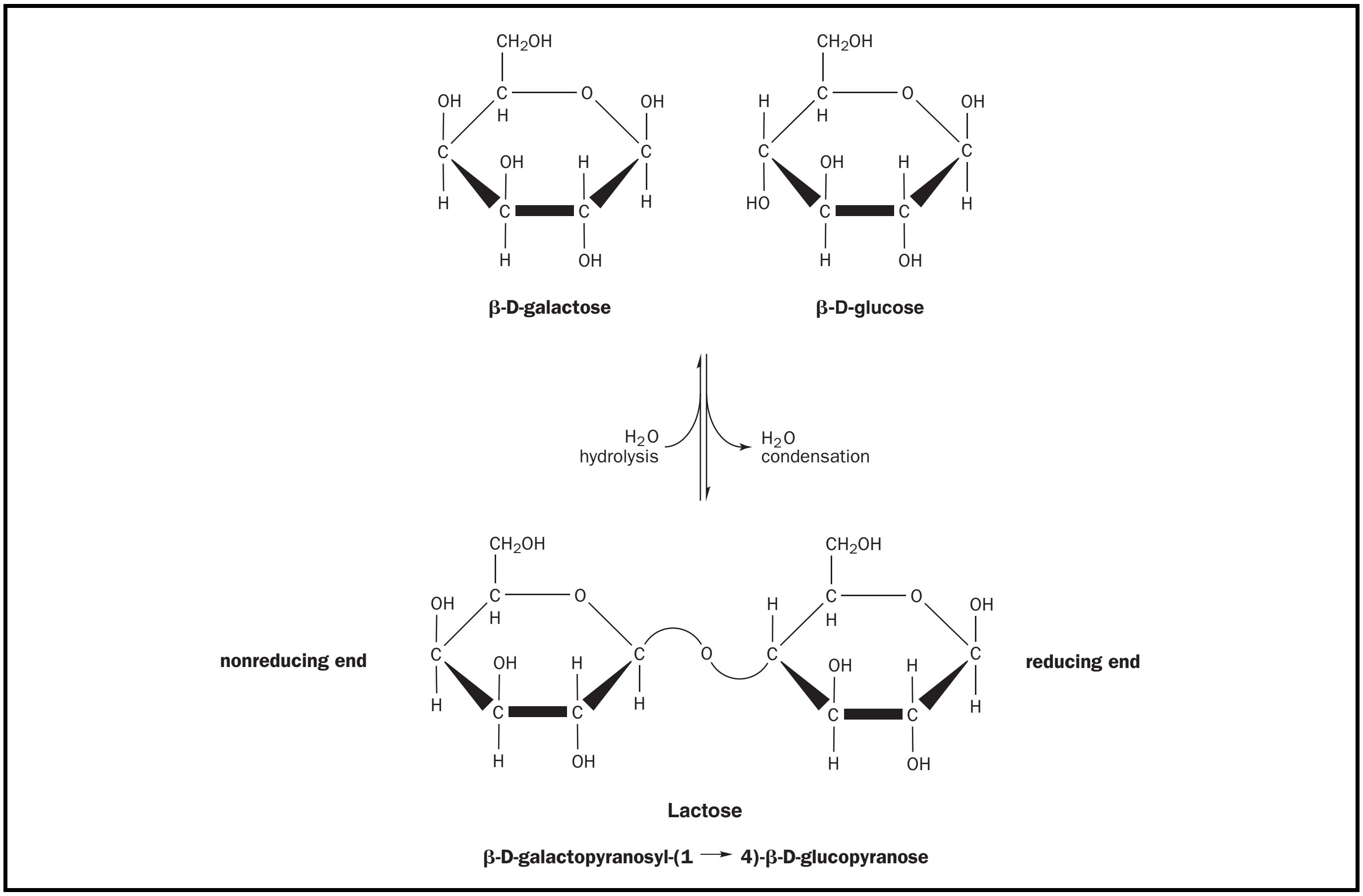
A common disaccharide is lactose, which is found only in milk. Lactose is formed from monosaccharides *β*-D-**galactose** and *β*-D-**glucose**. The anomeric carbon of the *β*-D-galactose molecule reacts with the C-4 hydroxyl group of the *β*-D-glucose molecule to form the glycosidic bond (see Figure 1). The bond is designated a *β*(1→4) bond, indicating the configuration of the anomeric carbon (*β*), the number of the anomeric carbon (1), and the number of the carbon (of the second sugar) to which it is linked (4). The correct specification of the configuration of the anomeric carbon is critical: an *α*(1→4) linkage is not the same thing as a *β*(1→4) linkage. Lactose is a reducing sugar; the *β*-D-glucose residue has a free anomeric carbon, and therefore the glucose residue is on the reducing end.

galactose: six-carbon sugar

glucose: common hexose monosaccharide; monomer of starch and cellulose; also called grape sugar, blood sugar, or dextrose

Lactose is hydrolyzed to glucose and galactose in the intestine by the enzyme lactase. People who are lactose-intolerant lack this enzyme. In these people, lactose advances in the digestive tract to the large intestine, where it is fermented by intestinal bacteria to produce large amounts of carbon dioxide and organic acids. Today, people with lactose intolerance can purchase milk in which the lactose has already been hydrolyzed, or can buy lactase supplements.

Figure 1. Formation of a glycosidic bond.



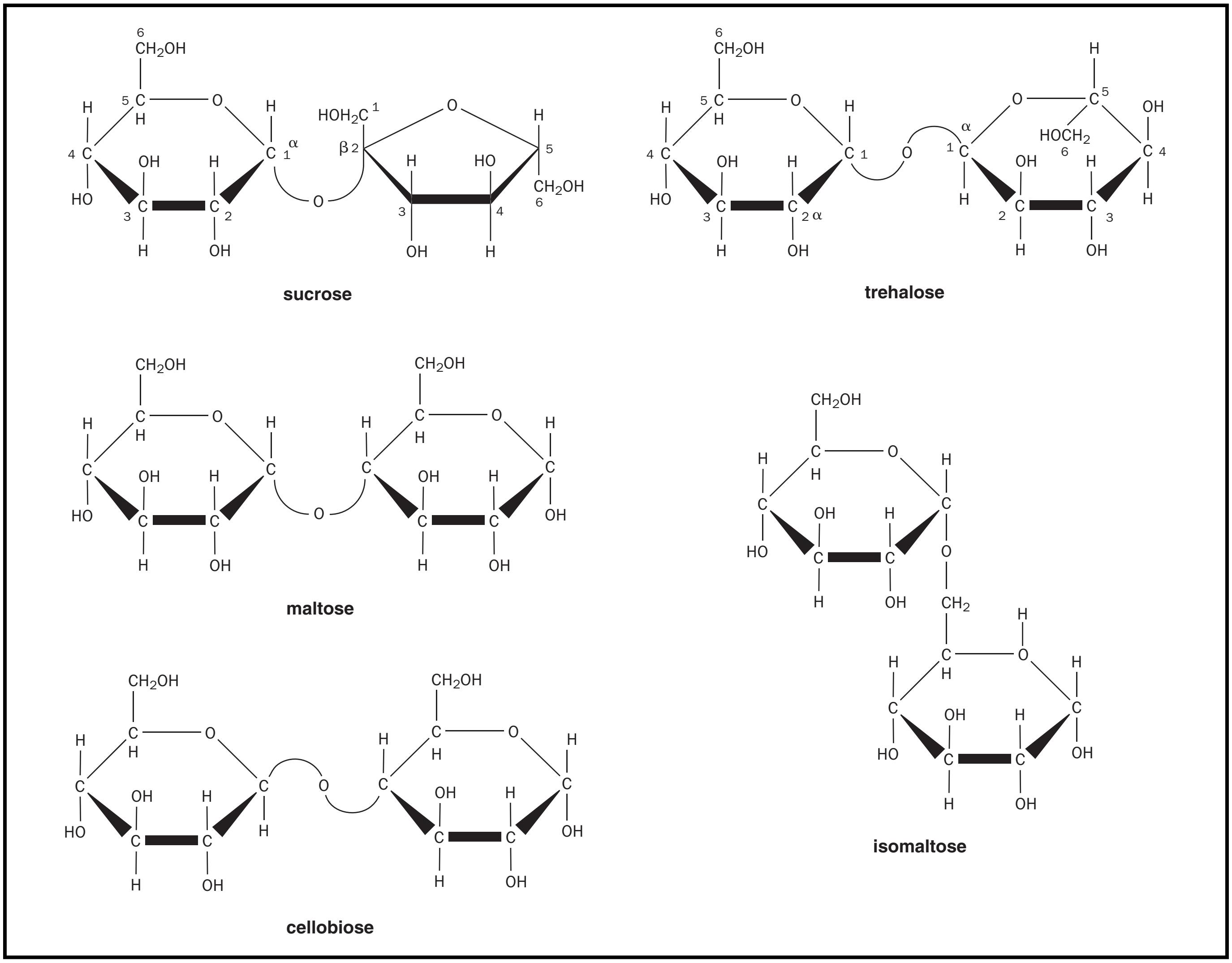


Figure 2. Selected disaccharides.

photosynthesis: process by which plants convert carbon dioxide and water to glucose

In contrast, most people are fond of and tolerate sucrose (see Figure 2). Sucrose is produced by plant cells; it is one of the major products of **photosynthesis**. It contains glucose and fructose molecules linked across the anomeric carbons of both (the C-1 of glucose and the C-2 of fructose). The systematic name is α-D-glucopyranosyl-(1→4)-β-D-fructofuranoside. Because it lacks a free anomeric carbon, sucrose is a nonreducing sugar. Sucrose is hydrolyzed in the intestine by the pancreatic enzyme sucrase.

A third prevalent disaccharide is trehalose (see Figure 2). Like sucrose, trehalose is a nonreducing sugar. It is composed of two glucoses in an $\alpha(1 \rightarrow 1)\alpha$ linkage. Trehalose is the principal sugar in the hemolymph of insects.

Other disaccharides are the product of the breakdown of larger polysaccharides. Maltose, cellobiose, and isomaltose are all composed of glucose residues (see Figure 2). Maltose and isomaltose both contain α-glucoses: in $\alpha(1 \rightarrow 4)$ linkages in the case of maltose, and in $\alpha(1 \rightarrow 6)$ linkages in the case of isomaltose. Maltose results from the hydrolysis of starch, and isomaltose from the hydrolysis of dextrans. Cellobiose is composed of β-glucose occurring in $\beta(1\rightarrow4)$ linkages. It is a breakdown product of cellulose. SEE ALSO CARBOHYDRATES.

Stephanie E. Dew

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Disposable Diapers

During the past forty years, disposable diapers have become an important part of the economy. Since the average baby uses at least ten diapers per day for an average of two years, the convenience of the product has made it a very popular as well as controversial item. A recent survey by Texas A&M University reported that 81 percent of the participants exclusively used disposable diapers, 15 percent used cloth and disposables, while just 4 percent used only cloth diapers.

The disposable diaper of today is composed of an inner layer of polyester that allows liquids to pass through to a layer of absorbent material, and an outer waterproof plastic layer of polyethylene film. The design was developed by many researchers through trial and error.

History

It is not clear who should be credited as the inventor of the first disposable diaper. The need for disposable diapers arose during World War II because of a shortage of cotton, which was used in traditional diapers. One of the first effective disposable diapers was created by Marion Donovan during the postwar baby boom. She is also credited with inventing the first plastic covering for traditional cloth diapers. Using this plastic covering (made from a shower curtain) and layers of tissue paper as an absorbent inner material, Donovan devised the new diaper in 1950. These first diapers were rectangular in shape, resulting in a bulky fit. In the 1960s, pulp was substituted for the paper, improving the absorbency of the diaper. The top sheets of the diaper were modified by using rayon. These diapers still were quite thick and included no tape for closure. By the 1970s the demand for disposable diapers had increased, and more improvements were added. New tapes were added for ease of fastening, and the shape was changed from rectangular to "hourglass."

During the early 1980s, modifications were made to respond to the demand for a better-fitting and biodegradable product. Starch was added to the outer sheet to enhance its biodegradability. Elastic was added to the

This baby is wearing a disposable diaper. Various technologies have improved the fit, absorbency, and biodegradability of the product.

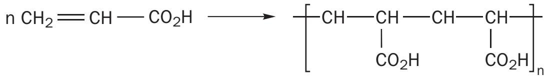
waist and to the leg openings for a better fit. Unfortunately this added a nonbiodegradable component to the product. A new tape system was developed to allow for several tapings and retapings without tearing the diaper. In response to a greater demand for a more environmentally friendly product, a new filler, cellulose mixed with crystals of polyacrylate, was developed. The cellulose is processed from pine trees and milled into "fluff pulp." The pulp consists of long cellulose fibers that provide a strong capillary effect, which helps to draw in the liquid. The surface tension binds the water once it has been absorbed.

The polyacrylate (known as a "superabsorbent polymer" or SAP by the diaper industry) is distributed throughout the fluff pulp. Another name for these crystals is Waterlock™. It is also used for plants to help retain water in the soil. The polyacrylate under pressure can hold an amount of liquid that is as much as thirty times its weight. This correlates to the compression (pressure) that occurs when a baby would sit or lie on the diaper. The polyacrylate allowed the manufacturers to reduce both the weight and thickness of the diaper by 50 percent and increase its absorbency.

Polymer Chemistry

The polyacrylate used in the diaper is a large-molecular-weight compound called a polymer. It consists of small repeating units called *monomers.* The length of the chain as well as the properties of the polymer may be changed by varying the reaction conditions. If two monomers are used in the **synthesis** of the polymer, the resultant polymer is referred to as a copolymer. The polymer used in disposable diapers is prepared by using acrylic acid as the monomer:

synthesis: combination of starting materials to form a desired product



$$n\,CH_2{=}CH{-}CO_2H \longrightarrow \left[-CH-\underset{CO_2H}{\underset{|}{CH}}-CH-\underset{CO_2H}{\underset{|}{CH}}-\right]_n$$

To obtain the properties needed for the diaper, sodium acrylate is used in the polymerization. The reaction is said to use "partially neutralized acrylic acid." The exact proportion of the two monomers (acrylic acid and sodium acrylate) present influences the character of the polymer formed. The length of the chains (represented by *n*) also is modified by reaction conditions and can change the characteristics of the polymer.

In addition to forming the chains of polyacrylate, the chains are cross-linked. This is a process in which two or more chains are held together by other compounds in a network. Typical cross-linkers for this polymer include di- and tri-acrylate esters. The swelling and elasticity of the polyacrylate polymer depends on the structure of this network and the number of cross-links. The swelling capacity of the polymer decreases with increased cross-link density. After formation, the polyacrylate is dried and formed into microparticles of irregular shape that can be stored for a long time.

When these particles come in contact with water, urine, or other **aqueous solutions**, they quickly swell and absorb the liquid. Typically it takes no more than five to ten seconds for this to occur. The ability to swell and absorb the water is dependent upon the **ionization** of the acid groups on the polymer chain. The amount of water uptake increases with the increase in concentration of ionized groups. This is due to an increase in repulsion between the ionized groups in the polymer. This allows for a greater amount of swelling of the polymer. The amount of liquid that is absorbed depends partly on the nature of the liquid. The polymer absorbs more pure water than it does solutions. This means that more urine, an aqueous solution, would be absorbed than pure water.

aqueous solution: homogenous mixture in which water is the solvent (primary component)

ionization: dissociation of a molecule into ions carrying + or − charges

New Advances

Diapers continue to become thinner and more absorbent. During the 1990s a modification of the SAP was developed. It uses a surface cross-linker to reduce the "gel block" problem: If the absorbent is saturated with a liquid, it prevents the liquid from moving.

Independent inventors also are continuing to modify the diaper. Marlene Sandberg of Stockholm has constructed a diaper that is 70 percent biodegradable. She uses cornstarch in the preparation of the outer layer of the diaper. This allows her to reduce the amount of polyacrylate used by designing channels in the fill material that help disperse the urine. Other workers in the field dispute that the diaper is 70 percent biodegradable: They say the diapers will not **degrade** that much in a landfill—their ultimate destination.

degrade: to decompose or reduce the complexity of a chemical

Controversy

As with all products, there are advantages and disadvantages to disposable diapers. The new polyacrylate gel has been linked to some side effects, including allergic reactions such as skin irritations, and to toxic shock syndrome. In addition, the dyes in the diapers have been linked to damage of the central nervous system, and disposable diapers may contain low concentrations of dioxin, a by-product of the bleaching process used in the production of the paper pulp found in the absorbent layer. Dioxin has been linked to liver damage and immune system suppression.

Disposables are also considered to be an environmental threat. Only some of the materials used in the diapers are biodegradable (the wood pulp and SAP). The polyethylene and polyester sheets are not biodegradable; neither is the elastic used for better fit, nor the polypropylene used for the tape that is employed as a fastener. Disposable diapers account for up to 2 percent of the total volume of landfills in the United States. The lifetime of the diaper in the landfill depends on several environmental factors: soil condition, groundwater flow, and the presence of other materials in the soil. SEE ALSO Materials Science; Polymers, Synthetic.

Catherine H. Banks

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DNA *See* ***Deoxyribonucleic Acid.***

DNA Replication

prokaryotic: relating to very simple cells of the type found in bacteria

eukaryotic cell: cell characterized by membrane-bound organelles, most notably the nucleus, and that possesses chromosomes whose DNA is associated with proteins

Before one cell can divide into two cells, the cell must make a copy of the cellular DNA so that after cell division, each cell will contain a complete complement of the genetic material. Replication is the cellular process by which DNA or the cellular genome is duplicated with almost perfect (and sometimes perfect) fidelity. The replicative process in **prokaryotic** cells, such as *Escherichia coli* (*E. coli*) cells, is best understood and will be described in detail, and the aspects that differ in replicating **eukaryotic cells** will be noted.

synthesis: combination of starting materials to form a desired product

Replication starts by the separation of the strands of DNA and the formation of a local "bubble" at a specific DNA site called the origin of replication (ori). A helicase enzyme uses energy from ATP hydrolysis to effect this action. Single-strand DNA binding proteins stabilize the strands during the subsequent steps. The original DNA strands will function as the templates that will direct **synthesis** of the complementary strands. A nucleotide on the template strand will determine which deoxyribonucleotide (dNTP) will be incorporated in the newly synthesized strand. This replica-

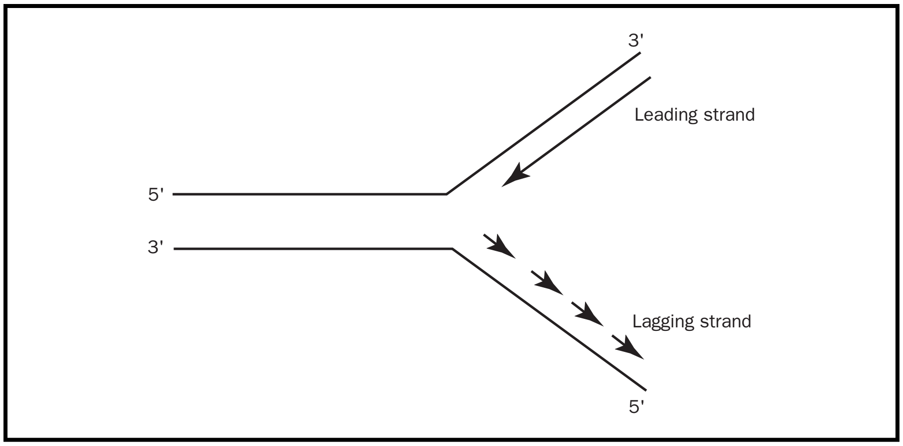

Figure 1. Replication model.

tion model is called semiconservative replication. The opening of the DNA produces two replication forks (see Figure 1), both of which will be the sites for replication. The forks will move in opposite directions relative to the replication machinery, with DNA replication occurring bidirectionally.

To initiate the synthesis of the two strands, a primer strand is needed, which is made by the enzyme primase. This small primer is an **RNA** molecule, which has a **5′-** and a **3′-end**. Replication requires the 3′-hydroxyl group of the deoxyribose. This group is "attacked" by the phosphate of the incoming dNTP, because all DNA polymerases can extend DNA only from the 3′-end (synthesis occurs in the 5′→3′ direction on the primer strand). Because the strands of DNA have opposite orientations, the replication process for each strand is considerably different. Extension of each strand requires very different operations that involve synthesis of a leading strand and a lagging strand. Leading strand synthesis, which progresses toward the fork in a continuous manner, begins with primase synthesizing a short RNA primer at the ori, followed by the action of DNA polymerase III, which incorporates deoxyribonucleotides into the strand, until strand synthesis is complete. If an incorrect nucleotide in incorporated, a proofreading activity in the mechanism removes it and the synthesis continues. Lagging strand synthesis progresses in the direction opposite to fork movement, with the new DNA strand synthesized in 1,000 to 2,000 nucleotide fragments called Okazaki fragments. Each fragment must also be initiated with a primer, followed by synthesis utilizing DNA polymerase III. When the Okazaki fragments are completed, DNA polymerase I both removes the RNA primers and simultaneously replaces the RNA with DNA. This occurs similarly for the single primer on the leading strand. The DNA fragments are then sealed together to produce a continuous strand by the enzyme DNA ligase.

RNA: ribonucleic acid, a natural polymer used to translate genetic information in the nucleus into a template for the construction of proteins

5′ end: situation in nucleic acids in which the phosphate group is attached at the fifth carbon atom from where the base is attached

3′ end: situation in nucleic acids in which the phosphate group is attached at the third carbon atom from where the base is attached

The size of the genomic DNA in eukaryotic cells (such as the cells of yeast, plants, or mammals) is much larger (up to 10^{+11} base pairs) than in *E. coli* (ca. 10^{+6} base pairs). The rate of the **eukaryotic** replication fork movement is about fifty nucleotides per second, which is about ten times slower than in *E. coli*. To complete replication in the relatively short time periods observed, multiple origins of replication are used. In yeast cells, these multiple origins of replication are called autonomous replication sequences (ARSs). As with prokaryotic cells, eukaryotic cells have multiple DNA polymerases. DNA polymerase δ, complexed with a protein called proliferating

eukaryotic: relating to organized cells of the type found in animals and plants

nuclear: having to do with the nucleus of a cell

cell **nuclear** antigen (PCNA), is thought to synthesize the leading strand, whereas DNA polymerase α is the replicase for the lagging strand. Eukaryotic genomes have linear DNA strands and require a special enzyme, called telomerase, to replicate the ends of the chromosomes. SEE ALSO BASE PAIRING; DEOXYRIBONUCLEIC ACID (DNA).

William M. Scovell

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Dopamine

Dopamine belongs to a family of biological compounds called catecholamines (see Figure 1). Dopamine is synthesized from the compound L-dihydroxyphenylalanine (L-dopa) via the enzyme dopa decarboxylase. In noradrenergic neurons and in the adrenal glands, dopamine is the precursor for the neurotransmitter norepinephrine. In dopaminergic neurons, dopamine itself acts as a neurotransmitter. Although dopaminergic neurons are not as widely distributed in the brain as noradrenergic neurons, they act to coordinate movement, to control the secretion of some hormones, and to regulate mood and emotional stability.

Dopamine's role in the coordination of movement can be partially understood by examining Parkinson's disease. This illness is associated with low levels of dopamine in the brain and is characterized by spastic motion of the eyelids as well as rhythmic tremors of the hands and other parts of the body. One method of treating Parkinson's disease is to increase the concentration of dopamine in the brain. This is most effectively accomplished by administering the precursor of dopamine, L-dopa. In order to prevent concentrations of norepinephrine from increasing as well, L-dopa is given in conjunction with a drug that inhibits norepinephrine **synthesis**.

synthesis: combination of starting materials to form a desired product

The role that dopamine plays in regulating mood and emotional stability can be at least partially grasped by examining dopamine's role in schizophrenia and drug addiction. Schizophrenia is a disorder characterized by delusions, hallucinations, withdrawal from external reality, and emotional unresponsiveness. The dopamine theory of schizophrenia, proposed in 1965, attributes the disorder to elevated brain concentrations of dopamine or to a hypersensitivity of dopaminergic **receptors**, especially the D_2 and D_4 receptor subtypes. Several drugs used to treat schizophrenic patients bind to D_2 and D_4 receptors and block the dopaminergic response.

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

amphetamine: class of compounds used to stimulate the central nervous system

Dopamine is also an important component of the brain's "reward system" and is believed to play a role in drug addiction. Increased levels of dopamine have been associated with cocaine, **amphetamine**, and marijuana use, as well as alcohol and nicotine addiction. SEE ALSO NEUROTRANSMITTERS.

Jennifer L. Powers

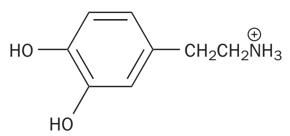

Figure 1. The structure of dopamine as it exists in solution.

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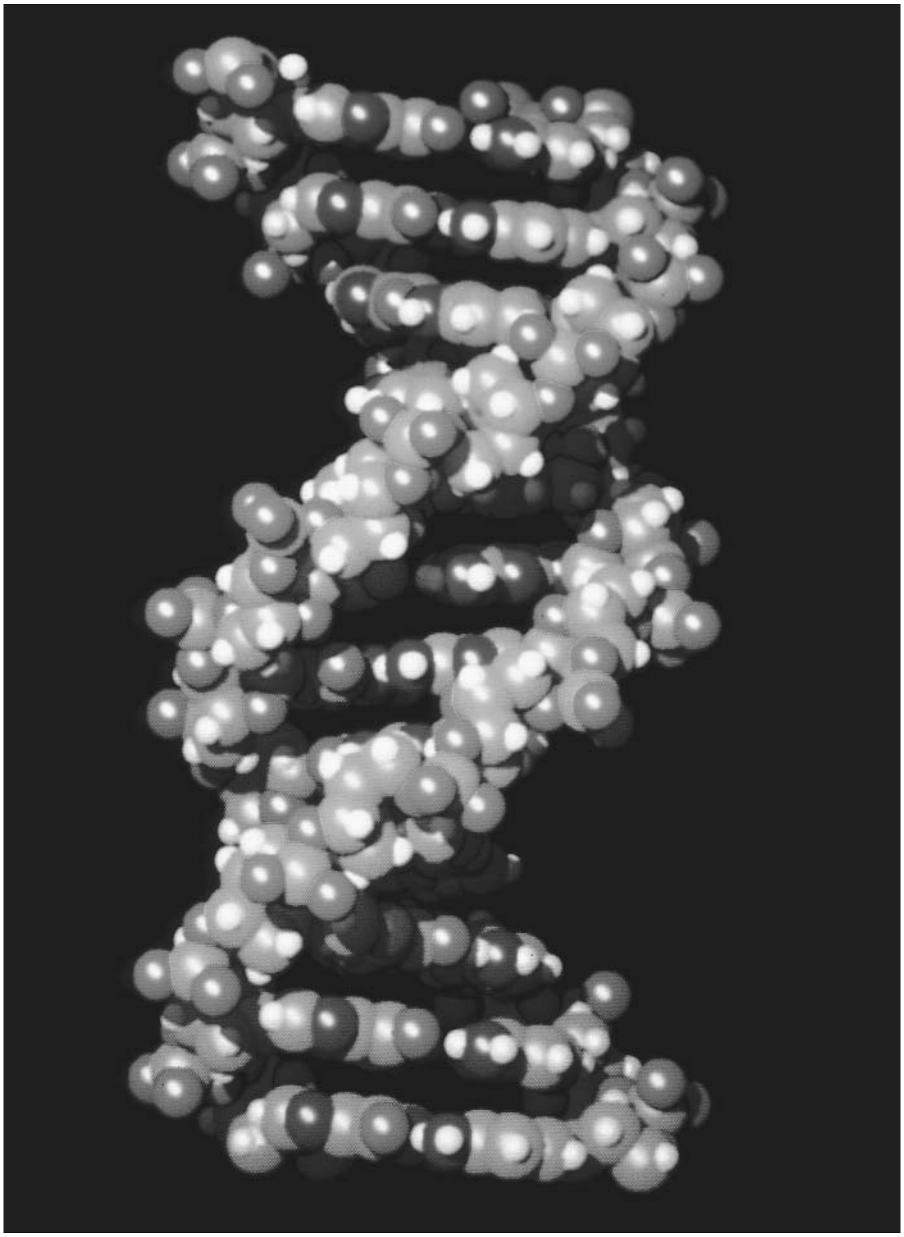
Double Helix

Described in 1953 by James Watson and Francis Crick, the double helix of **DNA** (deoxyribonucleic acid) is the cellular storehouse of genetic information. This biopolymer consists of a pair of complementary chains approximately 2.4 nanometers (9.5×10^{-8} inches) in diameter and composed of

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell



A computer-generation representation of the double-helix structure of DNA.

deoxyribose sugar molecules linked to each other by phosphoric acid, connecting the number three carbon of one sugar to the number five carbon of another. Attached to each sugar is a heterocyclic base: **adenine**, **guanine**, **cytosine**, or **thymine**. Each turn of the helix contains about 10.4 nucleotides.

These chains are said to be complementary: Guanine on one chain always pairs with cytosine on the opposite strand of DNA by forming three **hydrogen bonds**, and adenine on one chain pairs with thymine on the complementary chain, held in position by two hydrogen bonds. The interchain bonding forms an **attraction** between the two DNA chains and stabilizes the double helix against the strong **repulsive force** of the phosphoric acid residues. The chains are said to be antiparallel; that is, the two chains are held closely together but run in opposite directions, with the **3′ end** of one chain matching the **5′ end** of the other chain.

DNA performs two important functions. It contains the genetic **code** that provides directions for replication (**synthesis** of new DNA), and thus serves as a storehouse of genetic information, allowing the physical characteristics of parent organisms to be passed on to offspring. DNA also acts as a storehouse of synthetic information. The individual genes can be turned on or off, allowing the information of each codon within a gene to be converted into information contained in messenger RNA (a process known as **transcription**). This information can then be transcribed into protein having **catalytic** or structural properties. SEE ALSO BASE PAIRING; CODON; DNA REPLICATION; HYDROGEN; NUCLEIC ACIDS; WATSON, JAMES DEWEY.

Dan M. Sullivan

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du Pont, Éleuthère Irénée

FRENCH-AMERICAN INDUSTRIALIST
1771–1834

Éleuthère Irénée du Pont was born in France on June 24, 1771, and died on October 31, 1834, in the United States. He was the son of Pierre du Pont, an active member of the French government in the 1780s and 1790s before, during, and after the French Revolution. In keeping with the spirit of the times, Éleuthère Irénée was named for "liberty and peace." During the rise of Napoléon Bonaparte, Pierre was ordered into exile because of his continuing royalist sympathies. He took his family to the United States, where he later helped negotiate the U.S. purchase of the Louisiana Territory from France.

In 1787 Éleuthère Irénée du Pont worked at Antoine-Laurent Lavoisier's **saltpeter** plant in Essone, France. Here he was exposed to the craft of gunpowder manufacturing and to the application of Lavoisier's new chemistry to an industrial process. When du Pont arrived in the United States in 1800, he began to search for a potentially profitable business op-

CHARGAFF'S RULES

Erwin Chargaff found that the ratios of adenine to thymine and of guanine to cytosine were always 1:1, suggesting that these bases form pairs. The fact that the ratios are 1:1 is referred to as Chargaff's rules.

adenine: one of the purine bases found in nucleic acids, $C_5H_5N_5$

guanine: heterocyclic, purine, amine base found in DNA

cytosine: heterocyclic, pyrimidine, amine base found in DNA

thymine: one of the four bases that make up a DNA molecule

hydrogen bond: interaction between H atoms on one molecule and lone-pair electrons on another molecule that constitutes hydrogen bonding

attraction: force that brings two bodies together, such as two oppositely charged bodies

repulsive force: force that repels two bodies; charges of the same sign repel each other

3′ end: situation in nucleic acids in which the phosphate group is attached at the third carbon atom from where the base is attached

5′ end: situation in nucleic acids in which the phosphate group is attached at the fifth carbon atom from where the base is attached

code: mechanism to convey information on genes and genetic sequence

synthesis: combination of starting materials to form a desired product

transcription: enzyme-catalyzed assembly of an RNA molecule complementary to a strand of DNA

catalysis: the action or effect of a substance in increasing the rate of a reaction without itself being converted

saltpeter: potassium nitrate; chile saltpeter is sodium nitrate

French industrialist Éleuthère Irénée du Pont, who developed his company into the largest gunpowder manufacturer in the United States.

portunity and soon became aware of the unreliable and generally poor quality of domestic gunpowder at the time. After an unsuccessful attempt to purchase what was then the largest U.S. gunpowder plant located in Frankford, Pennsylvania, he purchased a mill on the Brandywine River in Delaware. This site had the advantage of existing mills with proven water power, nearby access to the port of Wilmington, local willow woods for charcoal, and a community of French-speaking workers. The mills were converted to the manufacture of gunpowder, and by 1811 E.I. du Pont de Nemours & Co. was the country's largest gunpowder manufacturing plant. It became the major supplier of gunpowder during the War of 1812.

On March 19, 1818, an accident at the plant triggered a series of explosions that killed thirty-six workers and destroyed five mill buildings. The company took years to rebuild and recover from this tragedy. In the process of rebuilding, safety became a lasting feature of corporate planning at DuPont. By the time of Éleuthère Irénée's death, DuPont was the primary manufacturer of gunpowder in the United States. As of 2003 it produces much more than gunpowder and is among the largest chemical manufacturers in the world. SEE ALSO Lavoisier, Antoine.

David A. Bassett

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Dyes

The great appeal of textiles lies in their colors and the way that color is used to create patterned effects. Color is applied by the process of dyeing, which in its simplest form involves the immersion of a fabric in a solution of a dyestuff in water. Patterned effects are obtained by selectively applying dyes to fabric, for example by roller printing. The amount of dyestuff required is very small, but its production and application require considerable skill. Changes in the ways of producing dyes during the nineteenth century heralded the modern science-based chemical industry.

Natural Dyes

Dyes obtained from natural products, such as plants and insects, have been used for decorative effect and as symbols of status for thousands of years. The mollusk-derived Roman purple, 6,6′-dibromoindigo, also called Tyrian purple, was remarkable for its fastness to light and washing; it was also an important mark of social distinction. The associated biblical blue holds great religious significance among observant Jews. In China, the emperor and empress wore yellow, the imperial ladies violet, and noblemen of the first grade blue. Explorers of the Americas came across many natural dyes, particularly dyewoods, not previously known in Europe. Native American peoples, such as Navajo and Hopi, were highly skilled dyers. In Europe the blue extracted from the woad plant was used for adornment, through the coloring of skin and later the dyeing of textiles.

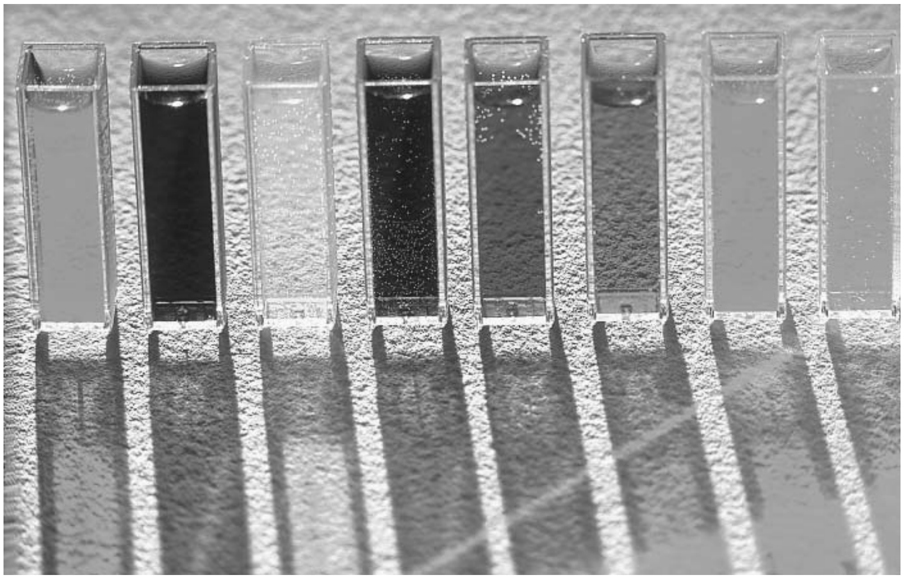
By the sixteenth century dyes played a major role in political and economic history as European nations vied for sources of new colors and the secrets of applying natural colors. *Indigo tinctoria* that yielded a brighter indigo blue than woad arrived in Europe from India and the East. Indigo and the red known as madder, from the roots of the madder plant, were the most important natural dyes. Indigo was used in kimono dyeing in Japan. Madder was the basis of the fiery Turkey red. England's King George II chose indigo for the color of British naval uniforms (hence "navy blue").

Indigo is a vat dye, which means that it was once applied in special vats. It and other vat dyes are insoluble in water. In dyeing, indigo is converted, or reduced, to a white form, which is soluble. Yarn or fabric is then dipped in the vat containing the reduced dye, which on leaving the vat is oxidized in the air back to blue. Tyrian purple and biblical blue are also vat dyes.

Dyes, Industry, and Science

Dyestuffs were central to the first **Industrial Revolution**, from the late eighteenth century, based on the production of and trade in textiles. This

Industrial Revolution: widespread replacement of hand tools by power-driven machines, beginning about 1750 (especially in England)



Containers of fabric dyes.

encouraged chemists to investigate the composition of natural dyes. They extracted the colorant in madder and gave it the scientific name alizarin. Dyes also played a prominent role in the second Industrial Revolution, commencing around 1870, when the quest for synthetic colorants led to the development of science-based industry.

The first of the modern synthetic dyes was invented in London in 1856 by the chemist William Henry Perkin when he was still a teenager. His product was first sold as Tyrian purple, but from 1859 on it was known as mauve, from the French word for the mallow flower. It was made from coal tar, the waste product of the coal gasification process. The coal-tar product benzene was converted in three steps to the dye. Perkin's teacher was the German chemist August Wilhelm Hofmann, who began research to identify the chemical constituents of the new coal-tar or "aniline" dyes. Chemistry in Germany was highly developed at this time, and many Germans journeyed to England to work in the new synthetic dye industry. Starting in the mid-1860s, they returned home, armed with the latest science and technology. The industry soon moved to Germany and Switzerland.

Particularly significant was the production of artificial alizarin red (in 1869), mainly in Germany, and indigo (1897), only in Germany. These synthetic products destroyed the trading monopolies in natural dyes by displacing the large-scale cultivation of madder and indigo. The other new dyes had no analogs in nature. In 1875 the dye chemist Otto N. Witt proposed a theory of color and constitution that is still used to explain how certain arrangements of atoms, called **chromophores**, give rise to color. Other groups called auxochromes enable the bonding to fiber and modify the color.

The development of the synthetic dye industry led to the emergence of classical organic chemistry. Its application in industry was rapid. From the end of the nineteenth century the **intermediates** employed in the manufacture of synthetic dyes were used to make pharmaceutical products such as aspirin. Some synthetic dyes exhibited bactericidal properties; they were called medicinal dyes. **Sulfonamides**, drugs introduced in the 1930s, are based on research into dyestuffs and their intermediates. Less fast dyes have

chromophore: part of the molecule that yields characteristic colors

intermediate: molecule, often short-lived, that occurs while a chemical reaction progresses but is not present when the reaction is complete

sulfonamides: first of a series of drugs used for the prevention and cure of bacterial infections in humans; sulfanomides are amides of sulfuric acids and contain the $-SO_2NRR_1$ group made color photography possible. Indigo is not fast to light and washing, and soon gives a faded effect. Since the 1960s that property has been used to advantage in fashionable denims.

The modern U.S. chemical industry emerged in 1915, when supplies of dyes were cut off by Germany, which required dyes and their intermediates for military purposes, including the manufacture of explosives, and also by the British blockade on German shipping. From the 1970s the by then mature industry declined in Europe and the United States, in part because of environmental difficulties facing dye manufacturers, such as the pollution of surface waters.

Making Colors Last

color fastness: condition characterized by a lack of removal of colored moieties from a base material

Color fastness is important in textiles. It is a measure of how well the dye is attached to fabric (substrate). In the early 1900s a new class of coal-tar dyes, known as the indanthrenes, was invented. Some blue indanthrenes displaced indigo, because they were faster to light and washing, and brighter. The most important of these colorants, collectively known as vat dyes, is vat jade green.

mordant dye: dye substance containing an acidic moiety, e.g., a carboxyl group, which binds metallic compounds, forming insoluble colored compounds

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Mordant dyes are those that can be applied only with a fixing agent, or mordant. The fixing agents are often **metal** compounds, particularly those whose cations form coordination complexes. Alizarin is a mordant dye, and with different metal compounds it gives a range of colors. The first synthetic dyes that attached to fabric without the need for a mordant were benzidine dyes, invented in the 1880s. However, early in the twentieth century some of them were found to cause bladder cancer. Their manufacture ceased by the early 1970s. In 1956 chemists at Imperial Chemical Industries (ICI) in England announced the first dyes that bonded chemically to fabric; these fiber-reactive colorants ensured great fastness.

Common Dyes

Fluorescent dyes, or whitening agents, alter the drab gray or yellow appearance of white fabrics that have been washed many times. They do this by absorbing ultraviolet (UV) light and reemitting the absorbed energy as fluorescence in the blue region of the spectrum. This “blueing” makes fabrics look whiter and brighter. Fluorescent dyes are also used as tracers in following sewage and contaminated sources of water, and are important in detection chemistry for drug development.

A wide variety of natural and synthetic dyes are used to color foodstuffs. Florida oranges, often a natural green color when ripe, are sometimes dyed orange with synthetic dyes. Since some synthetic dyes cause illness, their use is restricted, or excluded, even in the coloration of textiles. In the United States, the Pure Food, Drug, and Cosmetic Act enables the Food and Drug Administration (FDA) to control the dyes in foods. This is why these dyes are given names with the prefix FD&C or External D&C.

Hair dyes are of two types: permanent and semipermanent. Permanent dyeing is achieved with a synthetic dye, applied with hydrogen peroxide that first bleaches the natural pigment melanin. Semipermanent dyes are generally made with vegetable extracts, such as henna, that coat rather than penetrate the hair shaft. There are a number of questions about the safety of synthetic hair dyes, since some of the products they contain cause cancer.

TIE-DYEING

Tie-dyeing is, like textile printing, selective dyeing. If a piece of wool is bound tightly with cotton strips and then dyed by immersion in a dye bath, only those areas exposed to the dye will take on its color. After the fabric is removed and allowed to dry, and when the strips of cotton are untied, the tightly bound areas show no color from the dye. Omitting dye from an area creates what is referred to as a reserve. The whole piece can then be placed in a dye bath, so that the reserve areas are now dyed, and the previously dyed areas show the effect of two dyes. This process, called tie-dyeing, creates interesting patterns on fabric and is often used in producing T-shirts, shorts, or handkerchiefs.

Easter egg dyes are natural dyes that can be found around the home. They include blue from cabbage leaves or blueberries, orange from yellow onion skins, red from cranberries or raspberries, pale green from spinach leaves, and light yellow from orange or lemon peels. Dyes often have different colors in acidic and alkaline solutions. This enables them to be used as acid-base indicators. Many dyes are utilized as **biological stains**. SEE ALSO COSMETICS; PERKIN, WILLIAM HENRY; PIGMENTS.

biological stain: dye used to provide contrast among and between cellular moieties

Anthony S. Travis

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Dysprosium

66
Dy
DYSPROSIUM
162.50

MELTING POINT: 1,407°C
BOILING POINT: 2,567°C
DENSITY: 8,551/kg m^{-3}
MOST COMMON IONS: Dy^{4+}, Dy^{3+}, Dy^{2+}

Dysprosium, taking its name from the Greek word *dysprositos*, meaning "hard to obtain," is a metallic element, discovered, but not isolated, in 1886 in

rare earth elements: older name for the lanthanide series of elements, from lanthanum to lutetium

lanthanides: a family of elements from lanthanum to lutetium having from 1 to 14 4f electrons

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Paris by the French scientist Paul-Émile Lecoq de Boisbaudran. Its isolation was made possible by the development of ion-exchange separation in the 1950s. Dysprosium belongs to a series of elements called **rare earths**, **lanthanides**, or “4f elements.” The occurrence of dysprosium is low: 4.5 ppm (parts per million), that is, 4.5 grams per metric ton in Earth’s crust, and 2×10^{-7} ppm in seawater. Two minerals that contain many of the rare earth elements (including dysprosium) are commercially important: monazite (found in Australia, Brazil, India, Malaysia, and South Africa) and bastnasite (found in China and the United States). As a **metal**, dysprosium is reactive and yields easily oxides or salts of its triply oxidized form (Dy^{3+} ion).

alloy: mixture of two or more elements, at least one of which is a metal

nuclear: having to do with the nucleus of an atom

Dysprosium or its compounds are used in small quantities in several high-technological applications owing to their thermal, magnetic, and optical properties. For instance, dysprosium is susceptible to large magnetization and is a part of special magnetic **alloys** (e.g., those used for data storage on CDs). A cermet (a combination of a heat resistant ceramic with a metal) of dysprosium oxide and nickel enables the control of **nuclear** reactors, as it easily absorbs neutrons. Dysprosium is put into mercury-vapor lamps and several materials used to generate lasers, to enhance their optical properties. Dysprosium-cadmium chalcogenides are a source of infrared radiation. Some special purpose eyeglasses (e.g., those worn by glassblowers) contain dysprosium. SEE ALSO Cerium; Erbium; Europium, Gadolinium; Holmium; Lanthanides; Lanthanum; Lutetium; Neodymium; Praseodymium; Promethium; Samarium; Terbium; Thulium; Ytterbium.

Jean-Claude Bünzli

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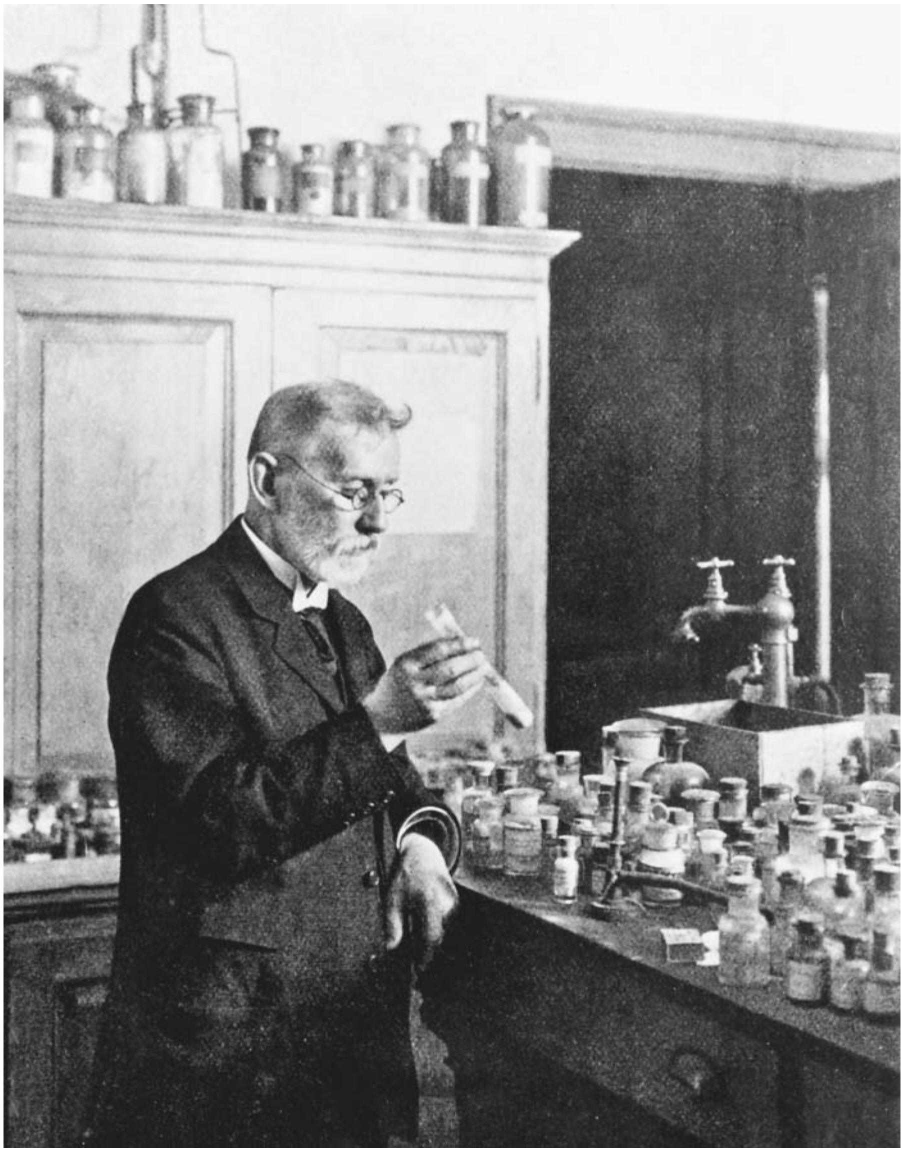
Ehrlich, Paul

GERMAN CHEMIST AND BACTERIOLOGIST
1854–1915

Paul Ehrlich made notable contributions in several areas of medicine including selective dye staining of cells, immunology, cancer research, and chemical therapy of infectious diseases.

Ehrlich was born in Strehlen, Germany, and attended school in Breslau where an older cousin, Carl Weigert, was a physician at a local hospital. Weigert was researching cell staining with synthetic dyes, a procedure that makes cells more visible under a microscope. Weigert demonstrated the technique for his teenage cousin who was immediately fascinated by the process.

As a medical student Ehrlich undertook his own investigations into cell staining techniques, observing that dyes could selectively stain different types of cells. Most of his dyes came from the flourishing German dye industry, and Ehrlich noted that different chemical structures of the dyes gave them different cell staining properties, leading him to the hypothesis that there was a very specific chemical attraction between the dye and certain cells or parts of cells. This concept of specific chemical attractions was to guide much of his life’s work.



German chemist and bacteriologist Paul Ehrlich, corecipient, with Ilya Ilyich Mechnikov, of the 1908 Nobel Prize in physiology or medicine, "in recognition of their work on immunity."

Following graduation from medical school in 1878, Ehrlich accepted a position at a Berlin hospital where he employed his knowledge and skill with synthetic dyes to make numerous important contributions to medicine. He was able to use dyes to differentiate several types of red and white blood cells, including leukemia cells, and to assist German bacteriologist Robert Koch in staining and identifying the tuberculosis bacterium. Cell staining remains in use to identify both healthy and cancerous cells.

In 1883 Ehrlich married a young woman named Hedwig Pinkus, to whom he was quite devoted. They had two daughters, Stephanie and Marianne. In 1888 Ehrlich himself developed tuberculosis, left employment at the hospital, and took a yearlong trip to Egypt where he recovered from the infection.

Ehrlich returned to Berlin in 1889 and established a small research laboratory where he began work on the chemical nature of immunity, antitoxin sera, and the nature of the binding of antibodies to antigens. Over a period of ten years this work led to his concept of complementary chemical binding of antigen to antibody and his famous side chain theory to explain why only part of an antigen was necessary to raise immunity. This work in immunology led to a 1908 Nobel Prize in physiology or medicine.

Ehrlich made significant contributions to understanding cancers, including developing a strain of mouse cancer cells known as Ehrlich ascites cells that are still used in cancer research. Ehrlich's work with the selectivity of staining dyes for specific cells, and the specific binding of one antigen to only one antibody, led to the hypothesis that it should be possible to develop drugs that were so specific to disease cells that they could be considered "magic bullets."

Ehrlich embarked on his search for magic bullets to treat parasitic disease with a vast supply of new chemicals from the German dye industry. In 1909 Ehrlich discovered the first effective cure for syphilis, "compound 606" (also called Salvarsan). For his insight and this achievement Ehrlich is known as the father of chemotherapy. SEE ALSO DYES.

Robert K. Griffith

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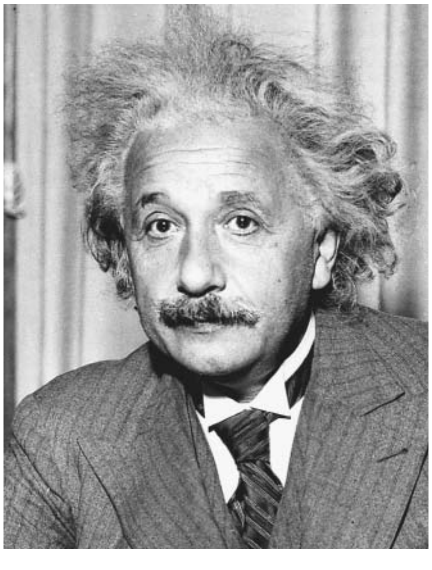
Einstein, Albert

GERMAN-AMERICAN PHYSICIST
1879–1955



American physicist Albert Einstein, recipient of the 1921 Nobel Prize in physics, "for his services to Theoretical Physics, and especially for his discovery of the law of the photoelectric effect."

nuclear: having to do with the nucleus of an atom

For most people asked to name a scientist, "Albert Einstein" is the first name that comes to mind. Einstein's life story, including his difficulties with math in high school, his time spent as a patent clerk in the Swiss Patent Office, his development of the theory of relativity, and his influence on the development of the **nuclear** bomb, is the stuff of legends. Indeed, many a struggling high school science student has sought refuge in the notion that Einstein did not do well in that capacity either.

Einstein is perhaps best known for his work on relativity, and his simple but elegant equation $E = mc^2$, which expresses an equivalence between energy and matter. It is this equation that describes the possibility of the transformation of mass into energy, and the phenomenon that is operational in a nuclear power plant or nuclear bomb. Very little matter can become an inordinate amount of energy, as the speed of light is a constant having an inordinately large value.

What is not so well known about Einstein is that he made contributions to the development of modern chemistry, particularly to the area of quantum mechanics. The Nobel Prize Committee awarded Einstein the Nobel Prize in physics in 1921 "for his services to Theoretical Physics, and especially for his discovery of the law of the photoelectric effect." His explanation of the photoelectric effect helped to validate Planck's view of quantized energy, and has become the basis of the quantitative laws of photochemistry.

The photoelectric effect had been observed as early as 1887, when the physicist Heinrich Hertz noted that light shining on metal decreased the amount of energy or **voltage** needed to eject electrons from the metal's surface. Further studies showed that the kinetic energy of the liberated electrons was independent of the intensity of the light; more light only produced more electrons. This kinetic energy was found to be dependent on wavelength. If the wavelength of the incident light was less than a threshold wavelength, no electrons were observed. Einstein explained the phenomenon in a paper published in the journal *Annalen der Physik* in 1905, the first of four papers by Einstein (all appearing in 1905) that changed science. In essence, Einstein argued that there is an intrinsic "work function" that is required to remove an electron from a metal, a specific amount of energy that depends only on the identity of the metal. The kinetic energy of the released electron is then the difference between the energy supplied by the incoming electromagnetic radiation (including visible light) and the work function. Subsequent experimental verification of Einstein's argument affirmed the claim that light was quantized.

voltage: potential difference expressed in volts

It is one of the ironies of twentieth century science that, although his work on the photoelectric effect helped to advance quantum mechanics, Einstein came to be its chief critic. It was his antagonism toward the probabilistic and nondeterministic nature of quantum phenomena that prompted Einstein to make the often-quoted remark, "I cannot believe that God would choose to play dice with the universe."

Einstein's explanation of the photoelectric effect was not his only contribution to chemistry. His Ph.D. dissertation, submitted in 1905, was entitled "A New Determination of Molecular Dimensions." His investigation of **Brownian motion** (the random movement of microscopic particles suspended in liquids or gases) was intended to establish the existence of atoms as being indispensable to an explanation of the molecular-kinetic theory of heat. And the concept of relativity has shed light on the motions of electrons in the core orbitals of heavy elements. SEE ALSO QUANTUM CHEMISTRY.

Todd W. Whitcombe

Brownian motion: random motion of small particles, such as dust or smoke particles, suspended in a gas or liquid; it is caused by collisions of the particle with gas or solvent molecules that transfer momentum to the particle and cause it to move

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Einsteinium

MELTING POINT: **1,133K**
BOILING POINT: **1,269K**
DENSITY: **8.8 +/- g/cc**
MOST COMMON IONS: Es^{3+}, Es^{2+}

99
Es
EINSTEINIUM
252

Einsteinium, the tenth member of the actinide series, was discovered in 1952. Einsteinium and fermium (element 100) were most unexpectedly produced

isotope: form of an atom that differs by the number of neutrons in the nucleus

atomic number: the number of protons in an atomic nucleus, expressed in terms of electric charge; it is usually denoted by the symbol Z

in the explosion of the first U.S. thermonuclear device, "Mike," tested at Eniwetok Atoll in the Pacific Ocean on November 1, 1952. Early analyses of debris from that explosion indicated that something unusual had occurred; the new, very neutron-rich **isotope** of plutonium, ^{244}Pu, was found during mass spectrometric analyses performed at the Argonne National Laboratory and another isotope of plutonium, ^{246}Pu, was detected at the Los Alamos Scientific Laboratory in the course of analyses of the Pu fractions. Scientists at the Radiation Laboratory at the University of California, Berkeley, using their previous experience with the separation of individual actinide elements, then joined in the search for trans-californium elements (elements of higher **atomic number** than californium). Tons of coral from the atoll were laboriously processed, and ^{253}99 (half-life 20 days) and ^{255}100 (half-life 20 hours) were positively identified based on the order of their elution (removal) from a cation-exchange resin column with an α-hydroxyisobutyrate solution. Because of the huge, nearly instantaneous neutron flux generated in the explosion, at least seventeen neutrons were successively captured by the ^{238}U in the thermonuclear device, producing uranium isotopes through ^{255}U, many of which β-decayed to higher atomic number elements, thus producing ^{253}Es and ^{255}Fm. After their declassification, these results were published jointly by the Berkeley Radiation Laboratory, the Argonne National Laboratory, and the Los Alamos Scientific Laboratory (Ghiorso et al., p. 1048[L], 1955).

***α*-particle:** subatomic particle with 2+ charge and mass of 4; a He nucleus

fission: process of splitting an atom into smaller pieces

lanthanides: a family of elements from lanthanum to lutetium having from 1 to 14 4f electrons

aqueous solution: homogenous mixture in which water is the solvent (primary component)

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

The name einsteinium was chosen for element 99, in honor of the great scientist Albert Einstein. Einsteinium isotopes of masses 241 through 256 are known. All are radioactive, decaying by ***α*-particle** emission, electron capture, spontaneous **fission**, and β-decay. The mass 241 isotope has the shortest half-life (8 seconds), and the mass 252 isotope has the longest (1.29 years). The ground state electronic configuration of the gaseous einsteinium atom is [Rn]5f^{11}7s^2, analogous to that of its **lanthanide** homologue (holmium). The most stable ion in **aqueous solution** is Es^{3+}, but Es^{2+} and Es^{4+} have been reported, and the **metal** is divalent. SEE ALSO Actinium; Berkelium; Einstein, Albert; Fermium; Lawrencium; Mendelevium; Neptunium; Nobelium; Plutonium; Protactinium; Radioactivity; Rutherfordium; Thorium; Transmutation; Uranium.

Darleane C. Hoffman

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Elastomer ***See Rubber.***

Electrochemistry

Electrochemistry deals with the links between chemical reactions and electricity. This includes the study of chemical changes caused by the passage of an electric current across a medium, as well as the production of electric energy by chemical reactions. Electrochemistry also embraces the study of **electrolyte solutions** and the chemical equilibria that occur in them.

electrolyte solution: a liquid mixture containing dissolved ions

Many chemical reactions require the input of energy. Such reactions can be carried out at the surfaces of electrodes in cells connected to external power supplies. These reactions provide information about the nature and properties of the chemical species contained in the cells, and can also be used to synthesize new chemicals. The production of chlorine and aluminum and the electroplating and electrowinning of **metals** are examples of industrial electrochemical processes. Electrochemical cells that produce electric energy from chemical energy are the basis of primary and secondary (storage) batteries and fuel cells. Other electrical phenomena of interest in chemical systems include the behavior of ionic solutions and the conduction of current through these solutions, the separation of ions by an electric field (**electrophoresis**), the corrosion and passivation of metals, electrical effects in biological systems (bioelectrochemistry), and the effect of light on electrochemical cells (photoelectrochemistry).

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

electrophoresis: migration of charged particles under the influence of an electric field, usually in solution; cations, positively charged species, will move toward the negative pole and anions, the negatively charged species, will move toward the positive pole

Electrochemical Cells

An electrochemical cell generally consists of two half-cells, each containing an electrode in contact with an electrolyte. The electrode is an electronic conductor (such as a metal or carbon) or a semiconductor. Current flows through the electrodes via the movement of electrons. An electrolyte is a **phase** in which charge is carried by ions. For example, a solution of table salt (sodium chloride, NaCl) in water is an electrolyte containing sodium cations (Na^+) and chloride **anions** (Cl^-). When an electric field is applied across this solution, the ions move: Na^+ toward the negative side of the field and Cl^- toward the positive side.

phase: homogeneous state of matter

anion: negatively charged chemical unit, like Cl^-, $CO_3{}^{2-}$, or $NO_3{}^-$

The half-cells are connected by a cell separator that allows ions to move between the half-cells but prevents mixing of the electrolytes. The separator can consist of a salt bridge, or tube of **aqueous solution** plugged at both ends with glass wool, or it can be an ion exchange membrane or a sintered-glass disk. In some cases both half-cells use the same electrolyte, so that the electrochemical cell consists of two electrodes in contact with a single electrolyte. Electrochemical cells are usually classified as either **galvanic** or electrolytic. In galvanic cells, reactions occur spontaneously at the electrode–electrolyte interfaces when the two electrodes are connected by a conductor such as a metal wire. Galvanic cells convert chemical energy to electric energy and are the components of batteries, which usually contain several cells connected in series. In electrolytic cells, reactions are forced to occur at the electrode–electrolyte interfaces by way of an external source of power connected to both electrodes. Electric energy from the external source is converted to chemical energy in the form of the products of the electrode reactions.

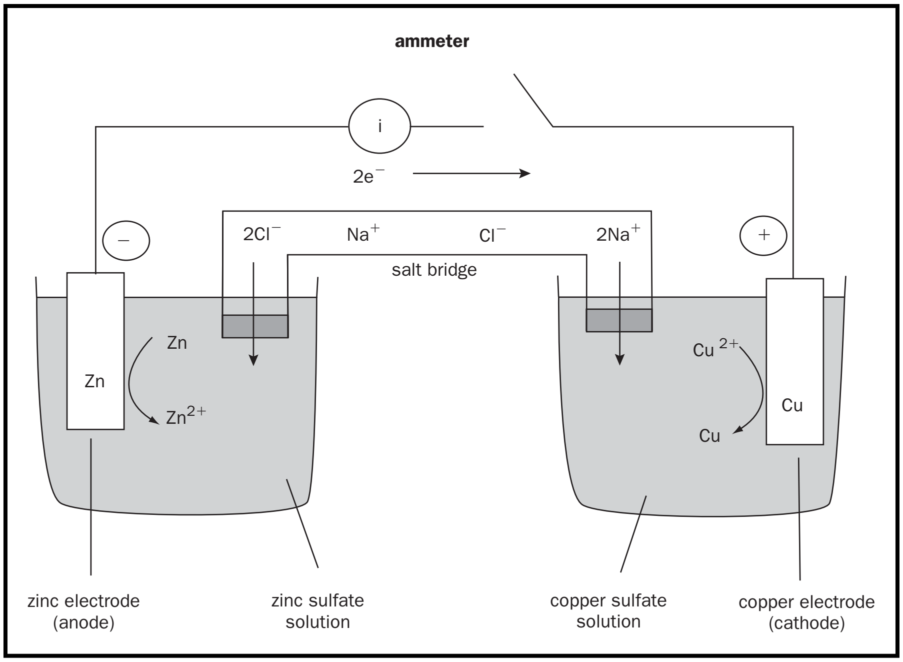
aqueous solution: homogenous mixture in which water is the solvent (primary component)

galvanic: relating to direct current electricity especially when produced chemically

The galvanic cell shown in Figure 1 is known as the Daniell cell and was used as an early source of energy. It consists of a zinc (Zn) electrode in contact with an aqueous zinc sulfate solution and a copper (Cu) electrode in contact with an aqueous copper sulfate solution. When the external switch is closed, an atom of zinc on the zinc electrode is oxidized to zinc ion, liberating two electrons.

$$Zn \rightarrow Zn^{2+} + 2e^- \tag{1}$$

Figure 1. Daniell Cell.



The electrons pass through the external wire and reduce a copper ion to an atom of copper metal on the surface of the copper electrode.

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad (2)$$

The electron flow in the external circuit represents an electric current produced by the cell. Ions flow within the electrolytes and across the salt bridge, as shown in the figure, to prevent an imbalance of ionic charge in the solutions that could result from the occurrence of these two electrode reactions. The overall cell reaction is the reduction of copper ion by zinc.

$$Cu^{2+} + Zn \rightarrow Cu + Zn^{2+} \qquad (3)$$

brine: water containing a large concentration of salts, especially sodium chloride (NaCl)

The electrolytic cell shown in Figure 2 is the industrial chloralkali cell in which **brine** (an aqueous sodium chloride solution) is electrolytically converted to chlorine and caustic soda (sodium hydroxide, NaOH). The external power source supplies electric energy to drive the overall reaction.

$$2Cl^- + 2H_2O \rightarrow Cl_2 + H_2 + 2OH^- \qquad (4)$$

Chloride ion is oxidized to chlorine gas at the carbon electrode, and water is reduced to hydrogen gas (H_2) and hydroxide ion (OH^-) at the iron electrode. The electrolytes are maintained as electrically neutral by a flow of sodium ions through the separator (such as an ion exchange membrane).

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

The electrode where **oxidation** occurs, the zinc electrode in Figure 1 and the carbon electrode in Figure 2, is called the anode, while the electrode where reduction occurs is called the cathode. Reactions (1) and (2) are known as half-reactions, whereas reactions (3) and (4) are called oxidation-reduction (redox) reactions.

Electrode Potentials

voltage: potential difference expressed in volts

Current and potential (or **voltage**) are the two electrical variables of greatest interest in electrochemical cells. Current is related to the rate of the elec-

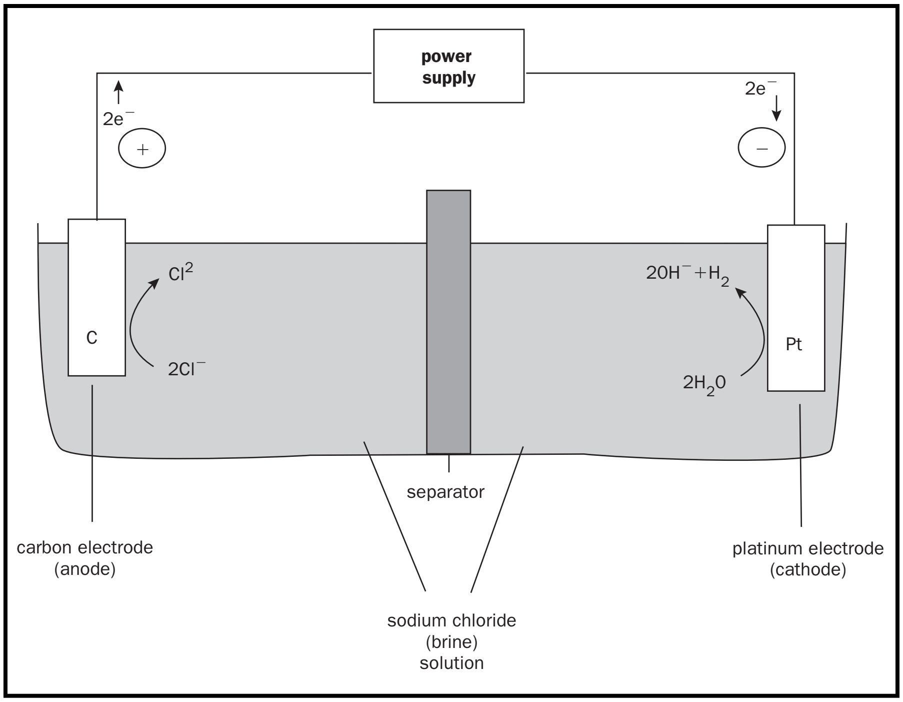


Figure 2. Electrolytic Cell.

trode reactions, and the potential, to the cell energetics. Current is measured in amperes (A), or the amount of electricity in coulombs (C) that passes across a medium per second(s). Potential between the two electrodes is measured in volts (V) with a voltmeter. Potential (V) has units of energy or work (joules, J) per amount of electric charge (C). That is, 1 V = 1 J/C, so that the cell potential is a measure of the energy of the cell reaction. The cell is said to be at open circuit when no current flows; that is, when there are no external connections to the electrodes. Under these conditions, no electrode reactions occur.

Measurements of the potentials of galvanic cells at open circuit give information about the thermodynamics of cells and cell reactions. For example, the potential of the cell in Figure 1, when the solution concentrations are 1 molar (1 *M*) at 25°C, is 1.10 V. This is called the standard potential of the cell and is represented by E°. The available energy (the Gibb's free energy $\Delta G°$) of the cell reaction given in equation (3) is related to E° by

$$\Delta G° = -nF\mathrm{E}° \tag{5}$$

where n is the number of electrons transferred in the reaction (in this case two) and F is a proportionality constant, called the Faraday (96,485 coulombs/equivalent). The cell potential is the difference in potential of the two half-cells. Tables of standard electrode potentials of half-reactions have been compiled; representative values are given in Table 1. These are frequently tabulated with respect to the standard or normal hydrogen electrode (SHE or NHE), which is arbitrarily assigned a half-cell potential of zero. Thus the value, +0.34 V, is assigned to the half-reaction $Cu^{2+} + 2e^{-} \rightarrow Cu$ and

$$\mathrm{E}° = +0.34 \text{ V vs NHE} \tag{6}$$

Similarly, the standard potential for the Zn/Zn^{2+} cell yields $Zn^{2+} + 2e^{-} \rightarrow Zn$ and

Table 1.

REPRESENTATIVE STANDARD POTENTIALS

Half Reaction	E^o vs NHE
$Li^+ + e^- \rightarrow Li$	−3.045
$Mg^{2+} + 2e^- \rightarrow Mg$	−2.356
$Al^{3+} + 3e^- \rightarrow Al$	−1.67
$Zn^{2+} + 2e^- \rightarrow Zn$	−0.7626
$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.424
$2H^+ + 2e^- \rightarrow H_2$	0.000
$Cu^{2+} + 2e^- \rightarrow Cu$	0.340
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.229
$F_2 + 2e^- \rightarrow 2F^-$	2.87

SOURCE: Bard, Allen J. et al., eds. (1985). *Standard Potentials in Aqueous Solutions.* New York: Marcel Dekker.

$$E^\circ = -0.76 \text{ V vs NHE} \tag{7}$$

The difference between these two half-cell potentials yields the standard potential of the Zn-Cu cell.

The standard potential applies to a half-cell when all the reactants are present at unit activity; that is, when the solution species are near a concentration of 1 molar. The actual half-cell potential *E* is a function of the solution concentrations and is related to these and to the standard potential E° by the Nernst equation. The Nernst equation for the generalized half-reaction

$$\text{Oxidized Species} + ne^- \rightarrow \text{Reduced Species} \tag{8}$$

is

$$E = E^\circ + \frac{RT}{nF} \ln \frac{[\text{Oxidized Species}]}{[\text{Reduced Species}]} \tag{9}$$

where *R* is the universal gas constant, *T* is the temperature on the Kelvin (absolute) scale, and the terms [Oxidized Species] and [Reduced Species] denote the activities of the species in the half-cells. The activities of pure solids and liquids are taken as unity. At 25°C, $(RT/F) = 0.025$ V.

Common Batteries

In most flashlights, toys, and remote controllers for televisions, primary batteries are used. The cell reactions in primary batteries are irreversible. During use, reactants are converted to products, and when the reactants are used up, the battery is "dead." The inexpensive flashlight batteries sold in retail stores use a design called a Leclanche dry cell. The body of the battery is made of zinc, which acts as the anode. A carbon rod in the center of the cell serves as the cathode. It is surrounded by a moist paste of graphite powder (carbon), manganese dioxide (MnO_2), and ammonium chloride (NH_4Cl). The anode reaction is the oxidation of the zinc cylinder to zinc ions. The cathode reaction involves the reduction of manganese dioxide. A simplified version of the overall reaction is

$$Zn + 2MnO_2 + H_2O \rightarrow Zn^{2+} + Mn_2O_3 + 2OH^- \tag{10}$$

Alkaline cells are similar, except that the zinc case is porous and the paste around the carbon cathode is moist manganese dioxide and potassium hydroxide. These are more expensive than ordinary zinc-carbon cells, but they maintain a high voltage longer.

The lead-acid storage battery used in automobiles is a secondary battery; it is rechargeable. That is, the automobile battery operates as a galvanic cell when used to start the engine (when discharging), and as an electrolytic cell when it is charged by the alternator or by an external battery charger. The anode consists of porous lead plates in contact with a sulfuric acid (H_2SO_4) solution. The cathode consists of lead dioxide (PbO_2) plates, also in sulfuric acid. Electrons flow from the lead plates to the lead oxide plates. As lead (Pb) loses electrons, it forms lead ions (Pb^{2+}) that react with sulfate ions ($SO_4{}^{2-}$) in solution to form insoluble lead sulfate ($PbSO_4$). When PbO_2 gains electrons, it too reacts with $SO_4{}^{2-}$ ions in solution to form solid $PbSO_4$. The cell reaction is

$$Pb + PbO_2 + 4H^+ + 2\ SO_4{}^{2-} \rightarrow 2PbSO_4 + 2H_2O \qquad (11)$$

and proceeds from left to right when the battery is discharging and from right to left when charging.

The rechargeable nickel-cadmium (Ni-Cad) batteries are used in a variety of cordless appliances such as telephones, battery operated tools, and portable computers. During discharge, cadmium metal (Cd) acts as the anode, and nickel dioxide (NiO_2) as the cathode. Both metals form insoluble hydroxides due to the presence of the potassium hydroxide electrolyte. The cell reaction during discharge is

$$NiO_2 + Cd + 2H_2O \rightarrow Ni(OH)_2 + Cd(OH)_2 \qquad (12)$$

The reaction is reversed during charging. SEE ALSO ALUMINUM; FARADAY, MICHAEL.

Cynthia G. Zoski

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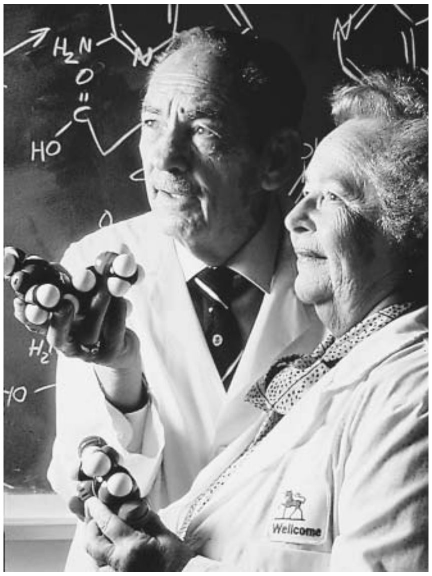
Electronic Materials ***See Semiconductors.***

Elion, Gertrude Belle

AMERICAN CHEMIST AND MEDICAL RESEARCHER
1918–1999

The Nobel Prize Committee rarely honors the work of scientists who develop new drugs. However in 1988, in awarding the Nobel Prize in physiology or medicine to Gertrude Elion and her colleague at the Burroughs



American chemist Gertrude B. Elion (right) with her colleague George H. Hitchings, recipients, with Sir James W. Black, of the 1988 Nobel Prize in physiology or medicine, "for their discoveries of important principles for drug treatment."

Wellcome Pharmaceutical Laboratories, George Hitchings, it recognized the work of this pair that led to the development of a series of important drugs, among these drugs used to treat malaria, the leukemias, viral infections, and some forms of impaired immune response.

Born on January 23, 1918, in New York City, Gertrude Elion graduated from Hunter College, in New York, in 1937 with an A.B. degree in chemistry. Unsuccessful in her efforts to enroll in graduate school, she worked for several years in pharmaceutical companies and as a teacher in New York City high schools while continuing her education part time. She earned an M.S. degree from New York University in 1941.

In 1944 Elion joined the Wellcome Research Laboratories, a subdivision of Burroughs Wellcome, as a senior research chemist; by 1967 she was head of their experimental therapy section. Probably the only woman to hold a top-ranking position in a major pharmaceutical company, in 1967 and for many years after, she is said to have felt that she experienced no discrimination at Burroughs Wellcome.

Her early work focused on the **metabolism** of nucleic acids. In 1944 little was known about these compounds beyond the fact that deoxyribonucleic acid (**DNA**) is the main component of the cell nucleus, and that DNA is composed of repeating units, called nucleotides, whose structures incorporate heterocyclic bases (that is, organic compounds with rings containing nitrogen atoms; the four bases involved are **adenine**, **cytosine**, **guanine**, and **thymine**). Elion's hope was that an understanding of the **synthesis** of nucleic acids in normal cells (and eventual comparisons with nucleic acid synthesis in malignant cells and in disease-causing microorganisms) would suggest ways to block selectively the metabolism of cancer cells or of pathogens without harming normal cells. She therefore proceeded to synthesize a number of compounds that resembled and that might mimic the substance used in DNA synthesis and in this way might block the formation of DNA in harmful cells.

metabolism: all of the biochemical processes that take place within living organisms; comprises processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those that break down complex food molecules, thus liberating energy (catabolism)

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

adenine: one of the purine bases found in nucleic acids, $C_5H_5N_5$

cytosine: heterocyclic, pyrimidine, amine base found in DNA

guanine: heterocyclic, purine, amine base found in DNA

thymine: one of the four bases that make up a DNA molecule

synthesis: combination of starting materials to form a desired product

Working with 2,6-diaminopurine (2,6-DAP), a derivative of adenine, Elion found that it inhibited nucleic acid synthesis in cancer cells and was effective in treating mouse leukemia. During the early 1950s, following the elucidation of the structure of DNA, interest in nucleic acid metabolism became intensified, and scientists investigating it, including Elion and her group, found themselves at the forefront of biochemical research. Elion synthesized 6-mercaptopurine (6-MP), another derivative of adenine, which also inhibited DNA synthesis. It was approved by the U.S. Food and Drug Administration in 1953 for the treatment of acute childhood leukemia. Its success led her to probe its exact mode of action using newly developed radiochemical techniques, a breakthrough in drug-related research that advanced considerably the rational design of therapeutic agents. Elion studied 6-MP as a possible inhibitor of antibody-forming cells. As a result, its derivative Imuran (azathioprine) has been used as an antirejection drug in kidney transplants.

Other notable research by Elion led to the development of the antiviral drug Acyclovir (acycloguanosine), which has been used to treat the herpes simplex viruses. Her studies during the 1970s showed that Acyclovir inhibited viral replication by interfering with viral DNA synthesis. The subsequent development of AZT (azidothymidine), which works in much the same way as Acyclovir against the human immunodeficiency virus (HIV), was carried out at Burroughs Wellcome after Elion retired in 1983 (although she worked after 1983 as a consultant).

In addition to the 1988 Nobel Prize (which she shared with Hitchings and British scientist Sir James Black), Elion received other awards and several honorary doctorates. Active in public service, she served on both national and international health committees. She died on February 20, 1999, in Chapel Hill, North Carolina. SEE ALSO DEOXYRIBONUCLEIC ACID (DNA); DNA REPLICATION; NUCLEIC ACIDS; NUCLEOTIDE.

Mary R. S. Creese

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Endorphins

Endorphins are small **neuropeptides** that are produced by the body and act to reduce pain—hence, the name endorphin (a shortened version of endogenous morphine). The term "enkephalin" (meaning literally "in the head") is also applied to endorphins, but usually refers to smaller molecules that have pain-relieving properties.

neuropeptide: neurotransmitter released into the bloodstream via nerve cells

Endorphins were discovered when scientists found sites where molecules such as morphine bind to nerve cells and reasoned that the body must use these sites to bind chemical compounds. Experiments showed that the compounds were small peptides, and the actions of endorphins were determined by a number of researchers.

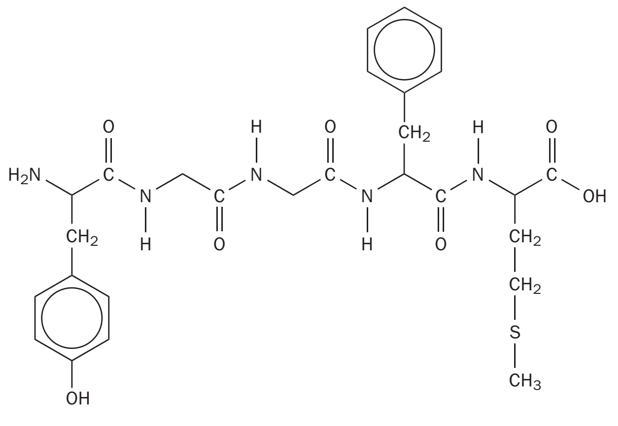
Although similar in primary structure to proteins, endorphins are smaller, ranging from five to forty or more amino acids in length. Endorphins are not considered to be neurotransmitter molecules, but are instead classified as neuromodulatory, that is, they modify the action of neurotransmitters through a number of effects associated with pain or pleasure.

Protein molecules are often synthesized in long chains by the body and cut apart to form functional individual protein units. β-endorphin molecules are produced by the body as portions of larger proopiomelanocortin (POMC) molecules, which are **coded** for by a single gene, synthesized as large molecules, and then cut by enzymes into active subunits. POMC also contains several hormones. The β-endorphin molecules function to relieve pain or produce pleasurable feelings and contain within their structure the pentapeptides met-enkephalin and leu-enkephalin. Composed of five amino acids joined by amide linkages, met-enkephalin (see Figure 1) and leu-enkephalin (see Figure 2) differ only in the amino acid present at the **carboxylic acid** (C-terminal) end.

code: mechanism to convey information on genes and genetic sequence

carboxylic acid: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the $-CO_2H$ functional group

Figure 1. Met-enkephalin



Tyrosine—Glycine—Glycine—Phenylalanine—Methionine—COOH
(Met-enkephalin)

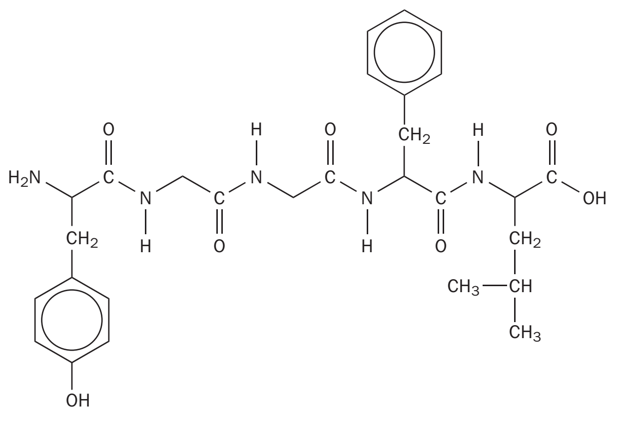
A wide range of physiological effects has been observed for endorphins, but the ultimate function and number of endorphins may not yet be known. Endorphins exhibit a number of **neurological** effects associated with the relief of pain. The administration of exogenous endorphins (those prepared outside the body) stimulates the release of many other hormones including prolactin, adrenocorticotropic hormone (ACTH), and antidiuretic hormone. The **analgesic** effects of morphine are commonly believed to be caused by binding to **receptor** sites for endorphins, but few beneficial effects of treatment with exogenous endorphins have been reported.

neurologic: of or pertaining to the nervous system

analgesic: compound that relieves pain, e.g., aspirin

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

Early speculations concerning the function of endorphins suggested that they were natural painkillers that the body produced to alleviate pain in circumstances requiring an individual to continue functioning in spite of injury or stress. Examples of such situations might include childbirth, exercise, and combat. In addition to affecting one's perception of pain, endorphins may be involved in other phenomena such as runner's high and acupuncture. Persons who exercise regularly have higher than usual amounts of β-



Tyrosine—Glycine—Glycine—Phenylalanine—Leucine—COOH
(Leu-enkephalin)

Figure 2. Leu-enkephalin

endorphin in their bloodstream, and the levels of β-endorphin molecules increase during exercise, perhaps accounting for the enhanced feelings of well-being experienced by long-distance runners. Acupuncturists insert and manipulate long needles at precise locations on the skin. After insertion of the needles, patients experience a reduction in pain or may have other physiological responses. In some cases, the stimulation of these acupuncture points by massage may result in the release of endorphins into the blood. Practices such as squeezing the upper lip to stifle a sneeze or massaging the fleshy area between the thumb and forefinger to alleviate a headache may be related to endorphin effects.

Healthy humans are able to overcome stress and pain, allowing them to continue functioning without being overcome by either. To some degree the response is probably psychological, but evidence that the endorphin effect is real exists in the relationship of the opioid-like drug naloxone to the placebo effect. Given a placebo (a so-called sugar pill), many patients report a decrease in pain. The placebo effect is reduced if naloxone, a drug used to treat the intoxicating effects of narcotics, is administered. The administration of naloxone also reduces the endorphin effect; if given naloxone, patients report increased sensitivity to pain. In addition, abnormal levels of endorphins may be associated with mental illness such as autism or depression. For example, an autistic patient might produce so much endogenous endorphin that he or she does not need to react to the world outside, and a depressed person might not produce enough endorphin to withstand the pain and pressures of daily life. SEE ALSO NEUROTRANSMITTERS; PEPTIDE BOND.

Dan M. Sullivan

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Energy

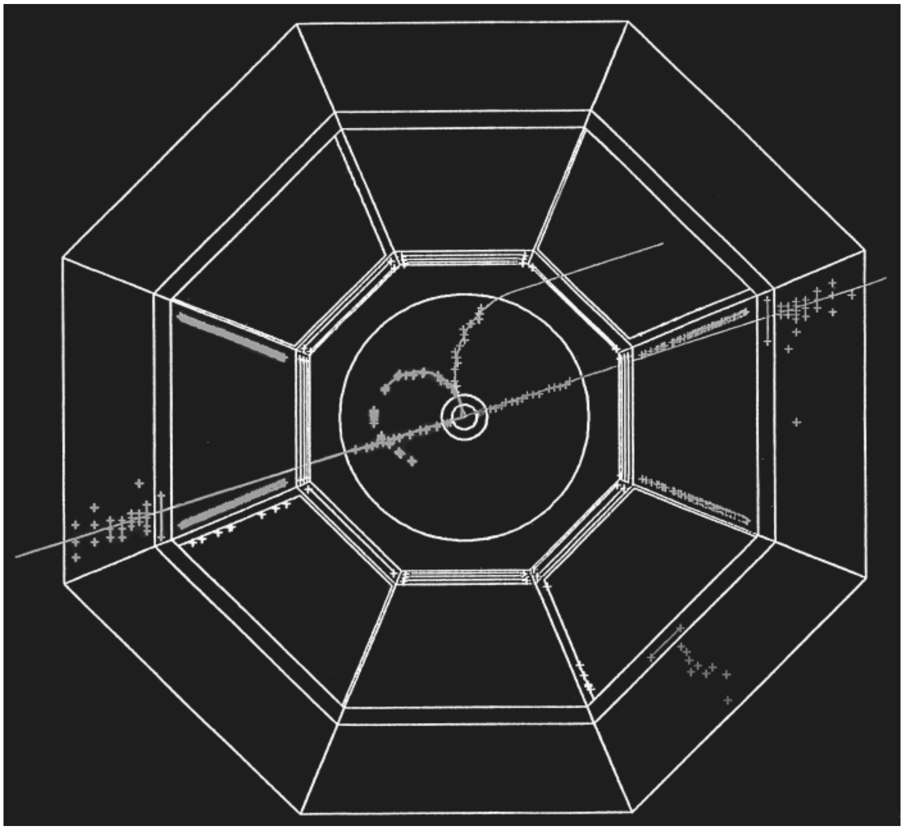
In the discussion of energy, the fundamental concept is that of work, which is motion against an opposing force. Energy is the capacity to do work. An object traveling at high speed and impacting on another object can do more work—can drive the object farther against an opposing force—than the same object moving slowly. This contribution to energy, the energy ascribed to motion, is called kinetic energy. The kinetic energy of an object of mass m traveling at a speed v is $\frac{1}{2}mv^2$. An object may also have energy by virtue of its position. An object high above the surface of Earth has more energy (can do more work) than one at its surface. This contribution to the total energy, the energy due to position, is called potential energy. The relation between the object's position and potential energy depends on the nature of the force field it experiences. The potential energy of a body of mass m at a height h above the surface of Earth is mgh, where g is the acceleration of free fall at the location. More important for chemistry is the potential energy of one charge near another charge. The Coulomb potential energy of a charge q_1 at a distance r from a charge q_2 is given by $q_1q_2/4\pi\epsilon_0 r$, where ϵ_0 is a fundamental constant called the vacuum permittivity. Energy is also stored in the electromagnetic field in the form of photons. The energy of a **photon** of radiation of frequency v is hv, where h is Planck's constant.

photon: a quantum of electromagnetic energy

Energy is conserved. That is, the sum of the kinetic and potential energies of a single body remains constant provided it is free of external influences (forces). Thus, a falling weight accelerates: The fall implies a reduction of potential energy and the acceleration implies an increase in kinetic energy; the sum, though, is constant. A generalization (which can be interpreted as an implication) of the conservation of energy is the first law of thermodynamics, which focuses on a property of a many-body system called the internal energy. The internal energy can be interpreted as the sum of all the kinetic and potential energies of all the particles comprising the system. The first law of thermodynamics states that the internal energy of an isolated system is constant. The first law is closely related to the conservation of energy, but it acknowledges the possibility of the transfer of energy as heat, which is outside the reach of mechanics itself.

The special theory of relativity states that the mass of a body is a measure of its energy: $E = mc^2$, where c is the speed of light. That is, energy and mass are equivalent and interconvertible. Changes in mass are measurable only when changes in energy are considerable, which in practice commonly means for **nuclear** processes.

nuclear: having to do with the nucleus of an atom



An electronic display of the decay of an upsilon particle in a CLEO detector.

In chemistry we are often concerned with the transfer of energy from one location (e.g., a reaction vessel) to another (the surroundings of that vessel). One mode of transfer is by doing work. For example, work is performed when gases evolved in a reaction push back a movable wall (e.g., a piston) against an opposing force, such as that due to the external atmosphere or a weight to which the piston is attached. Another mode of transfer is as heat. Heat is the transfer of energy that occurs as a result of a temperature difference between a system and its surroundings when the two are separated by a diathermic wall (a wall that allows the passage of energy as heat). A metal wall is diathermic, a thermally insulated wall is not diathermic. Finally, energy may leave a system as electromagnetic radiation, for example as in chemiluminescence—the emission of radiation from matter in energetically excited molecular states produced in the course of a chemical reaction, and as a result of **spectroscopic** transitions. We shall concentrate on the first two modes of transfer, work and heat.

spectroscopy: use of electromagnetic radiation to analyze the chemical composition of materials

At a molecular level, work is the transfer of energy that makes use of or drives the orderly motion of molecules in the surroundings. The uniform motion of the atoms in a piston driven back by expanding gas is an example of orderly molecular motion. In contrast, heat is the transfer of energy that makes use of or causes disorderly motion in the surroundings. When we say that a chemical reaction gives out heat, we mean that energy is leaving the reaction vessel and stimulating thermal motion (random molecular motion) in the surroundings.

The energy of a chemical system is stored in the potential and kinetic energies of the electrons and atomic nuclei. This stored energy is sometimes referred to as chemical energy; however, this is only a shorthand way of referring to the kinetic and potential energies of all the particles in an element or compound.

The internal energy of a system changes when a chemical reaction occurs because the electrons and nuclei settle into different arrangements, as in the change of partnerships of H and O atoms in the reaction $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(g)$. The energy released in a chemical reaction can be transferred to the surroundings (and put to use) in a variety of ways regardless of the manner in which the energy accumulated in the first place. Thus, energy may escape as heat and be used to raise the temperature of the surroundings, including raising the temperature of water that is then employed in a turbine to do work. The energy may also escape as work. We have already discussed expansion work, using the example of a piston being driven. The work may be accomplished electrically, as when electrons are driven through an external circuit and used to drive an electric motor.

Atomic nuclei are also centers of energy storage as a result of their internal structures. This energy is released when the nucleons (protons and electrons) undergo rearrangement and thereby change the strength of their interactions. The changes in energy are so great that they give rise to measurable changes of mass. For all chemical processes, the changes in mass accompanying acquisition or loss of energy are totally negligible. SEE ALSO CHEMILUMINESCENCE; CHEMISTRY AND ENERGY; ELECTROCHEMISTRY; HEAT; PHYSICAL CHEMISTRY; SPECTROSCOPY; TEMPERATURE; THERMODYNAMICS.

Peter Atkins

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Energy Sources and Production

Modern societies rely on a variety of energy sources to heat homes, propel transportation vehicles, and produce goods for shelter, food, health care, and entertainment. Some of these sources are renewable, whereas others are nonrenewable. A renewable energy source, for example, solar energy, is one that is virtually inexhaustible on the human time scale. A nonrenewable energy source, for example, natural gas, is one that can be either completely consumed (during a lifetime, or during several lifetimes) or depleted to such an extent that it is no longer economical for humankind to obtain it. Figure 1 shows energy consumption in both the world and in the United States in 2001 by source.

Fossil Fuels

About 80 percent of commercial energy is obtained from three kinds of fuel: oil, coal, and natural gas. These fuels burn in air with the release of energy. They are called fossil fuels because they are believed to have formed from the remains of plants and animals subject to heat and pressure for millions of years.

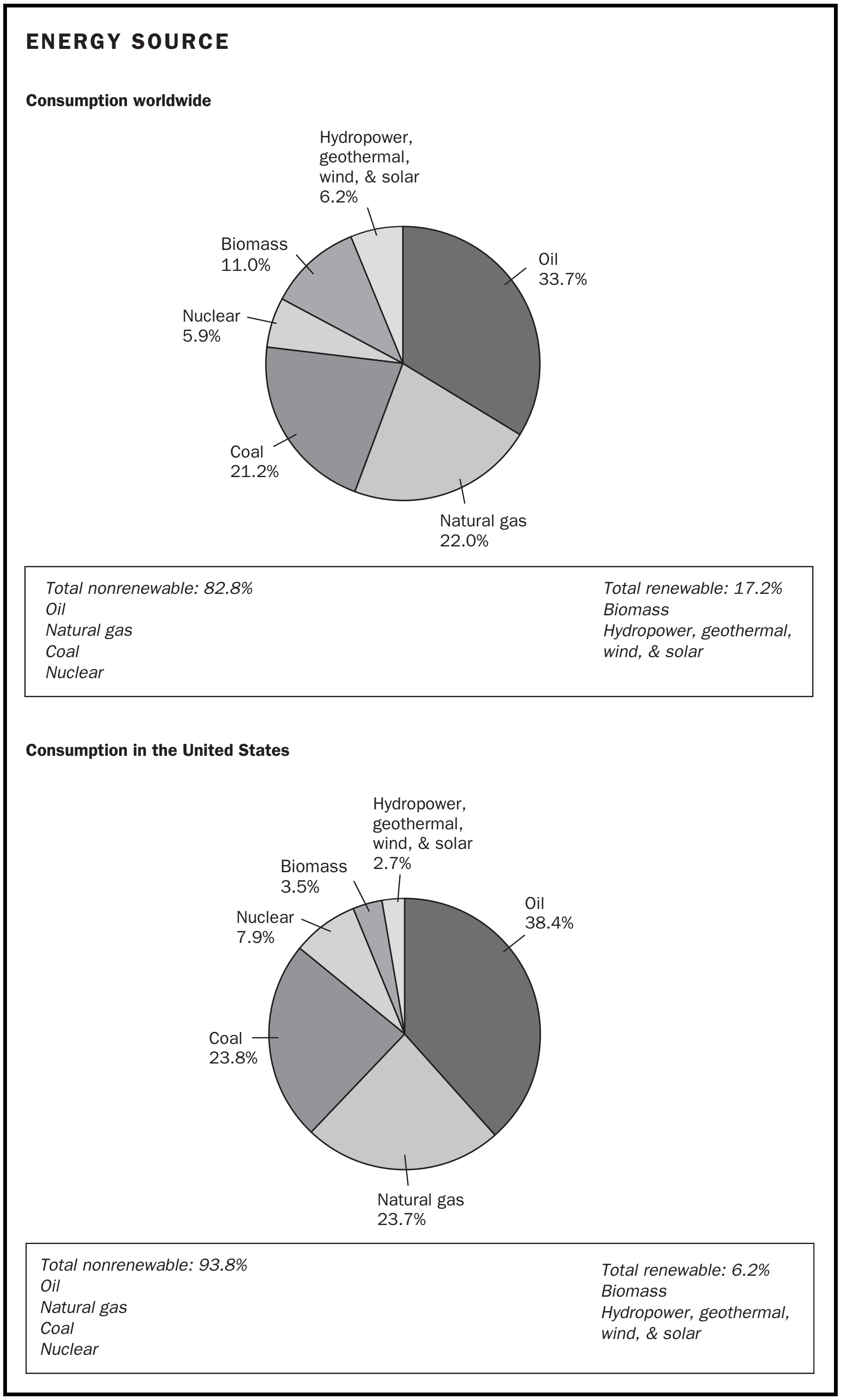

Figure 1. Sources of energy consumed worldwide and in the United States in 2001. In that year, the United States consumed a total of 1.0 x 10^{19} J of energy, whereas worldwide consumption was 4.2 x 10^{19} J. (Data was obtained from British Petroleum and the World Energy Council.)

Natural gas is a mixture of methane (CH_4), 60 to 90 percent, and smaller amounts of other gaseous hydrocarbons, including ethane (C_2H_6), propane (C_3H_8), and butane (C_4H_{10}). It is valued because it burns hotter and produces less air pollution than other fossil fuels. Complete **combustion** of a hydrocarbon substance produces carbon dioxide and water.

combustion: burning, the reaction with oxygen

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) \qquad \Delta H = 50.1 \text{ kJ/g}$$

In 2001, 2.39 trillion cubic meters of natural gas were consumed worldwide, with estimated remaining reserves of 150 trillion cubic meters.

Oil (also referred to as petroleum) is a complex liquid mixture of organic substances, principally of hydrocarbons containing five to sixteen carbon atoms. Most crude oil, once removed from a well, is sent by pipeline to a refinery, where it is distilled to separate it into gasoline, heating oil, diesel oil, and asphalt. The use of catalysts during the refining process increases the yield of gasoline. In 2001, 25.7 billion barrels of oil were used worldwide, with estimated reserves of 1.05 trillion barrels. (One barrel contains 159 liters.)

Coal is the most plentiful fossil fuel, comprising 80 percent of the fuel reserves of the United States and 90 percent of those of the world. It is a complex mixture of organic compounds and is anywhere from 30 to 95 percent carbon by mass. It also contains sulfur compounds. When coal is burned, the sulfur is converted to sulfur dioxide, a troublesome air pollutant. The description of coal as being of high quality is based on its having a low sulfur content and a high carbon content. Lignite coal (brown coal) has a low carbon content and produces the least energy upon combustion (about 15 kJ/g). Bituminous coal (soft coal) has a higher carbon content and produces more energy. It is the most extensively used coal. Anthracite coal (hard coal) has the highest carbon and heat content (about 30 kJ/g), but supplies of it are limited in most places. In 2001, 4.41 billion metric tons of coal were consumed worldwide, with estimated reserves of 985 billion metric tons. (A metric ton is 1,000 kilograms [2,679 pounds].)

Industrial Revolution: widespread replacement of hand tools by power-driven machines, beginning about 1750 (especially in England)

greenhouse effect: presence of carbon dioxide in the atmosphere prevents heat from escaping, thereby raising Earth's temperature

The combustion of fossil fuels produces carbon dioxide gas, a heat-trapping gas. For the past 250 years (since the beginning of the **Industrial Revolution**), the increased use of fossil fuels has caused the atmospheric concentration of carbon dioxide to increase by a factor of about 25 percent. It is now generally believed that this increase has produced higher global temperatures—a phenomenon called the **greenhouse effect**.

Nuclear Energy

fission: process of splitting an atom into smaller pieces

Commercial nuclear power is generated by nuclear **fission** reactions. When slow-moving neutrons strike nuclei of uranium-235 or plutonium-239, these nuclei are split, releasing energy. The energy is used to heat water and drive a turbine, in turn producing electrical energy. Currently nuclear power supplies more than 16 percent of the world's total electricity.

A typical nuclear reactor utilizes uranium oxide, whose uranium content is approximately 3 percent uranium-235, and 97 percent uranium-238, by mass. During the fission reaction, the uranium-235 is consumed and fission products form. As the amount of uranium-235 decreases and the amounts of fission products increase, the fission process becomes less efficient. At some point, the spent nuclear fuel is removed and stored. Some of the radioactive fission products, because of their radioactivity and long half-lives, must be stored securely for thousands of years. Thus, nuclear waste management poses a tremendous challenge.

Scientists hope to someday use controlled nuclear fusion to produce energy. Nuclear fusion, which involves the coming together of light nuclei to form heavier ones, is the process by which stars generate energy. In order for nuclear fusion to occur, the nuclei must have extremely high temperatures. Research has focused on the fusion of deuterium (hydrogen-2) nuclei and tritium (hydrogen-3) nuclei, a process that requires about 50 million degrees Celsius.

Renewable Energy Sources

The principal renewable energy sources are **biomass** from crops such as trees and corn, hydropower from flowing rivers, geothermal power from heat stored in Earth, wind energy from the movement of winds, and solar energy from the Sun.

biomass: collection of living matter

Wood is part of an array of plant matter referred to as biomass that can be burned to produce energy. The combustible substances in biomass are primarily carbohydrates (and of these, primarily cellulose). Cellulose, whose simplest or empirical formula is CH_2O, undergoes combustion to form carbon dioxide and water.

$$CH_2O(s) + O_2(g) \rightarrow CO_2(g) + H_2O(g) \qquad \Delta H = -14\ \text{kJ/g}$$

Wood fuels continue to be used in the rural areas of developing countries.

Hydroelectric power is a well-developed energy source. Today, hydropower provides about 19 percent of the world's electricity supply. Because it is a clean, renewable source of energy, hydropower should continue to serve as a vital energy source.

There has been a rapid growth in the use of wind turbines to generate electricity. In 2001 the amount of electricity generated in this way worldwide corresponded to the amount that would have been obtained from burning 15 million barrels of oil. Although this represents only about 0.05 percent of worldwide energy production in 2001, this fraction will increase.

Solar energy is the most significant and promising renewable energy source. Solar energy is converted to electricity by solar cells (also known as photovoltaic cells). A great deal of solar energy is used currently in what is known as passive heating (which can be directly experienced as the heat gain in a greenhouse caused by sunlight). SEE ALSO AIR POLLUTION; CHEMISTRY AND ENERGY; COAL; ENERGY; FOSSIL FUELS; GLOBAL WARMING; NUCLEAR FISSION; NUCLEAR FUSION; PETROLEUM; SOLAR CELLS.

H. Eugene LeMay Jr.

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Environmental Pollution

Environmental pollution is the release of chemical waste that causes detrimental effects on the environment. Environmental pollution is often divided into pollution of water supplies, the atmosphere, and the soil. In his book *Environmental Chemistry*, Stanley Manahan lists several different types of pollutants, including toxic inorganic and organic compounds, high concentrations of normally innocuous compounds, and heat and noise. While much pollution is produced by the chemical industry, domestic sources include human waste and automobile exhaust.

toxicology: division of pharmacology dealing with poisons, their identification, detection, effects on the body, and remedies

While physical sources, such as noise and light, of pollution are important, people most often notice the damage of chemical pollution on animals and plant life. These chemicals can react with tissues in the body and change the structure and function of the organ, cause abnormal growth and development of the individual, or bind with the genetic material of cells and cause cancer. The study of the effects of poisons on the body is called **toxicology**. One of the central tenets of toxicology states that the dose of a chemical determines its overall effects and that most chemicals can be dangerous at high exposures.

ultraviolet radiation: portion of the electromagnetic spectrum with wavelengths shorter than visible but longer than x rays

Individuals and chemical and petroleum companies contribute to the pollution of the atmosphere by releasing inorganic and organic gases and particulates into the air. The atmosphere is a paper-thin layer of gas (representing 1 percent of the mass of Earth) that protects the planet from damaging cosmic and **ultraviolet radiation**, contains life-giving oxygen, and allows the efficient cooling of the planet.

Atmospheric Pollution

chlorofluorocarbon (CFC): compound that contains carbon, chlorine, and fluorine atoms, which removes ozone in the upper atmosphere

acid rain: precipitation that has a pH lower than 5.6; term coined by R. A. Smith during the 1870s

combustion: burning, the reaction with oxygen

Some examples of atmospheric pollutants include nitrogen dioxide (NO_2), sulfur dioxide (SO_2), carbon monoxide (CO), and **chlorofluorocarbons (CFCs)**. The first two pollutants combine with water to form acids, which not only irritate the lungs but also contribute to the long-term destruction of the environment due to the generation of **acid rain**. Carbon monoxide, generated by the incomplete **combustion** of hydrocarbons, displaces and prevents oxygen from binding to hemoglobin and causes asphyxiation. Also, it binds with metallic pollutants and causes them to be more mobile in air and water. CFCs and other halogenated hydrocarbons react with light to form highly reactive species, called radicals, which destroy ozone in the upper atmosphere. These reactions greatly reduce the protective effects of ozone against ultraviolet radiation.

Water Pollution

heavy metal: by convention, a metal with a density greater than 5 g/cm^3; 70 elements are thus classified as heavy metals

transition metals: elements with valence electrons in d-sublevels; frequently characterized as metals having the ability to form more than one cation

Fresh, clean, and drinkable water is a necessary but limited resource on the planet. Industrial, agricultural, and domestic wastes can contribute to the pollution of this valuable resource, and water pollutants can damage human and animal health. Three important classes of water pollutants are **heavy metals**, inorganic pollutants, and organic pollutants. Heavy metals include **transition metals** such as cadmium, mercury, and lead, all of which can contribute to brain damage. Inorganic pollutants like hydrochloric acid, sodium chloride, and sodium carbonate change the acidity, salinity, or alkalinity of the water, making it undrinkable or unsuitable for the support of animal and plant life. These effects can result in dire consequences for higher mammals such as humans. A list of organic pollutants includes pesticides such as chlorpyrifos and paraquat, and their byproducts, such as dioxin. All of these substances are highly lethal to animals, and many can be readily absorbed through the skin.

Pesticides

The use of pesticides in agriculture contributes to environmental pollution. Pesticides are used to control the growth of insects, weeds, and fungi, which compete with humans in the consumption of crops. This use not only increases crop yields and decreases grocery prices, but also controls diseases such as malaria and encephalitis. However, the spraying of crops and the water runoff from irrigation transports these harmful chemicals to the habitats of nontarget animals. Chemicals can build up in the tissues of these animals, and when humans consume the animals the increased potency of the pesticides is manifested as health problems and in some cases death. Chemists have recently developed naturally occurring pesticides that are toxic only to their particular targets and are benign to birds and mammals. The most significant pesticide of the twentieth century was DDT, which was highly effective as an insecticide but did not break down in the environment and led to the death of birds, fish, and some humans.

Industrial Pollution and Love Canal

The infamous case of the pollution of Love Canal, on Lake Erie in New York, brought environmental pollution to the public attention in the 1970s, and the history of this incident has been thoroughly described at a University of Buffalo web site. From 1942 to 1953, several chemical companies dumped 20,000 metric tons of chemical waste at this site. In 1953 the land was sold to the local board of education, and the 99th Street School was constructed on the land. The school attracted families to the neighborhood, which grew to contain 800 single-family homes and 240 apartment units by 1978. Unfortunately, eighty different chemicals, including dioxins and polychlorinated biphenyls (PCBs), started to leach through the soil, and residents began complaining of odd smells in their houses and experiencing many unexplainable health problems. The school was closed in August 1978,

ERIN BROCKOVICH: THE STORY BEHIND THE MOVIE

In December 1987, Pacific Gas and Electric (PG&E) reported to the Environmental Protection Agency that it had detected levels of chromium (VI) at its natural gas compression station near Hinkley, California, that were ten times higher than those allowed by government standards. These reports devalued land in the community and sparked the curiosity of Erin Brockovich, who was working in a law office as a secretary. Her passionate investigation into the actions of the large public utility led to the discovery of a thirty-year cover-up of the improper disposal of cooling water contaminated with the chromium(VI). Dr. Robert A. Goyer has stated that chromium (VI) irritates the skin of humans and causes cancer in laboratory animals. According to an article by attorney Carole Bos on the *LawBuzz* web site, Erin Brockovich's work forced PG&E to pay damages of $300 million to the residents of Hinkley.

and the federal government contributed $10 million for the relocation of 200 families nearest the site. In 1980 President Carter sent additional funds, for the relocation of 700 more families. Today federal laws stipulate that generators of hazardous waste are responsible for the proper storage and disposal chemicals from the "cradle to the grave."

New Pollutants: Toxic Mold

Recently many people have complained of illnesses associated with the presence of toxic mold in their homes and workplaces. These molds, which thrive in damp surroundings, are members of the fungi kingdom and produce chemicals called mycotoxins that can produce a variety of health problems. Additionally, molds produce strong allergic reactions in some individuals. According to the Centers for Disease Control and Prevention (CDC), little strong evidence exists that can tie all of the health problems seen in damp or flooded areas to molds, but the CDC also recommends that one should repair leaking plumbing and all other causes of damp environments as soon as they occur.

While some of the environmental pollution created in society is avoidable, industrial nations will always produce a low level of pollutants. Pesticides greatly increase overall food production; pharmaceuticals, which require organic chemicals for their manufacture, extend life; and plastics are used in all aspects of medical and domestic life. Society must find a balance between the desire to minimize the cost of manufactured items and the desire to require industries and individuals to reduce pollution. SEE ALSO AIR POLLUTION; WATER POLLUTION.

G. Brent Dawson

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Enzymes

Enzymes are (mostly) proteins that catalyze biochemical reactions; that is, they increase the rate of a reaction but are not used up in the process. Their importance to life is underscored by the fact that many severe or fatal genetic diseases involve a missing or defective enzyme. Enzymes can also provide targets, with hitting the target the strategy for attacking disease-causing bacteria or viruses. One could design a drug that attaches to or occupies the active site of a target organism's enzyme. For example, penicillin destroys an enzyme crucial to the **synthesis** of bacterial cell walls. In the treatment of AIDS, HIV protease inhibitors target the viral enzyme protease.

synthesis: combination of starting materials to form a desired product

Properties and Mechanism

In some cases, the increase in the rate of an enzyme-catalyzed reaction versus the uncatalyzed rate is a millionfold. As soon as one reaction has been catalyzed, the enzyme is available for another round of **catalysis**—a phenomenon known as turnover. Enzymes operate near physiological temperature and pH, and they are also highly specific in their actions—for example, an enzyme called hexokinase will place a phosphate group only onto the sixth carbon of a D-glucose molecule. The enzyme has no activity toward L-glucose, and reduced activity toward other D-sugars. Enzymes can also be regulated so that they are switched on only when they are needed by the cell. They may consist of a single **polypeptide** chain of amino acids (RNAse contains 124 amino acids), or they may require an additional chemical called a coenzyme. Many of the **vitamins** as well as several **metals** act as coenzymes.

catalysis: the action of effect of a substance in increasing the rate of a reaction without itself being converted

polypeptide: compound containing two or more amide units—C(O)NH—produced by the condensation of two or more amino acids

vitamins: organic molecules needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

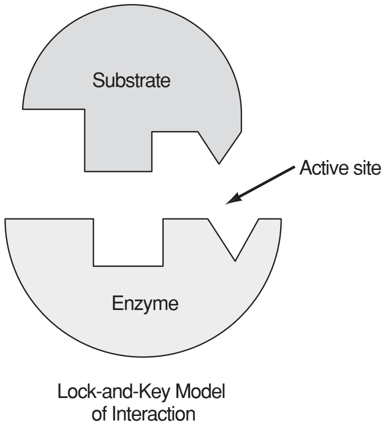
metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

A study of enzyme catalysis is a study of kinetics, which asks the question "how fast?" However, enzymes cannot alter the outcome or direction of a reaction. For instance, if one were to add a small amount of sodium chloride to a large volume of water, we know that the end result will be that the salt will dissolve in the water. However, the time dissolution takes depends on a number of factors: What is the temperature?; Is it being stirred? This is kinetics. We also know that a swinging pendulum will eventually come to rest at its **equilibrium** point, which in this case is its pointing straight down toward the center of Earth. Kinetics describes only the time it takes to reach that point. Enzymes cannot alter the equilibrium point of a reaction, only the time it takes to get there.

equilibrium: condition in which two opposite reactions are occurring at the same speed, so that concentrations of products and reactants do not change

To proceed to products, reactants must come together with sufficient energy to overcome an energy barrier known as the energy of activation. The apex of this barrier represents the transition state between reactants and products. Enzymes act to lower the energy of activation by stabilizing (lowering the energy of) the transition state.

Mechanistically, an enzyme will bind the reactant, called the substrate, at a very specific site on the enzyme known as the active site. This resulting enzyme–substrate complex (ES), described as a lock-and-key mechanism, involves weak binding and often some structural changes—known as induced fit—that assist in stabilizing the transition state. In the unique microenvironment of the active site, substrate can rapidly be converted to product resulting in an enzyme=product (EP) complex that then dissociates to release product.



A lock-and-key model of the interaction of an enzyme and substrate.

Nomenclature

Enzyme nomenclature has historically been at the whim of the discoverer of the enzyme. Many enzyme names give clues to their actions or to where they are found. The meat tenderizer papain can be obtained from the papyrus plant. Pepsin is a digestive enzyme found in the stomach. Lysozyme acts to lyse bacterial cell walls. Most enzymes are now named by their function along with the suffix "–ase." For instance, ethanol is metabolized in the liver by alcohol dehyrogenase. Phosphates are removed from molecules by phosphatases. An international body known as the Enzyme Commission (EC) has assigned numerical designations, called EC numbers, to enzymes. The EC has listed six categories based on type of activity (oxidation-reduction, hydrolysis, etc.), along with several subcategories, into which enzymes are placed. For example, alcohol dehydrogenase is EC 1.1.1.1.

Enzyme Kinetics

The rate of an enzyme-catalyzed reaction varies with the substrate concentration. At very low substrate concentrations, the rate will be directly proportional to the concentration of the substrate and will exhibit first-order kinetics. However, at very high substrate levels, all of the active sites are occupied and substrate molecules must wait their turn, just as the traffic at a line of tollbooths depends on how fast the cars can pass through the gates. This represents saturation, and the reaction rate is at its maximum and is designated V_{max}.

Other factors that influence enzyme activity include pH and temperature. Most mammalian enzymes operate maximally at around physiological pH and body temperature. There are several exceptions. The stomach digestive enzyme pepsin works best at around pH 2.0, the approximate pH of the stomach. Bacteria found in hot springs have enzymes that operate at or near the boiling point of water. In most cases, however, extremes of pH or temperature will destroy enzymes in an enzyme-unfolding process known as denaturation. Only one, very precise, three-dimensional configuration or fold of the chain of amino acids is functional. Denatured or unfolded proteins are inactive. Denaturation can be observed when an egg white is cooked: The proteins in the egg white unfold and form a gel-like aggregate with other unfolded proteins. The same occurs when bacteria spoil milk by lowering its pH sufficiently to unfold and curdle milk proteins.

RNA as an Enzyme

Although enzymes are considered to be proteins, enzyme activity has recently been found in ribonucleic acid (RNA) in certain organisms. These "ribozymes" may yield clues to the origins of life on Earth. **DNA** needs

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

enzymes to replicate, whereas enzymes need the instructions of DNA. This represents a "chicken-and-egg" question that has stumped researchers. Early life may have used RNA that was able to catalyze its own replication. SEE ALSO Catalysis and Catalysts; Coenzyme; Denaturation; Hydrogen; Inhibitors; Kinetics; Proteins; Ribonucleic Acid.

C. Larry Bering

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Epinephrine

adrenalin: chemical secreted in the body in response to stress

glucose: common hexose monosaccharide; monomer of starch and cellulose; also called grape sugar, blood sugar, or dextrose

Epinephrine, also known as **adrenalin**, is a hormone that is responsible for the "fight or flight" reaction in mammals. Chemically, it mobilizes the body's defense system, inducing the release into the blood of large amounts of **glucose** from stores in the liver and muscles. This burst of energy is the familiar "adrenalin rush" one experiences when frightened or excited. In some tissues, epinephrine also acts as a neurotransmitter, conveying signals between adjacent nerve cells.

tyrosine: one of the common amino acids

intermediate: molecule, often short-lived, that occurs while a chemical reaction progresses but is not present when the reaction is complete

Epinephrine (see Figure 1) is synthesized in several steps from either phenylalanine or **tyrosine** (both amino acids). Two adjacent hydroxyl groups are placed on the aromatic ring, leading to the ring structure called catechol. These hydroxylations form the **intermediate** L-dopa, which in turn is converted to dopamine (a neurotransmitter), norepinephrine (also a neurotransmitter), and finally epinephrine. Epinephrine together with norepinephrine and dopamine make up the family of biogenic amines called catecholamines.

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

synthesis: combination of starting materials to form a desired product

Nerve signals to the adrenal gland activate the conversion of stores of norepinephrine to epinephrine and its release into the bloodstream. The fight or flight reaction includes increased blood glucose, increased vasoconstriction in certain parts of the body, and increased heart rate. At the cellular level, epinephrine binds to liver and muscle cells at specific **receptors** on the outside surface of cell membranes. Such a receptor then activates a series of enzymatic reactions inside the cell, culminating in the **synthesis** of large amounts of cyclic adenosine monophosphate (cAMP). Epinephrine cannot cross the cell membrane, so its hormonal signal is transmitted inside the cell via cAMP, acting as a second messenger (epinephrine being the first messenger). CyclicAMP switches on a cascade of enzymes—mostly kinases that place a phosphate group at specific sites on other proteins or enzymes. These phosphorylations serve to activate (or in some cases inhibit) enzymatic reactions. The end result is the activation of glycogen phosphorylase, an enzyme that breaks down glycogen into its glucose units, and the release of glucose into the bloodstream.

metabolites: products of biological activity that are important in metabolism

The neurotransmitter action of epinephrine is terminated by reuptake into the neuron that released it, or breakdown to inactive **metabolites** by the enzymes catechol-O-methyl transferase (COMT) and monoamine oxidase (MAO). The second messenger effects inside the cell are terminated by enzymes that break down cAMP, and by phosphatases that reverse the action of the kinases by removing phosphates.

Epinephrine also acts at a crucial regulatory step in the synthesis of fatty acids. The activity of the first enzyme in fatty acid synthesis, acetyl-coenzyme A (AcCoA) carboxylase, is regulated by **phosphorylation**. The phosphorylated enzyme is inactive (and subsequent fatty acid synthesis is halted), whereas the dephosphorylated enzyme is active. Epinephrine, through the second messenger cAMP, prevents the dephosphorylation of AcCoA carboxylase, rendering it inactive and halting the synthesis of fatty acids. Indeed, during the fight or flight reaction, the organism needs to release energy in the form of glucose and fatty acids rather than store energy as glycogen or fat.

Clinically, epinephrine plays a lifesaving role in countering the effects of anaphylactic shock. Histamines released in large amounts upon the body's exposure to an allergen (bee stings in certain individuals, for instance) can constrict smooth muscle, including that in the airway passages. Epinephrine does the opposite: It relaxes smooth muscle, though at different receptors. Its effects on heart muscle (increasing the heart rate) can be used as a lifesaving measure when a patient's heart has stopped. Epinephrine is also used in conjunction with local anesthetics such as lidocaine. By constricting blood vessels near the site of the injection, it keeps the anesthetic from diffusing away from the site. SEE ALSO Kinase.

C. Larry Bering

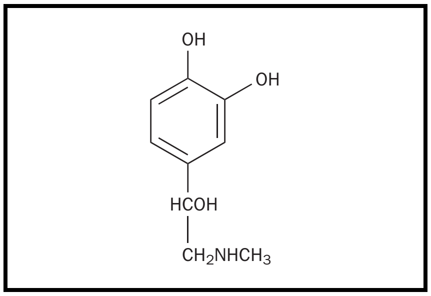

Figure 1. Chemical structure of epinephrine.

phosphorylation: the process of addition of phosphates into biological molecules

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Equations, Chemical

Chemical reactions convert reactants to products, whose properties differ from those of the reactants. Chemical equations are a compact and convenient way to represent chemical reactions. They have the general form

$$\text{Reactant(s)} \rightarrow \text{Product(s)}$$

The arrow in the equation means "changes to" or "forms." The reaction of gaseous nitrogen with hydrogen to produce ammonia, NH_3, is represented by the chemical equation

$$\underbrace{N_2 + 3\ H_2}_{\text{Reactants}} \rightarrow \underbrace{2\ NH_3}_{\text{Product}}$$

Although there are thousands of chemical reactions, a significant number of them, especially those that are not organic reactions, can be classified according to four general patterns: combination, decomposition, displacement, and exchange.

1. Combination. A combination reaction is one in which two or more substances (the reactants) are combined directly to form a single product (the product). An example is the reaction in which sodium (Na) combines with chlorine (Cl_2) to form sodium chloride, or table salt (NaCl).

A reaction of sodium with chlorine to produce sodium chloride is an example of a combination reaction.

$$2\ \mathrm{Na} + \mathrm{Cl_2} \rightarrow 2\ \mathrm{NaCl}$$

The physical states of reactants and products are included where necessary. The symbols used are: (*s*) for solid, (*l*) for liquid, (*g*) for gas, and (*aq*) for aqueous (water) solutions. In the case of sodium chloride formation, the equation is modified accordingly.

$$2\ \mathrm{Na}\ (s) + \mathrm{Cl_2}\ (g) \rightarrow 2\ \mathrm{NaCl}\ (s)$$

2. Decomposition. A decomposition reaction can be considered to be the reverse of a combination reaction. In a decomposition reaction, one substance (the reactant) decomposes to form two or more products. For example, calcium carbonate (limestone) decomposes at high temperatures to calcium oxide (lime) and carbon dioxide. This reaction is used industrially to produce large quantities of lime.

$$\underset{\substack{\text{calcium}\\ \text{carbonate}}}{\mathrm{CaCO_3}\ (s)} \rightarrow \underset{\substack{\text{calcium}\\ \text{oxide}}}{\mathrm{CaO}\ (s)} + \mathrm{CO_2}\ (g)$$

3. Displacement. A displacement reaction (also called a single replacement reaction) occurs when an element reacts with a compound to form a new compound and release a different element. An example is the reaction that releases silicon (Si) from silicon dioxide (sand), SiO_2, via its reaction with carbon. Carbon monoxide, CO, is the reaction's other product. When further purified, the silicon can be used in computer chips.

$$\mathrm{SiO_2}\ (s) + 2\ \mathrm{C}\ (s) \rightarrow \mathrm{Si}\ (s) + 2\ \mathrm{CO}\ (g)$$

4. Exchange. During an exchange reaction, "partners" in compounds exchange their partners. One type of exchange reaction is called a neutralization reaction, the reaction between an acid and a base. The reaction of sodium hydroxide (lye), NaOH, with hydrochloric acid, HCl, to produce NaCl and water is such a reaction. In this case, Na^+ switches partners from OH^- to Cl^-, and H^+ from $Cl^-$to OH^-.

$$\mathrm{NaOH}\ (aq) + \mathrm{HCl}\ (aq) \rightarrow \mathrm{NaCl}\ (aq) + \mathrm{H_2O}\ (l)$$

Organic chemical reactions, those in which carbon plays a predominant role, are very important in biochemical systems and industrial processes. These reactions can also be represented by balanced chemical equations, a few examples of which are given.

The fermentation of glucose to produce ethyl alcohol (ethanol)

$$\underset{\text{glucose}}{\mathrm{C_6H_{12}O_6}} \rightarrow 2\ \underset{\text{ethanol}}{\mathrm{C_2H_5OH}} + 2\ \mathrm{CO_2}$$

The synthesis of acetylsalicylic acid (aspirin) from the reaction of salicylic acid with acetic anhydride

$$2\ \underset{\substack{\text{salicylic}\\ \text{acid}}}{\mathrm{C_7H_6O_3}} + \underset{\substack{\text{acetic}\\ \text{anhydride}}}{\mathrm{C_4H_6O_3}} \rightarrow 2\ \underset{\text{aspirin}}{\mathrm{C_9H_8O_4}} + \mathrm{H_2O}$$

The formation of a triglyceride (a fat), such as the biochemical synthesis of tristearin via the reaction of stearic acid with glycerol:

$$3\ \underset{\substack{\text{stearic}\\ \text{acid}}}{\mathrm{C_{18}H_{36}O_2}} + \underset{\text{glycerol}}{\mathrm{C_3H_8O_3}} \rightarrow \underset{\text{tristearin}}{\mathrm{C_{57}H_{110}O_6}} + 3\ \mathrm{H_2O}$$

Matter is conserved in chemical reactions: *The total mass of the products equals the total mass of the reactants.* Chemical equations reflect this conservation. It is why chemical equations must be balanced. Atoms have mass, and the numbers of each kind of atom on each side of the equation must be the same. Coefficients, the numbers to the left of the formulas, are used to balance equations. Many equations can be balanced directly by simply adjusting the coefficients, as illustrated in the equations given above. Other equations are more difficult to balance, such as that for the decomposition of nitroglycerine (an explosive)

$$4\ C_3H_5(NO_3)_3\ (l) \rightarrow 12\ CO_2\ (g) + 10\ H_2O\ (l) + 6\ N_2\ (g) + O_2\ (g)$$

and this complicated reaction involving several reactants and products

$$\begin{aligned}&4\ CuSCN + 7\ KIO_3 + 14\ HCl \rightarrow \\ &\qquad 4\ CuSO_4 + 7\ KCl + 4\ HCN + 7\ ICl + 5\ H_2O\end{aligned}$$

Balanced chemical equations provide a significant amount of information. Consider the equation for photosynthesis, the natural process by which green plants form glucose, $C_6H_{12}O_6$, and oxygen from the reaction of carbon dioxide with water.

$$\underbrace{6\ CO_2 + 6\ H_2O}_{\text{Reactants}} \rightarrow \underbrace{C_6H_{12}O_6 + 6\ O_2}_{\text{Products}}$$

This balanced equation and its coefficients can be interpreted as indicating that six carbon dioxide molecules and six water molecules react to form one molecule of glucose and six oxygen molecules, each containing two oxygen atoms. A coefficient multiplies the term following it. The "6 CO_2" denotes six CO_2 molecules containing a total of six carbon atoms and twelve oxygen atoms.

$$6\ CO_2\ \text{molecules} \times \frac{1\text{C atom}}{1CO_2\ \text{molecule}} = 6\ \text{C atoms}$$

$$6\ CO_2\ \text{molecules} \times \frac{2\ \text{O atoms}}{1CO_2\ \text{molecule}} = 12\ \text{O atoms}$$

Applying these concepts to the remainder of the balanced equation yields information that confirms that the equation is balanced—the atom counts for both sides of the equation are the same.

Reactants	Products
Carbon atoms = 6	Carbon atoms = 6
Hydrogen atoms = 12	Hydrogen atoms = 12
Oxygen atoms = 12 + 6 = 18	Oxygen atoms = 6 + 12 = 18

Coefficients also apply to a larger scale, in which the counting unit is the mole (there are 6.02×10^{23} molecules per mole of a compound), rather than individual molecules. Thus, this balanced equation also represents the reaction of six moles of glucose with six moles of water to produce one mole of glucose and six moles of oxygen.

Oxidation-reduction (redox) reactions are an important, general kind of reaction, one involving the transfer of electrons. Oxidation is the *loss* of an electron or electrons from an element, ion, or compound. Reduction is the *gain* of an electron or electrons from an element, ion, or compound. The two processes occur simultaneously; electrons released during oxidation are gained in a reduction process. In every redox reaction, a reactant is oxidized (loses electrons) and a reactant is reduced (gains electrons). During a redox reaction there is a change in oxidation numbers—evidence of a redox reaction. An oxidation number compares the charge of an uncombined atom, one not in a compound, with its actual or relative charge when it is part of a compound. Oxidation numbers are zero, positive, or negative.

These guidelines are used to determine oxidation numbers.

- Atoms of pure elements, that is, atoms not combined with any *other* element, have an oxidation number of zero. For example, sodium in metallic sodium, Na; oxygen in molecular oxygen, O_2; and chlorine in molecular chlorine, Cl_2, each have an oxidation number of 0.
- Monatomic ions have an oxidation number equal to the charge of the ion. Thus, a sodium ion, Na^+, has an oxidation number of +1; that of chlorine in a chloride ion, Cl^-, is −1.
- Generally, hydrogen atoms in compounds have an oxidation number of +1; oxygen atoms in compounds are typically −2.
- The sum of oxidation numbers in a neutral compound is zero. Water, H_2O, is an example. Hydrogen: $2\ H \times (+1/H) = +2$; oxygen: $1\ O \times (-2/O) = -2$; $(+2) + (-2) = 0$
- The sum of oxidation numbers of the atoms in a polyatomic ion equals the charge on the ion. For example, the sulfate ion, SO_4^{-2}, a polyatomic ion, has a net charge of −2. Each oxygen in a sulfate ion has an oxidation number of −2, and four oxygens add up to −8. For the sulfate ion to have a net −2 charge, sulfur must have a +6 oxidation number: $-2 = 4(-2) + 6$.

Oxidation numbers and their changes can be used to identify the reaction of sodium with chlorine to form NaCl as a redox reaction.

$$2\ Na + Cl_2 \rightarrow 2\ NaCl$$

Reactant	Products
Oxidation number	Oxidation number
$Na = 0$	$Na^+ = +1$
$Cl = 0$	$Cl^- = -1$

During this reaction, reactant sodium atoms (oxidation number 0) are converted to sodium ions (oxidation number +1); reactant chlorine atoms (oxidation number 0) are transformed to chloride ions (oxidation number −1). Because there is a change in the oxidation numbers of the reactants during the reaction, this is a redox reaction. The definitions of oxidation and reduction can be broadened a bit using oxidation numbers: Oxidation is an *increase* in oxidation number; reduction is a *decrease* in oxidation number. The gain in oxidation number occurs because electrons are lost during oxidation; the gain of electrons during reduction causes a decrease in the oxidation number. This can be shown by using so-called half-reactions for each process.

$$\text{Oxidation half-reaction: } Na \rightarrow Na^+ + e^-$$

$$\text{Reduction half-reaction: } Cl_2 + 2\ e^- \rightarrow 2\ Cl^-$$

Notice in the balanced equation that two moles of Na were used to react with the two moles of chlorine atoms in one mole of Cl_2. Each mole of Na lost one mole of electrons; each mole of chlorine atoms gained a mole of electrons. Two moles of electrons were transferred to form two moles of NaCl. The overall reaction is the sum of the two half-reactions; the moles of electrons cancel, and the sodium ions and chloride ions combine to form sodium chloride. Note that the sum of the oxidation numbers in sodium chloride is zero: (+1) + (−1) = 0.

$$\text{Oxidation half-reaction: } 2\ \text{Na} \rightarrow 2\ \text{Na}^+ + 2\ e^-$$

$$\text{Reduction half-reaction: } \text{Cl}_2 + 2\ e^- \rightarrow 2\ \text{Cl}^-$$

$$\text{Overall reaction: } 2\ \text{Na} + \text{Cl}_2 \rightarrow 2\ \text{NaCl}$$

Oxidation-reduction reactions, even complex ones, can be balanced using either the half-reaction method or the oxidation number method. The half-reaction method will be discussed first, using the reaction of iron with chlorine to produce iron chloride.

$$\text{Fe} + \text{Cl}_2 \rightarrow \text{FeCl}_3 \text{ (unbalanced equation)}$$

Half-Reaction Method

Step 1. Divide the reaction into two half-reactions; one corresponding to oxidation, the other, reduction.

$$\text{Oxidation: Fe} \rightarrow \text{Fe}^{3+}$$

$$\text{Reduction: Cl}_2 + \rightarrow \text{Cl}^-$$

Step 2. Balance each half-reaction for mass and then charge. The iron half-reaction is balanced with respect to mass because there is one iron on each side. However, the charge is not balanced; the left side has a charge of zero, the right side has a charge of +3. Charge is balanced by adding three electrons to the right side.

$$\text{Fe} \rightarrow \text{Fe}^{3+} + 3\ e^-$$

The chlorine half-reaction is unbalanced in terms of mass and charge. Mass balance is achieved by using a coefficient of 2 on the right side.

$$\text{Cl}_2 \rightarrow 2\ \text{Cl}^-$$

Charge is then balanced by adding two electrons to the left side.

$$\text{Cl}_2 + 2\ e^- \rightarrow 2\ \text{Cl}^-$$

The two half-reactions indicate that three electrons are lost per Fe atom during oxidation, and that two electrons are gained as each Cl_2 molecule is reduced.

Step 3. Combine the two half-reactions in such a way as to balance the electrons lost and gained. The oxidation half-reaction lost three electrons; the reduction half-reaction gained two electrons. Therefore, to balance electrons lost and gained, multiply the oxidation half-reaction by 2 and the reduction half-reaction by 3. Add the resulting half-reactions to get the final balanced equation for the formation of $FeCl_3$. Note that, in doing so, the electrons cancel (as they should if the final equation is balanced).

$$2\ [\text{Fe} \rightarrow \text{Fe}^{3+} + 3\ \text{e}^-] \rightarrow 2\ \text{Fe} \rightarrow 2\ \text{Fe}^{3+} + 6\ e^-$$

$$3\ [Cl_2 + 2\ e^- \rightarrow 2\ Cl^-] \rightarrow 3\ Cl_2 + 6\ e^- \rightarrow 6Cl^-$$

The Fe^{3+} and Cl^- ions combine to form $FeCl_3$ and the overall balanced equation is

$$2\ Fe + 3\ Cl_2 \rightarrow 2\ FeCl_3$$

The half-reaction method can be applied to more complex redox reactions, such as the reaction of permanganate ion, MnO_4^-, with Fe^{2+} in acidic solution.

$$MnO_4^-\ (aq) + Fe^{2+}\ (aq) \rightarrow Mn^{2+}\ (aq) + Fe^{3+}\ (aq)\ \text{(unbalanced equation)}$$

Step 1. Oxidation: $Fe^{2+}\ (aq) \rightarrow Fe^{3+}\ (aq)$
Reduction: $MnO_4^-\ (aq) \rightarrow Mn^{2+}\ (aq)$

Step 2. Mass and charge balance are achieved this way:

The iron is balanced by adding one electron on the right

$$Fe^{2+}(aq) \rightarrow Fe^{3+}\ (aq) + e^-$$

To balance oxygen, we use H_2O on the right side; to balance hydrogen, we use H^+ on the left side (recall that the reaction is taking place in acidic solution)

$$8\ H^+\ (aq) + MnO_4^-\ (aq) \rightarrow Mn^{2+}\ (aq) + 4\ H_2O\ (l)$$

The reduction half-reaction has a net charge of +7 on the left [(8+) + (−1)] and +2 on the right [(+2) + 0]. Adding 5 electrons to the left side balances the charge.

$$8\ H^+\ (aq) + MnO_4^-\ (aq) + 5\ e^- \rightarrow Mn^{2+}\ (aq) + 4\ H_2O\ (l)$$

Step 3. Equalize the electrons transferred. Multiply the oxidation half-reaction by 5. Add the half-reactions, canceling the electrons.

$$5\ Fe^{2+}\ (aq) \rightarrow 5\ Fe^{3+}\ (aq) + 5\ e^-$$

$$8\ H^+\ (aq) + MnO_4^-\ (aq) + 5\ e^- \rightarrow Mn^{2+}\ (aq) + 4\ H_2O(l)$$

Balanced equation: $5\ Fe^{2+}\ (aq) + 8\ H^+\ (aq) + MnO_4^-\ (aq) \rightarrow$
$5\ Fe^{3+}\ (aq) + Mn^{2+}\ (aq) + 4\ H_2O\ (l)$

Oxidation Number Method

$MnO_4^-\ (aq) + Fe^{2+}(aq) + H^+\ (aq) \rightarrow$
$Mn^{2+}\ (aq) + Fe^{3+}\ (aq)\ H_2O\ (l)$ (unbalanced equation)

As in the half-reaction method, H_2O is used to balance oxygen, and H^+ is used to balance hydrogen.

Step 1. Identify the oxidation number of each element on each side of the equation. Determine which has undergone oxidation and which has undergone reduction. This is indicated in Table 1.

Element	Oxidation Number as Reactant	Oxidation Number as Product	Change in Oxidation Number	Oxidation or Reduction
Mn	+7	+2	Decrease by 5	Reduction
O	−2	−2	0	Neither
Fe	+2	+3	Increase by 1	Oxidation
H	+1	+1	0	Neither

Table 1.

Step 2. Use coefficients so that the total increase in oxidation number equals the total decrease. In this case, the total decrease is 5 (Mn^{+7} becomes Mn^{2+}), and the total increase must also be 5; each iron must be multiplied by 5: (5 Fe^{2+} becomes 5 Fe^{3+}). Balance hydrogen and oxygen in the usual manner. The balanced equation is

$$MnO_4^- (aq) + 5\, Fe^{2+} (aq) + 8\, H^+ (aq) \rightarrow Mn^{2+} (aq) + 5\, Fe^{3+} (aq) + 4\, H_2O\, (l)$$

SEE ALSO Chemical Reactions; Inorganic Chemistry; Mole Concept; Organic Chemistry.

Conrad L. Stanitski

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Equilibrium

A state of equilibrium exists in a process when the rate of the forward process equals the rate of the reverse process. The equilibrium condition exists in relation to thermal, mechanical, and chemical changes. For example, within a closed flask, liquid water evaporates to form vapor, and at the same time the vapor condenses to form liquid. When the rate of evaporation equals the rate of condensation, the system is said to be in a state of equilibrium:

$$\textbf{liquid} \underset{\text{condensation}}{\overset{\text{evaporation}}{\rightleftharpoons}} \textbf{vapor}$$

A state of thermal equilibrium exists when the heat loss of a system is equal to the heat gain. Chemical equilibrium exists when a reversible chemical reaction occurs within a closed system, such as a sealed flask, and the rate of the reaction in the forward direction equals the rate of the reaction in the reverse direction. For example: $N_2 + 3H_2 \rightleftarrows 2NH_3$.

In this reaction, nitrogen and hydrogen gases react to form gaseous ammonia, NH_3. When nitrogen and hydrogen are first introduced into the reaction chamber, they begin to form ammonia molecules. As the concentration of ammonia increases, ammonia molecules start to decompose, forming nitrogen and hydrogen. When the rate at which ammonia is formed equals the rate at which it decomposes, the system is at equilibrium. A reaction at equilibrium never goes completely to completion; molecules of reactants continue to collide to form product molecules, and product molecules constantly decompose to form reactant molecules.

A state of mechanical equilibrium is a special physical state in which the external forces and moments on an object are zero. All forces are balanced, and the object is at rest. Examples of systems in mechanical equilibrium include a ball hanging motionless on a string and a mass suspended motionless from a spring.

Every equilibrium system follows predictable mathematical rules. The law of mass action states that the product of the concentrations of a reaction's products, each raised to the power of the coefficient of the species, divided by the product of the concentrations of the reactants, each raised to the power of the coefficient of the species, is a constant at constant temperature. Thus for the ammonia reaction:

$$N_2 + 3\ H_2 \rightleftarrows 2\ NH_3$$

The equation describing the equilibrium reaction is called an equilibrium expression, and K_{eq}, the equilibrium constant, is a definite numerical value for each equilibrium reaction. The equilibrium constant for a particular reaction is specific for that reaction and changes only with variations in temperature. The presence of a catalyst does not alter K_{eq} but does cause the reaction to reach equilibrium more rapidly.

The size of K_{eq} can be used to predict whether the reaction goes further toward completion (results in the formation of large quantities of products) or favors reactants (results in higher concentrations of reactants present at equilibrium). For example, hydrogen and iodine react at 200°C (392°F) to form hydrogen iodide in the following equilibrium reaction: $H_2 + I_2 \rightleftarrows 2HI$. The value of K_{eq} for the reaction has been determined to be 50, experimentally. At equilibrium, if the concentrations of hydrogen and iodine were 1.0 moles per liter, the concentration of hydrogen iodide would be $\sqrt{50}$ or 7.1 moles per liter.

$$K_{eq} = \frac{[NH_3]^2}{[N_2]\ [H_2]^3}$$

Le Châtelier's principle states that if a stress is brought to bear upon a system at equilibrium, the equilibrium reaction shifts in a direction that relieves the stress. Put more simply, if the concentration of one of the reactants or products is increased at equilibrium, the reaction moves in the direction that consumes the added material. Adding hydrogen and iodine to the reaction mixture above would result in the formation of more hydrogen iodide.

STP: standard temperature and pressure

Similarly, adding hydrogen and nitrogen to the reaction mixture that forms ammonia would result in the formation of more ammonia, and removing ammonia would shift the equilibrium to the right, forming even more ammonia. Ammonia, hydrogen, and nitrogen are all gases, and one mole of each gas occupies a volume of about 22.4 liters at **STP**. In the reaction $N_2 + 3H_2 \rightleftarrows 2NH_3$, 22.4 liters of nitrogen react with 3 times 22.4 liters of hydrogen to form 44.8 liters of ammonia. This means that 4 times

22.4 liters of reactants form 2 times 22.4 liters of products. Le Châtelier's principle predicts that increasing pressure on the system at equilibrium causes the equilibrium to shift to the right. Therefore, ammonia is manufactured in a continuous loop by pumping in N_2 and H_2 and removing NH_3 by liquefaction as it is formed, causing the unreacted N_2 and H_2 to form more ammonia. The presence of a catalyst helps the hydrogen and nitrogen molecules interact to form ammonia more rapidly.

Equilibrium constants are dependent upon the temperature of the system. Formation of ammonia is exothermic—heat is released as the reaction occurs: $N_2 + 3H_2 \rightleftarrows 2NH_3 + 93.7$ kilojoules of energy. Therefore, cooling the reaction mixture favors the formation of even more ammonia.

Systems may be in chemical or mechanical equilibrium, and they may also exhibit thermal equilibrium. If a hot object is placed in contact with a colder mass of the same material inside an insulated container, heat flows from the hot object into the colder object until the temperatures of the two are equal. Heat lost by the warm object is equal to the amount gained by the cold object. The amount of heat needed to raise the temperature of an object a certain amount is equal to the amount which that object would lose in cooling by the same amount. The amount of heat needed to warm or the amount lost when cooling equals the product of the specific heat (or heat capacity) of the substance, the mass, and the change in temperature. For example, if a 50-gram (1.8-ounce) piece of silver at 70°C (158°F) is placed in 50 grams (1.8 ounces) of water at 15°C (59°F), the principle of thermal equilibrium can be used to calculate the final temperature of the water and silver:

$$K_{eq} = \frac{[HI]^2}{[H_2]\ [I_2]} = 50$$

At equilibrium, if the concentrations of hydrogen and iodine were 1.0 mole/Liter, the concentration of hydrogen iodide would be $\sqrt{50}$ or 7.1 moles/Liter.

As a result of heat flowing from the silver into the water to establish a thermal equilibrium between the two, the final temperature of the silver and water is 18.1°C (64.6°F). SEE ALSO CHEMICAL REACTIONS; THERMODYNAMICS.

Dan M. Sullivan

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Erbium

MELTING POINT: **1,529°C**
BOILING POINT: **2,510°C**
DENSITY: **9.07 g cm^{-3}**
MOST COMMON ION: **Er^{3+}**

Er
68
167.26

Erbium is a chemical element. Its ground state electronic configuration is $[Xe]4f^{12}\ 6s^2$. Natural erbium is a mixture of six stable **isotopes**. Monazite

isotope: form of an atom that differs by the number of neutrons in the nucleus

rare earth elements: older name for the lanthanide series of elements, from lanthanum to lutetium

lanthanides: a family of elements from lanthanum to lutetium having from 1 to 14 4f electrons

and xenotime are the principal erbium ores, in which erbium occurs together with other members of the **rare earth elements**, or the **lanthanides**. It can be separated from the other rare earths by ion exchange or solvent extraction techniques. The discovery of erbium is attributed to Carl G. Mosander (1842). Its name is derived from Ytterby, a small town in Sweden, where the first rare earth mineral (gadolinite) had been found. The elements ytterbium, yttrium, and terbium have also been named after the town of Ytterby.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

ductile: property of a substance that permits it to be drawn into wires

Pure erbium **metal** was first prepared in 1934. It is a silver-white, malleable, and **ductile** metal. The metal is not oxidized as rapidly as other rare earth metals when exposed to air. Erbium chemistry is dominated by the trivalent erbium(III) ion, Er^{3+}. Its chemical behavior resembles that of yttrium and the heavy rare earth elements. The ground state electronic configuration of Er^{3+} is [Xe]4f^{13}. Because of erbium's narrow absorption band in the green region of visible light (at wavelengths of ca. 530 nanometers, or 2.09×10^{-5} inches), erbium(III) salts are pink. Due to the high chemical stability of trivalent erbium, erbium(III) oxide is used to color glassware pink. Erbium is of importance to the technology of optical amplification in glass fibers. Erbium-doped crystals can be used to generate laser beams having wavelengths in the vicinity of 2,900 nanometers (1.14×10^{-4} inches). Such lasers are being used in laser surgery. The laser beam is strongly absorbed by water, so that the energy in hitting its target is confined to the surface layer of tissue. Phosphors based on erbium can convert infrared light to visible light (upconversion). SEE ALSO Cerium; Dysprosium; Europium; Gadolinium; Holmium; Lanthanides; Lanthanum; Lutetium; Neodymium; Praseodymium; Promethium; Samarium; Terbium; Ytterbium.

Koen Binnemans

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dialcohol: organic molecule containing two covalently bonded –OH groups

ketone: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the FC(O)R functional group

biosynthesis: formation of a chemical substance by a living organism

intermediate: molecule, often short-lived, that occurs while a chemical reaction progresses but is not present when the reaction is complete

synthesis: combination of starting materials to form a desired product

androgen: group of steroids that act as male sex hormones

functional group: portion of a compound with characteristic atoms acting as a group

passive diffusion: mechanism of transporting solutes across membranes

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

Estrogen

Estrogen is not one hormone, it is the name used to denote either of two steroid hormones. These hormones are noted for their role in the development of the secondary sexual characteristics of females. In mammals the most abundant (and most potent) estrogen is estradiol (a **dialcohol**: note the "-diol" suffix), followed by estrone (a **ketone**: note the *-one* suffix). As is true for the other steroid hormones, the major **biosynthetic** pathway for estrogen begins with cholesterol (C$_{27}$). The figure shows the major metabolic **intermediates** in the usual **synthesis** of estrogen, starting with cholesterol, proceeding to pregnenolone (C$_{21}$), an **androgen** (C$_{19}$), and then estrogen (C$_{18}$). Estrogen has an alcohol **functional group** at the C3 and C17 positions, and a methyl group at C13. A unique aspect of estrogen biosynthesis is the conversion (catalyzed by the enzyme aromatase) of the A ring to an aromatic ring.

Estrogen is produced in the ovaries and secreted into the blood, whereupon it enters target cells throughout the body. It enters the cells via **passive diffusion** and binds to specific proteins called estrogen **receptors**,

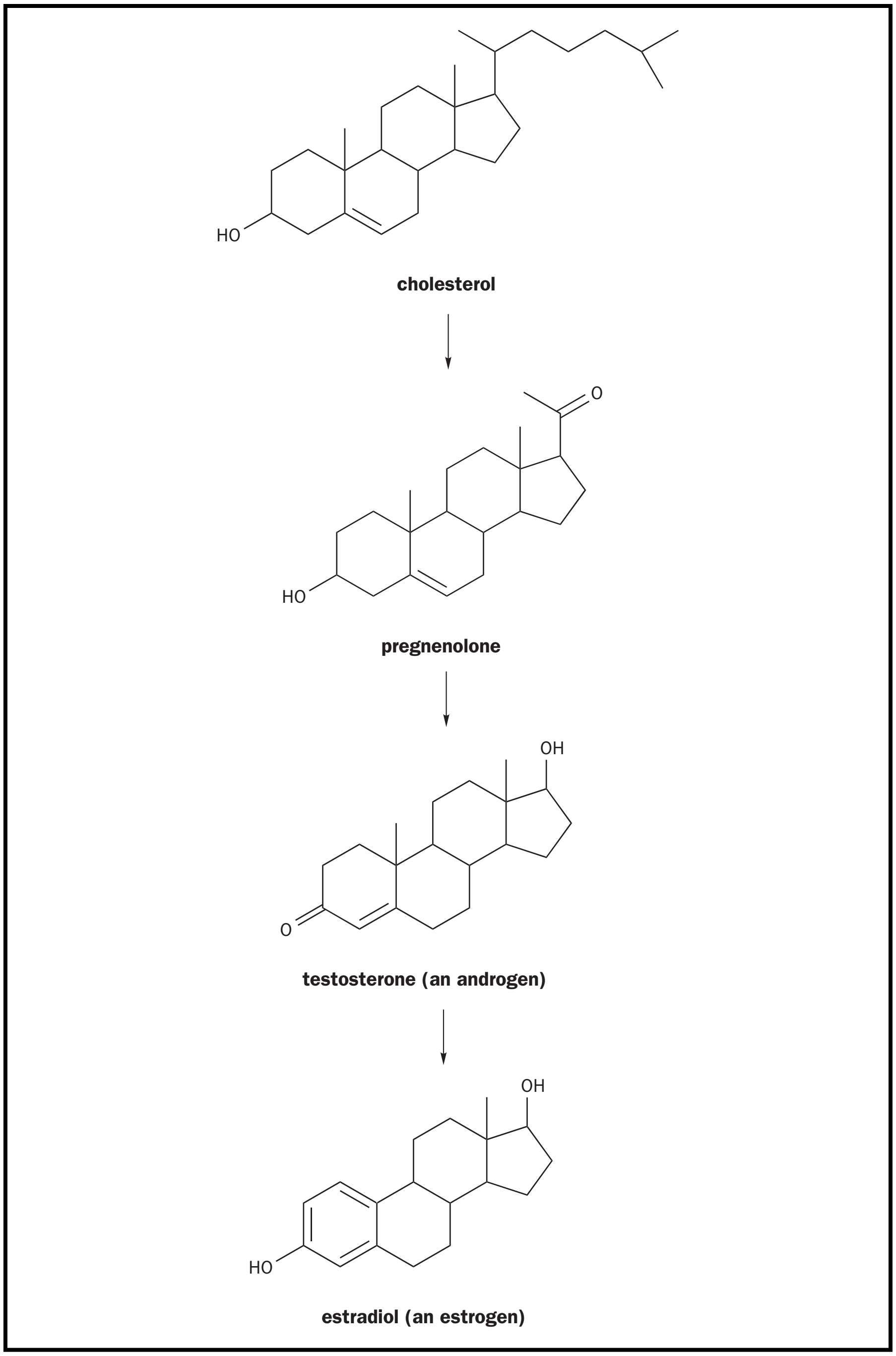

Figure 1. Major steroids in the synthesis of estrogen from cholesterol.

which reside in the cell nuclei. In the absence of estrogen, these receptors are functionally inactive. The binding of estrogen to a receptor activates the receptor, which can then bind to specific sites on the **DNA** to stimulate the **transcription** of a highly specific set of genes. As a result, the **metabolism** and the character of the cell changes.

In addition to its role in the development of the secondary sex characteristics in females, estrogen has important physiological functions in the cardiovascular, immune, and central nervous systems, as well as its effects on the growth and maturation of the long bones. It is also implicated in a number of diseases (including breast and uterine cancers) and in

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

transcription: enzyme-catalyzed assembly of an RNA molecule complementary to a strand of DNA

metabolism: all of the biochemical processes that take place within living organisms; comprises processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those that break down complex food molecules, thus liberating energy (catabolism)

EDWARD DOISY (1893–1986)

Before Edward Doisy earned the Nobel Prize for his research on vitamin K, he studied female hormones. It was at this time in 1936 that he isolated estradiol. In rodents without ovaries, small injections of this isolated compound were able to replicate the same behavior and biological processes as if the ovaries were still present.

—Valerie Borek

postmenopausal health problems, such as atherosclerosis, osteoporosis, and diminution of cognitive functions. Because these conditions, especially female cancers, are associated with estrogen, a number of anticancer treatments involve estrogen blockade: drugs that prevent estrogen from binding to its receptors. As a result, the receptors remain in an inactive form. SEE ALSO STEROIDS.

William M. Scovell

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Ethics

Chemistry, like any discipline, has a social structure. It relies on the interactions, behaviors, and expectations of individuals in order to function. Every social structure has a code of practices that constitutes its behavioral norms, that is, a set of rules governing what are acceptable and unacceptable behaviors. These rules are the moral philosophy of that social structure. When people find themselves in a situation in which there is a conflict or dilemma, the decision-making processes that they use to make the behavioral choices that follow are called ethical decision-making skills. Ethics, then, is the process whereby an individual, faced with a moral dilemma, arrives at a morally defensible decision.

What do these ideas have to do with science? The answer is that science as an undertaking is a quite human process that relies on many decisions. For example, progress in science relies on the complete honesty of those who report their experimental results, because (among other reasons) those results are key to the understanding of the natural phenomena under investigation. In addition, because scientific results are generally made public and accessible to all, it is extremely important that scientific results are trustworthy. If results are not reported honestly, then anyone who uses these results in his or her work has had his or her trust violated, and the injured party has wasted time and other resources. When the results impact a field such as medicine, or bear on product safety, an immense number of people could be put in harm's way because of decisions made on the basis of false information.

A scientist's past experience of ethical decision making is embedded in every value judgment he or she makes, large and small. Aspects of scientific enterprise that require ethical decision making encompass a broad range of responsibilities, including experiment design, the interpretation and report-

Stem cell research, a recent technological advance in which cells are grown to generate new tissue, has the scientific community facing new ethical issues.

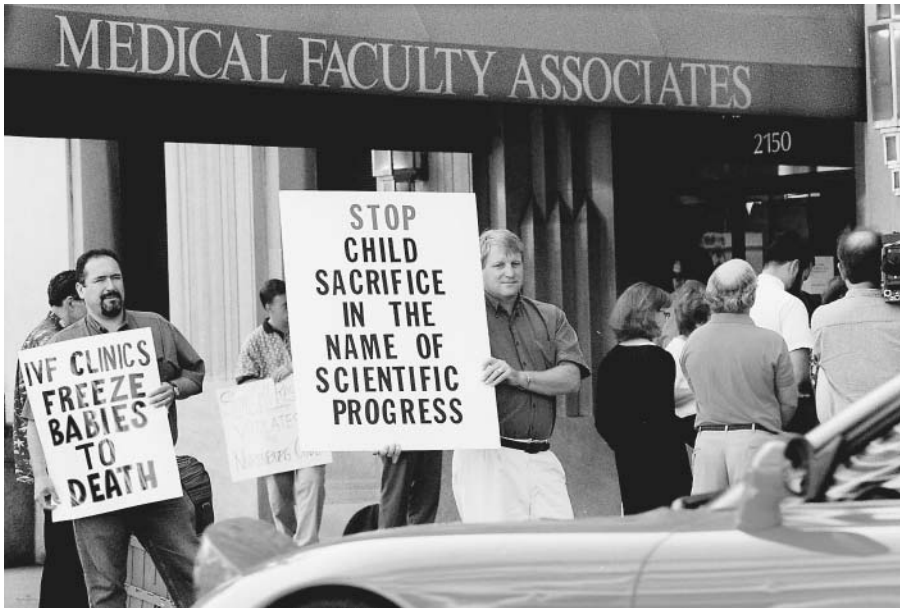
ing of data, interactions between collaborators, and the evaluation of colleagues.

When a scientist "cheats" for any reason, for instance by making up results or excluding selected data, the entire process of science is shaken. Other scientists and laypeople will make decisions based on the false reports that are generated, and these decisions could have devastating consequences. Imagine someone overseeing a clinical trial designed to test a medical treatment not disclosing a harmful side effect. Also imagine that people might actually be harmed because of such a nondisclosure. There are many reasons why a scientist might choose not to disclose potentially hurtful information. Perhaps he or she stands to make a financial profit from the sale of this medical treatment. Perhaps he or she is being pressured by a supervisor to report false results and is under threat of being fired. Personal gain at the expense of others is often the crux of willful misrepresentation of scientific experiments.

The use of human and animal subjects in drug testing is an area in which scientists must practice ethical reasoning in order to explore complex and contradictory ideas. There are all sorts of views held by all sorts of people on whether drug testing should be conducted on living beings. It is important for scientists to consider the moral philosophies that underlie these different perspectives, as they will have to make the decisions to proceed (or not) with such testing. Apart from the responsibilities of scientists, a nonscientist must sometimes decide, for example, whether she or he wants to be part of an organization that participates in such testing.

Topical Categories

Some ethical reasoning topics have been well debated over time, although every new technological advance spawns a new set of debates (for example, debates having to do with the uses of genetic information or research



Demonstrators outside George Washington University Hospital, Washington, D.C., protesting embryonic stem cell research.

involving stem cells). A violation of the standards of ethical scientific practice is called scientific misconduct. Some major categories of scientific misconduct, as outlined by the U.S. Department of Health and Human Resources, are:

- *Falsification of data.* Data fabrication (creating data that never existed). Selective reporting of findings. Omission of data that conflicts with other data (leaving out information in order to make one's story seem better). Willful suppression of data (not revealing relevant information) and/or distortion of data (exaggeration, for example).
- *Plagiarism.* Stealing the language, ideas, or thoughts of another and representing them as one's original work.
- *Improprieties of authorship.* Giving credit improperly or not giving credit at all in published materials. Publishing the same results in more than one place and claiming that each is an exclusively published report. Listing as authors individuals who have not made a definite contribution to the work published. Submission of multiauthored manuscripts to publishers without the agreement of all authors on the content of the text.
- *Misappropriation of the ideas of others.* An important aspect of scholarly activity is the exchange of ideas among colleagues. New ideas gleaned from such exchanges can lead to important discoveries. Scholars also acquire new ideas during the review of grant applications and scientific manuscripts. Improper use of information acquired in these ways could constitute fraud. Wholesale stealing of such material constitutes scientific misconduct.
- *Violation of generally accepted research practices.* Serious deviation from accepted practices in proposing or carrying out research. Any manipulation of experiments to bring about desired results. Deceptive statistical or analytical manipulation of results or improper reporting of results.

- *Material failure to comply with federal requirements affecting research.* Includes but is not limited to serious or substantial, repeated and/or willful violations involving the use of funds, care of animals, human subjects, investigational drugs, genetic products, new devices, or radioactive, biologic, or chemical materials.
- *Inappropriate behavior in relation to misconduct.* An inappropriate accusation of misconduct. Failure to report known or suspected misconduct. Withholding or destroying information relevant to a claim of misconduct. Retaliation against any person taking part in the allegation or investigation.
- *Deliberate misrepresentation of qualifications, experience, or research accomplishments (one's own or another's) to advance a research program, to obtain external funding, or to further other professional advancement.*
- *Misappropriation of funds or other resources.* For example, use of funds for personal gain.

An Example from Practice

The reproducibility of results is a hallmark of establishing reliable knowledge in scientific practice. In 2000 Professor Gérard Buono reported the results of a series of experiments carried out by him and his coworkers in France (Buono et al. 2000, p. 2554). In late 2001, Buono published a retraction of these results (Buono 2001, p. 4536). The retraction and accompanying story recounted in the text are an example of the self-correcting nature of ethical scientific practices. Buono describes how he was contacted by the editor of the journal that published the results and by Professor Scott E. Denmark, a scientific leader in the relevant area of chemistry who had not been able to reproduce the experimental results. In his retraction Buono writes, "At this stage, I asked my co-workers to check the experimental procedures and analytical conditions and to try to reproduce the described results. I was provided with experimental data and material that fully confirmed our original claims." After repetition of the experiments and upon close examination of his students' work, however, Buono saw evidence of error. He writes that he "noticed several inconsistencies with the analytical material the students had previously provided. Therefore, I decided to reproduce *personally* and *independently* the whole experimental procedures from the very beginning." Buono could not reproduce the results originally reported by him and his coworkers, but obtained the results reported by Denmark and his coworkers. Buono concluded this episode by writing that he wished "to withdraw [the original] communication. Other pieces of work based on related experimental results that were published elsewhere will also be withdrawn."

A Moral Education

Where and how do students learn about these ethics-related scientific practices? Historically, for scientists in training the process has been rather learn-as-you-go. It is generally assumed that senior scientists and teachers follow a code of defensible moral behavior and that, by their example, valuable lessons are transmitted to their students. Unfortunately, these assumptions are not necessarily valid, and cases of scientific misconduct surface in the news fairly regularly. By making ethical reasoning and the expectation of moral scientific behavior a more explicit part of education, it is hoped that the number of such cases can be reduced. The strategies for making rules of conduct explicit vary, and it is also hoped that many messages from many sources will impact the way scientists and future scientists make decisions.

In 1994 the editors of the Publications Division of the American Chemical Society (ACS) began publishing a series of articles titled "Ethical Guidelines to Publication of Chemical Research" in ACS journals. (See, for example, the *Journal of the American Chemical Society* [1994] 116[13]: 8A–10A.) These guidelines, revised in January 2000, define the ethical obligations of each participant in the science community who is responsible for bringing a scientific publication to that community, namely, the editors, authors, reviewers, and scientists publishing in the more popular science venues. As stated in the introduction to these guidelines, one characteristic of a profession is for its members to have an accepted code of behaviors, responsibilities and obligations, to one another and to the public. The advancement of science requires sharing information in an utterly honest and open fashion. Editors need to give unbiased consideration to all scientific reports submitted for publication in a timely and fair manner. Those who have the privilege of reviewing unpublished scientific results cannot use or disclose that information prior to its publication. Reviewers must also be sensitive to conflicts of interest; for example, a reviewer should not review a manuscript if it is authored by a person with whom the reviewer has a close personal relationship, or a relationship which would otherwise bias the reviewer's ability to judge the manuscript fairly. Authors are obliged to provide an accurate and honest account of their work, with enough information so that reviewers and readers can properly evaluate the validity of the information and reproduce the results.

In scientific research, as in business and medicine, the writing of and analysis of case studies are an effective formal vehicle for ethics instruction. Students, having been given an authentic narrative scenario to consider and debate, can practice ethical reasoning as they think through the moral issues that have been raised by a particular case. A case study debated in a classroom is a safe proceeding, because it is not an actual circumstance in which a student might face serious personal consequences. Educators hope that students, having to think through ethics-related dilemmas in classroom settings, can acquire the reasoning skills they are going to need when they are confronted with actual situations. The following is an excerpt from a case study.

> After only a few days in your new lab, you notice that one of the senior students is quite open about what appear to be many questionable experimental practices: he does not really keep a notebook, but numbers a new page for each reaction he performs and scribbles out a little information about what he had done, sometimes only the date and the starting time. . . . By now, his practices are quite well known in your particular lab room, and a number of jokes and asides by your labmates affirm your perceptions. Indeed, even the senior student has been heard to quip: "If I had done this the right way, I think the yield would have been 75%." When the research advisor comes to lab for a weekly update on progress, this student presents the data on the purified materials and reports a 75% yield. The research advisor and this student

have already published 3 papers based on his previous results. Who is potentially affected by this student's behavior? What are your options for possible actions? (Coppola, pp. 1506–1511)

It is important to understand that the educative development of ethical reasoning skills neither represents nor advocates a prescribed moral position, and does not commit a student in advance to dogmatic solutions to all moral problems. Ethics, or ethical reasoning, is the process by which the most defensible resolution to a moral dilemma is sought.

Brian P. Coppola

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Europium

MELTING POINT: **1,099K**
BOILING POINT: **1,800K**
DENSITY: **5,244/kg m^{-3}**
MOST COMMON IONS: **Eu^{3+}, Eu^{2+}**

63
Eu
EUROPIUM
151.97

Europium is a metallic element discovered in 1901 in Paris by the French scientist Eugène-Anatole Demarcay. It belongs to a series of elements called **lanthanides**, or 4f elements, extending from lanthanum (atomic number 57) to lutetium (atomic number 71). These elements have low abundances: Europium occurrence in Earth's crust is only 2.1 ppm (parts per million), that is, 2.1 grams (0.07 ounces) per metric ton, and in seawater, its concentration is as low as 4×10^{-8} ppm.

lanthanides: a family of elements (atomic number 57 through 70) from lanthanum to lutetium having from 1 to 14 4f electrons

As a **metal**, europium is very reactive so that one usually finds it under its trivalent, triply oxidized form (Eu^{3+} ion) in oxides or salts. A divalent form (Eu^{2+}) also displays some stability. Two minerals that contain many of the lanthanide elements, which are separated by liquid-liquid extraction, are commercially important: monazite (found in Australia, Brazil, India, Malaysia, and South Africa) and bastnasite (found in China and the United States).

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

A very interesting property of the europium ions is their bright red (Eu^{3+}) and bright blue (Eu^{2+}) luminescence. The red luminescence has been instrumental in identifying the element and it is of great practical use today. For instance, the red color seen on computer and television screens derives from red light emitted by a europium-containing phosphor (an inorganic compound with 4–7% Eu^{3+}). The same type of material is used in energy-saving fluorescent lamps: Those displaying a warm light contain Eu^{3+}. In medicine, **antibodies** (molecules generating an antibody response, e.g., certain hormones) labeled with a europium-containing compound react with specific antigens, forming antigen-antibody complexes, and the red luminescence helps to quantify these hormones in biological fluids (e.g., blood, urine). SEE ALSO Cerium; Dysprosium; Erbium; Gadolinium; Holmium; Lanthanides; Lanthanum; Lutetium; Neodymium; Praseodymium; Promethium; Samarium; Terbium; Thulium; Ytterbium.

antibody: protein molecule that recognizes external agents in the body and binds to them as part of the immune response of the body

Jean-Claude Bünzli

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Explosions

An explosion is a sudden, violent change of potential energy to work, which transfers to its surroundings in the form of a rapidly moving rise in pressure called a blast wave or shock wave. The shock wave can cause substantial damage. Potential energy may exist in either of three forms before an explosion occurs: **nuclear**, chemical, or physical. Generally, nuclear explosions are much larger and more destructive than chemical or physical explosions. Chemical explosions are more frequent than nuclear or physical explosions. Although chemical explosions are usually deliberate, they may also occur accidentally. Large physical explosions are relatively rare and usually accidental.

nuclear: having to do with the nucleus of an atom

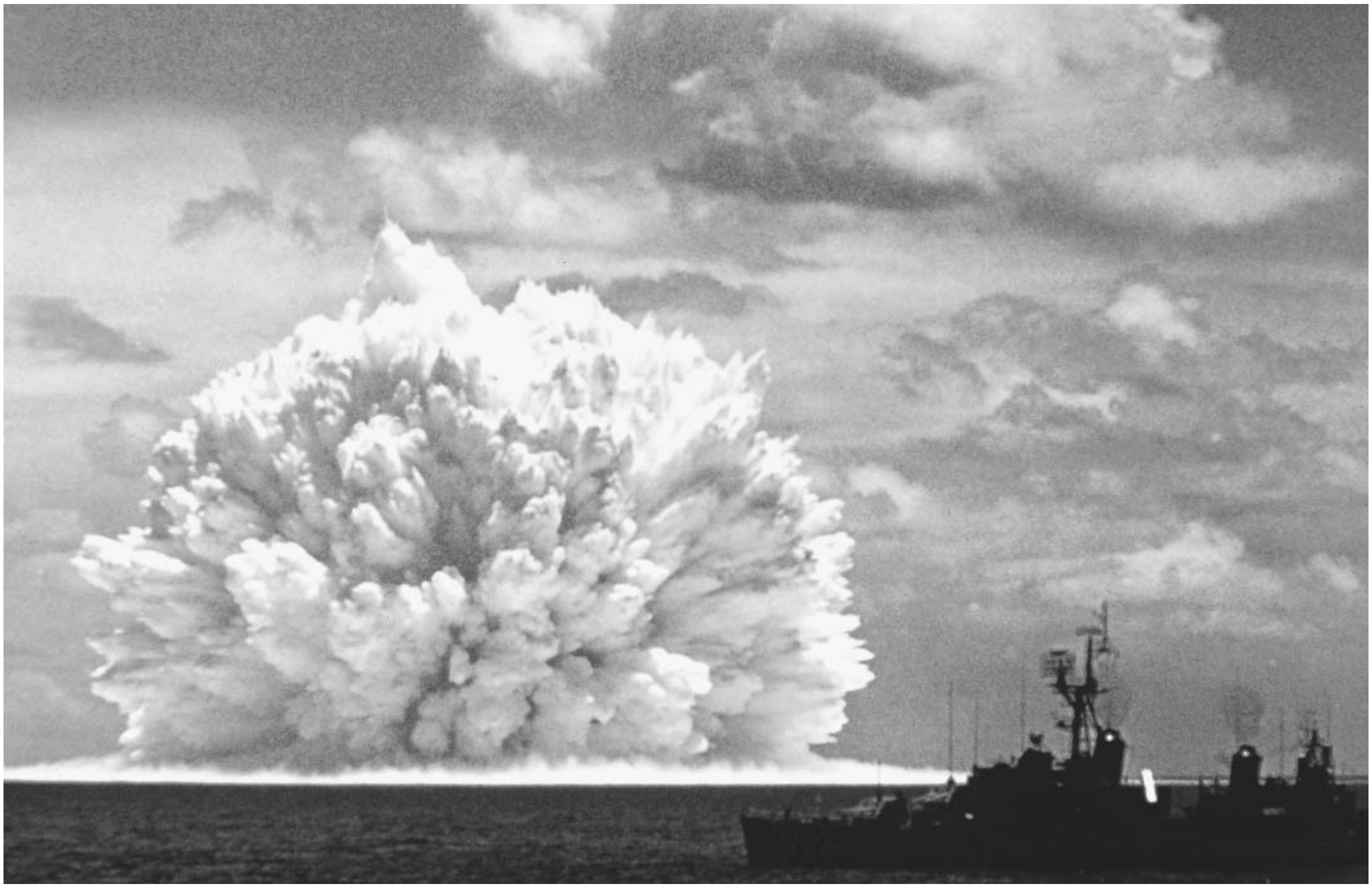
Nuclear Explosions

Nuclear explosions may be caused by either fusion or **fission** reactions. In a **fusion** reaction, the nuclei of two small atoms combine to form a single larger atom, sometimes accompanied by a neutron. The mass of the products of the reaction is less than the mass of the reactants, and that difference in mass is converted to energy according to Einstein's well-known equation $E = mc^2$ where E is the energy produced, m the mass converted to energy, and c the speed of light. The speed of light is very large, and only a small amount of mass must be converted to result in a significant explosion.

fission: process of splitting an atom into smaller pieces

fusion: process of releasing nuclear energy by combining lighter elements such as hydrogen into heavier elements

In a fission reaction, a single large atom, such as uranium, is bombarded with neutrons, causing the nucleus of the atom to split into two smaller nuclei and several neutrons. The combined mass of the product atoms and neutrons is less than the mass of the original atom, and the mass loss is converted to energy according to Einstein's equation. The neutrons produced by the fission reaction cause other large atoms to fission, and their neutron production causes still other atoms to fission, leading to a chain reaction that continues exponentially (i.e., 2, 4, 8, 16, 32, 64 . . .). The entire process is very rapid, taking only a few millionths of a second. The resulting energy production heats the surrounding air and causes it to expand in the form of a blast wave.



A nuclear explosion at sea.

Both fusion and fission reactions can be used in bombs. The fusion reactions require a very high temperature to get started, so they are initiated by fission reactions. (When controlled at slower rates in nuclear reactors, fission reactions are used to produce power and additional nuclear fuel.)

Chemical Explosions

Chemical explosions may be either decomposition or combination reactions. In either case, the reaction is exothermic and the energy released by the reaction is partially converted to work. Decomposition reactions occur in materials such as trinitrotoluene (TNT) and nitroglycerine. The molecules of these materials contain oxygen. When the molecule decomposes, the products are **combustion** gases, which are produced at high temperatures. The volume of the gases is much larger than the volume of the explosive, generating high pressures at the reaction zone. The rapid expansion of the gases forms the shock wave that provides the explosive effect. Even some hydrocarbons that have no oxygen in their molecules, such as acetylene, can decompose explosively.

combustion: burning, the reaction with oxygen

Combination reactions require that two or more components react together exothermically to produce hot gases. Some examples are ammonium nitrate and fuel oil (ANFO), gunpowder (potassium nitrate, carbon, and sulfur), and fireworks. In these explosions, the reactants that make up the explosive must be carefully mixed to assure that the reaction will continue.

The damage caused by an explosion depends partly on how fast the explosive reaction occurs. Decomposition reactions generally occur much faster than combination reactions. They are more likely to be used for military applications because they are more destructive. They also have a stronger shattering effect (called brisance) than combination reactions. Combination explosions are frequently used in mining operations because they have lower brisance and occur at slower rates.

There is a special case of explosion known as a vapor cloud explosion that can occur when a fuel (such as ordinary propane) is mixed with the atmosphere. If the cloud is ignited, the burning rate may be fast enough to form a shock wave. Although the overpressure in the shock wave may not be very high compared to other explosions, it is strong enough to damage or destroy structures. In a vapor cloud explosion, the result is called a deflagration if the shock wave moves slower than the speed of sound and a detonation if the shock wave moves faster than the speed of sound. Detonations are more destructive than deflagrations because of their stronger shock waves.

It should be kept in mind that explosives are generally unstable compounds. Once the exothermic decomposition or combination reaction is started, the temperature rises and the reaction accelerates; it usually cannot be stopped.

Physical Explosions

Physical explosions are those in which no chemical or nuclear reaction occurs. The most frequent example is the rupture of a vessel whose contents, either gas or liquid, exist under high pressure. If the containing vessel bursts, its contents are free to expand and a shock wave is formed. Even a common automobile tire can explode if it is highly overinflated.

Liquids that have a normal boiling point well below ambient temperatures are sometimes stored (under their own vapor pressure) at pressures well above atmospheric pressure. If the tank holding the liquid bursts, part of the liquid vaporizes extremely rapidly and expands, forming a shock wave. This process is called a boiling liquid expanding vapor explosion (BLEVE) and the resulting explosion can be very destructive.

Explosions can be used for constructive purposes, such as mining and road building; for entertainment, such as fireworks; or for destructive purposes, such as military weapons and terrorist bombs. They may be either deliberate or accidental. Explosive materials must always be handled with extreme care to prevent accidents. Such caution must be exercised with not only industrial explosives, but also commonly encountered materials such as fireworks, laboratory and industrial chemicals, and flammable gases. SEE ALSO Fire, Fuels, Power Plants; Fireworks; Kinetics; Nuclear Fission; Nuclear Fusion; Thermodynamics.

J. Reed Welker

Fahrenheit, Daniel Gabriel

GERMAN PHYSICIST

1686–1736

Observations are the heart of the scientific method, but human perception is faulty when it comes to observing "absolutes." That is, one may be able to say that this liquid is hotter than that liquid, but not by how much, nor their exact temperatures. For science to be meaningful and its results reproducible, some external mechanism for making (and comparing) measurements that can be used by scientists must exist.

Daniel Gabriel Fahrenheit was a German physicist living in the Netherlands in the early eighteenth century. Like many of his contemporaries, he was interested in a great many phenomena, but the one phenomenon that really seized his attention was the boiling of liquids. Fahrenheit discovered that pure liquids boil at fixed temperatures, which are not influenced by the continued application of heat. He described his reaction to this discovery in his *Philosophical Transactions* (1724): "I was at once inflamed with a great desire to make for myself a thermometer of the same sort [a water-based thermometer], so that I might with my own eyes perceive this beautiful phenomenon of nature, and be convinced of the truth of the experiment."

Fahrenheit could not make a "thermometer of the same sort," despite repeated attempts. The type of thermometer that he was trying to make used water, open to the atmosphere, as the fluid of expansion. His original thermometers were thus sensitive to air pressure, and acted as both barometers and thermometers at the same time.

Fahrenheit subsequently recognized that both alcohol and mercury expanded with heat. He built closed bulb thermometers that contained alcohol (1709) and mercury (1714), thereby inventing the modern thermometer. With these instruments, he was able to make much more accurate and more consistent measurements of temperature. And he discovered, among other things, that water can be supercooled (cooled below its normal freezing point), and that the boiling point of a liquid is not a constant, but is a function of atmospheric pressure. Fahrenheit used supercooled water (from a mixture of water, ice, and sal ammoniac [ammonium chloride]) to establish his zero point, and his own body temperature to establish what would be 100 degrees. (Of course, we now gauge normal body temperature to be 98.6°F.) Fahrenheit's thermometers were the first to enable accurate and reproducible measurements of temperature.

Until the 1970s, the Fahrenheit scale was in common use in all English-speaking countries. Since then, the Celsius scale has been adopted by most countries (not including the United States). SEE ALSO TEMPERATURE.

Todd W. Whitcombe

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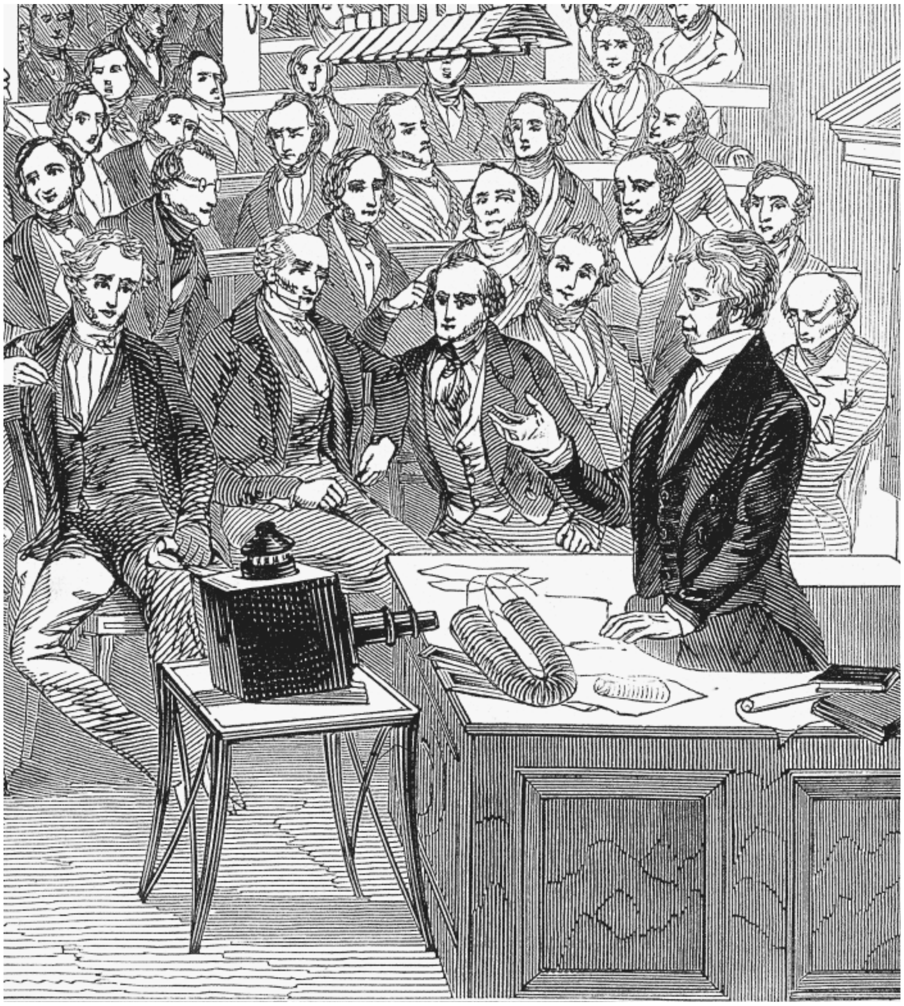
Faraday, Michael

ENGLISH CHEMIST AND PHYSICIST
1791–1867

Michael Faraday, the leading chemist and natural philosopher in England during the middle third of the nineteenth century, discovered the principle behind the electric motor (1821), benzene (1825), the electric transformer



English chemist and physicist Michael Faraday, who developed the field theory of electromagnetism.

and generator (1831), the laws of electrolysis (early 1830s), and the magneto-optical effect and diamagnetism (1845), which enabled him to develop the field theory of electromagnetism, one of the cornerstones of modern physics.

Faraday was born on September 22, 1791, in Newington Butts, south of London. His father, a blacksmith, belonged to the Sandemanians, a small literalist sect (in which the members believe in the literal truth of the Bible) of Christianity. Faraday was fully committed to this sect, becoming a deacon in 1832 and an elder in the 1840s and again in the 1860s. He married a fellow Sandemanian, Sarah Barnard, in 1821 and died on August 25, 1867, in his "grace and favour" house (a house given by a monarch to a subject in recognition of worth and of need) at Hampton Court. In his scientific research, Faraday sought to determine the laws of nature that he believed God had written at the creation of the universe. Although it was only toward the end of his life that problems began to emerge between some types of Christianity and science, mostly in response to Charles Darwin's theory of natural selection, published in 1859, Faraday did not see any conflict between them.

Faraday attended a day school and in 1805 he began an apprenticeship as a bookbinder, which was to last for seven years. During this time he developed a strong interest in science, particularly chemistry, and in 1812, the final year of his apprenticeship, he attended four lectures delivered by Humphry Davy at the recently founded (1799) Royal Institution in London's West End. Faraday sent his notes on Davy's lectures to Davy asking for a job in the field of science; he was eventually appointed as an assistant in the Royal Institution's laboratory. Between the fall of 1813 and spring of 1815 he toured Europe with Davy and helped him establish the fact that iodine was a chemical element. Returning to England, Faraday was reappointed to the Royal Institution and promoted through the ranks, becoming the director of its laboratory in 1825 and first Fullerian Professor of Chemistry in 1833. In these roles, Faraday established Christmas lectures for children and Friday evening discourses, both of which series still continue.

During the 1820s much of Faraday's work centered on chemistry. He aided Davy in his disastrous efforts to protect electrochemically the copper bottoms of ships and with the equally unsuccessful project to improve optical glass. In 1823 Faraday liquefied the gas chlorine for the first time and in the 1840s he liquefied several more gases. His **liquefaction** of chlorine resulted in a bitter break with Davy, by now president of the **Royal Society**, who believed that Faraday had not given him sufficient credit for his part in the work. Davy thus tried, albeit unsuccessfully, to block Faraday's election to the Royal Society. Two years later Faraday discovered, but did not investigate fully, a new chemical that he named "bi-carburet of hydrogen." Nearly ten years later Eilhardt Mitscherlich, a chemistry professor in Berlin, first undertook a detailed study of the substance that he renamed benzene. Faraday, nevertheless, is credited with benzene's discovery, and in 1925 there were major celebrations throughout England marking the 100-year anniversary of Faraday's discovery.

liquefaction: process of changing to a liquid form

Royal Society: The U.K. National Academy of Science, founded in 1660

Following his 1831 electromagnetic work, Faraday turned his attention to electrochemistry. The decomposition of chemical compounds was a standard test for the presence of electricity. In his extensive use of this test, he observed phenomena contradicting Davy's theory that electrochemical decomposition occurred at the **metal** pole. Faraday found that decomposition occurred in the substance itself and the poles did not need to be metal. All this led Faraday to develop a new language of electrochemistry. With a number of classical scholars, notably William Whewell, Faraday introduced terms such as electrolysis, electrolyte, electrode, anode, cathode, and ion (although he said there would be little need for this last term).

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Faraday was thus able to enunciate his two laws of electrolysis. His second law implied that both matter and electricity were atomic in nature. Faraday was deeply opposed to atomism, especially the theory proposed by John Dalton, and indeed held a very antimaterialist view. It was clear to Faraday, however, that the law of definite proportions also required some sort of **atomic theory**. What Faraday proposed in the 1840s was that matter was perceived where lines of force met at a particular point in space. A direct experimental outcome of this radical theory was Faraday's discovery in 1845 of the magneto-optical effect and diamagnetism. The field theory that Faraday developed from this was able to solve a number of problems in physics that were not amenable to conventional approaches. This was one reason why field theory was taken up quite quickly by elite natural philosophers such as William Thomson (later Lord Kelvin) and James Clerk Maxwell.

atomic theory: concept that asserts that matter is composed of tiny particles called atoms, the particular characteristics of which determine the form and type of matter.

Nevertheless, the theory was not generally accepted for some time because it was seen by many physicists as opaque and, in origin, nonmathematical. However, as the German organic chemist Justus von Liebig pointed out, this occurred because physicists did not recognize Faraday's background as a chemist, a factor Liebig thought crucial in the development of Faraday's theory: "To physicists, who have approached physics by the road of chemistry, Faraday's memoirs sound like admirably beautiful music" (Hofmann, p. 1100). SEE ALSO DALTON, JOHN; DAVY, HUMPHRY; ELECTROCHEMISTRY; IODINE; LIEBIG, JUSTUS VON; MAXWELL, JAMES CLERK.

Frank A. J. L. James

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Fats and Fatty Acids

Fats occur naturally in food and play a significant role in human nutrition. Fats are used to store energy in the body, insulate body tissues, cushion internal organs, and transport fat-soluble **vitamins** in the blood. Fats also play in an important role in food preparation: They enhance food flavor and food texture, make baked products tender, and conduct heat during cooking.

vitamins: organic molecules needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

Fats are the most prevalent class of compounds (in living systems) referred to as **lipids**. Lipids are cellular compounds that are insoluble in water. Fats are soft, low-melting solids, with a density less than that of water. They have a greasy feel and are slippery. Because fats are insoluble in water and less dense than water, after meat that has a lot of fat in it has been cooked, upon cooling a layer of fat often appears on top of the juices. Fats and closely related oils are mixtures of compounds consisting of fatty acids combined with glycerol (commonly known as glycerin) via **ester** linkages. Fatty acids are long, straight chain carboxylic acids. A fat (or oil) is formed when three fatty acid molecules react with a glycerol molecule to yield a triglyceride (and three water molecules). (See Figure 1.) Fats in the body are transported and stored as triglycerides.

lipid: a nonpolar organic molecule; fatlike; one of a large variety of nonpolar hydrophobic (water-hating) molecules that are insoluble in water

ester: organic species containing a carbon atom attached to three moieties: an O via a double bond, an O attached to another carbon atom or chain, and an H atom or C chain; the R(C═O)OR functional group

Fat molecules are characterized as monoglycerides, diglycerides, or triglycerides, depending on whether there are one, two, or three fatty acid chains present in the molecules. Fatty acids in nature generally have an even number of carbon atoms because they are synthesized in cells via successive

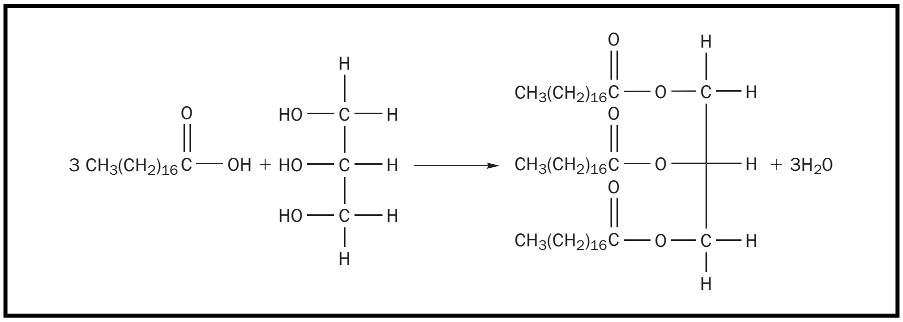

Figure 1. The formation of a triglyceride of stearic acid.

additions of two-carbon acetate groups in a stepwise cyclic reaction. Some fatty acids found in nature are shown in Table 1.

Fats and Oils

Dietary fats and oils are both triglycerides. Fats are generally solids and oils are generally liquids at ordinary room temperatures. The characteristics of fats and oils are related to the properties of the fatty acids that they contain. The larger the number of carbon atoms, the higher the **melting point**; the larger the number of double bonds, the lower the melting point. Oils contain a higher percentage of unsaturated fatty acids than fats. Fats from animal sources tend to be solids and fats from vegetable sources tend to be liquids. Thus fats are often referred to as "animal fats" and "vegetable oils."

melting point: temperature at which a substance in the solid state undergoes a phase change to the liquid state

When fats or oils are exposed to air, they react with the oxygen or water vapor to form short-chain carboxylic acids. The short-chain acids are **volatile** and have unpleasant smells and tastes. For example, the strong smell and sour taste of vinegar are due to acetic acid, a two-carbon **carboxylic acid**. The **oxidation** process is called rancidification and can make foods unpalatable. The characteristic smell of rancid butter is due to the presence of butyric acid (a four-carbon acid). (Rancidity can also be the result of the hydrolysis of fats or oils.)

volatile: low boiling, readily vaporized

carboxylic acid: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the $-CO_2H$ functional group

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

Unsaturated Fatty Acids

There are about forty naturally occurring fatty acids. The fatty acids without carbon-carbon double bonds are classified as saturated, and those containing carbon-carbon double bonds are classified as unsaturated. Palmitic and stearic acids are the most common saturated fatty acids, and oleic and linoleic acids are the most common unsaturated fatty acids. Oleic acid is monounsaturated because it has only one carbon-carbon double bond. Linoleic, linolenic, and arachidonic acids are polyunsaturated because they have two, three, and four carbon-carbon double bonds, respectively. A way to measure the relative degree of unsaturation of a fat or an oil is to determine its iodine number. The iodine number is the mass of iodine, in grams, that is consumed by (reacts with) 100 grams of a fat or an oil. Iodine reacts with the carbon-carbon double bonds. Thus the greater the number of double bonds, the higher the iodine number. In general, fats have lower iodine numbers than oils because oils have greater percentages of carbon-carbon bonds that are double bonds. For example, typical iodine numbers for butter are 25 to 40, and for corn oil, 115 to 130.

Table 1.

FATTY ACIDS

Common Saturated Fatty Acids

Number of Carbon Atoms	Formula	Common Name	Source
4	$CH_3(CH_2)_2COOH$	Butyric acid	Butter
6	$CH_3(CH_2)_4COOH$	Caproic acid	Butter
8	$CH_3(CH_2)_6COOH$	Caprylic acid	Coconut oil
10	$CH_3(CH_2)_8COOH$	Capric acid	Coconut oil
12	$CH_3(CH_2)_{10}COOH$	Lauric acid	Palm kernel oil
14	$CH_3(CH_2)_{12}COOH$	Myristic acid	Oil of nutmeg
16	$CH_3(CH_2)_{14}COOH$	Palmitic acid	Palm oil
18	$CH_3(CH_2)_{16}COOH$	Stearic acid	Beef tallow
18	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	Oleic acid	Olive oil
18	$CH_3(CH_2)_4CH{=}CHCH_2CH(CH_2)_7COOH$	Linoleic acid	Soybean oil
18	$CH_3CH_2(CH{=}CHCH_2)_3(CH_2)_6COOH$	Linolenic acid	Fish oils
20	$CH_3(CH_2)_4(CH{=}CHCH_2)_4(CH_2)_2COOH$	Arachidonic acid	Liver
22	$CH_3(CH_2)_{20}COOH$	Beheric acid	Sesame oil

Common Unsaturated Fatty Acids

Number of Carbon Atoms	Formula	Common Name	Source
16	$CH_3(CH_2)_5CH{=}CH(CH_2)_7COOH$	Palmitoleic acid	Whale oil
18	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	Oleic acid	Olive oil
18	$CH_3(CH_2)_4CH{=}CHCH_2CH(CH_2)_7COOH$	Linoleic acid	Soybean oil, safflower oil
18	$CH_3CH_2(CH{=}CHCH_2)_3(CH_2)_6COOH$	Linolenic acid	Fish oils, linseed oil
20	$CH_3(CH_2)_4(CH{=}CHCH_2)_4(CH_2)_2COOH$	Arachidonic acid	Liver

Hydrogenation

In addition to their reacting with iodine, unsaturated fats and oils react with hydrogen. Like iodine atoms, hydrogen atoms add across the carbon-carbon double bonds. Vegetable oils, with their higher degrees of unsaturation, can be converted to solids via reaction with hydrogen in a process called hydrogenation. A polyhydrogenated fat is one that has been altered by such a reaction. The reaction may cause the oil to become a solid. Margarine and shortening are vegetable-based oils that have undergone partial hydrogenation. Because the amounts of hydrogen added can be controlled, the products of these reactions can be engineered to have specific properties, such as degrees of softness and a chosen melting point. The peanut oil in peanut butter usually has been hydrogenated to prevent it from separating. Another product of partial hydrogenation is a class of fats called *trans* fatty acids. Foods high in *trans* fatty acids (for example, margarine, shortening, and commercially fried food) tend to raise cholesterol levels in the blood.

Composition of Fats and Oils

Fat and oil glyceride molecules can contain a single fatty acid species or any combination of up to three fatty acids. Most naturally occurring fat and oil molecules contain a combination of fatty acids. As indicated previously, the greater the percentages of carbon-carbon bonds that are double bonds

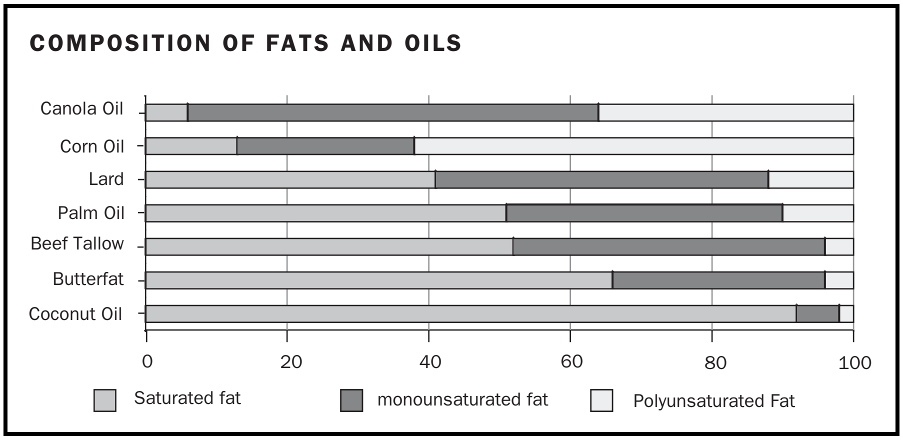

Figure 2.

in the fatty acids of a glyceride, the lower is the melting point and the more likely the glyceride will exist as a liquid at room temperature. Figure 2 shows the composition (in terms of their saturated, monounsaturated, and polyunsaturated portions) of some common fats and oils. Note that the oils tend to contain fewer saturated fatty acids. Coconut oil is an exception; although it does contain an ample amount of saturated fatty acids, approximately two-thirds of its fatty acid content is derived from lauric and myristic acids. Lauric and myristic acids have shorter chains of 12 and 14 carbons, respectively, and they are responsible for the low melting point of coconut oil.

Saponification

Because fats and oils are triesters of glycerol, they react with water to form fatty acids and glycerin. When the reaction is carried out in a basic solution, salts of the fatty acids are produced instead of the fatty acids themselves. The salts of fatty acids are soaps and an individual molecule is characterized by an ionic end (the salt part) and a **nonpolar** end (the hydrocarbon part). The ionic salt end is water-soluble and the nonpolar hydrocarbon end is water insoluble. The process of making soaps by treating fats and oils with basic substances is called saponification (which means "soapmaking"). Pioneers made soap by adding lye (the base sodium hydroxide) to animal fat, and then heating the mixture. The soap rose to the top of the pot and solidified upon cooling and the glycerol remained at the bottom.

nonpolar: molecule, or portion of a molecule, that does not have a permanent, electric dipole

Fats and oils can be characterized by their saponification numbers. The saponification number is defined as the number of milligrams of potassium hydroxide needed to saponify completely one gram of a fat or an oil. One mole of fat requires three moles of potassium hydroxide for complete saponification. If a fat contains fatty acids of relatively high molecular weights, then one gram of the fat will consist of fewer moles. Thus, fats having greater percentages of high molecular weight fatty acids will have lower saponification numbers than fats having greater percentages of lower molecular weight fatty acids. Lard, which contains mostly 16- and 18-carbon fatty acids, has a saponification number range of 190 to 200. Coconut oil, which is about 50 percent lauric acid, a 12-carbon fatty acid, has a saponification number approaching 260.

Fats in the Diet

Fats are necessary to maintain the body. Dietary fats exist mainly in the form of triglycerides. Fats are classified as high-energy food. They provide about 9 kilocalorie (kcal) of energy per gram consumed. In contrast, both carbohydrates and proteins provide about 4 kcal of energy per gram consumed. As a result, fat is the most efficient way to store energy. If one consumes more calories than he or she needs, some of the excess calorie source is converted to fat.

It is generally recommended that not more than 30 percent of one's dietary calories should derive from fat (and of this 30 percent, 10 percent should be monounsaturated, and 10 percent, polyunsaturated). It appears that consumption of greater amounts of saturated fats (compared to amounts of monounsaturated and polyunsaturated fats) is related to higher levels of cholesterol in the blood and a greater risk of heart disease. In the United States the average diet is about 34 percent fat and (13 percent saturated fat).

Fat Substitutes

Because an average American diet tends to be higher in fats than what is recommended, there have been quests for substitutes for fat. Three products were first marketed as fat substitutes in the 1990s. The first was Simplesse, made by G.D. Searle. It is a low-calorie fat substitute made from milk protein (whey). The whey is made to undergo a microparticulation process that produces microparticles and prevents the formation of larger particle aggregates. The small size and uniformly spherical shape of Simplesse particles are responsible for this product's resemblance to a creamy fluid. The texture of Simplesse is similar to that of fats, and its use in frozen desserts can inhibit the growth of ice crystals. Simplesse is used in cheeses, frozen desserts, dressings, spreads, and puddings. It cannot be used in foods that require baking or frying.

Another product is Olestra, made by Procter and Gamble, and it is sold to food producers as Olean. It is an ester of sucrose (instead of glycerol), and it is used as a substitute for fats in potato chips, crackers, and tortilla chips. Olestra's similarity to fats with respect to molecular structure contributes to its ability to mimic the mouth-feel of fat. However, it is much bulkier than a triglyceride-containing food, and this bulkiness prevents it from being digested and absorbed by the body. Thus it has no dietary caloric content. Potato chips fried in Olestra have 75 calories (instead of the 150 calories corresponding to chips fried in fat the traditional way). Like fat, Olestra is nonpolar and can dissolve other fat-soluble substances, including the fat-soluble vitamins A, D, E, and K. It is problematic that Olestra absorbs these vitamins that are stored in fat and are necessary for good health. Olestra is therefore fortified with vitamins A, D, E, and K to prevent it from depleting the body's supply of these vitamins. Although the U.S. Food and Drug Administration has found Olestra to be safe and has approved its use in snack foods, it required warnings on products containing Olestra because of undesirable side effects, such as diarrhea and abdominal cramping.

A third fat substitute, Z-Trim, has been developed by the U.S. Department of Agriculture. Originally called Oat-Trim, it is made from agricultural by-products, such as the hulls of oats, peas, soybeans, and rice, or bran from corn or wheat. Because it is made from natural dietary fibers, it is digestible. Not only does it lower fat consumption, it also provides fiber for the diet. Z-Trim can be used as a fat substitute in cheese products, baked goods, and hamburgers. Brownies containing Z-Trim are 16 percent fat (compared to 25 percent for traditional brownies).

Although fat substitutes may reduce the caloric contents of the foods in which they are used, caution is still necessary. Foods labeled "fat free" are not "calorie free." If an individual feels that he or she can eat more of a food containing a fat substitute, his or her total caloric intake may actually increase. SEE ALSO DETERGENTS; LIPIDS; SOAP.

Jerry L. Sarquis

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Fermi, Enrico

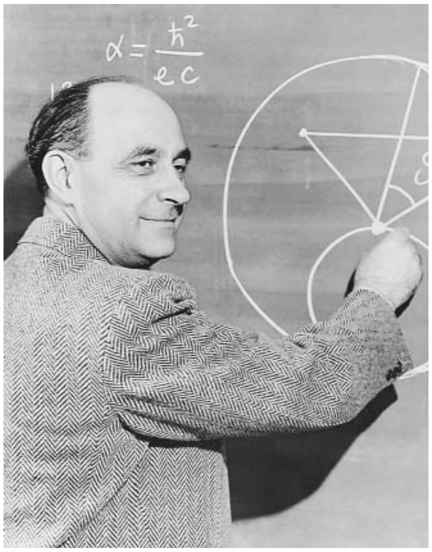
AMERICAN PHYSICIST
1901–1954

Enrico Fermi was born in Rome, the son of Italy's chief railroad inspector (Alberto Fermi) and a schoolteacher (Ida de Gattis). While he was attending Ginnasio Liceo Umberto I, an associate of his father recognized Fermi's talents in physics and mathematics and encouraged him to master several challenging scientific treatises. At the University of Pisa and the Scuola (1918–1922), Fermi published two papers on relativistic electrodynamics and one on general relativity. He completed doctoral theses at each institution. After holding several short-term positions, Fermi attracted the attention of Italian senator and chemist Orso M. Corbino, who helped establish for Fermi the country's first chair of **theoretical physics** at the University of

theoretical physics: branch of physics dealing with the theories and concepts of matter, especially at the atomic and subatomic levels

Rome. In 1928 Fermi married Laura Capon, and the couple had two children.

As a chair at the University of Rome, Fermi did much of his most important work between 1927 and 1938. Along with the English physicist Paul Dirac but independently, he developed quantum-mechanical statistics that measure particles of half-integer spin (now known as fermions); between 1929 and 1932 he reformulated more simply and elegantly Dirac's then recent work on quantum electronics. In 1933–1934, he published a theory of β-decay that included what became known as the Fermi interaction, Fermi interactions, and the Fermi coupling constant. He also theorized and named the neutrino ("little neutral one"), originally hypothesized by Wolfgang Pauli but not detected experimentally until 1956.


American physicist Enrico Fermi, recipient of the 1938 Nobel Prize in physics, "for his demonstrations of the existence of new radioactive elements produced by neutron irradiation, and for his related discovery of nuclear reactions brought about by slow neutrons."

α-particle: subatomic particle with 2+ charge and mass of 4; a He nucleus

nuclear: having to do with the nucleus of an atom

Manhattan Project: government project dedicated to creation of an atomic weapon; directed by General Leslie Groves

fissionable: of or pertaining to unstable nuclei that decay to produce smaller nuclei

After 1933 Fermi turned increasingly to experimental physics. Inspired by recent work in which artificial radioactive substances were produced by **α-particle** bombardment, Fermi and several collaborators used neutron bombardment to create several "transuranic" elements heavier than uranium, including plutonium. This work, and his finding that slow neutrons produce **nuclear** reactions more efficiently than fast ones, earned Fermi wide acclaim and the 1938 Nobel Prize in physics. After accepting the prize in Sweden, Fermi and his Jewish wife immigrated to the United States to escape the Nazis.

After replicating the German fusion of the uranium atom in early 1939, Fermi was recruited to join the secret U.S. atomic bomb project, the **Manhattan Project**. He initially worked at the project's metallurgical laboratory at the University of Chicago, where he was chief designer of an atomic pile that achieved a sustained nuclear reaction on December 2, 1942. Throughout the war he worked on reactor design and **fissionable** fuel production at several project facilities.

Fermi became a naturalized U.S. citizen on July 11, 1944. Short in stature and barrel-like, he retained a thick Italian accent and refreshingly unassuming manner throughout his life. Although he supported the atomic bombing of Japan, after the war, as a member of the powerful General Advisory Committee of the Atomic Energy Commission, he opposed the development of a hydrogen bomb. Fermi moved into new areas of research, including cosmic rays (the "Fermi mechanism" modeled their acceleration) and elementary particle physics. In addition to the Nobel Prize, Fermi was honored with many other distinguished awards, including the Presidential Medal of Merit (1946), the Franklin Medal (1947), the Max Planck Medal (1954), and the Fermi Award (1954). The latter, as well as the Fermi National Accelerator Laboratory in Batavia, Illinois, were named in his honor. SEE ALSO NUCLEAR CHEMISTRY; PAULI, WOLFGANG.

David B. Sicilia

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Fermium

100
Fm
FERMIUM
257

MELTING POINT: 1800K
BOILING POINT: unknown
DENSITY: unknown
MOST COMMON IONS: Fm^{3+}, Fm^{2+}

Fermium, the eleventh member of the actinide series, was discovered in 1952. Fermium (element 100), together with einsteinium (element 99), were unexpectedly produced in the explosion of the first U.S. thermonuclear device, "Mike," tested at Eniwetok Atoll in the South Pacific on November 1, 1952. Fermium was first identified in the form of the ^{255}Fm (half-life 20 hours). The name fermium was chosen for element 100, in honor of the great physicist Enrico Fermi. Fermium **isotopes** of masses 242 through 260 are known. All are radioactive, decaying via **α-particle** emission, electron capture, and spontaneous **fission**. The isotope of mass 258 has the shortest half-life (0.4 milliseconds), and that of mass 257 has the longest (100.5 days). It is noteworthy that a predominantly symmetric mass division (during spontaneous fission) was first observed in ^{259}Fm. The ground state electronic configuration of the gaseous fermium atom is $[Rn]5f^{12}7s^2$, analogous to that of its **lanthanide** homologue (erbium). The most stable ion in **aqueous solution** is Fm^{3+}, although Fm^{2+} and Fm^{4+} have been reported. However, the claim of the identification of the latter two ions has not been substantiated. As with einsteinium, divalency is seen in the **metal**. SEE ALSO Actinium; Berkelium; Einsteinium; Fermi, Enrico; Lawrencium; Mendelevium; Neptunium; Nobelium; Plutonium; Protactinium; Radioactivity; Rutherfordium; Thorium; Transactinides; Transmutation; Uranium.

Darleane C. Hoffman

isotope: form of an atom that differs by the number of neutrons in the nucleus

α-particle: subatomic particle with 2+ charge and mass of 4; a He nucleus

fission: process of splitting an atom into smaller pieces

lanthanides: a family of elements from lanthanum to lutetium having from 1 to 14 4f electrons

aqueous solution: homogenous mixture in which water is the solvent (primary component)

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

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Fertilizer

A fertilizer is a plant nutrient added to a soil to increase its yield. Plants need nutrients to grow and produce fruits and vegetables. Two categories of nutrients have been identified in fertilization: **macronutrients** and micronutrients. There are only six macronutrients and they are required in large amounts by plants: nitrogen, phosphorus, potassium, sulfur, magnesium, and calcium. However, a larger number of micronutrients are required but in trace amounts: iron, manganese, boron, zinc, copper, molybdenum, chlorine, cobalt, nickel, sodium, and silicon. Eliminate any of these elements, and plants will display abnormal growth and deficiency, or they may not reproduce.

macronutrient: one of a number of substances, needed in relatively large amounts, that provide nourishment for living organisms

The most popular fertilizers contain the three major nutrients: nitrogen, phosphorus, and potassium, and they are therefore referred to as NPK fertilizers. To illustrate their importance in any economy, in 2000, the world consumption of the total fertilizer nutrient ($N + P_2O_5 + K_2O$) was 140

Fertilizer is being applied in a rice field.

million tons, representing 52 million tons for developed countries and 88 million tons for developing countries.

Nitrogen forms part of proteins, hormones, **chlorophyll**, **vitamins**, and enzymes, and promotes stem and leaf growth. Too much nitrogen can delay fruiting, while a deficiency of it can reduce yields and induce yellowing of leaves and stunted growth. Nitrogen fertilizers are applied in organic and/or inorganic forms. Organic nitrogen fertilizers are farmyard manure, guano (excreta and remains of seabirds), dried blood, hoof, and horn. However, organic nitrogen sources must undergo microbial processes that produce nitrate nitrogen.

chlorophyll: active molecules in plants undergoing photosynthesis

vitamins: organic molecules needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

Inorganic nitrogen sources are directly available to plants and include the following: sodium nitrate, calcium nitrate, ammonium sulfate, ammonium nitrate, urea, calcium cyanamide, and ammonia. In addition, atmospheric nitrogen may be used as a source of plant nitrogen by the process called "nitrogen fixation." Legumes and a few other plants, in association with **cyanobacteria** (microscopic aquatic bacteria, for example, *Anabaena azollae*), convert nitrogen to biologically useful ammonia. This process occurs in small growths on the roots called "nodules." Ammonia is subsequently available for many biological molecules, such as amino acids, proteins, vitamins, and nucleic acids.

cyanobacterium: eubacterium sometimes called "the blue-green alga"; it contains chlorophyll (the pigment most abundant in plants), has very strong cell walls, and is capable of photosynthesis

seed germination: beginning of the process by which a seed produces a new plant

photosynthesis: process by which plants convert carbon dioxide and water to glucose

Phosphorus plays an important role in **seed germination**, **photosynthesis**, protein formation, overall growth and **metabolism**, and flower and fruit formation. Phosphorus deficiency induces purple stems and leaves, poor flowering and fruiting. Low soil pH (<4) ties up phosphates by favoring the formation of insoluble aluminum and iron phosphates. Phosphorus fertilizers come from different sources: bones, rock phosphate, superphosphate (a mixture of calcium dihydrogen phosphate and calcium sulfate), nitrophosphate, ammonium phosphate, basic slag (by-product in steel manufacture), etc.

metabolism: the complete range of biochemical processes that take place within living organisms; comprises processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those that break down complex food molecules, thus liberating energy (catabolism)

Potassium contributes to the formation of sugars, carbohydrates, proteins and to cell division; adjusts water balance; enhances the flavor, color, and oil content of fruits; and is very important for leafy crops. Potassium deficiency produces a spotted, curled, or burned appearance to leaves and lowers crop yields. Potassium fertilizers are applied in the following forms: potassium chloride, potassium sulfate, potassium nitrate, and wood ash.

Other macronutrients are supplied as part of NPK fertilizers. First, sulfur is available from the sulfate of fertilizers. It contributes to the formation of amino acids, proteins, and enzymes, and is essential to chlorophyll. It also affects flavor in many vegetables. Second, magnesium is naturally present in the soil and is generally associated with potassium sulfate and calcium phosphate, used as NPK. It is a critical part of chlorophyll, and contributes to the functioning of enzymes for carbohydrates, fruit and nut formation, and the germination of seeds. Magnesium deficiency induces yellowing between the veins of older leaves, and leaves droop (hang down) as a result. Finally, calcium is also present in the soil and is available from calcium phosphate and nitrate, and lime. It activates enzymes, contributes to the structural part of cell walls, and influences water movement, cell growth, and division.

Micronutrients are not specifically applied to soil since they are naturally found in soils. However, there are some extreme cases where they must be supplied. For example, animal disorders have been linked to a lack of trace amounts of elements, not necessary for plant growth but essential for some species of animals. In some parts of Great Britain, for example, sheep and cattle suffered from "pining disease" that resulted in severe weight loss and general debilitation. The disease was found to result from a shortage of cobalt in the herbage. It has also been established that selenium deficiencies in some soils cause **muscular dystrophy**, while selenium excesses induce **selenium toxicity** in livestock. SEE ALSO Calcium; Carbohydrates; Enzymes; Magnesium; Nitrogen; Nucleic Acids; Phosphorus; Potassium; Proteins; Silicon; Sulfur.

muscular dystrophy: medical condition in which there is gradual atrophy of skeletal muscles

selenium toxicity: condition created by intake of excess Se from plants or seleniferous water; acute and chronic toxicity are known

Joseph Bariyanga

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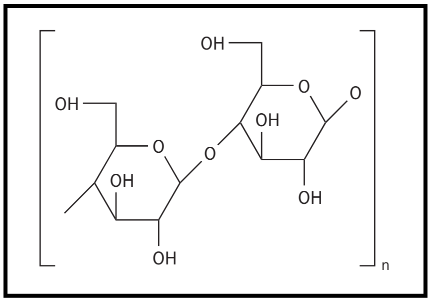
Fibers

Fibers are long strands of molecules interwoven to form a linear, stringlike structure. They may be natural or made by humans and are essential to clothing, industry, and our very bodies. Natural fibers are of plant or animal origin. In many cases, synthetic fibers mimic natural fibers.



A portion of a cellulose fiber.

Natural Fibers

Among the natural fibers are cellulose, the primary structural component of plants and bacterial cell walls; animal fibers such as wool and silk; and biochemical fibers. Plant fibers are composed of cellulose (see Figure 1), lignin (see Figure 2), or similar compounds; animal fibers are composed of protein (see Figure 3).

Cellulose, the most widespread organic molecule on Earth, is the major component of plant cell walls. Plants produce approximately 50 kilograms of cellulose daily for each person on Earth. A linear polymer made up of 10,000 to 15,000 glucose molecules bonded in a 1 → 4 glycosidic linkage, it is made up almost entirely of glucose. Cellulose molecules contain many polar hydroxyl groups, which allow them to interact with adjacent molecules to form fibers. These fibers are structurally strong and resistant to chemical attack, so wood products are widely used in construction and production of paper.

Cotton, a vegetable fiber that is almost pure cellulose, grew to become an important industrial commodity during the nineteenth century. Composed of cellulose strands in small springlike coils, cotton fibers have no surface scales and are softer than wool and less likely to provoke itching. First used as a textile material in India, cotton is now grown in every temperate part of the world and has been an important commodity in the southern United States. Cotton plants grow seed cases called bolls that yield tangled masses of fibers which are easily collected and spun. Processing cotton fibers is done in much the same way as wool.

Natural fibers such as cotton can be chemically modified to form rayon or acetate. Rayon was first called artificial silk. In the viscose process, cellulose is dissolved in sodium hydroxide, pushed through spinnerets, and treated with acid to harden. Treatment with copper compounds and ammonia is used to form hosiery yarns. Acetate (or cellulose acetate), produced by treating cotton with acetic acid and acetic anhydride, is also used in production of clothing.

Hemicellulose is similar in structure to cellulose, but chains of hemicellulose are shorter and less stable. Soluble hemicellulose chains attract water and form gels. Unlike cellulose, hemicellulose is a polymer of various monosaccharides, such as glucose, galactose, mannose, xylose, and arabinose.

polymer: molecule composed of many similar parts

Lignin **polymers** are often found in most plant structures in association with cellulose. The structure of lignin is not well defined, but lignin appears to be made up of polymers of propylbenzene with hydroxy and methoxy groups attached. Lignin is primarily hydrocarbon in nature and makes up a major portion of insoluble dietary fiber.

Animal Fibers. Animal hair composed of protein is a common biological fiber. Numerous types of hair have been used commercially for weaving, production of ropes, padding, and insulation.

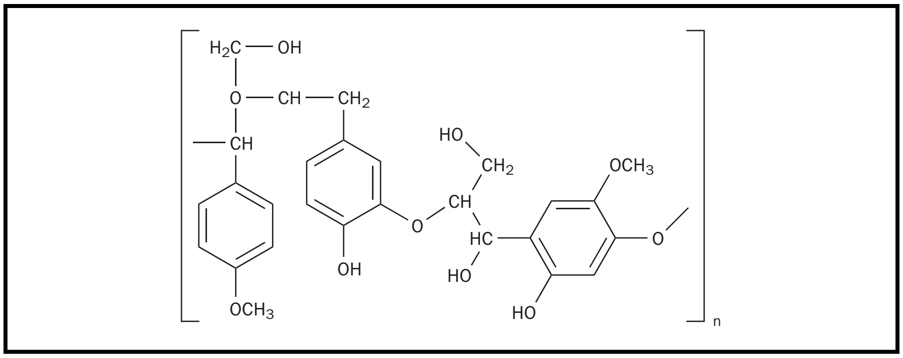


Figure 2. A portion of one of the many possible structures of lignin.

Wool fibers are made of animal hair, principally from sheep. Each hair is a complex structure made up of layers of protein molecules. Cloth made from wool has excellent insulating properties and resists wrinkling. Wool fibers can be stretched, dyed, and woven.

For centuries, sheep have been bred for their wool-bearing qualities. Production of woolen fabrics is a highly technical process. In its simplest form, sheep are sheared and the wool sorted and cleaned, then the wool is carded to straighten the fibers, spun into thin cords, and woven into fabrics. Each step in this process has been refined to provide a high-quality product of vast commercial importance.

Silk is an animal fiber valued for its texture, strength, and luster. First prepared in ancient China, silk fabric was expensive, luxurious, and soft; its popularity led to the development of a trade route known as the Silk Road leading from Asia to Europe. Early American entrepreneurs such as Benjamin Franklin promoted the silk industry in the colonies. Silkworms spin cocoons that are collected, steamed, and unwound to obtain the silk fiber by a process known as reeling. A number of fibers are twisted together to form a thread of raw silk. Threads are combined, cleaned, stretched, dyed, and woven into fine fabrics. Silk fibers have great tensile strength and are sometimes used in **cordage**.

cordage: rope or twine created by twisting individual fibers into strands and twisting strands into cords

Polymers of amino acids held together by amide linkages form the primary structures of proteins. In the portion of a protein molecule shown in figure 3, the amino acids glycine, cysteine, valine, and serine are joined by amide (peptide) bonds to form a tetrapeptide segment. In addition to hair and silk, proteins are found in some important cellular substances. Some fibers are single molecules; others are combinations of molecules lying side by side and covalently cross-linked or held in place by hydrogen bonds. Collagen fibers found in tendon, bone, and skin are side-by-side assemblies of tropocollagen. Each tropocollagen molecule consists of three polypeptide chains wound into a triple helix. Separation of collagen fibers by boiling produces gelatin. Bacterial flagella, the fibrin that helps to form blood clots, and muscle fibers also fall under the heading of fibers.

In the fine structure of cells, microtubules make up fibers such as the spindle fibers that attach to centromeres of chromosomes to pull chromatids apart during mitosis and meiosis. Microtubules function in a number of cellular processes, including motility of cells and subcellular components. Microtubules assemble into tubulin, a substance that can change the shape of cells.

A carpet trader in Sarajevo, Bosnia and Herzegovina. Wool fibers are refined to produce high-quality fabrics for numerous commercial purposes.

Actin and myosin fibers or filaments make possible the contraction of muscles. Actin and myosin fibers in muscle lie side by side and react chemically, sliding together and apart to shorten and lengthen in response to energy from adenosine triphosphate.

Inorganic Materials. A few inorganic materials form fibers. Fiberglass made of spun glass has excellent insulating properties. Mixed with epoxy resins, fiberglass is an important reinforcing component for use in such products as automobile bodies and boats. Steel fibers can be pressed into steel wool pads, widely used for their abrasive quality, or they can be braided or twisted into ropes.

Carbon can be treated at high temperature to form strong, light fibers that are mixed with other materials such as epoxy resin to form composites similar to those reinforced with fiberglass but lighter and stronger. Most

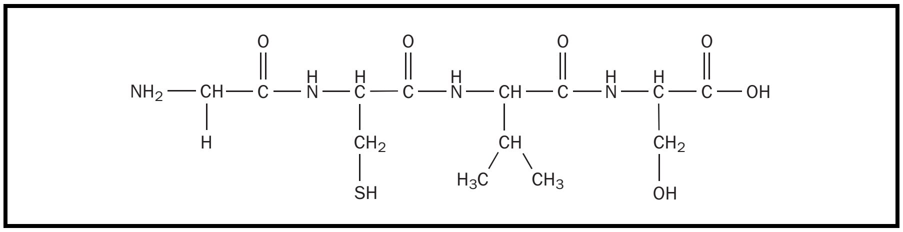


Figure 3. Glycylcysteinylvalylserine, a tetrapeptide portion of a protein molecule.

carbon fiber technology converts the carbon to graphite, which forms long, thin ribbons that pack together to form fibers. Carbon fibers show promise as components of composites for aircraft and autos, but the added expense has limited carbon fiber technology to production of high-quality devices such as golf clubs, fishing rods, bicycles, tennis rackets, and luxury autos. A new technique allows the formation of remarkably strong and light carbon nanofibers. These nanofibers show promise as bases for catalysts and as microconductors that may form important components of future computers.

Asbestos fibers occurring naturally in minerals such as serpentine were once valued for their insulating qualities and resistance to chemical attack. Locomotive and industrial boilers, pipes, and cargo compartments of ships were once coated with asbestos. However, there have been so many cases of workers in the asbestos industry developing respiratory illnesses such as asbestosis or mesothelioma that asbestos is no longer being used and in many places it is being removed.

Both gold and silver can be made into threads, which can be used as electrical conductors or in production of decorative fabrics. Many valuable examples of gold tapestries, carpets, or canopies for thrones exist. The durability and luster of gold undoubtedly contribute to its value.

Synthetic Fibers

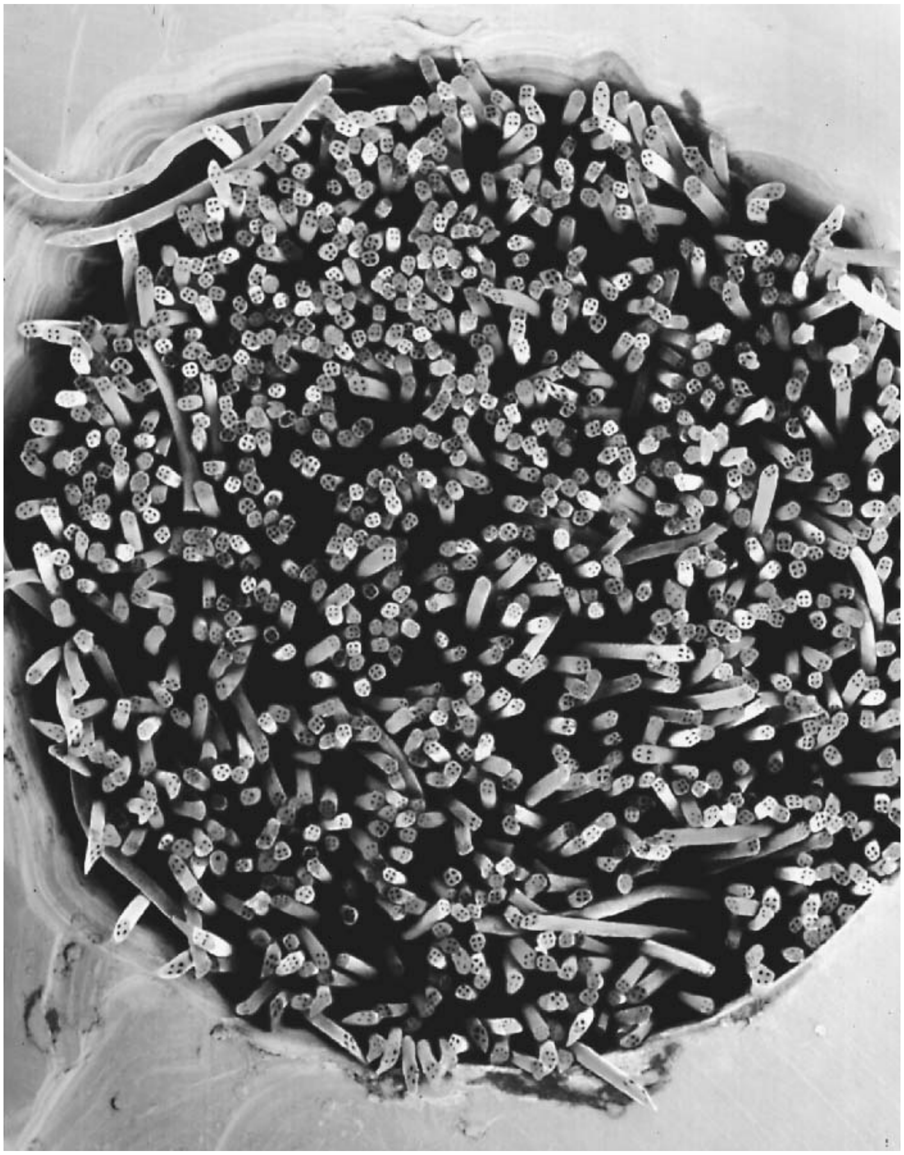
Synthetic fibers are usually polyesters or polyamides. The most important synthetic fibers are dacron, nylon, orlon, and polypropylene (primarily used for upholstery).

Acrylic fibers are vinyl polymers valued for resistance to chemical and biological degradation. Acrylonitrile (or vinyl cyanide) forms a homopolymer that is used in filters and artificial wool, which is widely used in sweaters.

Condensation fibers such as nylon and polyethylene terephthalate are formed when two or more different monomers react, releasing small molecules such as water, and forming amide or ester bonds between the monomers. Nylon, first produced by DuPont in 1938, became a mainstay of the hosiery industry and is now the most widely used fiber in carpet manufacture. Polyethylene terephthalate, produced by formation of an **ester** bond between terephthalic acid and ethylene glycol, is by far the most widely used synthetic fiber.

ester: organic species containing a carbon atom attached to three moieties: an O via a double bond, an O attached to another carbon atom or chain, and an H atom or C chain; the R(C=O)OR functional group

Teflon, discovered accidentally by Roy Plunkett at DuPont, is formed by polymerizing tetrafluoroethene. Teflon has a low coefficient of friction and is remarkably resistant to chemical attack. The ability of Teflon to flow under pressure makes it an ideal sealant for pipe threads and vessels, and



A microscopic view of dacron polyester fibers.

its low coefficient of friction makes it valuable as a component of self-lubricating bearings. The molecular weight of Teflon is high, but Teflon powders can be formed into many shapes, including artificial joints for use in the human body and fibers used in clothing.

Kevlar, a polymer of aromatic amides, is several times stronger than steel, but much lighter and also fire resistant. Kevlar fibers are formed into hollow cylinders that are then woven into fabrics useful in bullet-proof vests and manufacture of automobile tires. SEE ALSO CELLULOSE; POLYESTERS; POLYMERS, SYNTHETIC.

Dan M. Sullivan

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Fibrous Protein

Many of the familiar cells in your body use fibrous proteins to carry out important tasks. Skin, bones, muscles, tendons, and hair cells all rely on molecules in this class.

The amino acid sequences of fibrous proteins often contain repeating sets of **amino acid residues**. Such repeating sets tend to cause the protein to be both elongated and strong.

amino acid residue: in a protien, which is a polymer composed of many amino acids, that portion of the amino acid that remains to become part of the portein

Human hair provides a good example of how fibrous proteins have structural functions. The main protein in hair is called alpha-keratin. More than twenty-five variations of alpha-keratin are found in the cells of mammals. Individual molecules of alpha-keratin are not particularly large, but they provide the structure for hair by forming a coil of coils. Clustering several smaller structures to make a larger filament adds strength in the same way that strong ropes are made from groups of smaller twine.

Fibrous proteins also gain strength due to interactions between the side chains of the residues. The alpha-keratin **polypeptides**, for example, have a large number of cystine residues, which can form **disulfide bonds**.

polypeptide: compound containing two or more amide units—C(O)NH—produced by the condensation of two or more amino acids

disulfide bond: two bonding sulfur atoms, –S–S–

When a person gets a "permanent," the first chemicals that are applied break the disulfide bonds. The hair is then curled (or straightened), and

A scanning electron micrograph of eyelashes growing from the surface of human skin.

another chemical is applied to reform the disulfide bonds so the new style is retained permanently.

Coils such as those found in alpha-keratin are not the only structural motifs present in fibrous proteins. Silk, for example, is largely composed of fibrous proteins whose structures resemble interleaved sheets. SEE ALSO QUATERNARY STRUCTURE; SECONDARY STRUCTURE; TERTIARY STRUCTURE.

Thomas A. Holme

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Fire, Fuels, Power Plants

Fire is a phenomenon of combustion, usually the reaction of a substance with oxygen, producing heat, light, and gases. It has been used for entertainment, religious ceremonies, destruction, and energy. Typical fires involve wood, paper, or hydrocarbon fuels combining with oxygen in air, but many substances such as metals burn in atmospheres of chlorine or fluorine.

Fire, considered by ancient Greeks to be one of the four elements, has been worshiped and is often invoked in religious ceremonies. Fires provide a source of energy as well as adding to the entertainment of an evening at home or around a campfire.

The fire from candles has provided light for centuries. Capillary action carries melted wax along the wick from the candle to the flame. As the wax burns, it produces a characteristic teardrop-shaped flame as air is heated and expands, moving upward. In the microgravity of space, candle flames slightly influenced by gravity are round or dome-shaped.

oxidation: process involving the loss of electrons (or the addition of an oxygen atom)

Oxidation is a chemical process in which the substance being oxidized loses electrons to another substance that is simultaneously reduced. Magnesium metal burns vigorously in air, producing flames and magnesium oxide. The flames produced in this reaction are caused by heating magnesium oxide particles until they incandesce, radiating visible light. Similarly, when a hydrocarbon fuel burns, particles of carbon incandesce, emitting light and passing into the surrounding air as smoke.

Efficient and complete combustion of a hydrocarbon such as methane yields carbon dioxide and water:

$$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O + \text{heat}$$

Incomplete combustion caused by insufficient oxygen yields water and carbon monoxide or carbon in place of carbon dioxide. Small amounts of carbon monoxide in air are probably harmless, but carbon particles form soot, which often contains dangerous polycyclic hydrocarbons and may carry dangerous gases into the alveoli of lungs. Carbon monoxide is a colorless, odorless, poisonous gas. Furnaces are designed to burn natural gas with a blue flame, indicating production of little carbon, and probably little carbon monoxide.

Power Plants

Fire also provides energy for power plants. Energy is defined as the ability to do work, power is defined as the rate of doing work. An incandescent light bulb is rated in terms of power. A 100-watt bulb uses power at the rate of 100 watts. Power is commonly measured in watts or joules. One watt is equivalent to 1 joule per second, so a 100-watt incandescent bulb would use 100 joules of energy per second. Burning the electrical bulb for ten hours uses 1 kilowatt-hour of energy at the rate of 100 watts per hour. Homeowners purchase electrical energy, not power.

Power plants typically consist of a generator to produce electricity and a power source to operate the generator. The source of energy may be nuclear reactions or fossil fuels such as natural gas, oil, or coal. The fuel may be burned to boil water, producing steam, or burned in a diesel or internal combustion engine to turn the generator. Most thermal power plants burn fuel to boil water, forming steam, then pass the steam through turbines that spin generators, producing electricity.

The location of power plants is determined in part by the need for electricity, the availability of fuel, and water for cooling. The Four Corners power plant located at the junction of Colorado, New Mexico, Arizona, and Utah is one of the largest plants in the United States. It burns 28,000 tons of coal per day and produces 2,040,000,000 watts of power. Located far from urban areas, the plant's emissions originally seemed to pose less danger to humans than urban plants, but environmental concerns soon demanded more stringent emission controls. Emissions from the plant, located in a rural area, are now more carefully controlled, fuel from nearby coal mines is readily available, and cooling water from nearby rivers makes the energy-generation process more efficient.

Electrical energy is fed into power transmission grids that span several states. A number of power plants produce electricity that goes into the grids and is used by consumers many miles away. Distribution of alternating current allows the voltage to be stepped up by passage through transformers prior to distribution. High-voltage electricity can be transmitted more efficiently than low voltages, and the voltage is reduced through step-down transformers and transferred to distribution grids before use by consumers.

Nuclear power plants use **fissionable** materials such as uranium-235 as sources of energy. In the core of a nuclear power plant, rods of uranium dioxide (UO_2) are placed in a matrix containing moderators such as heavy water or graphite that slow neutrons so they can be captured. The neutrons impact uranium nuclei, splitting them to release lighter nuclei and converting a small amount of mass to energy. In order for a chain reaction to occur, a critical mass of fissionable material must be present.

fissionable: of or pertaining to unstable nuclei that decay to produce smaller nuclei

Nuclear power plants are designed to prevent accidents such as meltdown by careful control of fuel-rod placement and positioning of control rods made of boron or other materials that have high affinity for neutrons. If the core of the reactor should become overheated, the fuel rods are automatically pulled out of the reactor and the control rods drop in, cutting the supply of neutrons. In addition, the core of the reactor is positioned over a number of separate wells into which components would fall, separating the fissionable materials to less than a critical mass.

fusion: the act of releasing nuclear energy by combining lighter elements such as hydrogen into heavier elements

Fusion promises to provide a nearly inexhaustible supply of hydrogen fuel as well as less radioactive waste, but temperatures of fusion reactions are too high for present materials, and the huge amounts of energy needed to start fusion reactions would explode or melt any known construction materials. The fires of nuclear fusion in our Sun provided energy for early humans long before they discovered the art of combustion. SEE ALSO Chemical Reactions; Chemistry and Energy; Explosions; Fossil Fuels.

Dan M. Sullivan

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Fireworks

One of the most beautiful and entertaining uses of fire occurs in firework displays. Fireworks need a source of combustible material for energy such as black powder, a mixture of charcoal, sulfur, and saltpeter (an old name for potassium nitrate), or smokeless powder such as cellulose nitrate. In addition, fireworks contain substances that give off bright, colorful light when heated. A common example of such material is sodium in table salt. If salt is sprinkled into a flame, an orange color appears. The colored flame is a result of electrons in sodium ions absorbing energy and moving up to higher energy levels and then falling back to their ground state, emitting specific amounts of energy that correspond to colors of light. For centuries, this phenomenon has been the basis of flame tests in chemistry laboratories.

anions: negatively charged chemical unit, such as Cl^-, CO_3^{2-}, NO_3^-

oxidation: process involving the loss of electrons (or the addition of an oxygen atom)

Chemical ingredients of fireworks are chosen to produce specific colors. Barium compounds produce green colors when heated, copper salts produce green and blue flames, sodium salts are yellow in flame, lithium compounds produce red colors, magnesium metal produces brilliant white light when burned, and strontium compounds produce brilliant red colors. Salts used contain both metallic cations and nonmetallic **anions**. Anions such as chlorates, perchlorates, and nitrates also contribute **oxidizing** power to the chemical mixture.

Chemical Element	Color Produced
sodium	yellow
barium	green
strontium	red
copper	blue

While the metallic element dictates the color produced, the compound that contains the element has a profound effect on the type of flame. Calcium does not produce an exciting color by itself, but it enhances colors of other substances. Chlorine does not produce colored flames by itself, but the presence of chlorine greatly enhances the development of color from metallic elements. Chlorine-containing substances such as chlorate or perchlorate oxidizers or organic chlorine compounds such as polyvinyl chloride or hexachlorobenzene provide chlorine atoms to enhance volatility and light emission. Certain substances are included for specific effects. Iron filings sparkle and flash when mixed with other burning materials; the metallic iron oxidizes to produce Fe_2O_3, a process that produces a large amount of energy sufficient to cause the reacting iron particles to glow. Titanium metal is also used for production of sparks. Zinc is used in some smoke formulas and to produce star effects.

Fireworks consist of a source of energy such as a mixture of a fuel and an oxidizing agent that react to produce high temperatures and some substance that will emit brightly colored light. One of the simplest firework devices is a sparkler. Sparklers typically consist of a metal wire coated with a mixture of fuel and an oxidizer (mixed in proportions to allow burning), iron filings, and a glue to hold the components together. When the sparkler is ignited, the fuel and oxidizer burn, heating the iron filings so that they sparkle. Other substances such as zinc or magnesium alter the character of the sparks.

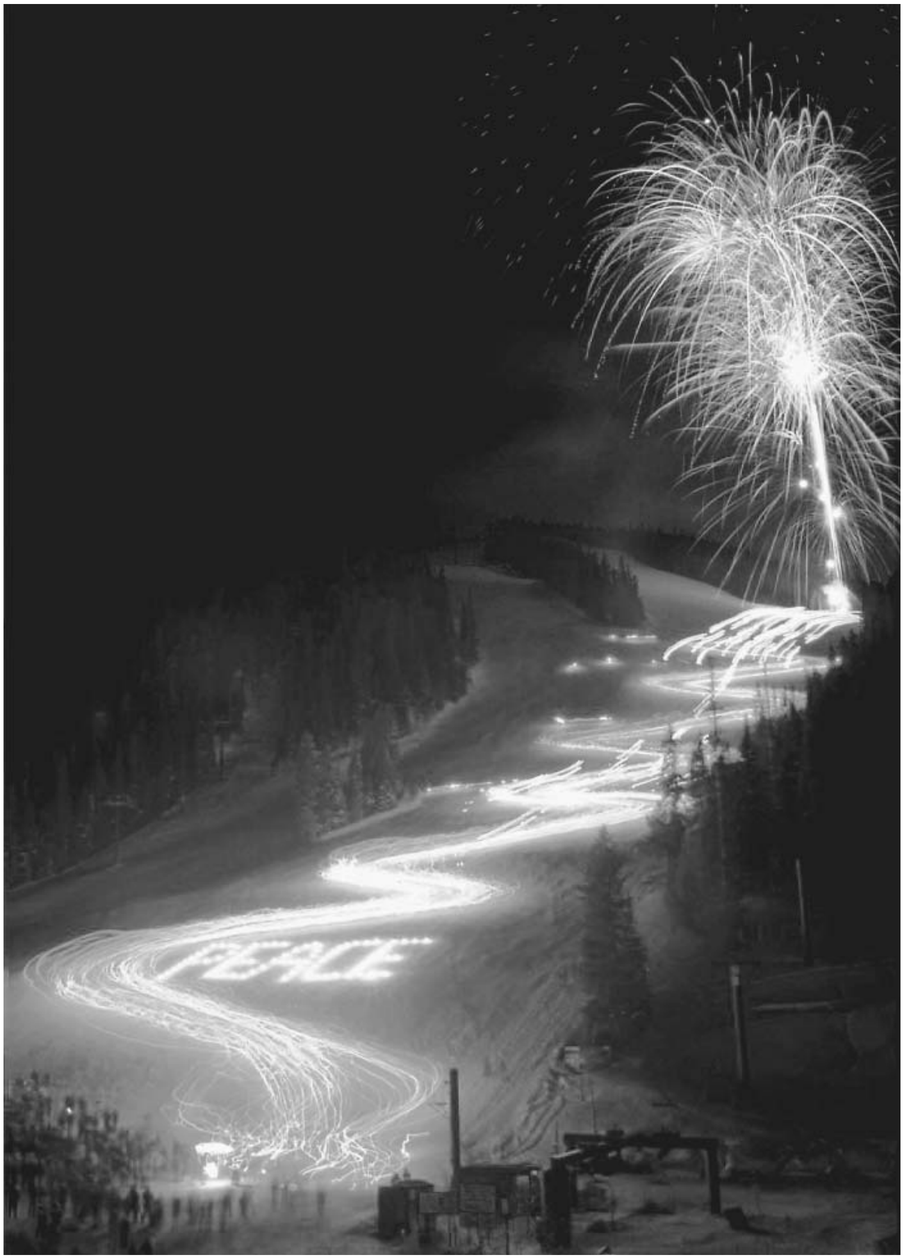
Firecrackers contain flash powder (a mixture of an oxidizer such as potassium chlorate or perchlorate and powdered aluminum or magnesium) or black gunpowder in a paper tube. An attached fuse ignites the flammable mixture, which burns explosively, producing gases that rapidly build up pressure and burst the container. Aluminum and magnesium components produce brighter flashes.

Aerial fireworks usually are of two types, aerial shells fired from tubes and the traditional skyrocket. Rockets are made of cardboard tubes filled with a mixture of fuel and oxidizer in proportions that allow continuous burning rather than explosion. Expulsion of gases from the tube propels it skyward. Rockets often contain explosive charges to explode after the propellant charge burns out; the composition of the explosive charge determines the colors produced.

Aerial shells are small balls of explosive material fired from a steel or cardboard tube or stand. A lifting charge throws the ball skyward, and the explosive charge fires when the embedded fuse burns down after a time period appropriate for the shell to reach the desired altitude. The shell usually contains a bursting charge and stars made up of cubes or spheres of material that will burn, sparkle, or explode. Multibreak shells are made up of combinations of shells designed so that the explosion of one shell ignites the next.

Shells designed to explode with a bang are called reports or salutes. The whistling effect of some devices is produced by packing techniques that cause intermittent burning. Specialized shells designed to burst forming patterns such as hearts or circles are made by surrounding the break charge with pellets containing explosive charges. When the break charge explodes, the pellets are blown outward, producing a pattern.

In addition to their value as entertainment, pyrotechnics have military applications as signaling, training, and combat devices. Burning naphthalene and anthracene produce black smoke that can be used to screen off an



Torchlight parade of skiers, Winter Park, Colorado, December 24, 1995.

area, but may be dangerous in populated areas. White smoke produced by vaporizing zinc chloride or oil or burning phosphorus is sometimes used to provide cover during combat; the hydrolysis of silicon chloride ($SiCl_4$) produces a white smoke as well.

$$SiCl_4 + H_2O \rightarrow SiO + HCl$$

The moisture in the air is usually sufficient for producing the desired reaction. Colored smokes for signaling are usually produced by volatilization of organic dyes. Burning mixtures that provide enough heat to vaporize the dye, but not enough to decompose it, are chosen. Dyes chosen must be volatile, but nontoxic.

A simple and safe home experiment can be carried out by squeezing an orange peel near a candle flame. The oils of the peel produce tiny flashes of light as they burn. Bananas contain large amounts of potassium; a banana peel in a bonfire shows the characteristic violet color of potassium flames. SEE ALSO CHEMISTRY AND ENERGY; EXPLOSIONS.

Dan M. Sullivan

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Fischer, Emil Hermann

GERMAN CHEMIST
1852–1919

Emil Hermann Fischer, born October 9, 1852, in Euskirchen, Germany, received the Nobel Prize in chemistry in 1902 for his elucidations of the structure of sugars and the **synthesis** of purines. His father, a very successful lumber merchant, intended Emil to join the family business upon completion of his secondary school education. Young Fischer showed exceptional abilities as a student in the natural sciences, particularly in physics. In 1859 he dutifully entered his father's business, but showed little aptitude for commerce. In frustration his father enrolled him at the University of Bonn in 1871 to study chemistry, which at least had practical applications.

synthesis: combination of starting materials to form a desired product

The following year he transferred to the University of Strasbourg, where he attended the lectures of Adolf von Baeyer. He gave up any remaining interest in physics for a career in organic chemistry. Fischer pursued graduate studies in chemistry under von Baeyer's mentorship, and was awarded a doctorate degree in 1874. In the course of his doctoral research he synthesized the compound phenylhydrazine, which would prove to be invaluable in his studies of carbohydrates (but would also, because of his prolonged exposure to it, leave him with cancer).

In 1875 Fischer followed von Baeyer to the University of Munich, and in 1881 he obtained his first academic post as professor of organic chemistry at the University of Erlangen. This was followed by his being called to the University of Würzburg in 1888, and finally, in 1892, to the University of Berlin, where he remained until his death in 1919. His son Hermann Otto (1888–1960) went on to have a distinguished career in biochemistry.

Fischer's most important scientific work was carried out between 1882 and 1906. Little was known about the naturally occurring sugars when Fischer began his investigations of them in 1884. Four sugars were known at that time: **glucose**, **galactose**, fructose, and sorbose, each having the formula $C_6H_{12}O_6$. It was known that each had a six-carbon chain, and five alcohol groups as well as a carbonyl (**aldehyde** or **ketone**) **functional group** attached to the chain.

glucose: common hexose monosaccharide; monomer of starch and cellulose; also called grape sugar, blood sugar, or dextrose

galactose: six-carbon sugar

aldehyde: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the RC(O)H functional group

ketone: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the FC(O)R functional group

functional group: portion of a compound with characteristic atoms acting as a group

Fischer saw in the sugars what no one else had seen. In 1874 Dutch chemist Jacobus van't Hoff had proposed that molecules in which a central carbon atom is bonded to four constituent atoms had a tetrahedral geometry in space, and that if a carbon atom were bonded to four different constituents, the molecule could exist in two forms (as stereoisomers) that were mirror images of one another. These two forms would possess distinct right- and left-handedness. Fischer realized that in glucose there were four carbon atoms that met the criteria for exhibiting stereoisomerism. A glucose molecule would exist as one of sixteen possible stereoisomers, each differing only by its orientation in space. Using the methods of chemical synthesis and degradation that were available to him, he was able by 1891 to identify the structures of all isomers of the naturally occurring D-glucose.

To enable representation of these isomers on the flat surface of a page, Fischer developed a notation system (Fischer projections). Fischer projections denoted right- and left-handed isomers. These were called D (dextrorotatory) and L (levorotatory), respectively, and the compound glyceraldehyde (which exists in two forms) was used as a reference.

With the Fischer projections, the constituents on the horizontal lines may be envisioned as coming out of the page, and the vertical constituents, as pointing backward, away from the onlooker. Fischer assumed the D isomer corresponded to the projection in which the OH group was to the right of the CH_2OH group. This assignment (which was a guess) was proven correct in 1954 when the orientations in space of the glyceraldehyde stereoisomers were established by x-ray analysis.

Fischer's identification of the stereoisomers of D-glucose (naturally occurring d-glucose was the sugar that Fischer worked with) was important validation of the ideas of van't Hoff.

In 1899 Fischer turned his attention to the study of proteins, wishing to understand their chemical structures. It was known at that time that proteins were composed of amino acids, and thirteen naturally occurring ones were identified. Fischer was able to isolate via the hydrolysis of proteins three additional naturally occurring amino acids: valine, proline, and hydroxyproline. Amino acids exhibit stereoisomerism, and Fischer was able to separate individual forms from mixtures of stereoisomers for several of these compounds.

Another Fischer achievement was the synthesis of small peptides via the condensation of amino acids. Fischer suggested that there was a common linkage that held pairs of amino acids together in all proteins—the peptide bond. He understood that proteins were tremendously complex, owing to the large number of constituents and the fact of stereoisomerism. By 1916 Fischer had synthesized and characterized 100 peptides, but knew they represented a tiny fraction of what was possible. SEE ALSO AMINO ACID; CARBOHYDRATES; ISOMERISM; VAN'T HOFF, JACOBUS.

Martin D. Saltzman

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Fission ***See Transmutation.***

Fleming, Alexander

SCOTTISH BACTERIOLOGIST
1881–1955

Alexander Fleming will always be remembered for turning a laboratory mishap into one of the great medical discoveries of the twentieth century. His discovery of penicillin in 1928 laid the foundation for modern antibiotic therapy and earned him a share of the 1945 Nobel Prize in physiology or medicine.

Fleming was born on August 6, 1881, at Lochfield near Darvel in Ayrshire, Scotland. He attended elementary and secondary school in Scotland and then moved to London to attend the polytechnic school. He graduated with distinction in 1906 from St. Mary's Medical School, London University, received a graduate degree in bacteriology from St. Mary's in 1908, and lectured there until 1914. After serving as a captain in the Army Medical Corps during World War I, Fleming returned to St. Mary's in 1918.

Throughout his career Fleming was intensely interested in naturally occurring antibacterial substances, and penicillin was actually the second antibiotic that he discovered. In 1922 he described the antibacterial properties of lysozyme, a substance found in egg whites, mucus, and tears, which lysed, or dissolved, certain bacteria. Fleming found that lysozyme could turn a thick, milky white suspension of bacteria into a clear solution in a matter of seconds.

Unfortunately, lysozyme failed to destroy bacteria that caused human diseases and was never used as a medicine. Despite the limited utility of lysozyme, Howard Florey and Ernst Boris Chain of Oxford University later determined both its structure and the mechanism by which it destroys bacteria. These two scientists would figure prominently in Fleming's greatest discovery: penicillin.

Fleming freely admitted that he was not looking for a new antibiotic when he discovered penicillin in 1928. In fact, he was working on a problem unrelated to antibiotics when he returned to his lab from a month-long vacation and observed that a blue mold, or fungus, had grown on a discarded **culture** plate of *Staphylococcus aureus* (a common bacteria that causes many diseases in humans). Fleming further observed that a bacteria-free zone had developed around the mold. The once thick cultures of bacteria near the mold had become translucent, or almost clear, and evidently a substance produced by the mold had diffused through the culture medium and killed the bacteria.

culture: living material developed in prepared nutrient media

Scottish bacteriologist Sir Alexander Fleming, corecipient, with Ernst Boris Chain and Sir Howard Walter Florey, of the 1945 Nobel Prize in physiology or medicine, "for the discovery of penicillin and its curative effect in various infectious diseases."

The extraordinary appearance of the bacteria-free zone interested Fleming, so he set out to isolate the mold in pure culture and to determine some of its properties. Fleming classified the mold as *Penicillium rubra*, hence, the name penicillin for the active substance.

excrete: to eliminate or discharge from a living entity

Fleming tested the purified mold against other bacteria and observed that some bacteria grew right up to the mold, while others grew only to within a few centimeters of it. He tested other molds for their ability to kill sensitive bacteria and found none. Fleming then grew the mold in a liquid medium and determined that the mold **excreted** penicillin into the culture medium. When he tested the medium against common bacteria, Fleming found that the growth of many disease-causing bacteria was inhibited. He even injected the medium into mice and observed no toxic effects from the new substance.

Although Fleming was convinced that penicillin had enormous potential value in medicine, he was unable to produce enough of it to demonstrate its value to the medical community. He published his findings in 1929, and penicillin seemed destined for obscurity. But in 1938, Florey and Chain began to reinvestigate penicillin and eventually produced enough pure material to demonstrate that Fleming's assertions were correct. Penicillin has indeed had enormous value in the treatment of infections worldwide. SEE ALSO ANTIBIOTICS; PENICILLIN.

Thomas M. Zydowsky

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Fluorine

9
F
FLUORINE
18.9984

MELTING POINT: −223°C
BOILING POINT: −188°C
DENSITY: 1.696 g/cm^3
MOST COMMON IONS: F^-

isotope: form of an atom that differs by the number of neutrons in the nucleus

Fluorine is a chemical element that in pure form occurs as a dimer of two fluorine atoms, F_2. The fluorine atom has the ground state electron configuration $1s^2 2s^2 2p^5$. There is only one stable, naturally occurring **isotope** of fluorine: ^{19}F. However, the radioactive isotopes ^{17}F, ^{18}F, and ^{20}F are known. The inclusion of the isotope ^{18}F (half-life 110 minutes) in bioorganic molecules is an important noninvasive technique used in the study of living tissue by positron emission tomography.

electronegative: capable of attracting electrons

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

Fluorine is the most **electronegative** element. It is the lightest and most reactive element in the **halogen** family. Fluorine is a poisonous, corrosive, pale yellow gas with an acrid odor. It is the most powerful oxidizing agent known. The low F–F bond energy and the high energy of bonds between fluorine and other elements combine to make reactions of fluorine exothermic.

Elemental fluorine was first prepared by Henri Moissan in France in 1886 via the electrolysis of anhydrous hydrogen fluoride in the presence of potassium fluoride. Fluorine forms compounds with all of the elements except helium, neon, and argon. In nature, fluorine is primarily found in the minerals fluorospar (CaF_2), cryolite (Na_3AlF_6), and fluoroapatite ($CaF_2 \cdot 3Ca_3(PO_4)_2$), together comprising 0.065 percent of Earth's crust (making fluorine the thirteenth most abundant element). These minerals are widely used as electrolytes in the preparation of aluminum, as fluxes in the **metallurgy** of iron, and as additives in ceramics.

Other important inorganic compounds of fluorine include uranium hexafluoride, UF_6, a **volatile** substance that was used to separate ^{238}U from the **fissionable** ^{235}U by gaseous diffusion in the **Manhattan Project**. Sodium fluoride, NaF, is often added to drinking water and to toothpaste in order to reduce the incidence of tooth decay.

When hydrogen is replaced by fluorine in organic compounds, the properties of the compounds are substantially altered. The new compounds have increased chemical, thermal, and oxidative stability. Low molecular weight **chlorofluorocarbons**, known as Freons, are nonflammable, dense, nontoxic compounds particularly useful as refrigerants and blowing agents. Substitutes for these ozone-depleting compounds are being developed.

Teflon (polytetrafluoroethylene) is a chemically **inert** polymer used to create nonstick frying pans. Polytetrafluoroethylene can be modified to form a coating, Gore-Tex, which allows the passage of water vapor, but not liquid water, and is used in many articles of clothing. Polymeric perfluorinated ethers are widely used as high performance oils and lubricants.

The introduction of one to three fluorine atoms to large organic molecules, such as steroids, has been shown to modify the biological activity of these molecules. Many of these fluorine-containing compounds that are useful as pharmaceutical agents have been prepared. The compound 5-fluorouracil is a widely used anticancer agent. Prozac (containing fluorine) is a well-known antidepressant drug. In addition, agrochemists have developed many herbicides (e.g., trifluralin), insecticides (e.g., diflubenzuron), and fungicides (e.g., flutriafol) that incorporate fluorine. Fluorinated dyestuffs and fluorinated liquid crystals have also found commercial use. SEE ALSO ATMOSPHERIC CHEMISTRY; HALOGENS; OZONE.

Suzanne T. Purrington

metallurgy: the science and technology of metals

volatile: low boiling, readily vaporized

fissionable: of or pertaining to unstable nuclei that decay to produce smaller nuclei

Manhattan Project: government project dedicated to creation of an atomic weapon; directed by General Leslie Groves

chlorofluorocarbon (CFC): compound that contains carbon, chlorine, and fluorine atoms; it can remove ozone in the upper atmosphere

inert: incapable of reacting with another substance

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Food Preservatives

Most foods contain enzymes or natural chemicals, such as acids or alcohols, that cause them to begin to lose desirable characteristics almost immediately after harvest or preparation. In addition, a host of environmental factors, such as heat and the presence of microorganisms, acts to change foodstuffs in ways that may harm the food product. Food preservation traditionally has three goals: the preservation of nutritional characteristics, the preservation of appearance, and a prolongation of the time that the food can be stored. Traditional methods of preservation usually aim to exclude air, moisture, and microorganisms, or to provide environments in which organisms that might cause spoilage cannot survive.

Ancient peoples are known to have had dried fruits, vegetables, and meats. The pemmican of Native Americans and the jerky consumed by present-day campers and hikers are both prepared by drying. The drying process can include smoking, which may actually add antibacterial agents. The processes of dehydration and freeze-drying, used today to produce such foods as powdered coffee and soup, are variations of drying.

Among the earliest preservatives were sugar and salt (NaCl), which produced food environments of high osmotic pressure that denied bacteria the aqueous surroundings they needed to live and reproduce. Jams and jellies are preserved as solutions of high sugar content, and many meats (e.g., hams) and fish are still preserved by salting. Unlike other microorganisms, molds can often withstand the effects of high salt or sugar concentrations in foods. Fortunately, they seldom cause illness.

paraffin: saturated aliphatic hydrocarbon (alkane), or hydrocarbon wax

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Early methods of air removal included the sealing of foods inside containers (such as jars), or the covering of food surfaces with hot **paraffin**. The invention of canning by Nicolas Appert enabled commercial preparations of foodstuffs. In response to a prize offered by Napoléon in 1795, Appert developed a method of canning and preserving fruits and vegetables in glass containers for sea voyages. His process was used commercially in 1910 by Peter Durand in England, using **metal** cans. During the earliest days of canning, some persons (including some Arctic explorers) probably died as a result of exposure to the lead that was once used to solder cans. Modern techniques of air removal include vacuum sealing and the use of plastic wrappings.

Along with cooking, which kills most bacteria, freezing stops or slows bacterial growth as well as changes in foods brought about by enzymes present in the foods. Unlike the slower freezing of foods in homes, quick freezing in commercial processing enables foods to retain more of their natural appearance and taste.

vitamins: organic molecules needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

Chemical preservatives include free radical scavengers (also known as antioxidants), such as **vitamin** C and compounds such as BHA (butylated hydroxyanisole), and bacterial growth inhibitors, such as benzoic acid, sulfur dioxide, and sodium nitrite ($NaNO_2$). Ethanol (CH_3CH_2OH) has long been used as a preservative, both of itself (as in wine), and of other foods (e.g., fruits stored in brandy). Some chemical preservatives may be harmful: Sulfur dioxide (often used to preserve wines) is irritating to the bronchial tubes of persons who have asthma, and nitrites have been implicated as carcinogens.

After Louis Pasteur proved that it was the presence of bacteria that caused food to spoil, there was a tendency to consider all microorganisms harmful. But in fact, microbial action is responsible for the production and preservation of some foods. The action of microbes is a part of the production of cheese and some flavoring agents. Sauerkraut is both processed

Nitrates are a common preservative in luncheon meats.

and preserved by lactobacilli, and yeast cells ferment sugars, producing alcohol, which may add zest to beverages as well as help to preserve them.

The irradiation of foods has the advantage of enabling food packaging and preparation in which there is less person-to-food contact, thus decreasing the possibility of contamination and decreasing the need for chemical preservatives, some of which may be harmful. The ionizing radiation that is used to irradiate foods, wherein the foods are exposed to bursts of high-intensity x rays or streams of electrons, disrupts bacterial **DNA**. Some persons have objected to the irradiation of foods because of an (unfounded) fear of radioactivity. As pathogens such as virulent strains of coliform bacteria have caused food poisoning, the irradiation of animal carcasses and, in particular, of hamburger during its preparation has become more desirable. Irradiation currently extends the shelf lives of foods such as strawberries. Irradiation does not make foods radioactive, but may cause changes in food color or texture. SEE ALSO Ascorbic Acid; Carcinogen; Kinetics; Pasteur, Louis.

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

Dan M. Sullivan

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Forensic Chemistry

Few processes are more important to society than solving crimes, both to protect the public from criminals and to protect the innocent from unjust punishment. Very often, the strength of a prosecution rests on the ability of law enforcement personnel to connect the accused with the victim by matching physical evidence from the crime scene or victim with trace evidence found on or about the person accused of the crime. Forensic investigators consult a wide range of experts who analyze evidence collected at crime scenes and brought to the crime laboratory for examination. Forensic chemists perform specialized analyses to identify materials and learn the nature of such evidence. A highly trained forensic chemist can determine the composition and nature of materials and predict the source as well as matching sample against sample. Modern chemistry employs a wide range of analytical techniques along with traditional methods of analysis.

Physical evidence collected at crime scenes is sealed in special containers to prevent contamination and degradation and is catalogued carefully. A **chain of custody** is established and documented as the evidence is sent to a forensic laboratory. At the laboratory, the evidence is examined by personnel trained in one of several fields: Forensic serologists examine body fluids, forensic pathologists examine human remains, firearms technicians classify and test firearms and explosives, and forensic chemists determine the composition and identity of materials.

chain of custody: sequence of possession through which evidentiary materials are processed

The History of Forensic Chemistry

Poisons were employed by early Egyptians and ancient Greeks and Romans. Democritus was probably the first chemist to study poisons, and he communicated some of his findings to **Hippocrates**. Poisons were used both for murder and as a means of execution; the philosopher **Socrates** was condemned to death by drinking **hemlock**. Ancient Roman civilization had laws against poisoning in 82 B.C.E. Before the development of systematic, scientific criminal investigation, guilt was determined largely by circumstantial evidence and hearsay. **Arsenic** was a popular poison in Roman times. It was referred to as inheritance powder in early France. The Blandy trial of 1752 was the first instance of an actual chemical test for poison, and the Marsh test, developed in 1836, was the first reliable analysis that could show scientifically that arsenic was present in the body of a victim.

Hippocrates: Greek physician of fifth century B.C.E. known as "Father of Medicine"

Socrates: Greek philosopher, ca. 470–399 B.C.E.

hemlock: poisonous herb of the genus Conium

arsenic: toxic element of the phosphorus group

Every chemist is schooled in general, organic, and analytical chemistry, but forensic chemists also specialize in specific areas of expertise. For example, an inorganic chemist may examine traces of dust by using **microchemistry** to identify the chemical composition of tiny particles. Another chemist might employ thin-layer **chromatography** during the analysis of

microchemistry: chemical investigation carried out on a small scale

chromatography: the separation of the components of a mixture in one phase (the mobile phase) by passing it through another phase (the stationary phase) making use of the extents to which the components are absorbed by the stationary phase

Forensic scientists examine evidence from crime scenes in an effort to solve crimes. This scientist is removing a piece of blood-stained material gathered at a crime scene for DNA testing.

blood or urine for traces of drugs, and still another might use chemical reactions in test tubes to identify larger samples of compounds.

What Do Forensic Chemists Do?

Forensic chemistry encompasses organic and inorganic analysis, **toxicology**, arson investigation, and **serology**. Each method of analysis uses specialized techniques and instrumentation. The process may be as simple as setting up a density gradient column to compare soil samples or as complicated as using a mass spectrometer or **neutron activation analysis** to characterize an unknown substance.

toxicology: division of pharmacology dealing with poisons, their identification, detection, effects on the body, and remedies

serology: the study of serum and reactions taking place within it

neutron activation analysis: method for detecting traces of elements by bombardment with high-flux neutrons and then measuring the decay rate of the radioactive products

A wide array of laboratory techniques and instrumentation is used in forensic studies. This includes ultraviolet, infrared, and visible spectrophotometry; neutron activation analysis; gas chromatography and mass spectrophotometry; high pressure liquid chromatography; and atomic absorption spectrophotometry. The techniques and instrumentation chosen depend on the type of sample or substance to be examined.

The fact that most samples examined are not pure substances, but are often mixed with dirt or debris, presents a major challenge to the forensic chemist. This may also be an advantage, as every substance collected at a crime scene is a unique mixture of chemical compounds that can ultimately be identified. Arsonists, for example, often use accelerants such as gasoline or kerosene to speed **combustion** and spread flames in the interior of a building. A forensic chemist may collect samples of burned and unburned materials, extract the **volatile** hydrocarbons, and separate the components for analysis by gas chromatography.

combustion: burning, the reaction with oxygen

volatile: low boiling, readily vaporized

Analytical Techniques and Instrumentation

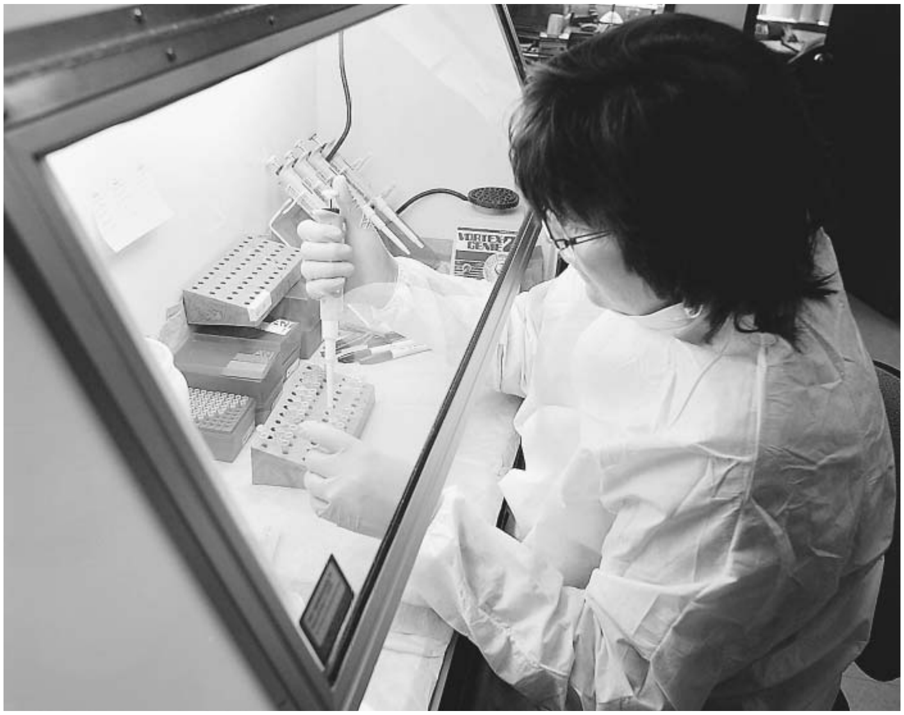
The gas chromatograph (GC) separates volatile substances into separate components by passing the volatile materials through a long absorbent column. The technique is highly reproducible and reliable; since each sample is likely to contain a definite number and type of impurities, it may provide a close match of the unknown accelerant to a known source such as a gasoline tank or hardware store. It may be necessary to vaporize a tiny sample of the material to provide volatile gases for analysis. The components of the vapor are then passed through the column and separated into a number of components, each of which can be captured and analyzed. In most cases, the accelerant will be mixed with portions of burned paint or building materials, making simple identification by examination impossible, but the ability of the GC to separate tiny portions helps in identification.

The GC is often connected to a mass spectrometer. Mass spectrometry (MS) breaks samples apart and separates the ionized fragments by mass and charge. Vast libraries of comparison fragments make computer-aided identification of materials possible even when the sample is very small. Most forensic laboratories have access to a combined gas chromatograph/mass spectrometer (GC/MS). High pressure liquid chromatography (HPLC) separates many types of drugs and may also be combined with MS.

Analysts may use several types of spectrophotometry. A typical spectrophotometer consists of a light source that provides light of a known wavelength; a holder to position solid, liquid, or gaseous samples; and a system of lenses and photocells that compare light shining on the sample with light passing through. A decrease in the intensity of light passing through the substance indicates the presence of materials that absorb light at that wavelength; the absorbance is quantitative and a measure of the concentration of material, and the wavelengths of maximum absorbance are characteristic of the type of material. Infrared spectrophotometry is especially useful for the identification of organic compounds, as bonds between certain atoms readily absorb infrared radiation (IR).

Ultraviolet (UV) spectrophotometry helps distinguish between samples of proteins and nucleic acids such as deoxyribonucleic acid (**DNA**). Atomic

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell



At the Colorado Bureau of Investigation in Boulder, lab agent Kathy Dressel works on DNA evidence in the JonBenet Ramsey murder investigation.

absorption spectrophotometry provides ways of determining absorption and emission spectra, useful tools in the analysis of **metals** such as bullet fragments.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

nuclear: having to do with the nucleus of an atom

Nuclear magnetic resonance spectrophotometry (NMR) makes use of the fact that nuclei of some molecules absorb radio frequency radiation in strong magnetic fields. Nuclei in certain molecules absorb radiation at characteristic frequencies, making the identification of even tiny or impure samples possible. X-ray analysis allows the forensic investigator to visualize foreign objects within the body.

In neutron activation analysis, a beam of neutrons from a nuclear reactor is directed at a sample of test material. The material becomes temporarily radioactive, emitting γ-rays that are characteristic of the composition; analysis of the γ-radiation provides a highly accurate and reproducible determination of the content of the sample. This technique has made possible the determination of arsenic in the hair of corpses buried for hundreds of years. In one case, the body of an Arctic explorer who had died under suspicious circumstances during the 1870s was found buried in a coffin surrounded by ice. Neutron activation analysis of hair from the body showed that hair that was several centimeters long contained little arsenic, but that shorter hair closer to the scalp (which had grown in the few days before death) contained high levels of arsenic, indicating that death was probably caused by arsenic poisoning.

Often, the presence of very small impurities makes comparison possible. For example, cars are painted with paints prepared to certain specifications of color and composition, and pigments and binders used vary from one manufacturer to another and even between models from the same distributor. A small sample of paint left at the scene of an accident may be checked for color by spectrophotometry and then analyzed for composition. Perpetrators of many hit-and-run crimes have been convicted on the basis of combined GC/MS analysis of paint chips.

Residues left by burning powder from firearms consist of patterns of particles that have both characteristic physical and chemical properties. Burned powder, for example, usually contains traces of nitrites that yield chemical reactions and traces of metals such as barium that are often present in primers. Both chemical reactions and microscopic analysis (including electron microscopy) are employed in the identification of powder residues on clothes and skin. An early method for detecting gunshot residue on the hands of suspects involved coating the hand with melted **paraffin**, allowing the paraffin to cool, and then stripping it off. Gunshot residues transferred from skin to paraffin turned blue or green in the presence of diphenylamine, but many common substances such as urine gave a false positive test. The Greiss **reagent** is much more definitive, and additional tests can identify traces of lead around bullet holes. Even microscopic particles are found to have definite compositions and can be unequivocally identified.

paraffin: saturated aliphatic hydrocarbon (alkane), or hydrocarbon wax

reagent: chemical used to cause a specific chemical reaction

Toxicology

Toxicologists examine a wide range of materials such as blood stains, urine, and blood gases for traces of poisons or drugs. Many businesses now require the drug screening of employees; it is the responsibility of the technician to distinguish between the presence of illegal drugs and **metabolites** from foods such as poppy seeds. Such tests may be as simple as paper or thin-layer chromatography or as complicated as gas chromatographic or electrophoretic and serological analysis of a blood sample. Following death by unknown cause, samples of the victim's lungs, blood, urine, vitreous humor, and stomach contents are examined for traces of poisons or medication. Insects found on or near corpses are also collected and examined; they may actually absorb traces of drugs or poisons from the body, and in fact, traces of poisons sometimes are found in the surrounding insects long after concentrations in the body have fallen below detectable limits.

metabolites: products of biological activity that are important in metabolism

Forensic biochemists perform blood typing and enzyme tests on body fluids in cases involving assault, and also in paternity cases. Even tiny samples of blood, saliva, or semen may be separated by **electrophoresis** and subjected to enzymatic analysis. In the case of rape, traces of semen found on clothing or on the person become important evidence; the composition of semen varies from person to person. Some individuals **excrete** enzymes such as acid phosphatase and other proteins that are seldom found outside seminal fluid, and these chemical substances are characteristic of their semen samples. The presence of semen may be shown by the microscopic analysis for the presence of spermatozoa or by a positive test for prostate specific antigen.

electrophoresis: migration of charged particles under the influence of an electric field, usually in solution; cations, positively charged species, will move toward the negative pole and anions, the negatively charged species, will move toward the positive pole

excrete: to eliminate or discharge from a living entity

In cases of sexual assault, tiny samples of DNA in blood, semen, skin, or hair found on the victim may be purified and the amount of DNA increased by the use of a polymerase chain reaction to produce quantities large enough to analyze. Since DNA is as specific to a person as fingerprints, matching the DNA of a perpetrator to a sample found on a victim is considered to be proof of contact. The Federal Bureau of Investigation (FBI) is currently in the process of establishing a national Combined DNA Index System (CODIS) that will collect data from many states and law enforcement agencies and index it so that particular DNA patterns from evidence collected at many crime scenes can be compared and matched. Many perpetrators of crimes have been convicted and many innocent persons set free after years in prison as a result of DNA analysis.

Testing for Alcohol

Accidents caused by intoxicated drivers kill nearly 15,000 persons a year in the United States alone (almost half of fatal auto accidents are alcohol-related), so a Breathalyzer kit is standard equipment in most police squad cars or state patrol vehicles. Breathalyzers are used to estimate the blood alcohol content of drivers suspected of being intoxicated; the driver may appear sober, but still have a blood alcohol level above the legal limit. Although it is impractical to take blood samples on the highway, research has shown that the concentration of ethanol in the breath bears a definite relationship to its concentration in blood. Many communities have now set a legal limit of 0.08 percent (meaning that 100 milliliters [3.38 fluid ounces] of blood would contain 0.08 grams [0.0028 ounces] of ethanol). In fact, authorities now consider that a person's driving ability is probably impaired at a blood ethanol level of 0.05 percent.

Several types of analytic devices are available to administer Breathalyzer tests. One test makes use of a portable infrared spectrophotometer, another uses a fuel cell, and the most common test employs several glass or plastic tubes and some common chemical reagents. The person being tested blows through a tube, which bubbles the breath through a solution of chemicals containing sulfuric acid, potassium dichromate, water, and silver nitrate. **Oxidation** of the alcohol results in the reduction of dichromate ion to chromic ion, with a corresponding change in color from orange to green. An electrical device employing a photocell compares the color of the test solution with a standard solution, giving a quantitative determination of the alcohol content. The test provides a quick and reproducible determination of the amount of alcohol in a person's breath and is a numerical measure of the amount of alcohol in the bloodstream. Use of a chemical test helps to avoid subjective opinions of sobriety and provides reliable evidence for court proceedings. The test can be readily and quickly administered by trained law enforcement personnel, but forensic chemists test and calibrate the equipment and testify to its accuracy.

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

Fingerprinting

Fingerprints on smooth surfaces can often be made visible by the application of light or dark powder, but fingerprints on checks or other documents are often occult (hidden). Occult fingerprints are sometimes made visible by the use of ninhydrin, which turns purple due to reaction with amino acids present in perspiration. Fingerprints or other marks are also sometimes made visible by exposure to high-powered laser light. Some fingerprints can be treated with chemical substances, resulting in a pattern that fluoresces when exposed to light from lasers. Cyanoacrylate **ester** fumes from glue are used with fluorescent dyes to make the fingerprints visible.

ester: organic species containing a carbon atom attached to three moieties: an O via a double bond, an O attached to another carbon atom or chain, and an H atom or C chain; the R(C═O)OR functional group

Forensic chemists are usually employed by laboratories in law enforcement agencies or by private testing laboratories and are often called on to provide testimony in court proceedings as expert witnesses. In these cases, the chemist may compare evidence in the case in question to a large number of similar cases he or she has examined and is often asked to give an expert opinion as to the quality of the evidence. Since forensic chemists usually have both a bachelor's degree in chemistry and an advanced degree in forensic science, their academic credentials, along with years of experience and the ability to compare the case in question with a large number of other cases, renders the testimony both valuable and believable. SEE ALSO Analytical Chemistry; Arsenic; Careers in Chemistry.

Dan M. Sullivan

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Formulation Chemistry

Formulation chemistry is the branch of manufacturing that addresses substances that do not react with each other, but have desirable properties as a mixture. These products include paints, varnishes, cosmetics, petroleum products, inks, adhesives, detergents, pesticides, and a broad range of household products.

Successful formulation requires a blend of art and science. Components are chosen for compatibility rather than reactivity. Formulation chemists think in terms of kilograms or tons rather than moles and place more emphasis on solubility than molecular weight.

Paints

Paints are suspensions of pigments, binders, drying agents, and vehicles. Vehicles are solvents in which the pigment is mixed. Pigments are powders made from insoluble chemicals, such as titanium dioxide, that give color to the preparation. Titanium and zinc oxides have largely replaced lead pigments in paint.

Binders bind pigments to surfaces. They solidify by drying, cooling, or reacting to produce polymers. Acrylic paints use polymer resins as vehicles. They can be thinned with water, but dry readily. Drying agents aid in the evaporation of a vehicle or help paint mixtures to polymerize.

Cosmetics

The cosmetic industry provides a wide assortment of formulated products. A typical bathroom contains a full range of perfumes, moisturizers, rouge, lipstick, antiaging skin products, face powder, emollients, nail polish, sunscreen, hair conditioning and coloring products, aftershave, drugs, and deodorants as well as medications.

Nail polish consists of flexible lacquers, pigments such as organic dyes, iron or chromium oxides, and ultramarine blue along with drying agents and binders or vehicles such as ethyl acetate that evaporate on drying. Nail polish remover is usually an organic solvent such as acetone or ethyl acetate.

Perfumes have been used since the days of ancient Egypt. Perfume bottles are among the most ancient glass items recovered in Asia, where perfumes were probably first extracted from plant materials such as roses, geraniums, or lemon oils. Later processes blended animal products such as ambergris and musk. The first perfumes were probably developed to mask the odors of disease or poor hygiene. Modern perfumes include components blended to produce a combination of scent that will last for several hours and provide a combination of notes (or fragrance impressions). The first note is the odor perceived when one sprays or applies perfume from a bottle. The second note or odor develops after the perfume has made contact with the skin, and the third note is the ability of fragrance to linger.

Most perfume preparations are not patented, but considered trade secrets, so manufacturers are not required to list their ingredients. High-quality perfumes are mixtures of substances that appeal to certain individuals. Typical ingredients include extracts of flowers and fragrances such as valerian, lavender, chamomile, passionflower, ylang-ylang or vanilla, geranium, mint, lemon, fixatives such as ambergris or musk, and water or alcohols. The formulation of perfumes is an art practiced by technicians who have developed abilities to perceive individual and blended fragrances. In addition to products for personal application, perfumes are used in numerous cleaning products.

Detergents

Detergents are among the most common household products and act as **wetting agents**. Water is a polar compound that readily dissolves most salts and polar compounds such as sugar. **Nonpolar** solvents such as gasoline or carbon **tetrachloride** (CCl_4) do not mix well with water, but dissolve nonpolar substances such as grease or oil.

wetting agent: molecule that, when added to a liquid, facilitates the spread of that liquid across a surface

nonpolar: molecule, or portion of a molecule, that does not have a permanent, electric dipole

tetrachloride: term that implies a molecule has four chlorine atoms present

Shampoo contains a mixture of ingredients, including detergents, that allow water to wet the nonpolar oils found in bodily secretions such as sebum, the oily substance which holds dirt and dead skin in hair. Common anionic detergents include sodium or ammonium lauryl sulfates. Cationic detergents, which act to condition hair as well remove dirt and oil from it, include alkyl ammonium compounds such as stearylammonium chloride or sulfate. Other components of shampoo include **surfactants** such as polyethylene glycol, antifoaming agents, thickeners, antistatic agents, and pH balancers. Formulation chemists add coloring or pearlizing agents and perfumes to shampoos to make them more attractive.

surfactants: surface-active agents that lower the surface tension of water; e.g., detergents, wetting agents

Much of the scum that forms on the walls of showers is a soap film, actually calcium or magnesium salts of fatty acids. Most soaps are sodium or potassium salts of fatty acids that function well as surface active or wetting agents, but calcium and magnesium ions in hard water form insoluble compounds with these fatty acids that dull shower walls. Shower cleaners typically contain chelating agents such as ethylenediamine tetraacetate (EDTA) that form soluble complexes with the ions. In addition, a surfactant such as an ethylene glycol ether wets the wall so water droplets run off. Isopropyl alcohol is a solvent both for the ingredients and for substances such as oils that are not water-soluble.

Sunscreen

A well-designed sunscreen does two things: It blocks harmful ultraviolet (UV) rays and allows the skin to tan. UV rays carry high energy and are suspected to cause cancer by damaging **DNA**. In addition, excess UV exposure causes increased wrinkling of the skin. Zinc oxide (ZnO) and titanium dioxide (TiO_2) are the long-term ingredients of most sunblockers, considered broad-spectrum agents because they block all UV light. Many sun worshipers or outdoors enthusiasts apply a coat of reflective zinc oxide and cream to their noses and ears for extra protection.

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

High energy in sunlight comes in two portions: UV-A (320–400 nanometers, or 1.2×10^{-5}–1.6×10^{-5} inches) and UV-B (290−320 nanometers, or 1.1×10^{-5}–1.2×10^{-5} inches). Since the light of shorter wavelength radiation is more energetic, UV-B causes burning, while UV-A promotes tanning. Although not as likely to result in sunburn as UV-B, exposure to UV-A does cause eventual wrinkling and aging of the skin. p-Aminobenzoic acid (PABA) in sunscreen absorbs the energy of UV-B while allowing UV-A to pass through. Other aromatic organic compounds such as benzophenone or oxybenzone are used with or in place of PABA. In the formulation process chemists must choose emollients and sunscreens that remain dispersed without precipitating from solution and feeling gritty.

Although probably harmless at the low concentrations used, most aromatic organic compounds pose some risk of cancer or of interference with bodily hormones, but this risk is probably lower than that of skin cancer or wrinkles. New technology allows encapsulation of the active ingredients of sunblockers in tiny polymer bags that keep the chemical agents away from the skin.

Dihydroxyacetone (DHA) acts as a self-tanning agent to give sunless tans. The browning action probably involves the reaction of DHA with free amino acids to form melanoidins. Melanoidins probably offer only slight UV protection.

Ancient Romans were aware of the bleaching effects of sunlight and used this and other processes to lighten hair. Modern bleaching is done with oxidizing agents such as hydrogen peroxide that destroy melanin, the natural pigment of hair. Hair containing no pigment is light-colored or white.

Hair Coloring Products

Hair coloring products are either temporary or permanent. Temporary hair colors attach to the surface of hair and wash out after repeated shampoos.

A dye is considered permanent if it penetrates into the hollow hair shaft. Coloring of hair starts with a treatment of substances such as hydrogen peroxide and ammonia. The ammonia causes hair shafts to swell and open, allowing dye **intermediates** and couplers to penetrate. Dyes applied during the second step of coloring react with the precursors to form pigments that remain in the hair.

intermediate: molecule, often short-lived, that occurs while a chemical reaction progresses but is not present when the reaction is complete

Melanin compounds may appear brown, black, or red. The type of melanin determines hair color, and the density of melanin granules determines the shade. Dark shades of dyed hair contain higher concentrations of dyes. Most hair colors are combinations of organic compounds chosen to produce particular shades. Resorcinol produces a yellow color; aminohydroxytoluene produces a redder hair, and nitrophenylenediamine dye results in very red hair. Graded dyes favored by men often contain lead acetate. The lead ions penetrate into hair and form lead sulfide (PbS), a dark-colored compound.

Deodorants

Deodorants and antiperspirants are frequently compounded together. Deodorants seldom actually remove odor; they simply mask odors or inhibit the microorganisms that cause body odor. Deodorants include several strong perfumes, often with minty or musky odors. Odors can be lessened somewhat by decreasing perspiration. Most underarm perspiration comes from the apocrine or eccrine glands. Perspiration probably functions primarily to cool the skin and get rid of excess heat, but may also carry pheromones and fatty acids and **excrete** excess salt. The active ingredients of antiperspirants are usually aluminum salts such as aluminum chloride ($AlCl_3$). Aluminum ions are absorbed by cells in the epidermis that squeeze the sweat gland ducts closed. Talcum powders may be used to absorb excess perspiration.

excrete: to eliminate or discharge from a living entity

Gasoline

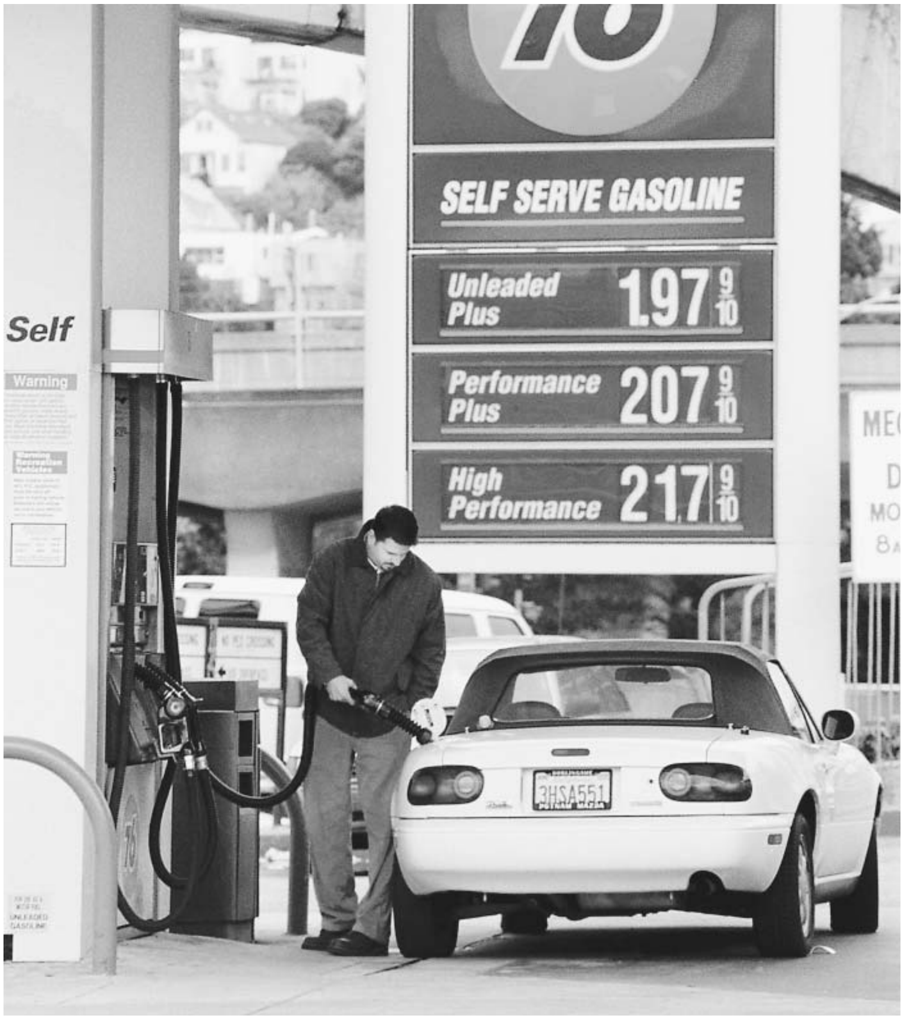
Civilization runs on gasoline. Gasoline is a solution of hydrocarbons chosen by composition and boiling point as a fuel for internal **combustion** engines. Petroleum from oil wells is a mixture of thousands of different hydrocarbons that must be refined and separated into useful components. In general, the longer and larger molecules vaporize at higher temperatures. Gasoline is a mixture of hydrocarbon chains typically seven to eleven carbons long.

combustion: burning, the reaction with oxygen

Gasolines are blended to produce mixtures that vaporize rapidly in carburetors or by passing though fuel injectors. In addition, blends are chosen to give certain octane ratings. The traditional octane rating system compares the knocking characteristics of fuels to *n*-heptane (C_7H_{16}), a fuel that knocks badly and is assigned an octane rating of zero, and isooctane (2,2,4-trimethylpentane, an **isomer** of octane, C_8H_{18}). Isooctane can be used without knocking in high-compression engines, yielding more power than low-octane fuels. The octane ratings of low-octane fuels can be raised by adding branched-chain or cyclic hydrocarbons, or by adding octane enhancers.

isomer: molecules with identical compositions but different structural formulas

The first octane enhancers were lead compounds such as tetraethyl lead (TEL) or tetramethyl lead (TML). A few milligrams of either converted inexpensive, low-octane gasoline into high-test fuels. As the danger of lead to



Gasoline, a mixture of hydrocarbon chains seven to eleven carbons long, is blended for different octane ratings.

the environment and to catalytic converters became apparent, lead compounds were phased out and lead-free gasolines introduced. Typically, lead-free gasoline contains cyclic compounds such as benzene and oxygenated additives such as ethanol, methanol, or methylcyclopentadienyl manganese tricarbonyl (MMT). Oxygenated fuels burn cleaner in cold engines.

Pesticides

Pesticides are chemical agents used to kill pests such as insects, snails, spiders, birds, or fish. Any living thing can be a pest at times; many weeds are simply plants growing in unwanted places, and prairie dogs look cute in the zoo, but their eating habits can cause widespread damage to cropland or livestock. Pesticides are, however, seriously poisonous substances.

Dichlorodiphenyltrichloroethane (DDT) is a halogenated hydrocarbon used during the 1940s to control mosquitoes and other disease vectors. Unfortunately, DDT accumulated in the environment until its high levels in the fatty tissues of birds began to cause thin eggshells and loss of life. Although its use is banned in many countries, including the United States, DDT remains a potent weapon against malarial mosquitoes in other parts of the world.

Organophosphate pesticides act by blocking cholinesterase, an enzyme that breaks down the neurotransmitter **acetylcholine** after a nerve impulse crosses the synapse. Most poisons require a lethal dose that depends on the weight of the animal. Because insects weigh much less than humans, the amount needed to kill an insect may be harmless to us. One early pesticide still in use is nicotine, an active ingredient of tobacco. Potent insecticide solutions can be made by soaking tobacco in water, but the formulation chemist produces safer preparations of standard toxicity. SEE ALSO COSMETIC CHEMISTRY; DETERGENTS; GASOLINE; PESTICIDES; SOLUTION CHEMISTRY.

acetylcholine: neurotransmitter with the chemical forumula $C_7H_{17}NO_3$; it assists in communication between nerve cells in the brain and central nervous system

Dan M. Sullivan

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Fossil Fuels

Since the beginning of the **industrial revolution**, fossil fuels have been important sources of energy. European industrialization began in the late 1700s in England, and coal soon became a major fuel. In 1850 wood was still the main energy source in the United States. During the latter half of the nineteenth century, the United States and other industrialized nations relied on coal (a fossil fuel) to provide the energy for industrialization. Coal remained the major fuel source for many years, and then, in the latter half of the twentieth century, oil and natural gas became the primary energy sources. The first oil well was drilled in Pennsylvania in 1859.

Industrial Revolution: widespread replacement of hand tools by power-driven machines, beginning about 1750 (especially in England)

In 2000, fossil fuels accounted for almost 90 percent of the world's energy production (see Table 1). **Nuclear** power and hydroelectric plants supplied about 13 percent and geochemical, wind, and solar energy sources supplied only a fraction of 1 percent. **Biomass**, including the burning of wood, is not included in the table because it is so difficult to estimate.

nuclear: having to do with the nucleus of an atom

biomass: collection of living matter

Although coal **combustion** produces substantially greater air pollution problems than does oil or natural gas combustion, because of its great abundance in the United States and other countries (such as Russia), there has been renewed interest in developing technology to burn coal more cleanly. However, all fossil fuels consist mainly of hydrocarbons (compounds that contain only carbon and hydrogen), which, upon complete combustion, yield carbon dioxide, a major greenhouse gas.

combustion: burning, the reaction with oxygen

WORLD ENERGY SOURCES IN 2000

Source	Percent of Energy
Petroleum	39
Natural Gas	24
Coal	24
Hydroelectric	7
Nuclear	6

Table 1.

It is widely accepted in the scientific community that fossil fuels (coal, oil, and gas) have a biological origin and are ultimately derived from the buried remains of plant and animal matter, although some still argue in favor of a nonbiological or inorganic source. It is believed that a small fraction (much less than 1%) of dead plant and animal matter accumulates as deposited matter, is removed from contact with atmospheric oxygen, is subject to elevated temperatures and pressures (inhibiting decomposition by bacteria), and over geological time, is transformed into fossil fuels.

Coal

Coal is considered the remnant of plants that grew in swamps hundreds of millions of years ago, and thus its source is often characterized as *terrestrial*, signifying its association with continental land masses. Terrestrial plant material characteristically contains *lignin*, a carbon-based natural polymer that provides rigidity to nonaquatic plants and enables them to stand upright against the pull of gravity. Lignin is much more resistant to bacterial degradation than other botanical components, such as cellulose, and is considered a significant contributor to the chemical composition of coal.

The extent to which lignin and other plant matter has been metamorphosed by the high temperatures and pressures associated with the gradual burial of this material determines the grade of the coal produced. As the process of coal formation (coalification) proceeds, the product is increasingly characterized by lower moisture content, greater carbon and energy content, and a greater hardness. Lignite is the softest and least metamorphosed type of coal, with a relatively high moisture content, a low fixed carbon (nonvolatile carbon) content, and a low energy content. *Subbituminous* coal is the next highest grade, and upon further coalification it can be transformed to bituminous coal, or ultimately to *anthracite*. Anthracite is the hardest coal, possessing about 95 percent fixed carbon, the lowest moisture content, and the best energy content. Coals from different sources also contain differing amounts of inorganic mineral matter (ash), which remains as a residue upon burning and thus lowers the energy content of the coal. Table 2 compares the compositions of the various types of coal.

One mineral often associated with coal is pyrite, FeS_2. The burning of coal contributes to pollution of the atmosphere, owing to the presence in coal of pyrite and organic sulfur-containing compounds. Coal is commonly burned in power plants that generate electricity, and both the inorganic (pyrite-containing) and organic forms of coal are oxidized to yield sulfur dioxide (SO_2). Sulfur dioxide reacts in air to form sulfuric acid (H_2SO_4), which is a major cause of **acid rain**. Sulfuric acid and sulfur dioxide are also lung irritants, and thus health hazards, and contribute to the corrosion of structures by their acidification of all forms of precipitation (rain, snow, fog, sleet). The impact of the atmospheric precipitation of SO_2 and H_2SO_4 has been minimized by chemical and physical processes that remove inorganic sulfur from coal (desulfurization), and by the use of coals with low sulfur content. One positive effect of higher H_2SO_4 levels in the atmosphere is the increase in cloud cover, due to the hygroscopic (water-absorbing) nature of this acid, and this may help to lower the average surface temperature of the planet—although CO_2 produced as a result of oxidization of the carbon in coal is a major contributor to global warming.

acid rain: precipitation that has a pH lower than 5.6; term coined by R. A. Smith during the 1870s

Table 2.

COAL COMPOSITION

Type of Coal	%C	%H	%O	%N	%Moisture	Heating Value (kcal/kg)
Anthracite	92–95	3–4	2–3	0–2	1–4	7500–8000
Bituminous	75–92	4–6	3–20	1–2	5–30	5000–8000
Lignite	60–75	4–6	17–35	1–2	30–50	3000–4500
Peat*	45–60	3–7	20–45	1–3	70–90	<3000

*Peat is a dark, woody soil that has not yet been coalified to lignite.

Coke

Coal can be transformed into coke and other fuels by various industrial and experimental processes. Coke is produced by the pyrolysis (heating in the absence of air) of coal and is used in the production of iron and steel. The coking procedure removes moisture and other volatile components from coal, yielding an extremely carbon-rich material. Coal can also be transformed (via intrafuel conversion) into relatively clean liquid and gaseous fuels (liquifaction and gasification). However, this is accomplished at high cost—in money and energy.

Petroleum

Petroleum is an extremely complex mixture of hydrocarbons, which can be separated into liquid (oil) and gas fractions. Compared to coal, petroleum being a liquid is easier to transport. It probably originated in marine sediments, in contrast to the terrestrial origins of coal.

Because petroleum varies greatly in composition and distribution throughout the world, elaborate systems of refining and transport have been developed. Major oil fields or giant petroleum fields ("giant" indicating oil fields capable of producing at least 500 million barrels of oil) are found primarily in the Middle East, North and South America, and countries that made up the former Soviet Union. The uneven natural distribution of oil, and the consequent need to transport oil across vast distances, has led to instances of contamination due to oil spills. Coastal waters are particularly vulnerable, not only to oil spills, but also to contamination by bilge water and tank-washing water from commercial oil tankers. Even though it is a major producer of oil, the United States has found it necessary to import significant additional amounts of oil in order to meet ever-increasing industrial and home-related energy demands. Most plastics and other petrochemicals are made from petroleum, along with almost all gasoline, diesel fuel, jet fuel, heating oil, and lubricants. However, Earth's supply of petroleum is limited. Some experts estimate that world production of oil could climax as early as 2004. Although most, if not all, of the major oil-producing fields associated with continental masses have been discovered, and many offshore wells have been drilled, there still may be other major oil discoveries in less accessible areas such as under the ocean—a largely unexplored territory.

Natural Gas

The history of natural gas dates back to 900 B.C.E., when its use was mentioned in China. It was apparently unknown in Europe until 1659, when it was discovered in England. It was not discovered in the United States until 1815 in West Virginia. In the early twenty-first century, natural gas has become the favorite fuel of industrial nations. The United States is the largest producer as well as the largest consumer of natural gas. The largest natural gas reserves are located in Russia, Kazakhstan, and Iran.

Natural gas, which consists mainly of methane (CH_4), can contain up to 20 percent of other gases—mainly ethane (C_2H_6), and possibly propane (C_3H_8), butane (C_4H_{10}), pentane (C_5H_{12}), carbon dioxide (CO_2), and nitrogen (N_2). Some natural gases contain small amounts of hydrogen, argon, carbon monoxide, or even hydrogen sulfide. Certain gas wells in Oklahoma also contain helium. In fact, they are a major source of helium in the United States. Natural gas is also colorless, odorless, and nontoxic but very flammable. (The odor we associate with natural gas is because of a mercaptan added to make gas leaks detectable.) Most natural gas is burned as fuel; however, ethane and the higher alkanes can be separated out and cracked to ethylene and propylene for making plastics. Although it is considered a "clean" and environmentally friendly fuel, compared to oil and coal, it is itself a major greenhouse gas and upon combustion yields carbon dioxide, the other major greenhouse gas. Like carbon dioxide, methane is also a greenhouse gas. However, natural gas fuel is thought to be only a minor contributor to methane in the atmosphere. Methane is constantly being generated by marsh and swamp terrain and by certain animals. Some experts believe that animals are the main source of atmospheric methane.

Other Sources of Fossil Fuels

Oil shales and tar sands also contain significant amounts of hydrocarbon materials that might eventually prove to be important energy sources. Oil shales are fine-grained sedimentary rocks (shales) that contain hydrocarbons that are dispersed within the matrix of the rock. A ton of shale contains from 10 to 100 gallons of kerogen, a waxy material that breaks down to oils when heated in the absence of air. It is estimated that three states (Utah, Colorado, and Wyoming) contain shale bearing more oil than exists in all the proven reserves in the world. Tar sands are the extremely viscous petroleum deposits associated with sedimentary rocks. They are mixtures of clay, sand, and extremely viscous oils called bitumens. The utility of oil shales and tar sands is currently limited, because of problems having to do with hydrocarbon recovery and the disposal of large amounts of inorganic residues. SEE ALSO Chemistry and Energy; Coal; Energy Sources and Production; Gasoline; Industrial Chemistry, Organic; Petroleum.

Mary L. Sohn

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Francium

MELTING POINT: 27°C
BOILING POINT: 677°C
DENSITY: unknown
MOST COMMON ION: Fr^+

87
Fr
FRANCIUM
223

The element francium is named for the country of France and its most stable **isotope** is known as actinium K. Dimitri Mendeleev assigned it the name eka-cesium prior to its actual discovery, although at this time it was also known as russium, virginium, and moldavium. Marguerite Perey, a one-time assistant of Marie Curie, discovered francium in 1939. It is not found in its elemental state and less than one ounce is thought to exist in Earth's crust at any one time.

isotope: form of an atom that differs by the number of neutrons in the nucleus

Although there are a number of isotopes of francium, most decay very rapidly to other elements. Most isotopes with masses of 223 AMU and lower emit **α-particles** (consisting of two protons and two neutrons) to become astatine. Some low mass francium isotopes can also undergo electron capture (the conversion of a proton to a neutron through the absorption of an electron) to become radon. Francium isotopes with masses of 220 AMU and higher can undergo β-decay (the conversion of a neutron to a proton through the emission of an electron) to become radium. Francium-223 is the most stable isotope and has a half-life of 21.8 minutes.

α-particle: subatomic particle with 2+ charge and mass of 4; a He nucleus

Naturally occurring francium is the product of a side reaction of the decay pathway of actinium. Actinium-227 generally undergoes β-decay to produce thorium-227, but about 1 percent of the actinium emits an α-particle to form francium-223. Francium can be produced in the laboratory via proton bombardment of thorium and during oxygen 18 (O-18) bombardment of heated gold.

Because of its extremely low abundance, short half-life, and high radioactivity, neither francium nor its compounds have economic applications. SEE ALSO Alkali Metals; Curie, Marie Sklodowska; Mendeleev, Dimitri; Radioactivity.

Nathan J. Barrows

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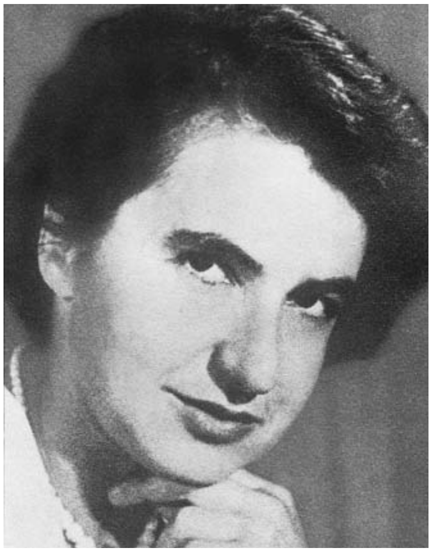
Franklin, Rosalind

ENGLISH MOLECULAR BIOLOGIST
1920–1958

Rosalind Elsie Franklin, the second of four children and the first daughter of Ellis Franklin, a wealthy Jewish banker, and Muriel Franklin (née Waley), was born on July 25, 1920, in London. Although raised in a happy home where children were encouraged to develop their individuality, Rosalind felt discriminated against because she was a girl, a feeling that surfaced again, along with an awareness of anti-Semitism, when she was working on **DNA** at King's College.

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell



English biophysicist Rosalind Franklin, who made important studies in the structure of DNA.

In 1938 Franklin graduated from St. Paul's Girls' School in London, where, at age fifteen, she decided to become a scientist. Although her father disapproved of college education for women, she attended Newnham College, a women's college at Cambridge University, from which she received a bachelor's degree in 1941. She spent a year (1941–1942) working with future (1967) Nobel chemistry laureate Ronald George Wreyford Norrish, after which she contributed to the World War II effort by working as a physical chemist for the British Coal Utilization Research Association (1942–1945). Her research on the structural changes caused by heating coal resulted in five publications, earned her a doctorate, and made her a recognized authority on crystallography and industrial chemistry.

Franklin's next three years (1947–1950) were spent as a research scientist at the Laboratoire Central des Services Chimiques de l'État in Paris. She became a researcher at King's College, London, in 1951, where she began to work on the structure of deoxyribonucleic acid (DNA), the physical basis of heredity. Her relationship with DNA coworker Maurice Hugh Frederick Wilkins (b. 1916), a biophysicist from New Zealand, soon degenerated into one of mutual dislike. In England two laboratories were working on the crystalline structures of biological materials: King's College was working on DNA, and the Cavendish Laboratory in Cambridge was working on proteins. The American James Dewey Watson (b. 1928) and the Briton Francis Harry Compton Crick (b. 1916) decided that DNA research was more exciting than the protein research in which they were thought to be engaging at the Cavendish.

monoclinic: one of several arrangements of atoms found in crystalline solids; characterized by a unit cell of three axes each of a differing length; two axes are mutually perpendicular while the third is at an oblique angle

Franklin discovered that DNA occurs in two forms (the "A" form, which is more crystalline, contains more water than the "B" form, which is the form that occurs in cells). When Watson and Crick visited King's, Wilkins showed them Franklin's x-ray diffraction photographs of the "B" structure. Her critique of Watson and Crick's earlier work helped them reformulate their structure. However, she failed to recognize the significance of the particular crystal symmetry system (**monoclinic** C2 symmetry) of "B" DNA. Crick, who was working on hemoglobin, which possessed C2 symmetry, recognized that this meant that the strands of nucleic acid are antiparallel, so they could serve as templates for each other. This insight, together with Watson's knowledge of Erwin Chargaff's base pairing, led to their final success. Watson, Crick, and Wilkins received the Nobel Prize in physiology or medicine in 1962.

Watson and Crick wished to publish quickly, before Linus Pauling, but were embarrassed that all the experimental work had been performed at King's, and Franklin's data had not been published. The heads of King's and the Cavendish approached the editors of *Nature*, who agreed to publish three articles in a single issue (April 25, 1953).

Watson and Crick's short paper was followed by an analysis by Wilkins, A. R. Stokes, and H. R. Wilson of the x-ray crystallographic data and Franklin and her graduate student Raymond G. Gosling's conclusion that the phosphate backbone of DNA lies on the outside of the structure. The Watson and Crick paper provided the experimental evidence for the helical structure of nucleic acids. Actually, Franklin and Gosling's paper provided the basis for Watson and Crick's structure, rather than being a confirmation of it.

Because Franklin and Wilkins were hardly speaking to each other, Franklin left King's College in 1953 for Birkbeck College, also in London, where she finished her DNA work and became head of the team studying tobacco mosaic virus. Franklin died of ovarian cancer on April 16, 1958, at the age of 37. SEE ALSO Deoxyribonucleic Acid (DNA); Double Helix; Pauling, Linus; Watson, James Dewey.

George B. Kauffman

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Freons

The trademark Freon refers to any of several gaseous chlorofluorocarbons, CFCs, with the general formula CF_xCl_{4-x} or $C_2F_xCl_{6-x}$. Due to their physical and chemical properties, these CFCs became the compounds of choice as propellants and refrigerants, substituting for the toxic and flammable sulfur dioxide and ammonia materials used until the early 1930s. Due to their long life, Freons drift for years in the atmosphere and eventually find their way to the stratosphere where they decompose and destroy the protective ozone layer. Current legislation calls for the elimination of Freons.

It was at an American Chemical Society (ACS) meeting in 1930 that Thomas Midgley Jr., of General Motors, announced the synthesis of dichlorofluoromethane by the “Swarts process”—a simple and inexpensive technique named after Belgian chemist Frédéric Swarts who worked on fluorine chemistry in the 1890s (Midgley and Henne, 1930, pp. 542–545). Seeking to make two points, Midgley inhaled the vapors and blew out a candle, thus demonstrating that dichlorofluoromethane was neither toxic nor flammable. The E. I. du Pont de Nemours & Co., working with the Frigidaire Division of General Electric in a joint research program called Kinetic Chemicals, registered these CFCs under the trademark of Freons.

Du Pont introduced a system of naming the CFCs according to the numbers of fluorine, hydrogen, and carbon atoms they contain. The number farthest to the right is the number of fluorines; the second digit from the right is the number of hydrogens plus one; and the third digit from the right is the number of carbons minus one. Thus, $CHClF_2$ is Freon 22; CCl_2F_2 is Freon 12; CCl_3F is Freon 11 (the zero, for the number of carbons, does not show); $C_2Cl_2 F_4$ is Freon 114; and Freon 113 is $C_2Cl_3F_3$.

Freons are essentially colorless, odorless, nonflammable, and nontoxic. Their low boiling points, low surface tension, low viscosity, insolubility in water, and general chemical inertness are quite remarkable: They remain stable in hot concentrated mineral acids and are unaffected by molten sodium. These properties result from the strong C–F bonds that become shorter as the fluorine atom to carbon atom ratio increases. Thus, the C–F bond length is 1.39 Å (angstroms) in CH_3F, 1.358 Å in CF_2Cl_2, 1.332 Å in CHF_3, and 1.323 Å in CF_4.

Because of their inert properties, Freons were quickly employed as ideal fire extinguishing, cleansing, and foaming agents, as solvents, and as aerosol propellants. Their low-pressure properties allow them to vaporize easily, and thus they were used as refrigerants. While their chemical inertness makes them valuable, it also creates a problem, as they persist in the environment for long periods, eventually diffusing into the stratosphere (altitudes of 25–40 kilometers; 15–25 miles) to decompose and then destroy the protective layer of ozone. This ozone is essential to human and animal life because it absorbs the Sun’s ultraviolet light. Without this protection, blindness, genetic damage, and skin cancers can result.

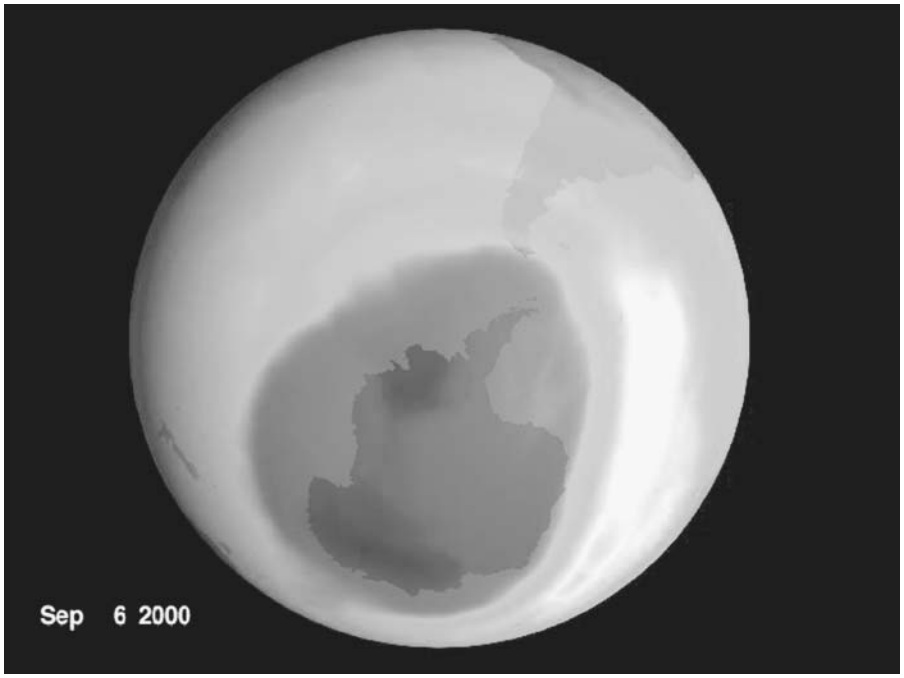
In the mid-1970s F. Sherwood Rowland and M. Molina showed evidence that Freons might drift freely and remain unaffected for up to 100 years, eventually move to the ozone layer, produce free chlorine atoms, and possibly destroy ozone (Molina and Rowland, 1974, pp. 810–812). They thus laid the foundation for a theory of ozone depletion and, together with Paul Crutzen of the Max Planck Institute, received the Nobel Prize for chemistry in 1995. In 1985 Joseph C. Farman, et al. published an article demonstrating the large volume of diminished ozone over Antarctica (Farman, Gardiner, and Shanklin, 1985, pp. 207–210).

In the stratosphere Freons decompose with exposure to ultraviolet light

$$CCl_2F_2(g) + \text{uv light} \rightarrow CF_2Cl(g) + Cl(g)$$

and the chlorine atoms destroy ozone

$$Cl(g) + O_3(g) \rightarrow ClO(g) + O_2(g)\ O(g) + ClO(g) \rightarrow Cl(g) + O_2(g)\ O(g) + O_3(g) \rightarrow 2\ O_2(g)$$



The decomposition of Freons in the atmosphere contributes to the destruction of the ozone layer. In this image, the ozone hole is visible over Antarctica.

The oxygen atom is formed in a separate reaction through the light-induced destruction of oxygen molecules.

$$O_2 + \text{uv light} \rightarrow 2\ O$$

It has been estimated that one chlorine atom has an atmospheric lifetime of one to two years and may destroy 100,000 ozone molecules, thus contributing to the mysterious "ozone hole." The British Antarctic Survey discovered the lowest ozone concentration in Earth's atmosphere ever recorded, in October 1984: nearly 40 percent less than the historical average for Antarctica. Atmospheric currents concentrate CFCs over Antarctica, creating the ozone hole that in 1984 was larger than the United States and taller than Mount Everest. The loss of ozone as a protective layer permits the penetration of increased levels of ultraviolet light to Earth's surface.

Today Freons are banned by an international agreement, and substitutes are sought. The United States has banned the production of CFCs since 1977. Non-ozone-depleting alternatives include hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs) such as CH_2FCF_3 (HFC 134a) and $CHCl_2CF_3$ (HCFC 123). In 1987 an international treaty, the Montreal Protocol, called for reducing CFCs, and a 1992 amendment to the treaty called for an end to CFC production. By 1993 CFC emissions had dropped dramatically. A total of 148 countries have now signed the Montreal Protocol calling for HCFCs to be phased out by 2020 and replaced by HFCs, which contain no chlorine and have a short lifetime. The black market of CFCs is of such proportion that *Scientific American* has reported (Beardsley, 1998, p. 32) that "the illegal CFC trade is one of the greatest threats to ozone-layer recovery." SEE ALSO ORGANIC HALOGEN COMPOUNDS; OZONE.

Erwin Boschmann

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Fuels *See Coal; Energy Sources and Production; Fire, Fuels, Powerplants; Gasoline; Petroleum.*

Fullerenes

inert: incapable of reacting with another substance

In 1985, while working in the laboratory of Richard Smalley at Rice University, graduate students Jim Heath and Sean O'Brien found that carbon aggregates in an **inert** atmosphere form C_{60} (and to a lesser extent, C_{70}) as the most abundant species. Previous work in the Smalley laboratory had involved clusters of atoms such as silicon, germanium, and gallium arsenide. The primary motive was to find out how elements like silicon contrive to minimize their "dangling bonds" on the surface of a small, nanoscopic bare cluster composed of only 10 to 100 atoms. Dangling bonds are ones found on the edges of the cluster that do not have the full complement of electrons that would be provided by bonding to other atoms. These workers had found that some silicon clusters adopt particularly stable structures, but never become so inert that they will not readily react with another silicon atom.

In the case of carbon, the specific cluster C_{60} was clearly behaving as if it had absolutely no dangling bonds as other carbon clusters continued to grow to even larger sizes in the condensing carbon vapor. Somehow the cluster had arranged in geometrical form to eliminate all dangling bonds. The only reasonable structure was a spherical one—a soccer ball—in which each carbon atom had the full complement of electrons. This epic-making work was published in the scientific journal *Nature* in 1985; senior investigators Richard E. Smalley, Robert F. Curl, and Harold W. Kroto were awarded the Nobel Prize in 1996.

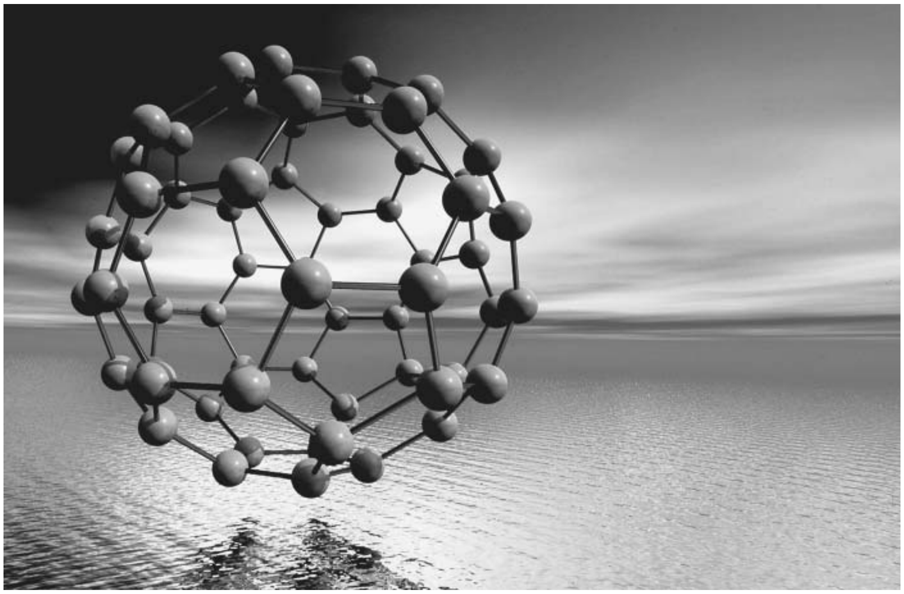

Figure 1. A computer graphic of a buckyball molecule, or carbon cluster, also called a Buckminsterfullerene, named after American engineer Buckminster Fuller.

As stated by Smalley, "the name [fullerene] was born in the dimmest early thinking of how a pure carbon cluster of 60 atoms could eliminate its dangling bonds" (Billups and Ciufolini, 1993, foreword vi). In an effort to make clear the shape of the cluster, Smalley asked Kroto the name of the architect who worked with big domes. The answer was Buckminister Fuller. Carbon clusters of all sizes were subsequently named Buckminsterfullerenes, fullerenes, or sometimes "buckyballs." A third allotrope of carbon had thus been added to the two (graphite and diamond) already known (see Figure 1).

Fullerenes were available initially only in vanishingly small quantities in the gas **phase**. An important breakthrough came in 1990 when Wolfgang Kratschmer of the Max Planck Institute for Nuclear Physics and Donald Huffman of the University of Arizona found that fullerenes could be synthesized in gram quantities by electric arc discharge between graphite electrodes immersed in a **noble gas**. The fullerenes C_{60} and C_{70} can be isolated readily from the crude soot along with several larger fullerenes. With an abundant supply of these fascinating new materials at hand, a flurry of activity directed at establishing a preliminary picture of fullerene chemistry ensued. The literature is now replete with descriptions of fullerenes that have been isolated using many of the **reagents** that are available to the organic chemist.

Fullerenes with **metals** trapped inside their cage may be formed when a graphite target is **doped** with the metal so that the fullerene grows around the metal. Chemists at Yale University have found that helium can be introduced by heating the fullerene under a high pressure of helium. In this way, a window is formed in the fullerene, which closes as the mixture is cooled, trapping the helium inside the fullerene. The **endohedral** fullerenes containing metals are promising candidates as magnetic resonance imaging agents.

Carbon nanotubes are fullerene structures played out as long strands rather than spheres. In 1993 Sumio Ajima working at the NEC Corporation in Japan discovered that carbon nanotubes could be created using a process similar to the one used by Kratschmer and Huffman to synthesize

phase: homogeneous state of matter

noble gas: element characterized by inert nature; located in the rightmost column in the Periodic Table

reagent: chemical used to cause a specific chemical reaction

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

dope: to add a controlled amount of an impurity to a very pure sample of a substance, which can radically change the properties of a substance

endohedral: descriptive term for a point within a three-dimensional figure

C_{60}. These nanometer-scale structures became the focus of enormous interest since they represent potential building blocks for nanostructured materials, composites, and novel electronic devices of greatly reduced size.

catalyst: substance that aids in a reaction while retaining its own chemical identity

Single-wall carbon nanotubes (SWNTs) can be prepared by laser-vaporization of a graphite source. A newer process uses carbon monoxide as the source of the carbon and is called the HiPco process. The **catalyst** is generated in situ from iron carbonyl. The SWNTs from the HiPco process are characterized by a smaller diameter and exhibit greater reactivity with organic reagents.

Since nanotubes are basically rolled-up sheets of graphite, many different tubes with different diameters and structures can be formed. Even a minor difference in the structure of the nanotube can make the material act like a metal or a semiconductor. Semiconducting nanotubes fluoresce upon exposure to light by emitting the light at a different wavelength. Since nanotubes fluoresce differently depending on their structure, it is possible to find an optical signal for each type of tube. In this way, a team of scientists at Rice University have identified thirty-three semiconducting varieties that are formed in the HiPco process, emphasizing the difficulty that researchers face as they attempt to carry out research with these materials. Nevertheless, carbon nanotubes hold great promise as precursors for strong fibers, electrical conductivity of copper and thermal conductivity of diamond, and perhaps even a means of perfecting deoxyribonucleic acid (DNA). see also Allotropes; Carbon; Nanochemistry.

W. E. Billups

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Fusion ***See Transmutation.***

Gadolin, Johan

FINNISH CHEMIST
1760–1852

lanthanides: a family of elements (atomic number 57 through 70) from lanthanum to lutetium having from 1 to 14 4f electrons

Johan Gadolin became an expert in the chemistry of the elements known as the **lanthanide** series of elements. From 1775 to 1779 he studied mathematics, then chemistry, in Åbo, Finland. From 1779 to 1782 he studied chemistry in Uppsala, Sweden. He received a master of science degree at the age of twenty-two, in 1782. During his Uppsala years he became friends with the Swedish chemists Carl Wilhelm Scheele (1742–1786) and Johan Gottlieb Gahn (1745–1818).

In 1786 he undertook a "grand tour" of Denmark, Germany, Holland, England, and Ireland. In Germany he met Lorenz Crell (1744–1816), the editor of the journal *Chemische Annalen.* They became friends, and it was in Crell's journal that many of Gadolin's research papers were eventually published in an international forum. In Ireland Gadolin worked with the Irish chemists Adair Crawford (1748–1795) and Richard Kirwan (1733–1812), investigating specific heat capacities and specific latent heats. After his return to Finland, Gadolin continued to his work in this area.

Gadolin is recognized for having discovered the element yttrium in 1794. He had been studying a black mineral that had been found by Karl Axel Arrhenius (1757–1824) in Ytterby, Sweden. The mineral was eventually named gadolinite. Working with the mineral, Gadolin was able to isolate an oxide substance (apparently the oxide of a new element) that was later named yttria. The existence of the new element, yttrium, was eventually confirmed.

In 1880 the French chemist Jean-Charles-Galissard de Marignac (1817–1894) studied samples of erbium **metal** that had been extracted from gadolinite. He discovered that the erbium metal contained minute amounts of a second metal. He named the metal (and the element) gadolinium, after the mineral.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

From 1785 to 1822 Gadolin was a professor of chemistry at the university in Åbo (formerly the Academy of Turku). He believed that students should learn chemistry by working in a laboratory and he enunciated that belief. Because the laboratory at the university was unsatisfactory, he built his own and invited his students to work there.

Gadolin added to the university's reputation, and when offered a chair at the university of Göttingen in Germany, he declined. Gadolin took part in the collective life of his motherland. Johan Gadolin is part of the Finnish national identity. SEE ALSO Erbium; Gadolinium; Lanthanides; Minerals; Scheele, Carl; Yttrium.

Ole Bostrup

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rare earth elements: older name for the lanthanide series of elements, from lanthanum to lutetium

lanthanides: a family of elements (atomic number 57 through 70) from lanthanum to lutetium having from 1 to 14 4f electrons

Gadolinium

MELTING POINT: 1,311°C
BOILING POINT: 3,233.0 °C
DENSITY: 7.89 g cm^{-3}
MOST COMMON ION: Gd^{3+}

64
Gd
GADOLINIUM
157.25

Gadolinium is a chemical element. Its ground state electronic configuration is $[Xe]4f^7 5d6s^2$. Monazite and bastnasite are the principal gadolinium ores, in which gadolinium occurs together with other members of the **rare earth elements** or the **lanthanides**. It can be separated from the other rare earths by ion exchange or solvent extraction techniques. Gadolinia, the oxide of gadolinium, was first extracted from the mineral gadolinite by Jean-Charles-Galissard de Marignac in 1880. (Gadolinite is named after the Finnish chemist Johan Gadolin.) In 1886 Paul-Émile Lecoq de Boisbaudran independently separated the oxide of gadolinium from Carl Mosander's "yttria" (impure yttrium oxide).

Gadolinium is a silver-white, malleable, and **ductile metal**. Gadolinium metal is ferromagnetic just below room temperature. Gadolinium chemistry is dominated by the trivalent gadolinium(III) ion, Gd^{3+}. This ion forms ionic bonds with **ligands** containing an oxygen or nitrogen donor atom. The ground state electronic configuration of Gd^{3+} is $[Xe]4f^7$. In **spectroscopic**

ductile: property of a substance that permits it to be drawn into wires

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

ligand: molecule or ion capable of donating one or more electron pairs to a Lewis acid

spectroscopy: use of electromagnetic radiation to analyze the chemical composition of materials

Gadolinium yttrium garnets are used in microwave devices, such as this oven.

analysis there are no absorption bands in the visible region of the electromagnetic spectrum, and gadolinium compounds are colorless.

reagent: chemical used to cause a specific chemical reaction

nuclear: having to do with the nucleus of an atom

Gadolinium(III) chelates are used as contrast **reagents** in magnetic resonance imaging (MRI). Due to the high magnetic moment of the paramagnetic Gd^{3+} ion (with its seven unpaired electrons), the relaxation time of water molecules in the proximity of Gd^{3+} ions is greatly reduced and signal intensity is thereby enhanced. MRI is a medical diagnostic technique that depends on the proton **nuclear** magnetic resonance (NMR) signal from water in its creation of a proton density map. Gadolinium is a major component of x-ray phosphors, such as $Gd_2O_2S{:}Tb^{3+}$, within which it dilutes the active emitter (Tb^{3+}) to avoid concentration quenching. Because gadolinium effectively absorbs neutrons, this element has found some use in control rods for nuclear reactors. SEE ALSO Cerium; Dysprosium; Erbium; Europium; Gadolin, Johan; Holmium; Lanthanides; Lanthanum; Lutetium; Neodymium; Praseodymium; Promethium; Samarium; Terbium; Ytterbium.

Koen Binnemans

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31
Ga
GALLIUM
69.72

Gallium

MELTING POINT: **29.78°C**
BOILING POINT: **2,250°C**
DENSITY: **5.907 g/cm^3**
MOST COMMON IONS: **Ga^{2+}, Ga^{3+}**

In 1870 Dimitri Mendeleev predicted many of the properties of an unknown element that he called eka-aluminum. The element was discovered in 1875 by Paul-Émile Lecoq de Boisbaudran who named it gallium from Gaul, the Latin name for France. The properties of the new element were those predicted by Mendeleev and helped to validate his Periodic Table of the elements.

Gallium can be obtained as a by-product of zinc and alumina production. The **metal** has an unusually low melting point but a very high boiling point. The liquid range is the largest known for any element, allowing gallium to be used in high-temperature thermometers. The liquid metal has a number of unusual properties: It has a tendency to supercool; to expand on **crystallization**; and does not crystallize in any of the common closely packed or body-centered cubic structures.

The chemistry of gallium is very similar to that of aluminum, its **congener**. Compounds of gallium almost always have a +3 **oxidation** state. While a few compounds with a +1 and +2 state have been postulated, these are controversial.

One of the most important uses of gallium is in electronic devices, usually in the form of gallium arsenide, which, together with other group-3 or group-5 elements, converts electrical energy to light, and is the basis of the light-emitting diode.

Metallic gallium and its salts have little or no toxicity, compared to the very toxic thallium salts. The toxicity of the aluminum ion is controversial. The gallium ion has been investigated as a possible antitumor agent, but no clinically useful compounds have been produced. SEE ALSO INORGANIC CHEMISTRY; MENDELEEV, DIMITRI; SEMICONDUCTORS.

Gus J. Palenik

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

crystallization: process of producing crystals of a substance when a saturated solution in an appropriate solvent is either cooled or some solvent removed by evaporation

congener: an element or compound belonging to the same class

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

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Gamma Rays ***See Radioactivity.***

Gardening

A successful garden represents a broad spectrum of chemical processes. Photosynthesis provides the route by which diverse chemical transformations use sunlight, water, carbon dioxide, and inorganic chemical elements to produce life-sustaining organic molecules and oxygen (Equation 1). This solar-powered rearrangement of matter is the foundation of almost all ecosystems and is an important example of how chemistry applies to the study of life.

$$6CO_2 + 12H_2O + \text{light energy} + \text{chlorophyll molecule} \rightarrow C_6H_{12}O_6 + 6\,H_2O + 6\,O_2 \quad (1)$$

Process of photosynthesis

The light reactions that occur in the chloroplasts, in addition to catalyzing the evolution of oxygen, also produce ATP and NADPH. ATP energy drives the endergonic reactions, and NADPH drives the reducing power required to bind the hydrogen ions to carbon atoms, and thus to synthesize all the organic compounds necessary for the growth and development of plants in a garden. Plants retrieve the needed ATP energy and reducing power by stripping away the energetic electrons and using them to make the high-energy compound ATP. This is possible because the electrons still carry the energy contributed by their encounter with the **photon** of light. When electrons are removed from chemical bonds, the food molecules are oxidized (i.e., lose electrons). Under **aerobic** conditions, the electrons that are harvested (as ATP is being formed) are eventually donated to oxygen gas, in a process known as cellular respiration (Equation 2).

photon: a quantum of electromagnetic energy

aerobic: involving oxygen or requiring it

$$\underset{\text{Aerobic (cellular) respiration}}{C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O + \text{energy (heat or ATP)}} \qquad (2)$$

Plants (including algae) are uniquely self-sufficient in that they are able to harvest and transform radiant energy into the chemical energy required to transform chemically simple molecules and elements (CO_2, H_2O, and nutrient elements) into substances (including carbohydrates, fats, proteins, alcohols, and hormones) needed for the garden plants to complete their life cycle, and to produce harvestable products.

Chemical processes that occur in the soil and aerial environment determine the extent and rate of all plant metabolic processes. The crop growth factors—water, light, essential nutrient elements (Table 1), temperature, and space—are utilized most efficiently when the chemical, physical, and microbiological interactions among the crops, soil, and air are optimal.

Almost all physiological processes in plants take place in the presence of water. Essential anabolic reactions (photosynthesis, assimilation, and protein synthesis), and catabolic ones (respiration and hydrolysis) occur in an aqueous cellular environment. Essential elements absorbed by plant roots, and the foods and other metabolites manufactured by the leaves and other tissues, move in aqueous solution from the regions of absorption or manufacture to other parts of the plant where additional **anabolic** reactions and ultimate food storage take place. Water is the major constituent of protoplasm, and is particularly abundant in young and growing tissues.

anabolic: characteristic of a reaction that builds complex molecules from simpler ones and requires energy

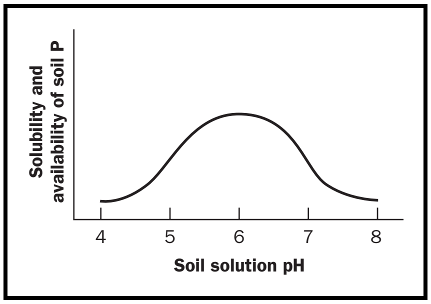

Figure 1. Solubility/availability of soil solution phosphorus as a function of soil pH. The relationship shown is for soil low in organic matter. As organic matter in the soil increases, the curve shifts to the left.

Good soil quality is essential for the crop's root system to function properly, and to ensure that all added chemicals are used efficiently. Incorporating into the soil the required amounts of lime (for soil pH adjustment) and fertilizer (all nutrients needed to amend the soil) is an important first step toward improving soil quality and creating a suitable rooting environment for crops. Deep placement of phosphorus in the soil is beneficial for several reasons. This element is sparingly soluble in the water present in the soil, especially when the soil is cold and/or when the soil pH is not properly adjusted (see Figure 1), and therefore phosphorus diffuses slowly to the site of uptake by roots. Phosphorus is the first essential mineral element the newly growing seedling requires from soil after the seed reserves (phytic acid) for this element are exhausted.

A healthy root system functions to absorb water and dissolved chemicals and translocate them to the above-ground tissues. Many crop growth regulators, hormones, and other chemicals crucial to providing biotic and

Table 1.

ELEMENTS ESSENTIAL[A] FOR CROP GROWTH, AND THE FORM MOST COMMONLY ABSORBED[B]

	Mostly from Air and Water	Mostly from Soil Solids/Fertilizer
Macronutrients[c]	Carbon (CO_2)	Nitrogen (NO_3^-, NH_4^+)
	Hydrogen (H_2O)	Phosphorus ($H_2PO_4^-$, HPO_4^{2-})
	Oxygen (O_2, H_2O)	Potassium (K^+)
		Calcium (Ca^{2+})
		Magnesium (Mg^{2+})
		Sulfur (SO_4^{2-})
Micronutrients[d]		Boron (BO_3^-)
		Chlorine (Cl^-)
		Cobalt (Co^{2+})
		Copper (Cu^{2+})
		Iron (Fe^{2+})
		Manganese (Mn^{2+})
		Molybdenum (MoO_4^{2-})
		Nickel (Ni^{2+})
		Zinc (Zn^{2+})

[a] Essential means that 1) without this element the plant cannot complete its life cycle (i.e., produce a viable seed), and 2) no other element may substitute for the element in question.

[b] Most readily absorbed form (i.e., most soluble in soil solution at suitable soil pH) in parentheses.

[c] Used in relatively large amounts (>0.1% of dry plant tissue).

[d] Used in relatively small amounts (<0.10% of dry plant tissue).

abiotic stress tolerance to the crop are synthesized in roots. Many of these chemical substances are translocated from root to shoot tissues in the same part of the vascular system (xylem tissue) as is the water, dissolved nutrient elements, and soil-applied pesticides. Some of the root-synthesized organic chemicals (such as the hormone abscisic acid) have a profound impact on the structure and function of above-ground tissues (leaf and reproductive tissue abscission and stomatal control of gaseous exchange, for example).

A healthy root system also will secrete organic chemicals (such as sugars, organic acids, and amino acids) into a cylindrical soil zone around the root system that is relatively rich in heterotrophic soil organisms. These soil microbes use these chemicals as energy and carbon sources for their own growth and reproduction, and catalyze many soil chemical transformations that are vital to the garden. With suitable soil moisture, temperature, and aeration, and in the presence of the appropriate microbes, a portion of the immobilized N, P, and S is converted to the inorganic form, and thus becomes available for plant uptake. Many of the essential elements cycle between organic and inorganic forms continuously throughout the growing season.

The key to ensuring that garden soil is in a proper chemical condition is to make certain that the soil pH and nutrient element status are correct for the crops of interest. Each crop has one pH value at which it grows best. Normally, the higher the amount of organic matter in the soil, the lower is the ideal soil pH.

Soil acidity commonly is decreased by supplying carbonates, oxides, or hydroxides of calcium and magnesium, compounds that are referred to as agricultural limes. Wood ashes (as from a fireplace) also are used to help raise soil pH. The primary sources of carbonates, and by far the most commonly used of all liming materials, are calcite, mostly $CaCO_3$, and dolomite, primarily [$CaMg(CO_3)_2$]. Given the fact that the balance of nutrients in plant tissues (the balance of N-P-K-Ca-Mg-S, for example) is even more important than the absolute amount of each nutrient present. Dolomite usually is the preferred liming material, because it supplies relatively equivalent quantities of two essential nutrients. Other sources of carbonates, such as marl, oyster shells, basic slag, and precipitated carbohydrates, all of which are relatively slow-acting, are also used to help control acidity.

Two additional sources of lime are noteworthy, especially when a rapid change in soil pH is desired. Calcium oxide (CaO), called quicklime or burned lime, and calcium hydroxide [$Ca(OH)_2$], called hydrated lime, are more irritating to handle, and more expensive, than is limestone, but are sometimes favored by gardeners who desire to adjust soil pH quickly.

All liming materials, whether oxide, hydroxide, or carbonate, react with soil water and carbon dioxide to yield the bicarbonate form when applied to acid soil. The partial pressure of carbon dioxide in the soil usually is several hundred times greater than that in atmospheric air, and drives the reaction that produces $Ca(HCO_3)_2$, which is very important in buffering the soil solution (see Equation 3).

$$CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2 \tag{3}$$

Reaction of lime with carbon dioxide

Two attributes are required of any liming material: 1) a cation capable of displacing soil colloid-adsorbed H^+ and Al^{+++}(also a source of soil acidity); and 2) an anion capable of neutralizing the displaced H^+ and Al^{+++} (see Equation 4).

$$\text{Soil colloid } -H^+ \ \& \ Al^{+++} + 2CaCO_3 + H_2O \rightarrow \text{Soil colloid—}2Ca^{2+} + Al(OH)_3 + 2CO_2 \tag{4}$$

Reaction of lime with soil colloids

The insolubility of $Al(OH)_3$ and the diffusion of CO_2 to the atmosphere drive this reaction to completion. Also, adsorption of cations onto the colloid complex raises the percentage base saturation (extent to which the colloidal complex is saturated with exchangeable cations other than hydrogen and aluminum, expressed as a percentage of the total cation exchange capacity) of the colloidal complex, increasing the pH of the soil solution accordingly.

Soil with an appropriate pH for the crops being grown will provide the essential nutrient elements in the most soluble form, and also will retain these elements in the effective rooting zone most fully, because the nutrients are more likely to be chemically adsorbed on the colloidal exchange complex, and less subject to leaching loss. One major problem resulting from raising the soil pH above about pH 6.5–6.7 is that several of the essential micronutrient elements begin to precipitate out of solution, becoming unavailable for uptake. Soils high in clay and/or organic matter are much harder to overlime, and generally require a slightly lower pH for optimal crop growth.

The vast majority of crops normally grown in most gardens are healthiest when the mineral soil pH is inthe 5.8–6.2 range. These crops grow equally well in soils fairly high in organic matter (2-5%) at a somewhat lower pH, in the 5.2–5.6 range.

The color of the blooms on the hydrangea plant, which can be pink, blue, or purple, are determined by the amount of acidity in the soil.

The decomposition of organic matter in the soil, and the reaction of NH_4^+-containing fertilizer materials in soil solution, contribute to an increase in soil acidity, especially when the soil is well-aerated and warm, and when the right kinds of bacteria are present (Equation 5). The process begins with the microbially-induced mineralization of nitrogen from organic to the NH_4^+ form, followed by a two-step nitrification process. In the first step, obligate autotrophic bacteria (*Nitrosomonas spp.*), that obtain their energy from the oxidation of nitrogen and their carbon from CO_2, oxidize NH_4^+ to NO_2^-. In the second reaction, NO_2^- is further oxidized to NO_3^- in the presence of autotrophic bacteria (*Nitrobacter spp.*). Under certain conditions other bacteria can be involved in both nitrification steps. The reaction rates associated with nitrification in most well-drained soils are NO_2^- to $NO_3^- > NH_4^+$ to NO_2^-. As a result, NO_2^- generally does not accumulate in soils, which is fortunate, because this ion is toxic to plant roots. The nitrate ion is more mobile than is the ammonium ion, and therefore much more highly leachable. Factors promoting nitrification in soils include 1) supply of ammonium, 2) population of nitrifying organisms, 3) soil pH, 4) soil aeration, 5) soil moisture, and 6) temperature. Because nitrification is suppressed in a cold soil, ammonium-containing fertilizers applied in the late fall or winter promote accumulation of ammonium rather than nitrate, and thus nitrogen is retained in the garden soil rather than being lost through leaching. Under wet soil conditions, and in the presence of anaerobic bacteria, the nitrate ion can be lost through denitrification to N_2, NO_x and N_2O, which is a greenhouse gas, and thus potentially a contributor to global warming (see Equation 5).

$$\text{Organic matter} \xrightarrow{\textit{Mineralization}} 2NH_4^+ + 3O_2 \xrightarrow{\textit{Nitrosomonas spp.}} 2NO_2^- \\ + 2H_2O + 4H^+ \; 2NO_2^- + O_2 \xrightarrow{\textit{Nitrobacter spp.}} 2NO_3^- \quad (5)$$

One of the greatest values of a properly limed and pH-adjusted soil is that applied fertilizer and pesticide materials are much more likely to remain in

A soil tilth test using compost.

the soil. This practice leads to the retention of more fertilizer elements in the effective rooting zone during periods of heavy rain. A higher proportion of a properly-limed soil colloid's cation exchange capacity is comprised of basic ions, such as calcium and magnesium, rather than hydrogen ions, thus reducing the potential for leaching loss of essential elements. Considering the relative strength of cation adsorption on the surface of soil colloids (both inorganic and organic), hydrogen ions are held the strongest, followed by aluminum, calcium, magnesium, potassium/ammonium, and finally sodium ions (held least tightly). The more fully the cation exchange capacity of a soil is satisfied by calcium and/or magnesium (i.e., the better limed it is), the lower is the leaching potential of applied nutrient elements such as potassium.

Another important reason for maintaining soil pH at the proper level is that most of the soil microorganisms that benefit the garden in so many ways (for example, decaying plant residues that otherwise would serve as a haven for pathogens and insects) function best in a well-limed soil. The bacteria that are able to produce nodules (tumor-like growths on the roots that serve as the site for symbiotic biological nitrogen fixation) on the roots of legume crops, for example, function best at pH 6.3-6.5. When the legume crop is healthy, and the proper strains of symbiotic bacteria are present (each legume requires its own bacterial strains), the nitrogenase enzyme (provided by the bacteria) within the nodule catalyzes the reduction of diatomic nitrogen gas to the ammonium form of nitrogen, one of the two forms of nitrogen (nitrate being the other) plants can readily use. Since the heterotrophic bacteria obtain their required energy (of ATP) from the host plant, this association is a true symbiosis. The legume plant dedicates about 14-18 moles of ATP for each mole of nitrogen gas reduced. When a legume crop is planted, and when this symbiotic relationship is functioning properly, no synthetic nitrogen fertilizer needs to be applied, and subsequent nonlegume crops planted in the same area will benefit from the residual nitrogen ultimately returned to the soil from the legume crop's residues.

A healthy garden represents a chemical laboratory in which a host of chemical processes are occurring in synchrony with our natural world. When the gardener has chosen adapted crop varieties, and has managed both soil and crops wisely, these chemical processes unfold in such a way that the garden harvests the sun's energy efficiently, and converts a portion into useful products. SEE ALSO AGRICULTURAL CHEMISTRY; HERBICIDES; INSECTICIDES; PESTICIDES.

Robert P. Patterson
Donald E. Moreland

Gases

A gas is a state of matter in which a substance does not have a specific shape or volume of its own, but adopts the form and size of its container. It was the early-seventeenth-century Flemish chemist-physician Jan Baptista van Helmont who coined the word "gas" (from the Greek *chaos*) in order to convey the idea that a gas had an indefinite shape and size. This is an apt name because, as was later hypothesized and confirmed, gas molecules are distributed uniformly throughout a container without any apparent spatial organization, and they undergo incessant, seemingly chaotic, random motion.

A liquid, like a gas, has no shape of its own, but it does have a definite volume. Both states of matter are referred to as fluids because of their mobility, or tendency to flow. A gas is actually a low density fluid because the molecules are much farther apart than in a liquid where molecules are in close contact with each other. For example, at room temperature and at atmospheric pressure the density of air is about 0.0012 grams (0.000042 ounces) per cubic centimeter (g/cm^3), whereas the density of liquid air is approximately 0.810 g/cm^3 (at its normal boiling point of −209°C, or −344°F). This corresponds to an average separation between molecules in the gas **phase** that is about nine times larger than that for the liquid. A liquid is thus called a condensed phase—or a high density fluid—and is roughly 1,000 times more dense than a gas.

phase: homogeneous state of matter

A compound exists in the gaseous state because the attractive forces between the molecules are weak and/or the average distance between them is large. Liquifaction, or condensation of the gas, may occur if the kinetic energy of the molecules is reduced (by cooling) and/or the intermolecular distance is made smaller (by compression).

Gas Properties

There are four intrinsic, measurable properties of a gas (or, for that matter, any substance): its pressure P, temperature T, volume (in the case of a gas, the container volume) V, and mass m, or mole number n. The **gas density** d is a derived quantity, which is m/V. Before the relationships between these properties for a gas are discussed, the units in which they are usually reported will be outlined.

gas density: weight in grams of a liter of gas

Pressure is defined as force per unit area. In the International System of Units (SI, or mks), unit pressure corresponds to one newton per square meter, which is denoted as one pascal or Pa (named after Blaise Pascal, the seventeenth-century French scientist). There are several other, more commonly used pressure units, however. One is the atmosphere or atm; it is based on the magnitude of the pressure actually exerted by Earth's atmosphere at sea level. Because atmospheric pressure varies, one atmosphere is simply defined as the pressure that is exerted by a 760-mm-high column of mercury, a dense liquid sometimes used to measure pressures. Note that 760 mm is equivalent to 29.91 inches, which is close to the value sometimes cited in weather reports of atmospheric pressure. Another pressure unit is the torr (named after the seventeenth-century Italian scientist Evangelista Torricelli). One torr is equivalent to one mm Hg.

One pascal corresponds to a very small pressure as compared with one atm, that is, $1 \text{ Pa} = 9.86923 \times 10^{-6}$ atm. The bar is another commonly used pressure unit. One bar is defined as 10^5 Pa and is equal to 750 torr.

Temperature is often reported in degrees Celsius. One Celsius degree is defined as 1/100 of the temperature difference between boiling water and freezing water (both at 1 atm pressure). In this scale, the temperature of pure water at its freezing point is 0°C (32°F) at 1 atm pressure. Another important temperature scale is the *absolute temperature*. The absolute temperature of pure liquid water in coexistence with ice and water vapor (the triple point) is defined as exactly 273.16 kelvins (K). This condition corresponds to 0.01°C, and thus the relationship between the Celsius *(t)* and Kelvin scales *(T)* is

$$t = T - 273.15°$$

The significance of the Kelvin scale is that 0 K represents the lowest temperature that can, in theory, be attained and corresponds to the condition in which molecular translational and rotational motion ceases.

The SI unit of volume is the cubic meter (m^3), but in most scientific applications, volumes are usually measured in cubic centimeters (cm^3) or liters (L). One liter contains 1,000 milliliters (mL), or equivalently, 1,000 cm^3.

The SI unit of quantity is called the mole (symbol n and abbreviation mol). It is derived from the Latin *moles* (meaning "a mass"). One mole of a substance contains Avogadro's number of elementary units of the substance. Because atoms and molecules are extremely small entities, Avogadro's number (N_A) is incomprehensibly large, 6.022×10^{23} particles/mol. Thus, one mole of hydrogen atoms contains 6.022×10^{23} H atoms, one mole of sucrose molecules consists of 6.022×10^{23} sucrose molecules, and so forth.

Relationships among Gas Properties

From the earliest days of quantitative inquiry, scientists have sought to uncover the mathematical relationships that describe natural phenomena, including the properties of gases. Because there are four fundamental properties of a gas, namely, P, T, V, and n, discovering the relationship between any two requires that the other two properties be kept constant. Some of the earliest quantitative studies of gases were reported in the mid-1600s by British chemist Robert Boyle, who found that for a fixed amount of a gas at a specific temperature (i.e., constant n and T), the volume was inversely proportional to the applied pressure. This V-P relationship, known as Boyle's law, is represented as

$$V = c/P$$

or

$$PV = c$$

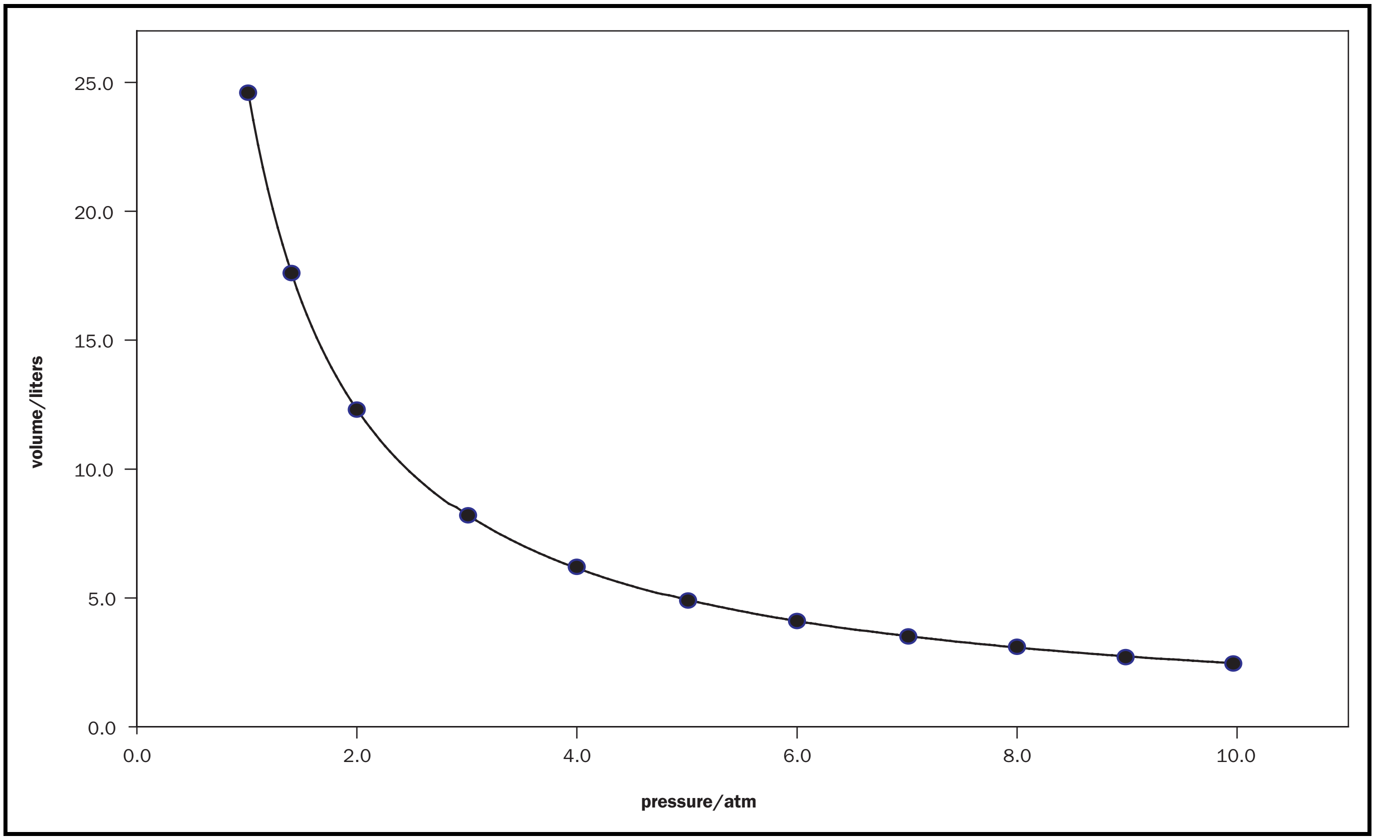

Figure 1. Illustration of Boyle's law. Plot of the volume, in liters, of 1.00 mole of an ideal gas at 300 K versus pressure, in atmospheres.

where c is an experimental constant that depends on the amount of gas and its temperature.

Figure 1 illustrates Boyle's law with a plot of the volume occupied by one mole of a gas at 300 K as a function of pressure.

In the later part of the eighteenth century, French chemist Jacques Charles studied the relationship between the volume of a fixed amount of gas and its temperature, while keeping the gas at constant pressure. He found that V was a linear function of the temperature. Figure 2 graphically represents this relationship, known as Charles's law, with a plot of the gas volume versus the temperature in Celsius, t.

Mathematically, Charles's law is expressed as

$$V = a + bt$$

where a and b are constants. The same data are plotted with expanded scales in Figure 3 to illustrate the fact that the x-intercept a has a value of $-273.15°\text{C}$, and it is evident that this value, called absolute zero, corresponds to the temperature at which the volume of a gas extrapolates to zero, its logically limiting value. This condition is the basis of the absolute temperature, or Kelvin scale, and was proposed in the mid-1800s by Lord Kelvin (British physicist William Thomson). Charles's law can be expressed in terms of the absolute temperature as

$$V = c'T$$

where c' is a constant; thus, the volume of a gas is directly proportional to its absolute temperature.

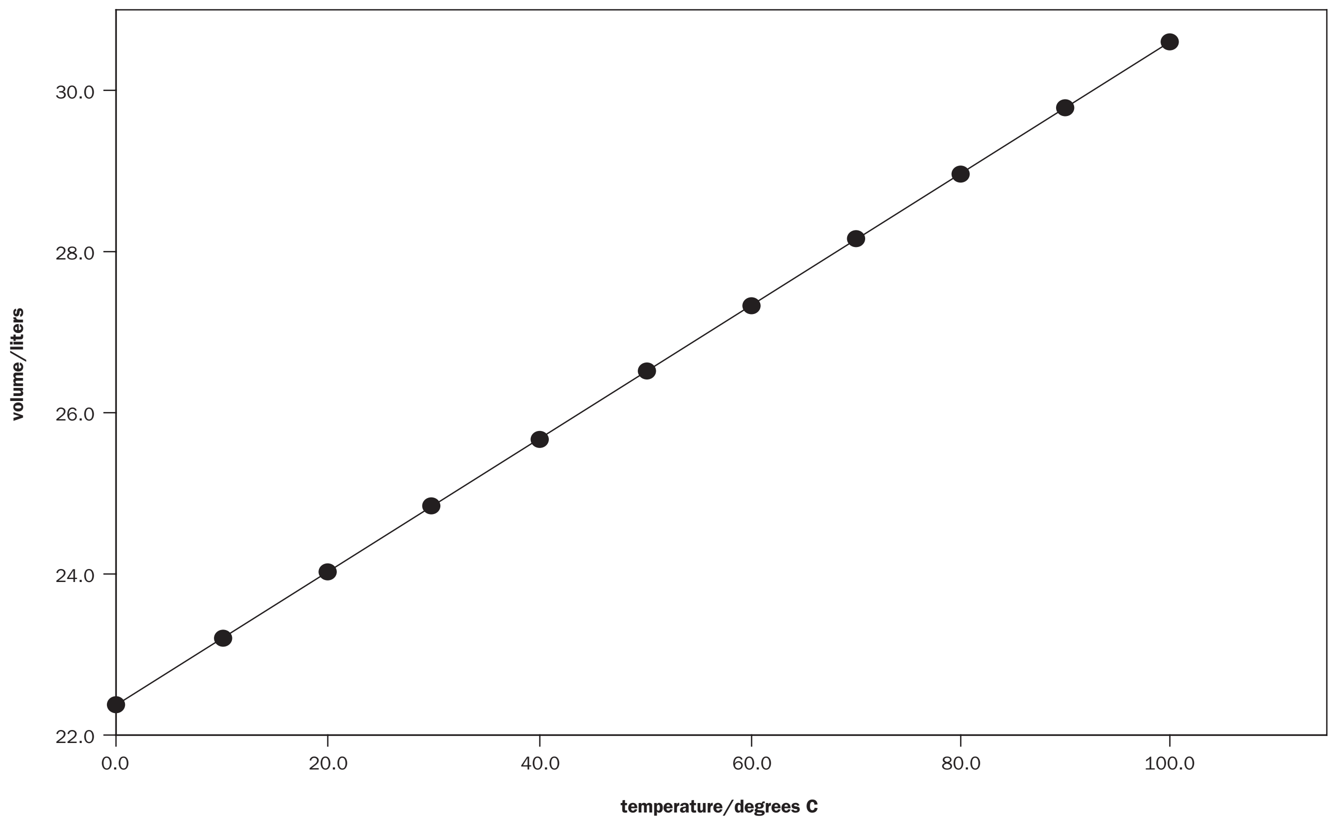

Figure 2. Illustration of Charles's law. Plot of the volume, in liters, of 1.00 mole of an ideal gas at 1.00 atm pressure versus temperature in degrees celsius.

The relationship between the volume of a gas and the quantity of the gaseous material, as represented by the number of moles, was established by Amedeo Avogadro in the early 1800s. He deduced from experiments performed by Joseph-Louis Gay-Lussac that equal volumes of different gases at the same temperature and pressure contained the same number of moles. This idea leads to Avogadro's law, which states that the volume of a gas at constant temperature and pressure is directly proportional to the number of moles of the gas, or

$$V = c''n$$

where c'' is a constant.

The three relations, Boyle's, Charles's, and Avogadro's laws, connecting the volume of a gas with its pressure, (absolute) temperature, and mole number, respectively, can be combined into one expression, called the ideal-gas equation of state, or $V = nRT/P$, in which R is a universal constant, valid for all gases. The value of R is 0.08206 L-atm/mol-K or, in SI units, 8.314 J/mol-K. The ideal-gas equation is usually expressed as

$$PV = nRT$$

A gas that obeys this equation is called an ideal or perfect gas. Notice that the identity of the gas is not represented in this equation; in this sense, an ideal gas is hypothetical. The ideal-gas equation works well in the limit of low pressures (where intermolecular interactions are negligible) and/or high temperatures.

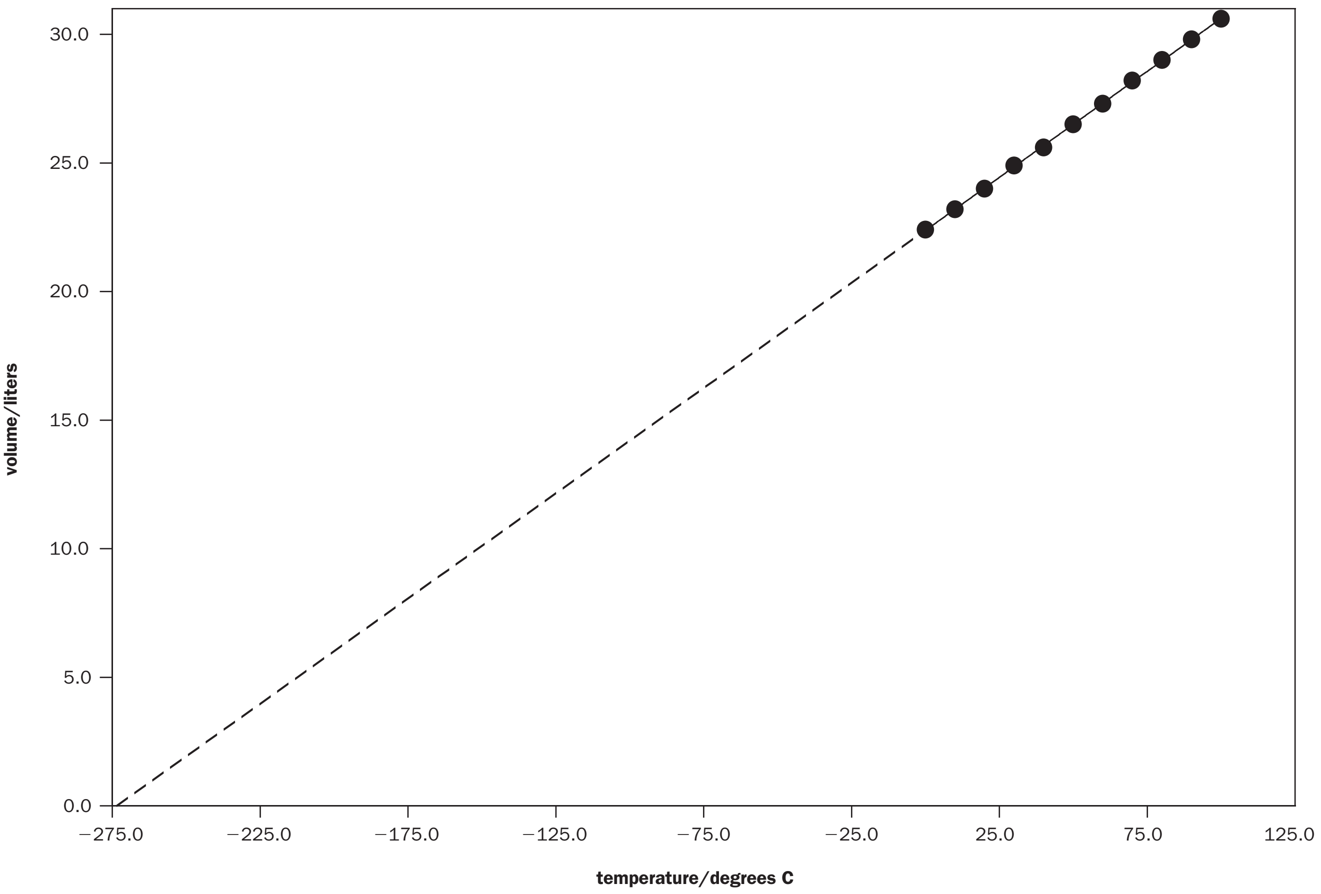

Figure 3. Plot of the data in Figure 2 showing the linear extrapolation to zero volume. The value of the x-intercept is −273.15°C.

There are many other equations of state, such as the van der Waals equation, that are designed to account for gas properties at higher pressures and/or lower temperatures. These equations contain one or more parameters whose values are specific for the gas in question.

Molecular Motion

Beginning with the empirical development of the gas laws, which explained how gases behave, scientists began to seek an understanding of the mechanism of this behavior. By the mid-1800s the work of several scientists, including James Joule, Rudolf Clausius, James Clerk Maxwell, and Ludwig Boltzmann, led to the development of the kinetic-molecular theory (KMT) of gases. This theory employed several assumptions: (1) Gas particles (i.e., atoms or molecules) are point masses—meaning they have negligible volume, (2) they undergo constant random motion involving frequent collisions, (3) attractive and **repulsive forces** between molecules are negligible, and (4) the average kinetic energy of molecules is proportional to the absolute temperature.

repulsive force: force that repels two bodies; charges of the same sign repel each other

According to this model, pressure is caused by the collisions that molecules make with the walls of its container. An analysis of this molecular motion using Newton's laws leads to an expression identical to the ideal-gas law. An important result of the theory is that the average kinetic energy of one mole of gas can be expressed in terms of the absolute temperature

Table 1. Composition of gases in Earth's atmosphere at sea level in volume (or mole) percent.

COMPOSITION OF GASES IN EARTH'S ATMOSPHERE AT SEA LEVEL IN VOLUME (OR MOLE) PERCENT

Component	Composition (% by Volume)[a]
N_2, nitrogen	78.084
O_2, oxygen	20.948
Ar, argon	0.934
CO_2, carbon dioxide	0.0345
Ne, neon	0.00182
He, helium	0.000524
CH_4, methane	0.000168
Kr, krypton	0.000114
H_2, hydrogen	0.00005
Xe, xenon	0.0000087

[a] Note that percent by volume is equivalent to percent by moles (Avogadro's law)

$$\frac{1}{2}Mu^2 = \frac{3}{2}RT$$

where *M* is the molar mass, *u* its average molecular speed, *R* the gas constant. The average kinetic energy of a gas depends only on *T* and is independent of its mass. The root-mean-square speed, u_{rms}, of a gas is equal to

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

and the KMT predicts that for methane, CH_4 ($M = 0.0160$ kg/mol), near room temperature (300 K) $u_{rms} = 394$ m/s (or 882 miles/hr!). Although this result seems very large, experimental measurements are consistent with this value. Another property obtained from the KMT is the mean free path λ, which is the average distance a molecule travels between collisions. Analysis shows that λ varies inversely with pressure, as well as the size of the molecule, a property not accounted for in simple KMT. For a pure gas,

$$\lambda = \frac{RT}{\sqrt{2}N_A d^2 P}$$

where *d* is the molecular diameter. For the oxygen molecule O_2, $d \approx 2.4 \times 10^{-10}$m, and $\lambda \approx 1.6 \times 10^{-7}$m at 300 K and 1 atm. Under these conditions, the molecule travels a distance that is about 670 times its diameter before it collides with another molecule.

Earth's Atmosphere

Perhaps the most important and ubiquitous gas is Earth's atmosphere, which is a complex mixture of compounds. The composition of gases in the atmosphere at sea level, excluding water vapor, aerosols, and particulate suspensions, which vary regionally and climatically, is listed in Table 1.

Although carbon dioxide (CO_2) is present in trace amounts, it is an exceedingly important constituent. Until about 1800 CO_2 composition was constant at about 0.028 percent. After that time it began to increase, presumably because of the **combustion** of fossil fuels. In 1900 the CO_2 level was ca. 0.0295 percent; currently it is 0.0345 percent. CO_2 and several other

combustion: burning, the reaction with oxygen

gases, such as methane (CH_4) and nitrogen oxides, which are, in part, anthropogenic, are called greenhouse gases because they absorb infrared radiation from Earth that would otherwise be transmitted into space. Thus, these gases, while transmitting visible light from the Sun, essentially retain heat in a way similar to the glass panels of a greenhouse. The apparent trend in global warming has been attributed to the rapid and continuing increase in the atmospheric composition of greenhouse gases observed in the past 50 to 100 years. SEE ALSO Avogadro, Amedeo; Air Pollution; Boltzmann, Ludwig; Boyle, Robert; Charles, Jacques; Gay-Lussac, Joseph-Louis; Maxwell, James Clerk; Noble Gases.

Arthur M. Halpern

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Gasoline

In 1859 Edwin Drake and E. B. Bowditch of the Seneca Oil Company drilled the first commercial oil well in the United States in Titusville, Pennsylvania. The well produced about 400 gallons of crude oil, less than ten barrels a day. Soon, similar wells all over western Pennsylvania were providing crude oil for kerosene production that was needed to fuel the nation's streetlights and house lamps. The lighter boiling component, gasoline, was discarded, since it had no market. There are historical reports that "waste" gasoline, which had been dumped into rivers, sometimes caught fire. In 1892 the first gasoline-powered engines, for both car and tractor, were developed: This soon provided a market for the once useless substance, gasoline.

Today gasoline is the most important product of a typical oil refinery: The entire refinery process is designed to maximize its production. Gasoline is a complex mixture of molecules with a boiling range of 40–200°C (104–392°F). To produce various grades, there is a blending of many refinery components, each of which promotes specific fuel qualities such as desired octane rating, volatility, and minimization of engine deposits.

Octane Quality

The most important quality parameter for gasoline is the octane quality. Octane number is a measure of the antiknock properties of the fuel. Knocking in a gasoline engine is a metallic clattering noise (pinging), which indicates excessive intensity in preflame reactions. Severe knocking can damage the engine.

Preflame reactions occur in the engine cylinders when portions of the fuel self-initiate **combustion** prior to the advancing flame from the spark plug. This additional combustion causes an excessive rate of energy release, which is knock. The tendency of a fuel to engage in preflame reactions is dependent upon the structure of its component molecules (see Figure 1);

combustion: burning, the reaction with oxygen

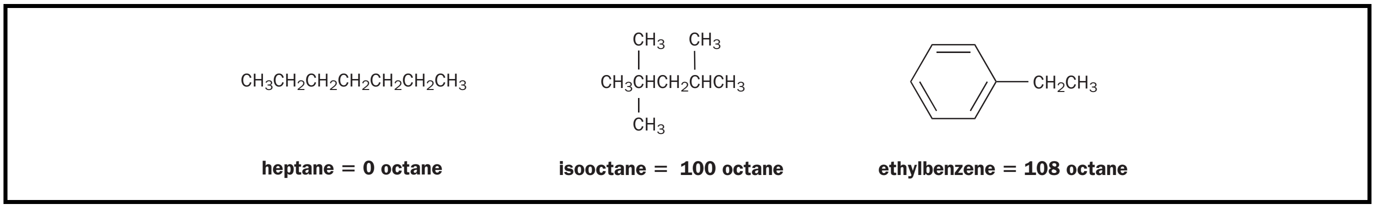


Figure 1. The tendency of a fuel to engage in preflame reactions depends on the structure of its component molecules.

the tendency for preflame reactions is high for straight chain hydrocarbons, medium for branched hydrocarbons, and low for aromatics.

The octane number for a test gasoline represents the percentage by volume of isooctane (2,2,4-trimethylpentane) in a reference fuel consisting of the mixture of isooctane and heptane that would be necessary to match the test fuel's knocking tendency. Isooctane burns with a minimal knocking and is given an octane rating of 100. This is in contrast to heptane, which burns with much knocking and is given an octane rating of 0. Thus, a gasoline that burns with the same amount of knocking as a mixture of 92 percent isooctane and 8 percent heptane is classified as a 92 octane gasoline.

The octane ratings of gasoline can be increased by the addition of small amounts of antiknock agents. The first commercially successful antiknock agent, tetraethyllead (TEL), was developed in the 1920s. TEL was used to promote the development of higher efficiency, higher compression engines. However, TEL is highly toxic and poisons **catalytic** converters. Since 1974 all new U.S. automobile engines have used catalytic converters in order to reduce exhaust emissions.

catalysis: the action or effect of a substance in increasing the rate of a reaction without itself being consumed.

Methyl *t*-butyl ether (MTBE) has been the antiknock agent of choice for unleaded gasoline. MTBE provides high-octane quality along with low volatility and is readily soluble in gasoline. However, leakage of gasoline from underground storage tanks has resulted in the detection of MTBE in the drinking water of several urban areas. This prompted the state of California to order the removal of MTBE from California gasoline by 2003.

Alcohols also have found use as octane enhancers. At higher concentration alcohols can be used as gasoline extenders, thus decreasing our dependency upon imported crude oil. A significant portion of all U.S. marketed gasoline is believed to contain ethanol.

Gasoline Additives

Trace amounts of olefins and diolefins found in gasoline are prone to reaction with oxygen dissolved in the gasoline. This process is referred to as autoxidation and involves a radical chain reaction that can incorporate oxygen

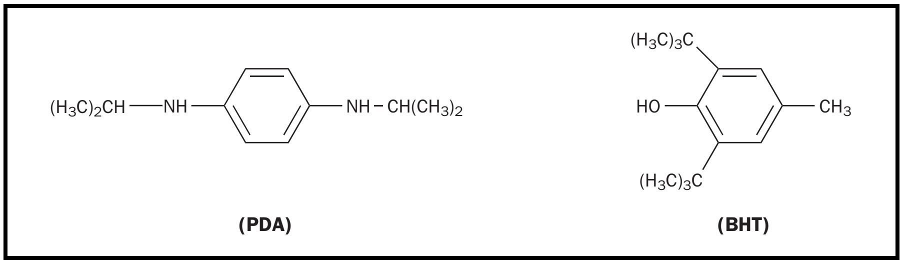


Figure 2. The chemical structures of the two different types of antioxidants used in gasoline are phenylenediamines (PDA) and hindered phenols (such as BHT).

into the olefin and also can promote a molecular size increase via polymerization reactions. The end result of this complex process is the formation of deposits and gums that can block fuel filters and interfere with the metering of fuel and air in the carburetor. This can result in adverse engine performance. Additives are frequently added to gasoline to address oxidative stability and other issues; they include antioxidants, **metal** deactivators, and detergents.

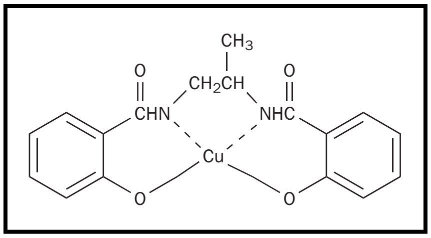


Figure 3. Structure of the copper complex of the most widely used metal deactivator N, N′-disalicylidene-1,2-propanediamine.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Antioxidants are additives that minimize autoxidation reactions. They function as hydrogen atom donors that stop the chain oxidation process of the olefins. The two different types of antioxidants used in gasoline are phenylenediamines (PDA) and hindered phenols (such as BHT).

Trace levels of soluble metal compounds, particularly copper, catalyze the oxidative degradation of gasoline by promoting the formation of gums and deposits. Metal deactivators overcome this problem by chelating the metal and rendering it inactive. The most widely used metal deactivator is N, N′-disalicylidene-1,2-propanediamine, the copper complex of which is shown in Figure 3.

Detergents minimize fuel system deposits at low concentrations, and at high concentrations can remove deposits that have already formed. Detergents are molecules that have a highly polar end group and a **nonpolar** hydrocarbon tail. A conventional amino amide type detergent is shown in Figure 4.

nonpolar: molecule, or portion of a molecule, that does not have a permanent, electric dipole

Presumably, the polar groups in the detergent attach themselves to metal surfaces and to polar deposits on these surfaces. The nonpolar tails of these molecules “stick out” into the fuel in such a way that a monomolecular film is formed on the metal surface, preventing deposition and particle aggregation. This process is also believed to solubilize any deposits already on the metal surface. The detergent monolayer is also believed to prevent the build-up of ice on carburetor surfaces during winter. Thus, detergents can also function as anti-icing additives.

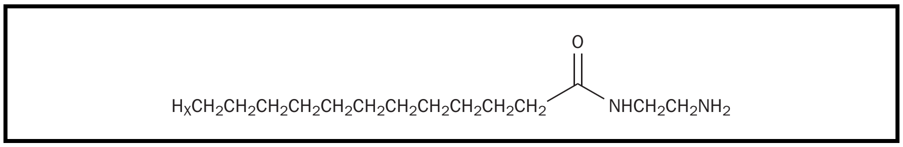
Gasoline Production

The production of gasoline begins with desalting the viscous crude oil. Salts and metals in the crude oil promote corrosion and poison processing catalysts. Thus, the crude oil is heated (to decrease viscosity) and extracted with water to remove the salts and metals. Frequently this process results in the formation of an oil/water mixture referred to as an **emulsion** (suspension). This emulsion is typically broken by the addition of a chemical **surfactant** (demulsifier) that promotes the separation of discrete oil and water layers. After separation of the aqueous layer, the oil is heated to about 400 °C (752°F): This converts the oil into gaseous products and increases the fluidity of the remaining liquid. In this form, the gaseous mixture enters the fractionating column, where the process of atmospheric **fractional distillation** separates the crude oil into different components based upon boiling point.

emulsion: immiscible two-phase mixture in which one phase is dispersed (as small droplets) in the other phase

surfactants: surface-active agents that lower the surface tension of water; e.g., detergents, wetting agents

fractional distillation: separation of liquid mixtures by collecting separately the distillates at certain temperatures



$H_xCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2C(=O)NHCH_2CH_2NH_2$

Figure 4. A conventional amino amide type detergent.

The lightest boiling fractions are molecules that are gases under ambient conditions: methane, ethane, propane, butane, and olefins derived from these compounds. Uses for this distillate stream include burning as a fuel at the refinery; as petrochemical feed stocks; or processing into liquefied petroleum gas (LPG). There are three other major distillate streams collected during atmospheric distillation: the naptha fraction, which has a boiling range of 30 to 180°C (86–356°F); the kerosene fraction, which distills at between 180 and 240°C (356–464°F); and the gas oil fraction, which distills at between 240 and 355°C (464–671°F).

catalyst: substance that aids in a reaction while retaining its own chemical identity

In order to meet current environmental regulations for the sulfur content in fuel products, the three-distillate streams are subjected to the process of hydrodesulfurization. In the presence of a **catalyst**, distillates are heated in the presence of hydrogen to reduce various organosulfur compounds to simple organic compounds and H_2S. The hydrogen needed for this process is a by-product of the catalytic reforming process. The H_2S product can be readily removed. In this process the refiner can control the octane number of the gasoline blending stock. By heating the naphtha fraction in the presence of an especially designed platinum catalyst, straight-chain hydrocarbons are cyclized, and saturated cyclic hydrocarbons are converted into aromatic compounds. In addition, this process converts straight-chain hydrocarbons into branched hydrocarbons. Catalytic reforming facilitates the production of gasoline blending stocks with octane ratings of from 90 to 100+.

Redistilling the atmospheric residue at a temperature of less than 400°C (752°F) under vacuum produces a vacuum gas oil. Typically, the vacuum gas oil is subjected to fluid catalytic cracking (FCC) to produce lower-boiling liquids that can be blended to make gasoline. This is achieved by breaking large molecules of the vacuum gas oil into smaller, lower-boiling molecules. An important gasoline blending component that can be produced in this manner is alkylate. It is a mixture of highly branched hydrocarbons produced by the acid-catalyzed reaction of isobutene and light olefinic hydrocarbons. Alkylate is a valuable blending component because of its high-octane quality and the absence of aromatics or olefins, which can lead to environmental and oxidative stability problems.

The 1990 Clean Air Act required the Environmental Protection Agency (EPA) to issue regulations that required gasoline to be "reformulated," resulting in significant reductions in vehicle emissions of ozone-forming and toxic air pollutants. This cleaner gasoline is called reformulated gasoline (RFG). RFG is required in the nine major metropolitan areas in the United States having the worst ozone problems. In addition, several other areas with ozone levels exceeding the public health standard have voluntarily chosen to use RFG.

volatile: low boiling, readily vaporized

Use of RFG decreases the amounts of **volatile** organic compounds (VOCs) and oxides of nitrogen (NO_x) in the atmosphere that react in the presence of sunlight to produce ozone, a major component of smog. Vehicles also release toxic emissions, one of which (benzene) is a known carcinogen.

RFG contains 2 percent by weight oxygen additives (oxygenates), such as MTBE or ethanol. Oxygenates increase the combustion efficiency of gasoline, reducing vehicle emissions of carbon monoxide, a serious public health threat. The appearance of MTBE in some urban water supplies has resulted in legislation pending in the U.S. Congress to phase out the use of MTBE in RFG. Ethanol would then most likely become the primary oxygenate for future RFG.

Gasoline is the most important product of the oil refinery. The most important quality parameter for gasoline is its octane number. Additional quality characteristics for gasoline are controlled by the use of additives, for example, antioxidants, metal deactivators, and detergents. By blending various refinery streams and additives a gasoline formulation can be achieved that minimizes environmental degradation. Such a fuel is called reformulated gasoline. SEE ALSO DETERGENTS; ENERGY SOURCES AND PRODUCTION; FOSSIL FUELS; PETROLEUM.

Bruce Beaver

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Gay-Lussac, Joseph-Louis

FRENCH CHEMIST AND PHYSICIST
1778–1850

Joseph-Louis Gay-Lussac was one of the great scientists of the industrial age. Born on December 6, 1778, in St. Léonard in central France, he was the eldest of five children. His father was a public prosecutor and judge advocate, and the political unrest surrounding the French Revolution played an early role in young Joseph's development. When his father was arrested in 1794 (he was later released) as a member of the bourgeois establishment, Gay-Lussac was sent to a boarding school in Paris.

Three years later Gay-Lussac was accepted to the newly founded and elite École Polytechnique in Paris, where he initially studied mathematics and engineering. However, he soon fell in love with science and especially chemistry. This was in no small part due to the influence of the renowned scientist Claude-Louis Berthollet (1748–1822), a lecturer at the École who was also a contemporary of Antoine Lavoisier. It was Berthollet who took Gay-Lussac under his wing as his student and laboratory assistant.

The research for which Gay-Lussac is perhaps most famous involves the experiments with gases he completed early in his scientific career. Upon graduation from the École in 1800, he remained Berthollet's assistant and a frequent guest at his country house at Arcueil, near Paris. With the encouragement of Berthollet, mathematician Pierre-Simon de Laplace, and others, Gay-Lussac began his own research in the winter of 1801 and 1802.

Among Gay-Lussac's early work was an extensive investigation of how the volume of various gases changes with temperature. The English scientist John Dalton was independently studying the same phenomenon. Both found that the volume V of all gases studied increased similarly with higher temperature T when pressure P was held constant ($V \alpha T$ at constant P). Each published his results around 1802, with Gay-Lussac's experimental work being both more thorough and more precise than that of Dalton. However,


French chemist and physicist Joseph-Louis Gay-Lussac, who published the "Law of Combining Volumes of Gases."

the credit for this discovery typically goes to neither Dalton nor Gay-Lussac, but instead to Jacques Charles. Charles had done some initial work on the thermal expansion of gases in 1787. Although Charles never published the results of his experiments, in his own scientific memoirs Gay-Lussac acknowledged hearing of Charles's work. Thus, the law governing the thermal expansion of gases, while sometimes called Gay-Lussac's law, has come to be known largely as Charles's law.

Gay-Lussac's studies were not limited to the physical properties of gases. In 1804 Gay-Lussac took advantage of the world's growing interest in ballooning and made multiple flights to study both Earth's magnetic field and how the temperature and composition of the atmosphere changed with increasing altitude. On his second flight, he took samples of air while reaching an altitude of 23,018 feet in a hydrogen balloon, a record that lasted for almost fifty years. Upon his return to Earth, he compared the gas samples to those taken at ground level and concluded that they were essentially identical—this despite making note of a headache during the flight that very possibly resulted from the decreased oxygen levels at high altitude.

In 1808 Gay-Lussac published his "Law of Combining Volumes of Gases." He determined that when different gases reacted, they would always do so in small whole number ratios (e.g., two volumes of hydrogen would react with one volume of oxygen in forming H_2O). This was one of the greatest advancements of its time and helped form the basis for later **atomic theory** and how chemical reactions occur.

atomic theory: concept that asserts that matter is composed of tiny particles called atoms the particular characteristics of which determine the type and form of the matter

With his colleague Louis-Jacques Thénard (1777–1857), Gay-Lussac did considerable work with electrochemistry to produce significant amounts of elemental sodium and potassium, highly reactive and useful substances that were used to isolate and discover the element boron. Gay-Lussac also completed extensive studies of acids and bases and was the first to deduce that there were binary (two element) acids such as hydrochloric acid (HCl) in addition to the known oxygen-containing acids like sulfuric acid (H_2SO_4). Additionally, he was able to determine the chemical composition of prussic acid to be hydrocyanic acid (HCN) and was considered the foremost practitioner of organic analysis.

In later years, Gay-Lussac continued to advance science. He developed a precise method for analyzing the alcoholic content of liquors and patented a method for the manufacture of sulfuric acid. His last publication on aqua regia (a mixture of nitric and hydrochloric acids that dissolves gold or platinum) came out the year before his death in 1850. Gay-Lussac was a top-notch experimentalist and theoretician. More than twenty-five years after Gay-Lussac died, the prominent chemist Marcellin Bertholet (1827–1907) once said, "We all teach . . . the chemistry of Lavoisier and Gay-Lussac" (Crosland, p. 248), a fitting tribute to two outstanding scientists of the era. SEE ALSO ACID-BASE CHEMISTRY; BERTHOLLET, CLAUDE-LOUIS; CHARLES, JACQUES; DALTON, JOHN; DAVY, HUMPHRY; LAVOISIER, ANTOINE.

David A. Dobberpuhl

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Gelatin *See Collagen.*

Gemstones

There are several thousand known minerals in nature (with estimates ranging from 2,000 to 7,000), but fewer than a hundred are considered gem minerals. Of these, only about a dozen or so are actually valuable enough to be important gemstones on the world market. In order to be considered a gemstone, a mineral must first of all be beautiful. In addition, it must be hard and durable. Its value increases if it is also rare.

The beauty of a gem is measured in terms of its clarity, brilliance, and color. Its natural beauty can be enhanced by the way it is cut. There are two basic kinds of gem cuts: faceted and cabochon. The faceted cut has many flat cut surfaces (facets) with an overall shape that might be round, oval, square, rectangular, or pear-shaped. Faceted cuts are preferred for brilliant transparent stones such as diamond. The cabochon cut has a smooth rounded top, usually with a flat base, and it is mainly used for opaque or translucent stones.

Hardness is measured using the Mohs' scale, on which 10 is hardest. (Diamond has a hardness of 10.) Gemstones should have a Mohs' hardness of 6 or more. A really durable gem should have a hardness of at least 7, which is the hardness of quartz. Table 1 shows the hardness of some familiar minerals on the Mohs' scale.

The value of a gemstone depends on its beauty and its rarity, but also the size of the stone. Size is measured in terms of weight using the carat as a unit. A carat is 0.2 grams (0.007 ounces). (A 10-carat diamond weighs 2 grams, or 0.07 ounces.) There are 100 points in a carat, so a 30-point diamond weighs 0.3 carat, or 0.06 grams (0.002 ounces). Since gemstones vary in density (weight per unit volume), several different 1-carat stones may vary in size, the stones with the greatest density being smaller than the others.

Some Important Gemstones

Diamond is the hardest substance known to occur in nature, measuring 10 on the Mohs' scale. It is pure carbon in a tightly packed cubic structure. Diamonds are usually graded on the basis of four Cs: carat, cut, clarity, and color. Carat refers to the stone's weight and degree of flawlessness. As for color, diamonds are usually colorless, but sometimes they do exhibit color. The famous Hope diamond, for example, is blue. Most diamonds come from mines in Africa, especially southern Africa, although Russia and Australia also have diamond mines. Industrial-grade diamonds have even been made synthetically at very high pressures and temperatures. A number of other softer colorless stones are often sold as imitation diamonds.

Ruby is a variety of corundum (Al_2O_3) with a Mohs' hardness of 9. Its red color results when chromic ions (Cr^{3+}) replace some of the aluminum ions in the crystal. The finest rubies come from Myanmar (formerly Burma) or Kenya. Star rubies are stones with a special starlike appearance. They usually have a cabochon cut and appear to show a 6-pointed star due to microscopic inclusions. Rubies of very high quality are sometimes made synthetically.

Sapphire, like ruby, is made of corundum (Al_2O_3) and has a hardness of 9. However, instead of Cr impurities, the crystal contains iron and titanium

Table 1.

Mohs' HARDNESS SCALE

Mineral	Chemical Composition	Hardness
Talc	$Mg_3Si_4O_{10}(OH)_2$	1
Gypsum	$CaSO_4$	2
Calcite	$CaCO_3$	3
Fluorite	CaF_2	4
Apatite	$3\ Ca_3(PO_4)_2 \cdot CaF_2$	5
Feldspar	$K_2Al_2Si_6O_{16}$	6
Quartz	SiO_2	7
Topaz	$Al_2SiO_4F_2$	8
Corundum	Al_2O_3	9
Diamond	C	10

ions, which produce a blue color, ranging from very pale to very dark blue. Sapphires are found in Cambodia and other places in Southeast Asia and Australia, as well as Montana in the United States. Also, as in the case of rubies, there are star sapphires, which exhibit a 6-pointed star. Pure corundum (white sapphire) was the first gem to be produced synthetically. It was a poor substitute for diamond, however, because of its low refractive index. Adding about 0.1 percent chromium, however, produces rubies of excellent quality; and the addition of iron and titanium yields beautiful blue sapphires. Even star sapphires and rubies that rival natural stones can be made synthetically.

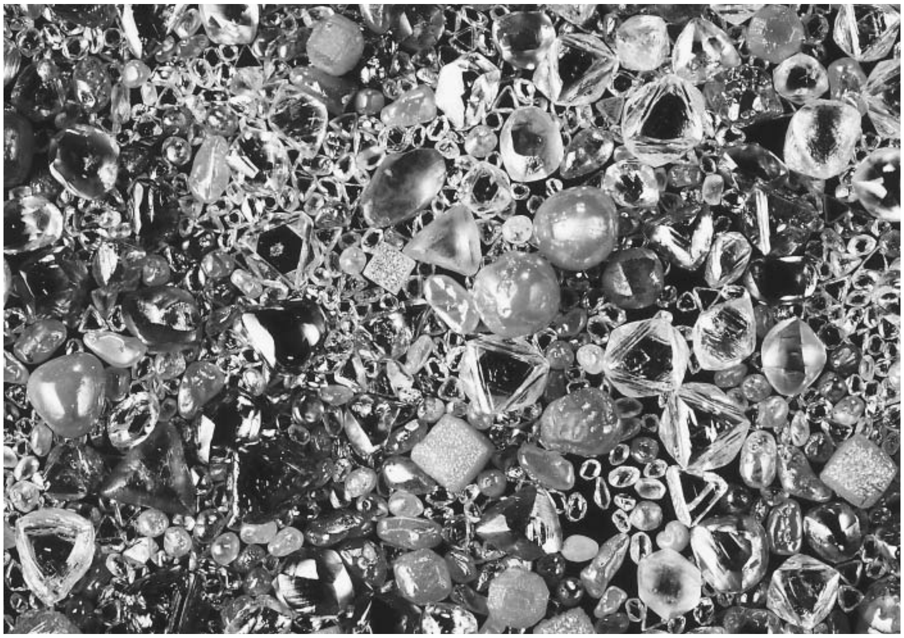
Emerald is a variety of beryl, a beryllium silicate, with a hardness of 7.5 to 8. It has a beautiful deep green color, and it is one of the most expensive gems, sometimes outranking diamond in value. The green color results from small amounts of chromic oxide (Cr_2O_3). The oldest emerald mines were in Egypt near the Red Sea, but the best emerald mines today are in Colombia. There are others in Brazil, Pakistan, and Africa; synthetic emeralds of excellent quality have also been manufactured.

Aquamarine, like emerald, is a transparent variety of beryl, or beryllium silicate. Its light blue to blue-green color results from small amounts of iron in the crystal. Like most beryl stones, it measures 7.5 to 8 on the Mohs' hardness scale. Most aquamarine gemstones come from Brazil.

Topaz is a rather rare silicate mineral with a Mohs' hardness of 8. It comes in many colors from yellow to pink to purple to blue, depending on what ions are present in the crystal. It can even be colorless. However, the favorite variety is orange to brown in color and called "imperial topaz." Much of the best topaz comes from Brazil. The gem called London blue topaz can be made from the colorless variety by treatment with heat and radiation.

Cubic zirconia (ZrO_2), with a Mohs' hardness of 8, is a beautiful, usually colorless, stone that is made synthetically. Although not as hard as diamond, cubic zirconia has much fire and brilliance, and it is popular as an imitation diamond. Zirconia normally has a **monoclinic** crystalline structure at room temperature, but when heated to about 2,300°C (4,172°F), it takes on a cubic structure. Ordinarily, it would revert to the monoclinic structure on cooling, but the addition of yttrium oxide (Y_2O_3) or calcium oxide (CaO)

monoclinic: one of several arrangements of atoms found in crystalline solids; characterized by a unit cell of three axes each of a differing length; two axes are mutually perpendicular while the third is at an oblique angle



A mixture of natural and synthetic diamonds. Diamonds are the hardest natural substance known.

can stabilize the zirconia so that it retains the cubic structure at room temperature. Cubic zirconia has optical properties very close to those of diamond, and it is clearly the best of all the various diamond imitations.

Zircon is native zirconium silicate ($ZrSiO_4$) that exhibits beautiful transparent crystals and a Mohs' hardness of 7.5. The tetragonal crystals are usually brownish yellow in color. Also known as jargon or jargoon, zircon is a stable and durable silicate crystal. Small crystals of zircon are among the oldest mineral grains ever found on Earth.

Opal is a hydrous silica (SiO_2), sometimes thought of as an amorphous silica gel. It is a fairly soft gem, measuring only 5 to 6 on the Mohs' scale. It is relatively common in nature except in its "precious" form, which comes mainly from Australia. In Switzerland, since 1970, opal of precious quality has been made synthetically. Usually cut in the cabochon shape to permit its rainbowlike display of color, opals come in white, black, and fire varieties. "Black" opals are dark gray to blue, and fire opals, which are more transparent than other opals, are usually orange-red in color.

Amethyst is a variety of quartz (SiO_2) that is violet to purple in color, probably because of iron and manganese impurities. It measures 7 on the Mohs' hardness scale and is obtained from many places, but mainly from India and Brazil. It should not be confused with oriental amethyst, which is a purple native variety of alumina (Al_2O_3).

Spinel is a colorless magnesium aluminate ($MgAl_2O_4$) of cubic structure. It is hard and durable, but, like white sapphire, it is not a good diamond substitute because it has a low refractive index and lacks brilliance. However, it is readily **doped** to produce other gems of various colors. Artificial ruby, for example, is often natural red spinel, and most synthetic blue sapphires on the market are actually blue spinel.

dope: to add a controlled amount of an impurity to a very pure sample of a substance, which can radically change the properties of a substance

Peridot is the gem variety of olivine, a magnesium silicate containing iron (about 9 Mg atoms for every Fe atom). Peridot is usually transparent,

A handful of a variety of gemstones. The beauty of gemstones is measured by their clarity, brilliance, and color.

with a color ranging from greenish yellow to brownish green. Much peridot comes from an island in the Red Sea, but it is also found in Myanmar and an Apache reservation in Arizona.

Garnet is actually a group of related silicates containing various amounts of magnesium, calcium, aluminum, iron, manganese, and chromium. Garnets have a hardness of 6.5 to 7.5, depending on their composition, and their color also varies along with their composition. The popular dark red garnets are found in many gem sites in the Czech Republic, but garnets of many colors are also found in other parts of the world, such as India, Tanzania, Russia, and Brazil.

Tourmaline is a highly complicated silicate, with a wide range of compositions and colors. It probably exhibits more colors than any other kind of gemstone. Sometimes there are several different colors in the same crystal. “Watermelon” tourmaline, for example, is green on the outside but red in the middle.

Lapis lazuli is a deep blue gemstone that is a complex copper silicate mineral varying widely in composition. It often contains sparkles of iron pyrite or calcite. The best source is probably Afghanistan. A pale blue variety is found in Chile. Some material sold as lapis lazuli is actually artificially colored jasper from Germany.

Onyx is a striped variety of the common silicate mineral called agate, with alternating black and white bands. It comes mainly from India and South America. Sardonyx is a variety of onyx with brown and white bands.

“Organic” Gems

The aforementioned gemstones, unless they are synthetic, usually occur in underground deposits from which they are mined. However, there are some gems that come from once living material.

Pearls are little spheres of calcium carbonate ($CaCO_3$) that form in mollusks (**invertebrate** shellfish) such as oysters, usually because of some sort of irritation. They are normally white or off-white in color, but they can have bluish or pink tints, and sometimes they are dark gray. Although many pearls form naturally, pearl production has been greatly increased by the "cultured" pearl industry, which raises beds of oysters into which irritants are routinely introduced. The irritants are usually bits of mother-of-pearl, the lining that forms inside oyster shells.

Amber is fossilized tree resin that hardened over millions of years and now is valued as a gem. Baltic amber is thought to be hardened sap from pine trees. It is normally yellow-brown in color, but the shades vary from almost white to almost black. Although sometimes completely clear, amber often contains inclusions of insects or other matter, often considered desirable. Much amber is obtained along the shores of the Baltic Sea, but it is also found along the coasts of Sicily, Romania, and Myanmar.

AMBER AND ELECTRICITY

Ancient Greeks called amber *elektron.* When they rubbed it with a cloth, it became charged and attracted bits of paper. The word "electricity" derives from the Greek word *elektron.*

invertebrate: category of animal that has no internal skeleton

Coral, like pearls, is calcium carbonate ($CaCO_3$) derived from living matter. It is the outer shells of small marine animals. It occurs in many colors, from white to deep pink and red. The greatest demand is for red coral. The best coral comes from the Mediterranean Sea, along the coasts of Algeria and Tunisia.

Ivory is a bonelike material that comes from the tusks of animals (elephant, walrus, hippopotamus). It has become such a highly prized material that there are unscrupulous poachers who kill these animals in order to steal their tusks. The pale cream color of new ivory becomes darker with age and turns yellow. Ivory is brittle, but it does not peel as do its plastic substitutes.

Jet is actually just a very hard and dense kind of lignite coal. It was probably plant material millions of years ago that has become fossilized and blackened over time. It often comes from northeast England, where it is derived from fossil driftwood buried under the sea. Its primary drawback as a gemstone is that it will burn (since it is basically just highly polished coal). SEE ALSO GLASS; MINERALS.

Doris K. Kolb

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Genes

A gene is a unit of genetic information that codes for a single biological function or product. Genes are found on chromosomes and are made up of nucleic acid (deoxyribonucleic acid [**DNA**] for most organisms) and proteins.

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

Table 1.

COMPARISON OF GENE NUMBERS AND DNA FROM DIFFERENT SPECIES

Organism	Number of genes	Number of base pairs (millions)
Yeast	5,800	12
Caenorhabditis elegans (worm)	19,099	97
Fruit fly	13,601	116
Arabidopsis (plant)	25,498	115
Human	30,000–40,000	2,700

SOURCE: Bork, Peer, and Copely, Richard (2001). "The Draft Sequence: Filling in the Gaps." *Nature* 409:818–820.

The information is contained in the sequence of the four nucleic acid components much like the way written information is contained in the sequence of letters in a sentence.

helix: form of a spiral or coil such as a corkscrew

DNA is measured in base pairs (bp) since it occurs as a double **helix**. The sum total of all genetic information in an organism is its genome. Different organisms have different sized genomes with different numbers of chromosomes, genes, and base pairs. Table 1 shows the values for several organisms, including the preliminary results for the human genome from the Human Genome Project (HGP) report. One surprising finding of the HGP was that only 30,000 to 40,000 genes were found. The human genome has almost 3 billion base pairs and many different gene products, so scientists were expecting over 100,000 genes. Results from the HGP suggest that about 75 percent of DNA is "nongene." This DNA is often referred to as "junk" or "selfish" DNA, but some portions do have important functions in maintaining the structure of chromosomes.

code: mechanism to convey information on genes and genetic sequence

eukaryotic: relating to organized cells of the type found in animals and plants

Genes "tell" a cell which molecules to synthesize based on the genetic **code** that those genes contain. The amount of code needed varies widely. Genes vary greatly in size, from those that code for small transfer RNA molecules (tRNAs) and have 73 base pairs, to those that code for very large proteins and have 250,000 base pairs (Maulik and Patel, p. 26). A **eukaryotic** gene for a large protein may be much larger than its coding region due to intervening noncoding sequences (introns). Each gene has two or more coding regions (exons) separated by introns. The introns are "cut out" of the genetic information during expression and do not show up in the final gene product. Some genes have as much as 90 percent intron DNA. Sometimes the exons are cut and pasted from the same gene in different ways, creating two or more different gene products issuing from the same gene. This added flexibility opens the door to even more debate about how genes and gene products are controlled. Although each gene codes for one or sometimes a few gene products (due to splicing variations), biological functions often require many genes working together or in sequence. The proper interplay of genes produces healthy cells. Some forms of cancer occur when certain genes, called oncogenes, become uncontrolled. SEE ALSO CHROMOSOME; DOUBLE HELIX; GENETIC ENGINEERING; GENOME; NUCLEIC ACIDS; PROTEINS.

David Speckhard

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Genetic Code ***See Codon.***

Genetic Engineering

Genetic engineering is a discipline represented by the ability to isolate, modify the expression of, or transfer genetic material. Genetic engineering was born in 1973 when Stanley Cohen and Herbert Boyer reported the successful transfer of reptile **DNA** into bacteria. Practical applications quickly followed, and in 1980 Genentech became the first publicly traded genetic engineering company. Genentech's main product was human insulin produced in bacteria. It was marketed for diabetic patients who had developed allergies to the pig or sheep insulin used to treat diabetes. The enthusiastic response from investors led to many new genetic engineering companies. Many of the newest of their products are produced in genetically engineered animals. This practice is called pharming.

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

Insulin was just the first of many genetically engineered products. In 1995 there were over 100 genetically engineered therapeutic products approved by the U.S. Food and Drug Administration (FDA) or in clinical trials. They ranged from hormones like insulin and human growth hormone to vaccines, and included many products created to treat serious diseases such as muscular dystrophy, multiple sclerosis, and cancer. Genetic engineering has allowed scientists to explore genetic material in detail. In 2001 the preliminary report of the Human Genome Project was released, containing the nucleotide sequence of nearly all of the human genome (International Human Genome Sequencing Consortium 2001, pp. 860–921; Venter et al. 2001, pp. 1304–1351). A better understanding of human genetic makeup will allow scientists to understand both healthy cells and diseases better. Scientists are predicting that in a few years a patient will receive a DNA scan that will allow a doctor to prescribe medicines that match that patient's genetic makeup. These genetically tailored medicines are expected to be more effective and to have fewer side effects than their predecessors. A new scan technique called "DNA microarray" or "gene chip" is now available. With this technique a scientist or doctor can scan the identity of all the genes that a given tissue or cell is using at any time. This tool will be very powerful in helping to unravel the complex interactions of genes in diseases like cancer. It has already helped to identify the ways in which chemotherapy drugs interact, so that new more effective drug combinations may be developed. The same tool will help scientists to investigate cell growth and development. One important question that can now be asked is: Which genes are turned off or on as a cell ages?

Corn embryos are being removed to be grown in controlled conditions for desired genetic traits at Sungene Technologies Lab, Palo Alto, California.

One of the most exciting branches of therapeutic genetic engineering is human gene therapy. A single defective gene is often the cause of a disease, for example as with cystic fibrosis or sickle cell anemia. Gene therapy would allow doctors to transfer the healthy gene to the patient, and possibly allow replacement or removal of the harmful gene. For the first time doctors could cure genetic defects instead of being able only to treat the symptoms the defects cause. Trials of human gene therapy began in 1994 with some success (Anderson 1995, pp. 124–128), but much remains to be done before gene therapy can be used routinely. In addition, there are important ethical questions having to do with which genes will be identified as defective and which gene replacements will be allowed.

toxin: poisonous substance produced during bacterial growth

Agriculture is another area in which genetic engineering has become increasingly important. Many genetically engineered products are used in veterinary medicine and to enhance livestock-related production. For example, Bovine Somatotropin is used to increase milk production in dairy cows. It is becoming more common to use genetically engineered crops. Two of the most common examples are genetically engineered corn and beans. A kind of corn called Bt corn is engineered to contain and put to use a gene from a strain of bacteria that produces a **toxin**. This toxin kills insects that attack the corn so that farmers can use less insecticide on the field. Many soybeans are engineered to withstand a particular herbicide. Farmers can apply the herbicide to kill weeds in a planted field without harming the soybeans. All of these innovations have been very successful, but have provoked some concerns about human exposure to the new products, as well as new ecological concerns about "escape" of these genes into the environment. In one case Bt corn that had not been approved for human consumption accidentally made its way into human food products, and in another case the effects of Bt corn pollen on monarch butterflies have been questioned, but no answer is yet forthcoming. Genetically modified animals used to produce nonfoodstuffs such as those produced in pharming, and as laboratory models, are becoming more common. SEE ALSO AGRICULTURAL CHEMISTRY; CHROMOSOME; CLONES; GENOME; RECOMBINANT DNA.

David Speckhard

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Internet Resources

Human Genome Project. More information is available from <http://www.nhgri.nih.gov/HGP/>.

Genome

An organism's genome is the complete set of genetic instructions, passed from one generation to the next. The genome consists of a set of instructions for building each of the components of a living cell or virus. The information is found in nucleic acids: usually deoxyribonucleic acid (**DNA**), but sometimes ribonucleic acid (RNA).

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

Genetic information is organized into units called genes, each of which provides instructions to build one cellular component. Genes are parts of large strands of DNA called chromosomes. Much of what we know about human chromosomes comes from the Human Genome Project, begun in 1990. In February 2001 David Baltimore of the International Human Genome Sequencing Consortium and J. Craig Venter of Celera Genomics separately announced initial results on the complete sequencing of human DNA. More information about this project is available online. Scientists were able to determine the chemical **code** of chromosomes by applying recombinant DNA techniques, whereby millions of copies of human DNA were reproduced in bacteria, and polymerase chain reaction (PCR), which copies small sections of DNA for sequencing, to amplify a few strands of human DNA into more than a trillion strands, enough to detect in the sequencers. Enough DNA was produced to enable determination of the genetic code. Recombinant DNA also provides the basis for the construction of transgenic species such as Bt corn, which contains a gene from the bacteria *Bacillus thuringiensis* that ultimately helps to protect the corn plant from insects. The terms "biotechnology" and "genomics" are used to describe the application of these new techniques and new genetic information to produce new products. Examples of new biotech products include medical

code: mechanism to convey information on genes and genetic sequence products such as cloned human insulin, human growth factor, and human clotting factors. These products are used to treat diseases caused by genetic errors. The new cloned materials are cheaper and safer than animal substitutes or isolated human materials. Another new biotech product is the herbicide-resistant soybean. These plants allow farmers to kill weeds in fields already planted with soybeans, without affecting the growth of soybeans. SEE ALSO AGRICULTURAL CHEMISTRY; CHROMOSOME; GENES; NUCLEIC ACIDS; POLYMERASE CHAIN REACTION (PCR); RECOMBINANT DNA.

David Speckhard

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Internet Resources

Human Genome Project. More information is available from <http://www.nhgri.nih.gov/HGP/>.

Germanium

32
Ge
GERMANIUM
72.61

MELTING POINT: **937.4°C**

BOILING POINT: **2,830°C**

DENSITY: **5.323 g/cm^3**

MOST COMMON ION: **Ge^{4+} Ge^{2+}**

Germanium has chemical and physical properties similar to those of silicon. It was predicted as an element ("eka-silicon") by Dimitri Mendeleev in 1871 from calculations made during the construction of his periodic table, and it was discovered by Clemens Winkler in 1886. It is 10,000 times less abundant than silicon, and it occurs as a **trace element** in silicate minerals (1–2 ppm). The element is usually obtained via the acid leaching of mineral dusts, especially certain coals and zinc ores (using H_2SO_4) formed during ceramic processing, followed by addition of hydrochloric acid, to form the **volatile** germanium **tetrachloride** ($GeCl_4$), which is easily separated from coprecipitated zinc compounds. Its low abundance and complicated processing make germanium an expensive material: Although some of its semiconducting properties are superior to those of silicon, its use in the electronics industry is limited. Like silicon, germanium forms gaseous hydrides (e.g., GeH_4) and volatile halides (e.g., GeF_4 and $GeCl_4$).

trace element: element occurring only in a minute amount

volatile: low boiling, readily vaporized

tetrachloride: term that implies a molecule has four chlorine atoms present

Germanium is more reactive than silicon, and the chemistry of its 2+ **valence** state is better developed: Binary solids such as GeF_2 and $GeCl_2$ are known, in addition to the tetrahalides. The monoxide GeO (a dark brown solid) occurs, although the dioxide, GeO_2, is more stable. Germanium dioxide has octahedrally coordinated germanium atoms; the tetrahedrally coordinated quartz phase is stable only at high temperature, although it exists metastably at ambient conditions. This contrasts with SiO_2: The corresponding octahedrally coordinated compound **isostructural** with the

valence: combining capacity

isostructural: for minerals, relating to an arrangement of atomic constituents that is geometrically the same although different atoms are present mineral **rutile** (TiO_2) form is prepared only at high pressure (>90,000 atmospheres). High pressure treatment of germanium nitride, Ge_3N_4, gives (as with like treatment of silicon nitride) a new high-density form with the same structure as the mineral **spinel** ($MgAl_2O_4$), containing octahedrally coordinated (GeN_6) groups. Like silicon, germanium forms "Zintl" phases with electropositive **metals** (e.g., KGe, $BaGe_2$) that contain unusual polyanions with Ge in negative **oxidation** states, and "semiconductor clathrates" (e.g., Na_8Ge_{44}; $Na_{16}Cs_8Ge_{136}$) with open framework structures constructed from Ge atoms in tetrahedral coordination that are structurally analogous with H_2O-ice clathrates, and with alkali or alkaline earth atoms occupying "cages" in the structure. SEE ALSO MENDELEEV, DIMITRI; SILICON.

Paul F. McMillan

rutile: common name of TiO_2; also a common structural type for compounds with the general composition AB_2

spinel: name given to a group of minerals that are double oxides of divalent and trivalent metals, for example, $MgO \cdot Al_2O_3$ or $MgAl_2O_4$; this mineral is called spinel; also a structural type

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

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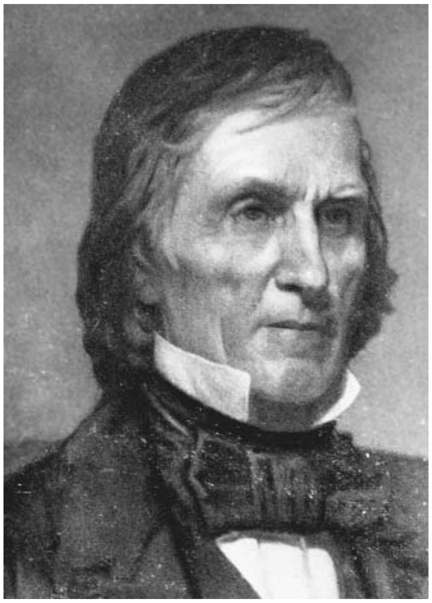
Gibbs, Josiah Willard

AMERICAN MATHEMATICIAN AND PHYSICIST
1839–1903

Josiah Willard Gibbs was born in New Haven, Connecticut, on February 11, 1839, into a family of academics whose connection to higher education dates back to the 1600s. Gibbs entered Yale University (where his father served as librarian) in 1854, graduated in 1858 with distinction in mathematics and Latin, and continued his studies there, in 1863 earning the first Ph.D. in engineering in the United States. He was appointed tutor and taught Latin and natural philosophy until 1866, whereupon he left New Haven to study in Europe. He attended lectures by the eminent scientists of Paris, Berlin, and Heidelberg, returning home in 1869. He was appointed professor of mathematical physics at Yale in 1871, a post he held until his death in 1903.

In 1873 Gibbs published the first two of his revolutionary papers, which unveiled graphical methods for visualizing properties such as stability, equilibrium, and critical states for thermodynamic systems. One of his major accomplishments was showing the usefulness of the "entropy" quantity that the German mathematical physicist Rudolf Clausius had posited in 1865. This was followed in 1876 by his famous "On the Equilibrium of Heterogeneous Substances" paper, in which he introduced the field of chemical thermodynamics, advancing the concept of chemical potential. Gibbs's free energy G determines whether it is favorable that chemicals will react. Gibbs employed a completely general treatment, making almost no assumptions about the properties of the interacting substances. His celebrated phase rule allowed for the identification of the number of coexisting phases in a system.



American physicist Josiah Willard Gibbs, creator of the field of chemical thermodynamics.

When one aspect of Gibbs's work in thermodynamics, the phase rule, is considered, just how important the discovery of this theoretical system was becomes clear. The phase rule allows one to determine the number of coexisting phases of any system, no matter how complicated. The rule relates the number of independently changeable intensive variables, or degrees of freedom, F, the number of components (i.e., substances) C, and the number of phases in equilibrium P, as follows:

$$F = C - P + 2$$

Thus, in a one-component system (such as pure water), at temperature and pressures where one phase is present ($F = 1 - 1 + 2 = 2$), those variables can be varied independently (carving out an area of coexistence on a phase diagram). In order to keep two phases in coexistence ($F = 1 - 2 + 2 = 1$), like water and ice, varying the pressure necessitates a specific change in the temperature (which forms a coexistence line on a phase diagram). Where all three phases (ice, water, and vapor) coexist, there are no degrees of freedom, which translates to a single point, the triple point, on a phase diagram. In other words, there is only one temperature and pressure where all three phases of water are in equilibrium. More complicated systems have more intricate phase diagrams, but the phase rule allows one to, relatively, easily determine the phase properties of any system.

Due in part to his mathematically demanding and abstract style of writing, and also since his papers were published in the obscure *Transactions of the Connecticut Academy of Arts and Sciences*, Gibbs's work was not immediately embraced by the scientific community, with the notable exception of the Scottish physicist James Clerk Maxwell. Consequently, many of Gibbs's results were not discovered until years or decades later by scientists ignorant of his work.

quantum mechanics: theoretical model to describe atoms and molecules by wave functions

Gibbs also wrote an influential book on statistical mechanics, which developed a molecular theory of thermodynamic properties from first principles, with a treatment that was general enough to accommodate **quantum mechanics**, a theory that had not even been imagined yet. He championed the now standard use of vector notation over William Rowan Hamilton's quaternion algebra and wrote several seminal papers on electromagnetism in the 1880s that supported Maxwell's theory. SEE ALSO EQUILIBRIUM; MAXWELL, JAMES CLERK; THERMODYNAMICS.

Michael J. Fosmire

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Glass

Glass is a state of matter. It is a solid produced by cooling molten material so that the internal arrangement of atoms, or molecules, remains in a random or disordered state, similar to the arrangement in a liquid. Such a solid is said to be *amorphous* or glassy. Ordinary solids, by contrast, have regular crystalline structures. The difference is illustrated in Figure 1.

Many materials can be made to exist as glasses. Hard candies, for example, consist primarily of sugar in the glassy state. What the term "glass" means to most people, however, is a product made from silica (SiO_2). The

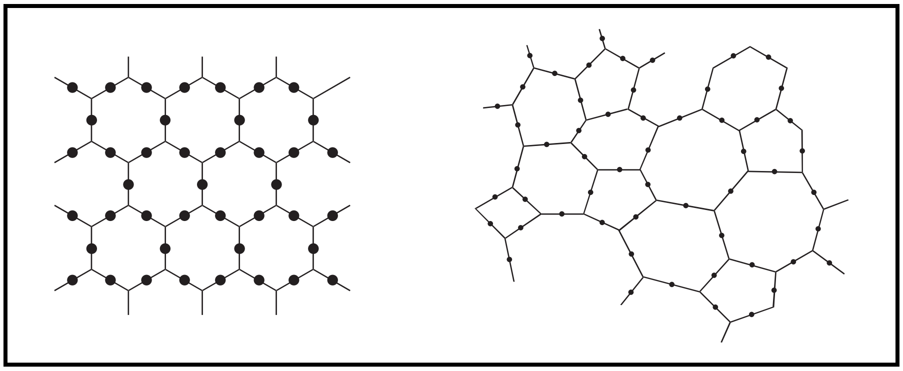

Figure 1. Structures of a typical solid (l.) and glass (r.).

common form of silica is sand, but it also occurs in nature in a crystalline form known as quartz.

Pure silica can produce an excellent glass, but it is very high-melting (1,723°C, or 3,133°F), and the melt is so extremely viscous that it is difficult to handle. All common glasses contain other ingredients that make the silica easier to melt and the hot liquid easier to shape.

Natural Glass

Probably as early as 75,000 B.C.E., long before human beings had learned how to make glass, they had used natural glass to fashion knives, arrowheads, and other useful articles. The most common natural glass is obsidian, formed when the heat of volcanoes melts rocks such as granite, which then become glassy upon cooling. Other natural glasses are pumice, a glassy foam produced from lava; fulgurites, glass tubes formed by lightning striking sand or sandy soil; and tektites, lumps or beads of glass probably formed during meteoric impacts.

Manmade (Synthetic) Glass

When, where, or how human beings discovered how to make glass is not known. Very small dark-colored beads of glass have been dated back to 4000 B.C.E. These may well have been by-products of copper smelting or pottery glazing. By 2500 B.C.E. small pieces of true synthetic glass appeared in areas such as Mesopotamia, but an actual glass industry did not appear until about 1500 B.C.E. in Egypt. By this time various small vases, cosmetic jars, and jewelry items made of glass had begun to appear.

All the ancient glasses were based on silica (sand), modified with considerable amounts of various metal oxides, mainly soda (Na_2O) and lime (CaO). This is still the most common glass being used today. It is known as soda lime glass. However, the ancient glass was usually colored and opaque due to the presence of various impurities, whereas most modern glass has the useful property of transparency.

Hundreds of thousands of different glass compositions have been devised, and they have been used in different ways. Much has been learned about which combination of chemicals will make the best glass for a particular purpose. For example, in 1664 an Englishman named Ravenscroft found that adding lead oxide (PbO) to a glass melt produced a brilliant glass that was much easier to melt and to shape. Since that time lead glass has been used to make fine crystal bowls and goblets and many kinds of art glass.

An important kind of glass was developed in the early 1900s to solve a serious problem—the inability of glass to withstand temperature shock. This failure resulted in tragic accidents in the early days of the railroads. Glass lanterns used as signals would get very hot, and then, if it started to rain, the rapid cooling would sometimes cause the glass to break and the signal to fail. The problem was solved by replacing much of the soda in the glass with boron oxide (B_2O_3). The resulting glass, called borosilicate, contains about 12 percent boron oxide and can withstand a temperature variation of 200°C (392°F). It also has greater chemical durability than soda lime glass. Today borosilicate glass is used in most laboratory glassware (beakers, flasks, test tubes, etc.) and in glass kitchen bakeware.

For even greater heat shock resistance and chemical durability, alumina (Al_2O_3) can be used instead of boron oxide. The resultant aluminosilicate glass has such resistance to heat shock that it can be used directly on the heating element of the kitchen stovetop. It is also used to make the special bottles used for liquid pharmaceutical prescriptions, and to produce the glass thread that is woven into fiberglass fabric.

High silica glass (96.5–100% silica) remains difficult to make because of the very high melting point of pure silica. However, it is made for special purposes because of its outstanding durability, excellent resistance to thermal shock or chemical attack, and ability to transmit ultraviolet light (an ability that ordinary glass does not have). Spacecraft windows, made of 100 percent silica, can withstand temperatures as high as 1,200°C (2,192°F). Table 1 lists the five major types of glass along with properties and uses.

Glass Composition. The making of glass involves three basic types of ingredients: formers, fluxes, and stabilizers. The glass former is the key component in the structure of a glassy material. The former used in most glasses is silica (SiO_2). Pure silica is difficult to melt because of its extremely high melting point (1,723°C, or 3,133°F), but fluxes can be added to lower the melting temperature. Other glass formers with much lower melting points (400°C–600°C, or 752–1,112°F) are boric oxide (B_2O_3) and phosphorus pentoxide (P_2O_5). These are easily melted, but because their glass products dissolve in water, they have limited usefulness.

Most silica glasses contain an added flux, so that the silica can be melted at a much lower temperature (800°C–900°C, or 1,472–1,652°F). Standard fluxes include soda (Na_2O), potash (K_2O), and lithia (Li_2O). Frequently the flux is added as a carbonate substance (e.g., Na_2CO_3), the CO_2 being driven off during heating. Glasses containing only silica and a flux, however, have poor durability and are often water-soluble.

To make glasses stronger and more durable, stabilizers are added. The most common stabilizer is lime (CaO), but others are magnesia (MgO), baria (BaO), and litharge (PbO). The most common glass, made in largest amounts by both ancient and modern glassmakers, is based on silica as the glass former, soda as the flux, and lime as the stabilizer. It is the glass used to make windows, bottles, jars, and lightbulbs.

Colored Glass. The natural glasses used by the ancients were all dark in color, usually ranging from olive green or brown to jet black. The color was

MAJOR GLASS TYPES AND THEIR USES

Glass Type	Properties	Limitations	Uses
Soda lime	Inexpensive; easy to melt and shape; most widely used glass	Poor durability; not chemically resistant; poor thermal shock resistance	Windows; bottles; light bulbs; jars
Lead glass (often 20–30% Pb oxide)	High density; brilliant; very easy to melt, shape, cut, and engrave	Poor durability; easily scratched	Fine crystal radiation windows; TV tube parts
Borosilicate (usually 5–13% B_2O_3)	Very good thermal shock resistance and chemical durability; easy to melt and shape	Not suitable for long-term high temperature use	Labware; kitchenware; special light bulbs; glass pipe; sealed beam headlights
Aluminosilicate (usually 5–10% Al_2O_3)	Excellent thermal resistance; durability	More difficult to melt and shape than borosilicate	Top-of-stove cookware; high quality fiberglass
High silica (Vycor 96.5%; fused quartz 100%)	Outstanding thermal resistance	Difficult to make; very expensive	Spacecraft windows; labware; fiber optics

Table 1. Major glass types and their uses.

due to the presence of significant amounts of metal impurities, especially iron. Even today the ubiquitous presence of iron in nature causes most ordinary glass to have a slight greenish cast.

Many standard glass colorants are oxides of metals such as cobalt (blue), chromium (green), and manganese (violet). Yellow glass is usually made with cadmium sulfide, and red or pink glass usually contains selenium, although some ruby-colored glass has had gold added. The coloring of glass is not a simple subject. Glass color depends not only on which elements are added, but also on the composition of the glass, and on whether the furnace used was in an oxidizing or reducing mode. Copper, for example, can produce blue, green, or opaque red glass, depending on melting conditions.

The Egyptians of 1500 B.C.E. knew that they could make brightly colored glasses by adding certain metals (or their compounds) to the glass melt. The ancient Romans continued the science of making colored glass and expanded it. By the fourth century C.E. the Romans had learned how to produce a dichroic (two-color) glass. The most famous dichroic glass article left by the Romans is the Lycurgus Cup (now at the British Museum). It is green in reflected light (with the lamp in front of the cup), but red in transmitted light (the lamp behind the cup). This unusual glass contains microscopic particles of gold and silver.

Glass Forming

Ancient Methods. Shaping hot, molten glass into useful articles has long been a challenge. Molten glass is extremely hot, caustic, sticky, and difficult to handle. In the period extending from about 2000 B.C.E. to 50 B.C.E., there were three basic methods used to form glass. One of the earliest and most widely used was core forming. This involved distributing molten glass around a clay core on a metal rod. The rod with the clay core could either be dipped into molten glass, or the hot liquid glass could simply be poured over it. The outer glass coating was then rolled (marvered) on a flat stone surface to smooth it. Often the object was decorated by dribbling more glass, sometimes of a different color, onto its surface. The hot glass was then annealed (cooled slowly so as to relieve thermal stress), and the metal rod was removed and the clay core scraped out.

A second method involved sagging and fusing. It called for taking preformed glass rods or canes (which were often of different colors), placing them in or on top of a mold, and then heating the canes until they sagged and fused together and conformed to the shape of the mold. (Sheets of glass could also be sagged over shaped clay molds.)

The third method was casting, which called for pouring hot, molten glass into a mold. A variation on cast glass was faience, made from powdered quartz blended into molten glass. The mixture might be pressed between two molds to make a cast vessel such as a bowl.

All three of these methods were slow, and they generally produced small items that were rather thick. Glass pieces tended to be quite expensive, and, in antiquity, were affordable only by the very wealthy.

Glassblowing. It was probably in the Middle East during the first century B.C.E. that the important technique of glassblowing was discovered. A hollow metal rod (or pipe) was used to pick up a gob of molten glass; the act of blowing into the pipe generated a bubble of glass. If the bubble were blown into a mold, the molten glass could be given a desired shape. Wooden paddles and pincers were used to refine the shape even further. The blowing procedure was used to make glass objects that were larger and thinner than those that had been made previously, and it was much faster than previous glass-forming methods. As glass pieces became easier to make, they became cheaper and more available. The ancient Romans became particularly skillful at glassblowing. More glass was produced and used in the Roman world than in any other civilization of antiquity. During the Middle Ages, there was a great expansion of glassblowing activity, especially in Venice, the Middle East, and European countries such as Spain and Germany.

Some Modern Methods. Since the nineteenth century, many centuries-old glass-forming methods have been mechanized, greatly increasing the rate of production of glass objects, and lowering the prices of these objects. For example, the “ribbon machine,” developed in the 1920s for the automatic glassblowing of lightbulbs, is a milestone of mechanical glass forming. In the ribbon machine, puffs of air blow glass bubbles from a rapidly moving ribbon of molten glass into a moving stream of molds that give the bulbs their shape and then release them. Small lightbulb blanks can be made at the rate of 1,000 per minute.

With so many millions of windows in buildings and vehicles everywhere, we tend to take sheets of flat glass for granted. Throughout most of human history, however, there were no sheets of flat, transparent glass. Even as recently as the eighteenth century, glass windows were quite uncommon.

In a very limited way glass windows did start to appear in the Roman world during the third century, but they were generally small glass fragments set in bronze or wooden frames. In that era most windows were not glass, but were thin sheets of translucent horn or marble, or perhaps panes of mica (isinglass). Around 600 C.E., during the Byzantine period, glass windows (usually made of small pieces of colored glass) began to appear in the large churches, but glass windows in houses and other secular buildings remained quite rare until the end of the eighteenth century.

The principal method for making flat glass during the 1700s called for blowing a hot glass bubble, securing an iron rod to the bubble's other side, and then cutting the bubble free from the blowing pipe. The tulip-shaped hot glass was then rotated rapidly around the iron rod axis until the centrifugal force forced the glass tulip to open up and form a disk. The rod was then removed from the glass (leaving a spot in the middle of the glass disk that looked rather like a bull's eye). This method was the source of the old "bull's-eye" windows that can still sometimes be found in English pubs. The windows were limited in size and poor in optical quality (besides having a bull's-eye at their centers).

The chief method for making flat glass during the 1800s was the cylinder method. The first step was to blow a large glass bubble (compressed air was often used); it would then be swung back and forth until the bubble became elongated and acquired a cylindrical shape; finally the cylinder was split lengthwise, reheated, and allowed to flatten on an iron table. The resulting pane of glass was not really flat, and it had a lot of optical distortion, but the method was used widely to make sheet glass. For example, it was used to produce the 300,000 panes of glass that were used to build London's Crystal Palace, the huge greenhouse constructed for the London World's Fair Exhibition of 1851.

By the twentieth century these methods were replaced by an innovative technique invented by a Belgian named Foucault, who had learned how to draw up continuous sheets from a tank filled with molten glass. Even this glass was of nonuniform thickness and had some roughness at its surface, therefore, for high quality flat glass, it had to be ground and polished.

Then, in 1959, the Pilkington Glass Works in Britain introduced the "float glass" process. In the float process, molten glass is allowed to flow continuously onto a mirrorlike surface of molten tin at 1,000ºC (1,832ºF). At this temperature the glass spreads out and becomes a layer that is about 6 millimeter (1/4 inch) thick. If the layer is stretched as it cools, a thickness of 2 millimeter (0.08 inch) can be achieved. The glass is allowed to advance on the hot liquid tin until, at 600ºC (1,112ºF), it becomes solid enough to be lifted off the molten tin surface. It is then annealed (heated to relieve any strain) before being cut into desired sheet lengths. The float glass method rapidly replaced the Foucault drawing process, and today it is the standard method for making flat glass. A large modern float glass plant can produce 5,000 tons of glass sheet per week, and it can be operated 24 hours a day, 365 days a year, for several years before serious repairs are apt to be needed. Float glass has uniform thickness and bright fire-polished surfaces that need no grinding or polishing.

The drawing of glass fibers had long been of interest, but glass fibers found little use until the twentieth century. Articles such as wedding gowns made from glass fiber cloth were largely curiosities, made for show rather than use. In the 1930s glass researchers learned to feed molten glass into platinum bushings having hundreds of tiny holes. Fine glass filaments of 10 to 50 microns were rapidly drawn downward and assembled as bundles or strands of glass fiber. Today a major use of glass cloth or filaments is to strengthen the plastics used to make fiberglass-reinforced composites. These composites are widely used in making boats, from canoes to yachts, and bodies for cars, such as the Corvette.

An even larger poundage market is that of glass wool insulation. In a process much like that used to make cotton candy, fine glass fibers are spun, sprayed with an organic bonding agent, and then heat-cured and cut into mats of various sizes, to be used for insulating buildings and appliances.

Surely the most significant glass fiber development in recent times is fiber optics, or optical wave guides. These ultrapure, very fine glass fibers are a most crucial part of modern communications technology, wherein glass fibers link telephones, televisions, and computers. A single strand of glass optical fiber that has a protective plastic coating looks much like a human hair. The glass fiber has an inner core of ultrapure fused silica, which is coated with another silica glass that acts as a light-refractive barrier. Lasers are used to convert sound waves and electrical impulses to pulses of light that are sent, static-free, through the inner glass core. Glass fibers can transmit many times more information than can be carried by charges moving in a copper wire. In fact, one pound of glass optical wave guides can transmit as much information as can be transmitted via 200 tons of copper wire. Today millions of miles of optic fibers are crisscrossing not only the United States, but also the entire planet.

Windows need to be cleaned. In 2000 a new glass that largely cleans itself when it comes into contact with rain was introduced. This low-maintenance glass was developed by Pilkington Glass Works, the company that invented the float process. It is made by depositing a microscopically thin coating of titanium dioxide (TiO_2) on hot sheet glass during its manufacture in the float process. As dirt collects on the window, the Sun's ultraviolet rays promote a catalytic reaction at the glass surface that breaks down and loosens surface dirt. SEE ALSO Ceramics; Gemstones; Minerals.

Kenneth E. Kolb

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Global Warming

The term "global warming" refers to an increase in Earth's mean global temperature because a part of Earth's outgoing infrared radiation is retained by several trace gases in the atmosphere whose concentrations have been increasing because of human industrial, commercial, and agricultural activities. These gases have the ability to absorb radiation, leading to the tendency of the atmosphere to create warmer climates than would otherwise be the case. The most important naturally occurring trace gases that have the ability to absorb infrared radiation are water vapor (H_2O), carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and ozone (O_3). In addition, there are some industrial gases that are extremely effective absorbers of the radiation. Important among these are **chlorofluorocarbons (CFCs)**, perfluorocarbons, hydrochlorofluorocarbons, hydrofluorocarbons (HFCs), and sulfur hexafluoride (SF_6). These gases are analogous to the glass in a greenhouse, which also leads to the net trapping of infrared radiation, hence the terms "greenhouse gases" (GHGs) and "**greenhouse effect**." These GHGs act as a partial blanket for the thermal radiation from the surface and make the atmosphere warmer than it would otherwise be. Before human intervention, Earth's radiation balance was in **equilibrium**, resulting in a mean average temperature of Earth at 15°C (59°F). Without the presence of naturally occurring GHGs, Earth's average surface temperature would have been −18°C (−0.4°F). This difference of 33°C (91.4°F) is due to the natural greenhouse effect, which has made Earth a habitable planet. Although the level of naturally occurring GHGs may change naturally over time, their concentration has steadily increased since the **Industrial Revolution** that began around 1750, because of fossil fuel **combustion**, deforestation, **biomass** burning, drainage of wetlands, conversion of natural into agricultural ecosystems, and plowing/cultivation of soil.

The concentration of CO_2 has increased from about 280 parts per million by volume (ppmv) in the preindustrial era to about 370 ppm in 2000, and is increasing at the rate of about 1.5 ppm/yr (0.4 percent/yr). The

chlorofluorocarbon (CFC): compound that contains carbon, chlorine, and fluorine atoms, which remove ozone in the upper atmosphere

greenhouse effect: presence of carbon dioxide in the atmosphere prevents heat from escaping, thereby raising Earth's temperature

equilibrium: condition in which two opposite reactions are occurring at the same speed, so that concentrations of the products and reactants do not change

Industrial Revolution: widespread replacement of hand tools by power-driven machines, beginning about 1750 (especially in England)

combustion: burning, the reaction with oxygen

biomass: collection of living matter atmospheric concentration of CH_4 has increased from 700 parts per billion by volume (ppbv) to 1,720 ppbv, and is increasing at the rate of 10 ppbv/yr (0.6 percent/yr). Similarly, the concentration of N_2O has increased from 275 ppbv to 312 ppbv and is increasing at the rate of about 0.8 ppbv/yr (0.25 percent/yr) (Bruce, Lee, and Haites 1996). Because of the successful implementation of the Montreal Protocol in 1987, the concentration of industrial gases has been decreasing.

There are three anthropogenic human-derived sources of atmospheric enrichment of CO_2: (1) fossil fuel combustion; (2) cement manufacturing; and (3) land use change involving deforestation, biomass burning, and cultivation. Fossil fuel combustion annually emits 6.22 Pg C (1 Pg = 1 billion metric tons) as CO_2, 46 to 155 Tg of C (1 Tg = 1 million metric tons) as CH_4, and 0.7 to 1.8 Tg N as N_2O and NO_x. The fossil fuel emission has steadily increased over the last 150 years. The CO_2-C emission from fossil fuel combustion was negligible in 1850, 1,850 Tg/yr in 1900, 1.7 Pg/yr in 1950, and 6.2 Pg/yr in 1995 (Hansen, et al. 1998, pp. 12753–12758). Cement manufacturing emits 0.2 Pg C/yr as CO_2. Tropical deforestation and soil cultivation annually emit 0.6 to 2.6 Pg C as CO_2, 160 to 460 Tg of C as CH_4, and 2.2 to 6.8 Tg N as NO_x (Harvey 2000, pp. 16–20). From 1850 to 1998, approximately 270 (±30) Pg C has been emitted as CO_2 by fossil fuel combustion and cement production. During the same time, about 136 (±55) Pg has been emitted as a result of deforestation and land use change, of which 78 (±17 Pg) is due to depletion of the soil organic carbon pool (Watson, et al. 2000, p. 4; Lal 1999, p. 317).

The alteration in Earth's radiation budget because of an increase in atmospheric concentration of GHGs is referred to as "radiative forcing," and is measured in w/m^2. The radiative forcing of three gases (CO_2, CH_4, and N_2O) since the preindustrial era is 2.45 w/m^2, due to the accelerated greenhouse effect or global warming. The GHGs differ with regard to their radiative forcing and their life span, or residence time in the atmosphere. This relative ability of GHGs is called the global warming potential or GWP. The GWP is computed relative to CO_2, and is 1 for CO_2, 21 for CH_4, 210 for N_2O, 1,800 for O_3, and 4,000 to 12,000 for CFCs. It is estimated that the mean global temperature has increased by about 0.5°C (32.9°F) since the preindustrial era. With business as usual, the radiation budget of Earth may change within a short span of several decades to a century, with an attendant increase in Earth's mean temperature of 1 to 4°C (33.8 to 39.2°F). The projected increase will be less in the tropics than in the boreal, temperate, and cold regions. The greenhouse effect is tolerable (i.e., the biomes or ecological communities comprising plants and animals can adapt) if the rate of increase in Earth's mean temperature is about 0.1°C (32.18°F) per decade.

World soils constitute the third largest global C pool (after oceanic and geologic), and comprise 1,550 Pg of soil organic carbon (SOC) and 750 Pg of soil inorganic carbon (SIC). Thus, the soil C pool is 3.2 times the atmospheric pool (720 Pg), and 4.1 times the biotic pool (560 Pg). The C depleted from the SOC pool can be resequestered through adoption of appropriate land use and soil/crop/vegetation management practices (Lal and Bruce 1999, p. 182; Lal 2001a, pp. 171–172). Restoration of degraded soils and ecosystems and desertification control have a potential to sequester

C in soil and the biota and to decrease the rate of enrichment of GHGs in the atmosphere (Lal 2001b, p. 52; 2001c, p. 23).

There are short-term and long-term strategies of mitigating the accelerated greenhouse effect. In the short term, it is important to improve energy use efficiency and to identify strategies of CO_2 sequestration. In the long term, it is important to develop noncarbon fuel sources. Carbon sequestration in soil and vegetation through restoration of degraded soils and the ecosystem and adoption of appropriate land uses is a winning strategy. SEE ALSO AIR POLLUTION.

Rattan Lal

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Globular Protein

In a globular protein, the amino acid chain twists and folds in a manner that enhances the protein's solubility in water by placing polar groups of atoms at the protein's surface (where they can participate in attractive interactions with water molecules). This twisting and folding that determine the overall shape of a protein molecule (its tertiary structure) are due largely to the very complex interplay of **intramolecular forces** that exists among different groups of atoms within the molecule, and to intermolecular forces acting between groups of atoms on the protein and molecules in the protein's immediate surroundings. Some of the common amino acids have polar side chains; this polarity is the result of chemical bonds between atoms in these side chains that have very different electronegativities (for instance, oxygen and hydrogen). A protein's polar side chains tend to exert strong attractive forces toward other polar groups of atoms within the protein molecule, or toward polar molecules in the protein's surroundings. Similarly, **nonpolar** side chains exert attractive forces (of a different nature) toward other nonpolar side chains within the protein. The shape assumed by a globular protein molecule tends to maximize both types of attractive forces, whereby

intramolecular force: force that arises within molecules—essentially the force associated with chemical bonds

nonpolar: molecule, or portion of a molecule, that does not have a permanent, electric dipole

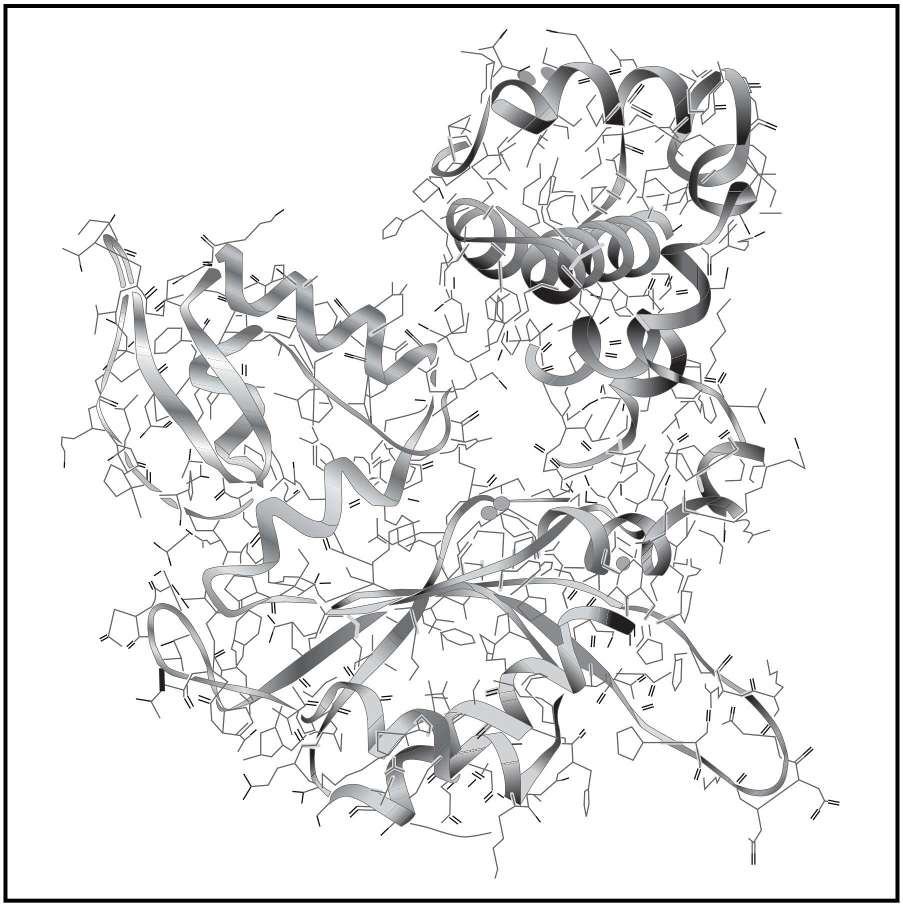

Figure 1. The 3-dimensional molecular structure of the globular protein polymerase β. The ribbon represents the backbone of the amino acid chain with the various amino acids depicted by shading. The side chains of the amino acids fill in the structure.

nonpolar side chains "point" inward and interact with one another and polar side chains are oriented outward such that they are exposed to adjacent polar water molecules. Over the last few decades, molecular shape and structure have been experimentally determined for several thousand proteins.

The aqueous solubility of globular proteins allows them to exist in biological fluids as individual molecules or in small clusters and to accomplish a wide range of critical biological functions, for example, the enzymatic **catalysis** of chemical reactions. Globular proteins also function as **antibodies** in the body's immune system and as transport vehicles for other molecules in circulating blood, and they are heavily involved in the replication and repair of **DNA**. Figure 1 shows the molecular structure of polymerase β, a much-studied globular protein that catalyzes reactions having to do with the repair of damaged DNA. The structure of polymerase β was determined by Huguette Pelletier and her coworkers using the technique of x-ray diffraction at the University of California, San Diego. SEE ALSO AMINO ACID; PROTEINS; TERTIARY STRUCTURE.

catalysis: the action or effect of a substance in increasing the rate of a reaction without itself being converted

antibody: protein molecule that recognizes external agents in the body and binds to them as part of the immune response of the body

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

Robert C. Rittenhouse

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Glycolysis

Glycolysis is the sequence of enzymatic reactions that oxidize the six-carbon sugar **glucose** into two three-carbon compounds with the production of a small amount of **adenosine triphosphate (ATP)**. Glycolysis has two basic functions in the cell. First, it metabolizes simple six-carbon sugars to smaller three-carbon compounds that are then either fully metabolized by the mitochondria to produce carbon dioxide and a large amount of ATP or used for the **synthesis** of fat for storage. Second, glycolysis functions to produce

glucose: common hexose monosaccharide; monomer of starch and cellulose; also called grape sugar, blood sugar, or dextrose

adenosine triphosphate (ATP): molecule formed by the condensation of adenine, ribose, and triphosphoric acid, HOP(O)OH–O–(O)OH–OP(O)OH–OH; it is a key compound in the mediation of energy in both plants and animals

synthesis: combination of starting materials to form a desired product

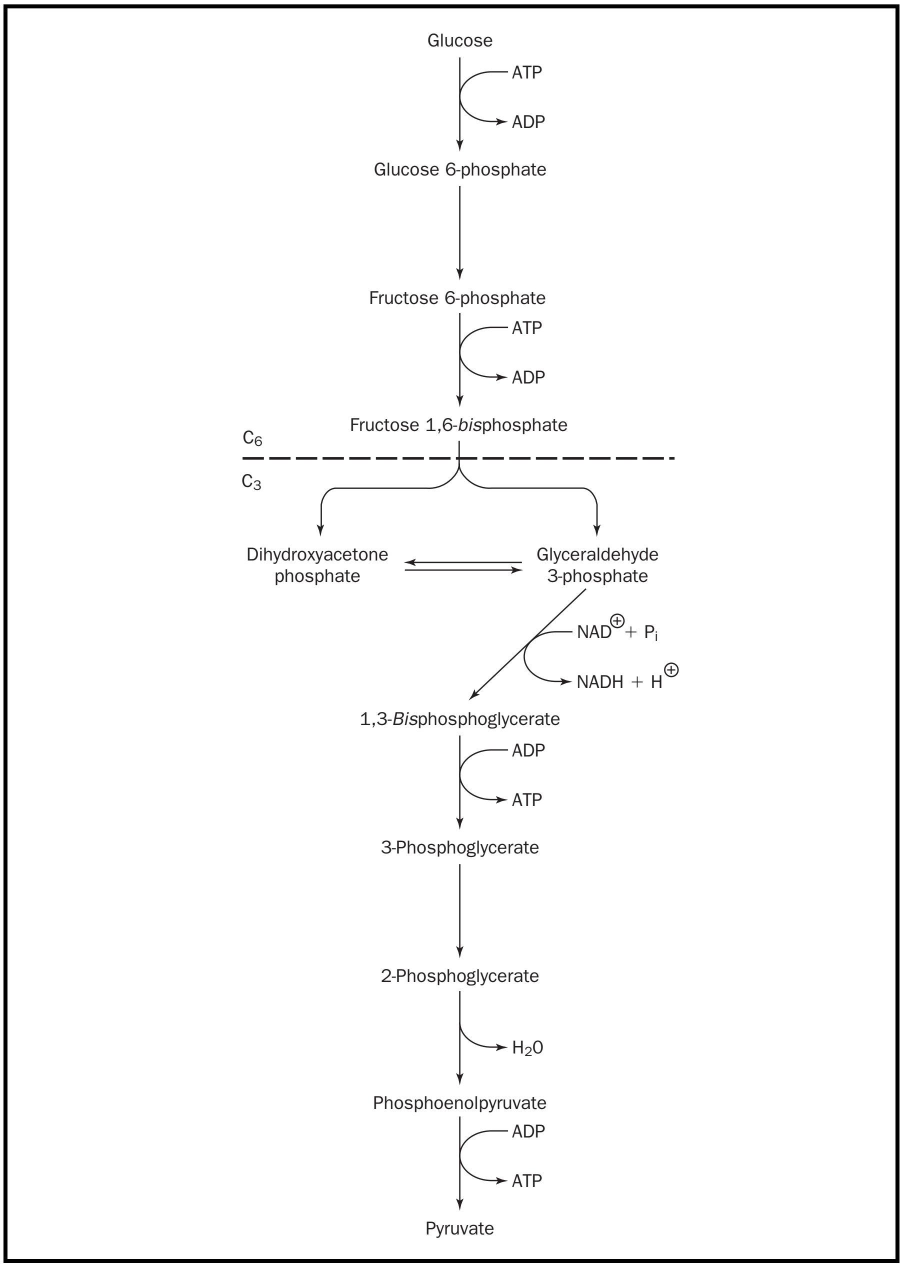

Figure 1. The glycolytic pathway.

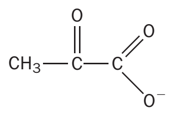

Figure 2. Structure of pyruvate.

monosaccharide: one class of the natural products called carbohydrates with the general formula $C_x(H_2O)_y$; monosaccharides have a weak sweet taste, are readily soluble in water, and are called sugars

galactose: six-carbon sugar

metabolism: the complete range of biochemical processes that take place within living organisms; comprises processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those which break down complex food molecules, thus liberating energy (catabolism)

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

adenine: one of the purine bases found in nucleic acids, $C_5H_5N_5$

pyruvate: anion of pyruvic acid produced by the reaction of oxygen with lactic acid after strenuous exercise

metabolize: performing metabolism—the processes that produce complex substances from simpler components, with a consequent use of energy (anabolism) and those which break down complex food molecules, thus liberating energy (catabolism)

a small amount of ATP, which is essential for some cells solely dependent on that pathway for the generation of energy.

The glycolytic pathway is nearly ubiquitous, being found in every cell of virtually all living creatures. It is catalyzed by soluble enzymes located in the cytosol of cells. Although the glycolytic pathway is most commonly thought of as metabolizing glucose, other common **monosaccharides** such as fructose, **galactose**, and mannose are also metabolized by it. The glycolytic pathway operates in both the presence (aerobic) or absence of oxygen (anaerobic).

The **metabolism** of fuel molecules in the cell can be thought of as an **oxidation** process. In glycolysis, glucose is the fuel molecule being oxidized. As the glucose is oxidized by the glycolytic enzymes, the coenzyme nicotinamide **adenine** dinucleotide (NAD^+) is converted from its oxidized to reduced form (NAD^+ to NADH). When oxygen is available (aerobic conditions), mitochondria in the cell can reoxidize to NADH to NAD^+. However, if either oxygen levels are insufficient (anaerobic conditions) or mitochondrial activity is absent, NADH must be reoxidized by the cell using some other mechanism. In animal cells, the reoxidation of NADH is accomplished by reducing **pyruvate**, the end-product of glycolysis, to form lactic acid. This process is known as anaerobic glycolysis. During vigorous exercise, skeletal muscle relies heavily on it. In yeast, anaerobic conditions result in the production of carbon dioxide and ethanol from pyruvate rather than lactic acid. This process, known as alcoholic fermentation, is the basis of wine production and the reason why bread dough rises.

Although some cells are highly dependent on glycolysis for the generation of ATP, the amount of ATP generated per glucose molecule is actually quite small. Under anaerobic conditions, the metabolism of each glucose molecule yields only two ATPs. In contrast, the complete aerobic metabolism of glucose to carbon dioxide by glycolysis and the Krebs cycle yields up to thirty-eight ATPs. Therefore, in the majority of cells the most important function of glycolysis is to **metabolize** glucose to generate three-carbon compounds that can be utilized by other pathways. The final product of aerobic glycolysis is pyruvate. Pyruvate can be metabolized by pyruvate dehydrogenase to form acetyl coenzyme A (acetyl CoA). Under conditions where energy is needed, acetyl CoA is metabolized by the Krebs cycle to generate carbon dioxide and a large amount of ATP. When the cell does not need energy, acetyl CoA can be used to synthesize fats or amino acids. SEE ALSO INSULIN; KREBS CYCLE.

Robert Noiva

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Glycoprotein

Glycoproteins are proteins that contain covalently attached sugar residues. The **hydrophilic** and polar characteristics of sugars may dramatically change the chemical characteristics of the protein to which they are attached.

hydrophilic: a part of a molecule having an affinity for water

The addition of sugars is often required for a glycoprotein to function properly and reach its ultimate destination in the cell or organism. Glycoproteins are frequently present at the surface of cells where they function as membrane proteins or as part of the extracellular matrix. These cell surface glycoproteins play a critical role in cell–cell interactions and the mechanisms of infection by bacteria and viruses.

There are three types of glycoproteins based on their structure and the mechanism of synthesis: N-linked glycoproteins, O-linked glycoproteins, and nonenzymatic glycosylated glycoproteins.

N-linked glycoproteins are synthesized and modified within two membrane-bound organelles in the cell, the rough **endoplasmic reticulum** and the Golgi apparatus. The protein component of the glycoprotein is assembled on the surface of the rough endoplasmic reticulum by the sequential addition of amino acids, creating a linear polymer of amino acids called a **polypeptide**. Twenty different amino acids can be used for the synthesis of polypeptides. The specific order of the amino acids in the polypeptide is critical to its function and is referred to as the amino acid sequence. One of the twenty amino acids used for the synthesis of polypeptides, asparagine ($C_4H_8N_2O_3$), is essential for the synthesis of N-linked glycoproteins.

endoplasmic reticulum: internal membrane system that forms a net-like array of channels and interconnections of organelles within the cytoplasm of eukaryotic cells

polypeptide: compound containing two or more amide units—C(O)NH—produced by the condensation of two or more amino acids

N-linked glycoproteins have carbohydrates attached to the R side chain of asparagine residues within a polypeptide. The carbohydrate is always located in amino acid sequences, where the asparagine is followed by some other amino acid and then a serine or threonine residue (-Asn-Xaa-Ser/Thr). Carbohydrate is not attached to the polypeptide one sugar at a time. Rather, a large preformed carbohydrate containing fourteen or more sugar residues is attached to the asparagine as the protein is being translated in the rough endoplasmic reticulum. The carbohydrate on the glycoprotein is then modified by enzymes that remove some sugars and attach others as the newly formed glycoprotein moves from the rough endoplasmic reticulum to the Golgi apparatus and other locations in the cell. Many N-linked glycoproteins eventually become part of the cell membrane or are secreted by the cell.

O-linked glycoproteins are usually synthesized by the addition of sugar residues to the hydroxyl side chain of serine or threonine residues in polypeptides in the Golgi apparatus. Unlike N-linked glycoproteins, O-linked glycoproteins are synthesized by the addition of a single sugar residue at a time. Many O-linked glycoproteins are secreted by the cell to become a part of the extracellular matrix that surrounds it.

Nonenzymatic glycosylation or glycation creates glycoproteins by the chemical addition of sugars to polypeptides. Since this type of glycosylation is nonenzymatic, the factors that control glycosylation are simply time and the concentration of sugar. Older proteins are more glycosylated, and people with higher circulating levels of glucose experience higher levels of nonenzymatic glycosylation. This is the basis of the glycosylated hemoglobin A1c diagnostic test used for the monitoring and long-term maintenance of blood sugar levels in diabetics. SEE ALSO CONCENTRATION GRADIENT; PROTEINS.

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Gold

79

Au

GOLD

196.96654

MELTING POINT: **1,064.18°C**
BOILING POINT: **2,808°C**
DENSITY: **19.32 g/cm^3**
MOST COMMON IONS: **Au^+, Au^{3+},**

Gold is a soft, malleable yellow **metal**. If finely divided, it may be black, ruby, or purple. The name of the element is derived from the Anglo-Saxon word *geolo*, meaning "yellow." The symbol Au is derived from the Latin word *aurum*, meaning "shining dawn."

Gold is the most malleable and **ductile** metal known. Approximately 28 grams (1 ounce) of gold can be hammered to form a piece that is 28 square meters (300 square feet). It is a good conductor of heat and electricity, and unreactive in air and most **reagents**. It forms ionic compounds primarily as a +3 ion; the most common compounds are gold (III) chloride ($AuCl_3$), and chlorauric acid ($HAuCl_4$).

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

ductile: property of a substance that permits it to be drawn into wires

reagent: chemical used to cause a specific chemical reaction

The relative abundance of gold is 0.004 part per million (ppm) in Earth's crust. Deposits of the metal are found in South Africa, Siberia, North America, and South America. Gold has one naturally occurring **isotope** (^{197}Au) and forty-five synthetic isotopes.

isotope: form of an atom that differs by the number of neutrons in the nucleus

Found in association with quartz or pyrite, gold occurs in veins and is traditionally isolated from rocks by panning or sluicing; these techniques take advantage of gold's high density. A modern method of isolation is the cyanide process, in which gold is leached from crushed rock with an aerated solution of sodium cyanide. The gold then precipitates upon addition of zinc dust and is purified by electrolytic refining.

Gold was used as early as the late Stone Age for ornamental purposes (e.g., jewelry and plating) and more recently as a monetary standard. It is a component of electrical connectors in computer equipment due to its high electrical conductivity. Its unreactivity in air leads to its use for corrosion-free contacts in electrical connections. As an excellent conductor of heat, it is used in the main engine nozzle of the space shuttle. Since gold is the most reflective of all metals, it is used as a coating for space satellites, face shields for astronauts, and windows. Chlorauric acid is used in photography; disodium aurothiomalate is given as a treatment for arthritis. SEE ALSO INORGANIC CHEMISTRY; RUTHERFORD, ERNEST.

Catherine H. Banks

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Goodyear, Charles

AMERICAN INVENTOR
1800–1860

American inventor Charles Goodyear, developer of the vulcanization process.

Charles Goodyear was born in New Haven, Connecticut, on December 29, 1800. Goodyear began his work on rubber in 1834, when rubber from Brazilian trees (*Hevea brasiliensis*) was first being imported to the United States in large quantities. He approached a rubber goods manufacturer with an idea for a valve for an inflatable life buoy, but was advised that the company's own products were failing because of the material's inherent flaws. Although it had outstanding qualities, it turned brittle and hard at low temperatures, and worse, into a gooey mass during warm weather.

Goodyear was determined to solve the problems inherent in natural rubber. With no formal training in chemistry, his work was based on trial and error, experimenting with different methods of processing and additives such as magnesia. The solution he discovered resulted partly from serendipity and partly from constant work.

The breakthrough came in 1839 while Goodyear was exhibiting his most recent samples at a general store in Woburn, Massachusetts. When he accidentally dropped a piece on a hot stove, it burned, but the uncharred part was transformed into a smooth, firm material that was not affected by high or low temperature. The additive in the sample was sulfur, but it took Goodyear several months to determine the right combination of heat, pressure, and sulfur to produce a stable compound. He found that the best material was produced when the compound was steam-heated under pressure at 120°C (248°F) for four to six hours. Its first commercial use was as elastic thread in men's shirts.

Goodyear vigorously promoted his product, but was forced to spend large sums of money defending his patent. In Britain, Thomas Hancock had received a patent for **vulcanized rubber** (after Vulcan, the Roman god of fire) a few months before Goodyear applied for his. Although Hancock offered to share his royalties, Goodyear took his claim of sole ownership to court and lost. He also lost his French patent, although he was eventually awarded the Cross of the Legion of Honor by Napoléon III for his important work.

vulcanized rubber: chemical process of mixing rubber with other substances like sulfur; it strengthened rubber so it could be used under hot or cold conditions; discovered by Charles Goodyear

Goodyear invented a material that would eventually be used in thousands of ways and opened the door for a huge industry. Today there is one rubber tree for every two people on Earth. Despite this, he died destitute in New York on July 1, 1860. Although the Goodyear Tire and Rubber Company was named in his honor, Goodyear's descendants had little to do with the rubber industry after his death. SEE ALSO Polymers, Natural; Rubber.

Andrew Ede

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Green Chemistry

Green chemistry is also known as environmentally benign chemistry, or sustainable chemistry. Perhaps the most widely accepted definition of green chemistry is the one offered by chemists Paul Anastas and John Warner, who defined green chemistry as the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances.

Milestones

The Pollution Prevention Act of 1990 set the stage for green chemistry: Its focus is the prevention of pollution at the source rather than the treatment of pollutants after they are formed. This goal became a formal objective of the Environmental Protection Agency (EPA) in 1991. Anastas coined the term "green chemistry" the same year. Two of the most prominent and early advocates of green chemistry were Kenneth Hancock of the National Science Foundation (NSF) and Joe Breen, who after twenty years of service at the EPA then became the first director of the Green Chemistry Institute (GCI) during the late 1990s.

Anastas and Warner formulated the twelve principles of green chemistry in 1998. These serve as guidelines for chemists seeking to lower the ecological footprint of the chemicals they produce and the processes by which such chemicals are made.

Starting in 1996, outstanding examples of green chemistry have been recognized in the United States each year by the Presidential Green Chemistry Challenge (PGCC) awards. These are the only awards in chemistry that are bestowed at the presidential level.

The EPA and the American Chemical Society (ACS) have played a major role in promoting research and development, as well as education, in green chemistry. In 2000 the GCI became a partner of the ACS. Chemical societies around the globe have recognized the importance of green chemistry and promote it through journals, conferences, educational activities, and the formation of GCI chapters. There are GCI chapter affiliates all over the world.

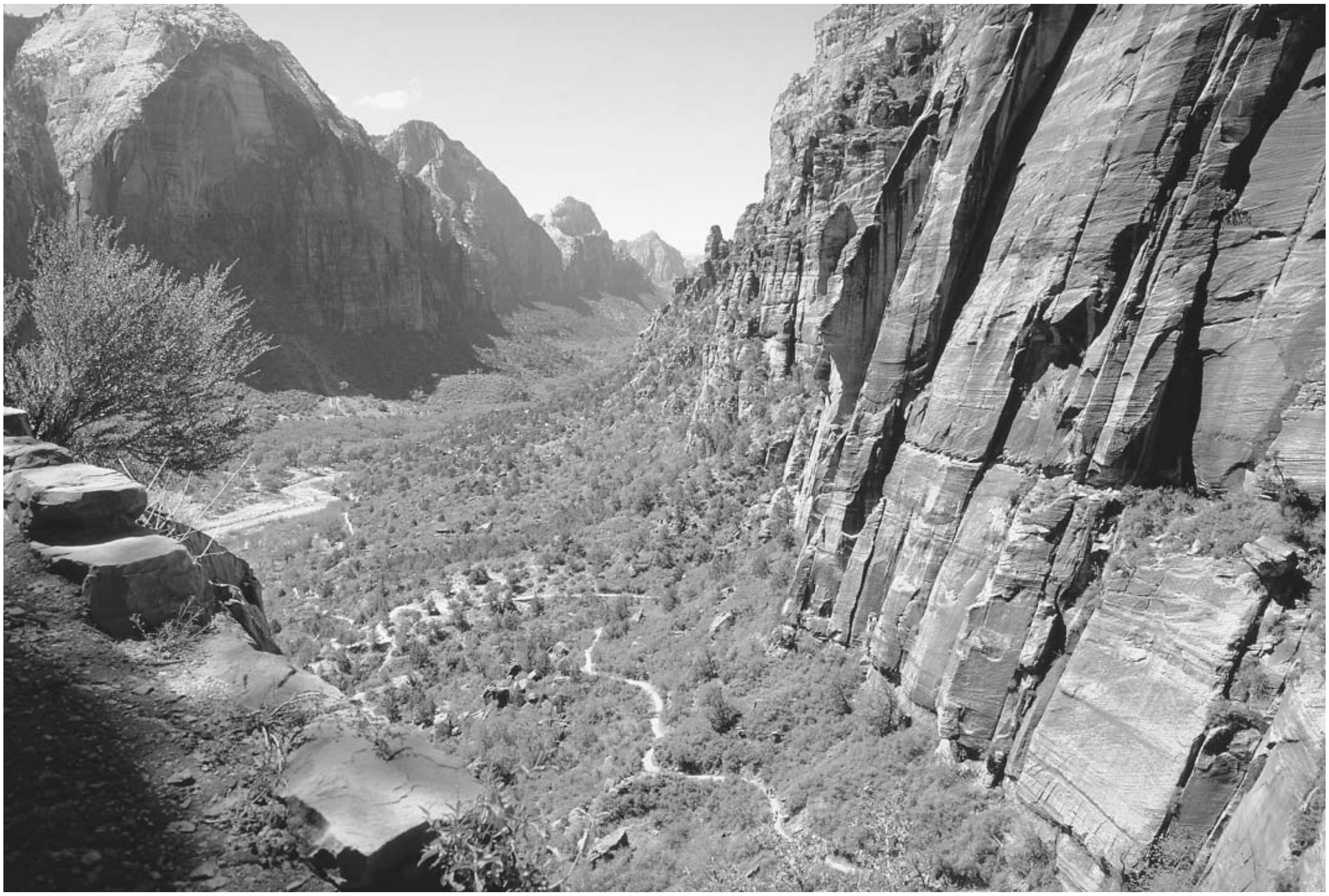
Importance to Industry: The Triple Bottom Line

During the 1990s many industries began to earnestly adopt green chemistry and other sustainable practices. Forward-looking companies realized that the practice of green chemistry not only leads to environmental benefits, but also economic and social benefits. The combination of these three benefits is known as the "triple bottom line" and provides strong encouragement for businesses to develop sustainable products and processes.

The following real-world examples of green chemistry represent the accomplishments of several winners of the PGCC awards. They illustrate how green chemistry impacts a wide array of fields including pharmaceuticals, pesticides, polymers, and many others.

The Concept of Atom Economy

When chemists are considering a compound, they are concerned with the chemical, biological, and physical properties of this compound, and the



Concerns over the pollution of natural resources such as this valley in Zion National Park, Utah prompted the development of green chemistry in the 1990s.

method by which the compound is prepared or its **synthesis**. In order to focus greater attention on waste by-products that are formed during a synthesis, Barry Trost of Stanford University developed the concept of atom economy. This concept deals with the question: How many of the atoms of the reactants are incorporated into the final desired product and how many are wasted by incorporation into by-products? An example of the application of this concept is discussed in the following synthesis of ibuprofen.

synthesis: combination of starting materials to form a desired product

Pharmaceuticals. Ibuprofen is the active ingredient in many **analgesic** and inflammatory drugs such as Advil, Motrin, and Medipren. Beginning in the 1960s, ibuprofen was produced by a six-step synthesis with an atom economy of only 40 percent. This meant that less than half (40 percent) of the weight of all the atoms of the reactants were incorporated in the ibuprofen, and 60 percent were wasted in the formation of unwanted by-products. The annual production of approximately 30 million pounds of ibuprofen by this method resulted in over 40 million pounds of waste. But during the 1990s, the BHC Company developed a new synthesis of ibuprofen with an atom economy of 77 to 99 percent. This synthesis not only produces much less waste, it is also only a three-step process. A pharmaceutical company can thus produce more ibuprofen in less time and with less energy, which results in increased profits.

analgesic: compound that relieves pain, e.g., aspirin

Pesticides. Dichlorodiphenyl trichloroethane (DDT) is one of the most well-known insecticides. During World War II it saved thousands of Allied

THE TWELVE PRINCIPLES OF GREEN CHEMISTRY

1. It is better to prevent waste than to treat or clean up waste after it is formed.

2. Synthetic methods should be designed to maximize the incorporation of all materials used in the process in the final product.

3. Wherever practical, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4. Chemical products should be designed to preserve efficacy of function while reducing toxicity.

5. The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary whenever possible and innocuous when used.

6. Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.

7. A raw material feedstock should be renewable rather than depleting whenever technically and ecomonically practical.

8. Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.

9. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10. Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.

11. Analytical methodologies need to be further developed to allow for real-time in-process monitoring and control prior to the formation of hazardous substances.

12. Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

Source: Anastas, Paul T., and Warner, John C. (1998). *Green Chemistry Theory and Practice.* New York: Oxford University Press.

lives by killing disease-carrying insects, but during the 1960s the significant environmental damage caused by DDT was brought to the public's attention by Rachel Carson in *Silent Spring* (1962). As a result of the controversy generated by this book and other media coverage, the substance's use was banned in the United States in 1973.

During the 1960s and 1970s organophosphates largely replaced organochlorine pesticides such as DDT. These pesticides rapidly **degrade** in the environment, but they are much more toxic to mammals. They are deadly to a wide array of insects and kill not only the target organism but also beneficial insects, such as bees and predatory beetles, and can also be harmful to humans.

degrade: to decompose or reduce to complexity of a chemical

One approach to producing less environmentally harmful pesticides is to use compounds that destroy only the target organisms. One manufacturer, Rohm & Haas, has developed insecticides that mimic a hormone used only by molting insects. Insects that do not molt are not affected, leaving many beneficial insects unharmed.

A more recent strategy for protecting plants from pests and disease involves the use of genetically altered plants. This method is controversial. Concerns include cross-pollination with unaltered plants and the entry of altered plants into the food supply.

Another approach to protecting plants from pests and diseases is to activate their natural defense mechanism against pests or diseases. EDEN Bioscience Corporation has developed what is known as harpin technology. Harpin is a naturally occurring protein that is isolated from genetically altered bacteria. When applied to the leaves and stems of plants, this protein elicits their natural defense systems. The EPA has classified harpin as Category IV, which is reserved for materials with the lowest hazard potential. As an added benefit, harpin also stimulates plant growth.

Polymers. Synthetic polymers or plastics are everywhere. They are used in cars, computers, planes, houses, eyeglasses, paints, bags, appliances, medical devices, carpets, tools, clothing, boats, batteries, and pipes. More than 60 million pounds of polymers are produced in the United States each year. The feedstocks that are used to produce these polymers are virtually all made from petroleum, a nonrenewable resource. Approximately 2.7 percent of all crude oil is used to generate chemical feedstocks.

In order to decrease human consumption of petroleum, chemists have investigated methods for producing polymers from renewable resources such as **biomass**. NatureWorks polylactic acid (PLA) is a polymer of naturally occurring lactic acid (LA), and LA can be produced from the fermentation of corn. The goal is to eventually manufacture this polymer from waste biomass. Another advantage of PLA is that, unlike most synthetic polymers which litter the landscape and pack landfills, it is biodegradable. PLA can also be easily recycled by conversion back into LA. It can replace many petroleum-based polymers in products such as carpets, bags, cups, and textile fibers.

biomass: collection of living matter

Computer Chips. The manufacture of computer chips requires excessive amounts of chemicals, water, and energy. Estimates indicate that the weight of chemicals and fossil fuels required to make a computer chip is 630 times the weight of the chip, as compared to the 2:1 ratio for the manufacture of an automobile. Scientists at the Los Alamos National Laboratory have developed a process that uses supercritical carbon dioxide in one of the steps in chip preparation, and it significantly reduces the quantities of chemicals, energy, and water needed to produce chips.

Dry Cleaning. Condensed **phase** carbon dioxide is also used as a solvent for the dry cleaning of clothes. Although carbon dioxide alone is not a good solvent for oils, waxes, and greases, the use of carbon dioxide in combination with a **surfactant** allows for the replacement of perchloroethylene (which is the solvent used most often to dry clean clothes, although it poses hazards to the environment and is a suspected human carcinogen).

phase: homogeneous state of matter

surfactants: surface-active agents that lower the surface tension of water; e.g., detergents, wetting agents

Other Examples. Some other examples of green chemistry include the following:

- taking chromium and arsenic, which are toxic, out of pressure-treated wood
- using new less toxic chemicals for bleaching paper
- substituting yttrium for lead in auto paint
- using enzymes instead of a strong base for the treatment of cotton fibers

Green chemistry reduces toxicity, minimizes waste, saves energy, and cuts down on the depletion of natural resources. It allows for advances in chemistry to occur in a much more environmentally benign way. In the future, when green chemistry is practiced by all chemists and all chemical-related companies, the term "green chemistry" will ideally disappear as all chemistry becomes green. see also Ibuprofen; Industrial Chemistry, Organic; Solution Chemistry.

Michael C. Cann

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Guanine *See Nucleotide.*

Haber, Fritz

GERMAN PHYSICAL CHEMIST
1868–1934

synthesis: combination of starting materials to form a desired product

Fritz Haber, born in Breslau, Prussia (now Wroclaw, Poland), successfully applied physical chemistry to technological problems. In 1918 he won the Nobel Prize in chemistry for his **synthesis** of ammonia from the elements, an important starting material in the production of fertilizers and explosives.

combustion: burning, the reaction with oxygen

Haber, whose father was a natural dyestuff importer, was destined to enter the family business at a time when synthetic dyes began to dominate the market, and his fortunes soon floundered. In 1894 the young Haber became assistant to Hans Bunte at the Technical University of Karlsruhe. Self-taught in physical and electrochemistry, he applied these new theories with impressive results to chemical technology, particularly to the **combustion** of hydrocarbons, the electrolysis of salts, and the fixation of nitrogen. In 1906 he was appointed professor at Karlsruhe, but he left six years later to become director of the new Kaiser Wilhelm Institute for Physical Chemistry in Berlin. During World War I, that institute was transformed into Germany's headquarters for chemical weapons research and production, with Haber remaining as its director. When the Nazis in 1933 began to dismiss all Jews from civil service, Haber, himself a Jew who had converted to Christianity, immediately resigned and emigrated to Great Britain. He was invited to head the physical chemistry section of the new Weizmann Institute in Palestine, but died shortly before its establishment.

The most abundant component of common air, elementary nitrogen, stubbornly resists chemical reactions. However, certain bacteria can transform it to ammonia (the so-called fixation of nitrogen) as the essential raw material for protein production in plants. That was already known in the late nineteenth century when a rapidly growing population required a more efficient agriculture to be supported by fertilizers including "fixed nitrogen." At that time natural niter (KNO_3), or guano from Chile, was virtually the only nitrogen source for fertilizers, so chemists were challenged to find ways to fix nitrogen from the air. In the early 1900s, several prominent physical chemists, including Henri-Louis Le Châtelier, Friedrich Wilhelm Ostwald, and Walther Hermann Nernst, were experimentally and theoretically working on this issue from two different approaches to nitrogen: **oxidation** to nitrogen oxide and reduction with hydrogen to ammonia.

German chemist Fritz Haber, recipient of the 1918 Nobel Prize in chemistry, "for the synthesis of ammonia from its elements."

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

equilibrium: condition in which two opposite reactions are occurring at the same speed, so that concentrations do not change

Although most researchers soon dropped the topic because of little success, from 1904 on Haber continued investigating both approaches under contract with the chemical company BASF (Badische Anilin- und Sodafabrik), who offered him money, equipment, and patent shares. The path to ammonia turned out to be more promising if the reaction rates were increased by catalysts at high temperature. Thermodynamics required low temperature, however, to move the **equilibrium** toward higher yields of ammonia. Because thermodynamics predicted the same effect at high pressure, Haber and his coworkers at BASF searched for temperature and pressure conditions that a reaction vessel could withstand and that resulted in acceptable yields. Success came only when they found more effective catalysts, at first with osmium and uranium. In addition, they pushed the equilibrium to the product side by continuously drawing off ammonia from the reaction mixture and continuously providing new reactants, resulting in 1909 in a steady flow reactor at about 100 atm and 500°C (932°F) with ammonia yields of some 10 percent.

Haber demonstrated that the production of ammonia from the elements was feasible in the laboratory, but it was up to Carl Bosch, a chemist and engineer at BASF, to transform the process into large-scale production. The industrial converter that Bosch and his coworkers created was completely revised, including a cheaper and more effective **catalyst** based on extensive studies in high-pressure **catalytic** reactions. This approach led to Bosch receiving the Nobel Prize in chemistry in 1931, and the production of multimillion tons of fertilizer per year worldwide. SEE ALSO AGRICULTURAL CHEMISTRY; CATALYSIS AND CATALYSTS; EQUILIBRIUM; LE CHÂTELIER, HENRI; NERNST, WALTHER HERMANN; OSTWALD, FRIEDRICH WILHELM.

catalyst: substance that aids in a reaction while retaining its own chemical identity

catalysis: the action or effect of a substance in increasing the rate of a reaction without itself being converted

Joachim Schummer

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72
Hf
HAFNIUM
178.49

Hafnium

MELTING POINT: 2,150.0°C
BOILING POINT: 5,400.0°C
DENSITY: 13.31g/cm^3
MOST COMMON IONS: Hf^{4+}

Hafnium was discovered in 1923 by Danish chemist Dirk Coster working together with Hungarian physicist György K. Hevesy. The electronic structure of hafnium had been predicted by Niels Bohr, and Coster and Hevesy found evidence of a substance whose pattern matched what had been predicted. The element predicted by Bohr was finally identified as being part of the mineral zircon by means of x-ray spectroscopy analysis. Due to its discovery in Copenhagen (whose ancient Latin name was Hafnia), the element was named hafnium.

Most zirconium-containing minerals are 1 to 3 percent hafnium. Hafnium is a ductile metal with a brilliant silver luster. The properties of hafnium are often difficult to ascertain, as measurements of these properties are sometimes distorted by the presence of zirconium impurities. Of all the elements, zirconium and hafnium are two of the most difficult to separate from one another. Hafnium is a group IV transition element.

Because hafnium has a high absorption cross-section for thermal neutrons (almost 600 times that of zirconium), has excellent mechanical properties, and is extremely corrosion resistant, it is used to make the control rods of nuclear reactors. It is also applied in vacuum lines as a "getter"—a material that combines with and removes trace gases from vacuum tubes. Hafnium has been used as an alloying agent for iron, titanium, niobium, and other metals. Finely divided hafnium is pyrophoric and can ignite spontaneously in air.

Melting near 3,890°C, (7,034°F), hafnium carbide (HfC) has the highest melting point of any known binary compound. Hafnium nitride (HfN) also has a very high melting point (around 3,305°C, or 5,981°F). Other hafnium compounds include hafnium tetrachloride ($HfCl_4$), hafnium tetrafluoride (HfF_4), and hafnium dioxide (HfO_2). SEE ALSO Bohr, Niels; Inorganic Chemistry; Zirconium.

Herbert W. Roesky

Hair Dyes and Hair Treatments

Hair has no vital function in the human body but provides an outward sign of health and social communication. The history of hair coloring dates from ancient dynasties of Egypt and China where mineral and plant dyes were widely available to cosmeticians. Through the ages, women in particular have dyed their hair to hide grayness and to improve their appearance.

General Features of Hair

In all mammals, hair develops as an epidermal structure from papillae deep in the skin and acquires characteristic patterns on the scalp, eyebrows, eyelashes, and elsewhere on the body. In humans, hair growth is continuous throughout life (declining with advancing age), occurs in cyclic patterns, and

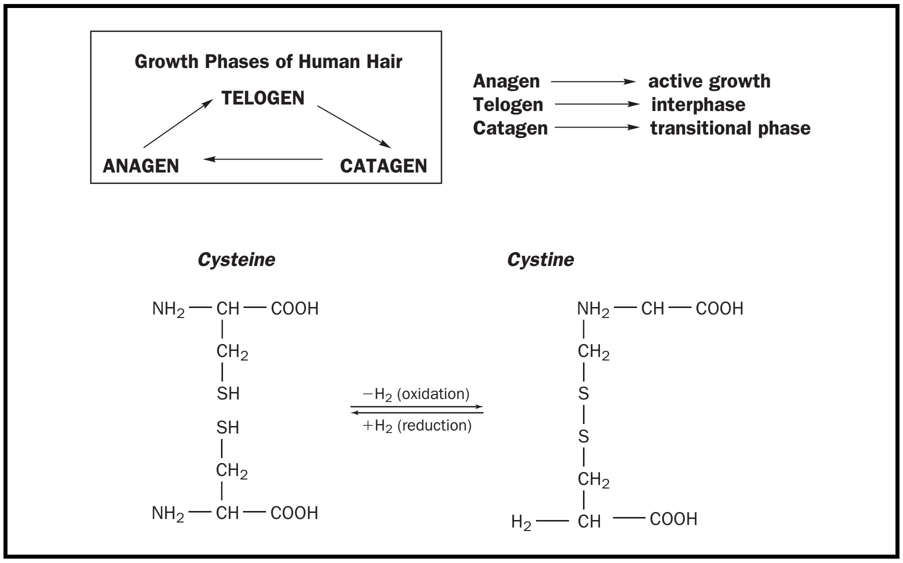

Figure 1.

is influenced by **androgens**, thyroid hormones, and dietary factors. Human hair is composed largely of keratin and consists of a narrow central medulla surrounded by a thick envelope (cortex) of elongate cells, which contain numerous melanin granules that determine the natural color. The hair is ensheathed in a multilayered cuticle of overlapping cells that become progressively imbricated (having edges overlapping in a regular arrangement) with continued growth. These cuticular cells are rich in cystine (**disulfide bonds**) and become rough or show a weathered appearance through exposure to environmental exposure or poor health.

androgen: group of steroids that act as male sex hormones

disulfide bond: two bonding sulfur atoms, –S–S–

Chemically, human hair contains approximately 85 percent protein, 7 percent water, 3 percent **lipid**, 4.7 percent protein-bound sulfur (as cystine), and low concentrations of trace minerals (e.g., iron, zinc, copper). The phosphorus content is approximately 80 milligrams per 100 grams (0.003 ounces per 3.5 ounces) of hair. Hair is normally associated with sebum and exocrine secretions from skin glands that confer greasiness but influence its water content and mechanical and physical properties.

lipid: a nonpolar organic molecule; fatlike; one of a large variety of nonpolar hydrophobic (water-hating) molecules that are insoluble in water

Hair follicles are determined prenatally; about 100,000 hairs are found on the scalp region of most adults. Hair density, color, and condition vary according to age, race, and genetic background. Natural hair colors vary from albino or white to blond, red, or intense black and reflect ethnic origin (Caucasoid, Negroid, etc.), age, diet, and health. While hair color is closely related to the density of melanin granules, impairment in a person's health or substances in the diet that influence the availability of trace minerals are potential causes of changes in hair color or condition. The configuration of the hair shaft (i.e., straight, wavy, spiral, or peppercorn) is attributable to the number and distribution of disulfide bonds. Hair straightening requires reduction of these disulfide bonds and fiber cross-linkages.

Hair serves to eliminate toxic materials (e.g., lead) and **metabolites** from the body, and may be used to monitor environmental contamination. For example, copper deficiency is a cause of Menke's "kinky" hair syndrome; protein deficiency leads to hair loss and discoloration. Hair keratin carries a strong negative charge and binds inorganic materials; it becomes prone to

metabolites: products of biological activity that are important in metabolism

discoloration through exposure to environmental chemicals (e.g., cobalt, tar in cigarettes, picric acid, trinitrotoluene, etc.). Prolonged exposure to copper in diet, tap water, or swimming pools is a cause of green hair.

Natural Hair Color and Its Control

tyrosine: one of the common amino acids

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

Melanin granules are secreted by melanocytes in the hair papilla and distributed to keratin in the hair cortex and inner layers of the hair sheath during normal development. Melanogenesis is subject to hormonal control and has been the focus of intensive genetic studies. Two main forms of melanin exist in human skin—eumelanin and phaeomelanin, both of which are derived from **tyrosine** through the action of tyrosinase (a cupro-enzyme) and possibly other key enzymes (with nickel, chromium, iron, and manganese as cofactors). Tyrosine is converted to dihydroxyphenylalanine and, via a series of intermediate steps, to indole-5,6-quinone, which polymerizes to eumelanin. Phaeomelanins are produced by a similar mechanism but with the incorporation of sulfur (as cysteine) by a nonenzymatic step in the **oxidation** process.

Hair color is a balance between these two melanins. Albino or white-haired individuals have latent melanocytes, but possibly show defects in tyrosinase-mediated events. Graying of the hair is age-related and possibly results from declining melanocytic function or retarded hair growth resulting from atrophy or degenerative changes in hair papillae. Hair melanin absorbs insufficient ultraviolet (UV) light energy to afford protection for most individuals against sunburn.

Hair Dyes and Cosmetic Coloring

A wide variety of dyes, dressings, and conditioners are available to men and women to enhance the color of hair or to alter its condition, providing the “feel good” factor. Natural hair dyes such as henna and mineral salts are still used, but hair dyeing increasingly involves careful chemical manipulation of the chemistry of hair fibers through bleaching or enhancement of natural colors. Additionally, social and cultural customs have led to the increasing demand for exotic colors (reds, greens, blues, yellows, etc.). Hair coloring is a well-defined science with intense study of the interaction between hair keratin and highly reactive organic dyes, oxidizing agents, and conditioners.

Available hair dyes include:

- Minerals such as lead acetate (<1% aqueous), lead sulfide (kohl); silver nitrate; salts of bismuth, copper, and cobalt (commonly called “gradual” colorants)
- Vegetable materials such as henna (flowers and leaves of *Lawsonia inermis* that contain acidic naphthoquinone, chamomile, and indigo)
- Synthetic dyes including a large number of organic dyes to provide permanent, semipermanent, temporary, or progressive color changes or to enhance natural colors

The dyeing process provides for temporary, semipermanent (direct dyes), and oxidation-type reactions (semipermanent or permanent colors). It may involve absorption or adsorption (electrostatic) of the colorant into/to the hair structure, bleaching or otherwise masking the natural melanin col-

Table 1.

COLOR INDEXED DYES USED AS TEMPORARY COLORS IN HAIR COSMETICS

CI Acid Yellow 1	
CI Acid Yellow 3	(D & C Yellow No.10)*
CI Acid Orange 7	(D & C Orange No. 4)
CI Acid Orange 87	
CI Acid Red 3	(D & C Red No. 33)
CI Acid Red 211	
CI Acid Violet 43	(D & C Violet No. 2)
CI Acid Violet 73	
CI Acid Blue 9	(FD & C Blue No. 1)
CI Acid Blue 168	
CI Acid Green 25	(D & C Green No. 5)
CI Acid Brown 19	
CI Acid Brown 45	
CI Acid Black 107	
CI Basic Yellow 57	(Arianor™ Straw Yellow)
CI Basic Red 76	(Arianor™ Madder Red)
CI Basic Blue 99	(Arianor™ Steel Blue
CI Basic Brown 16	(Arianor™ Mahogany)
CI Basic Brown 17	(Arianor™Sienna Brown)
Sunset Yellow	(FD & C Yellow No. 6)
Ponceau Red	(FD & C Red No. 4)
CI Solvent Brown 44	

*F - food color, D - drug additive, C- cosmetic coloring

ors, or alteration of the structure of the hair shaft, allowing deep penetration of the colorant. The hair cuticle provides a barrier to the absorption of hair dyes, particularly those of high molecular weight, but damaged fibers exhibiting higher negative charges and reduced phospholipid content are more porous. Dye uptake is determined by the partition coefficient between the hair and the dye carrier (water, alcohol, etc.), pH, and chemical charge (dye-fiber interaction). Thickeners and **surfactants** can also influence dye uptake.

surfactants: surface-active agents that lower the surface tension of water; e.g., detergents, wetting agents

The vast array of natural dyestuffs, metallic salts, and synthetic organic chemicals available to cosmeticians are regulated in the United States (by the Food and Drug Administration [FDA]), the European Union, and many other countries, and regulatory toxicity information is documented.

Henna. Henna is the oldest and most widely used vegetable dye utilized in hair coloring. A temporary chestnut color is produced in blond or auburn hair by applying a paste of henna flowers and leaves ground in hot water immediately before use. (The dye is unstable in **aqueous solution**.) The addition of indigo achieves darker blue-black shades; extracts of walnut shell or logwood enhance brown coloration.

aqueous solution: homogenous mixture in which water is the solvent (primary component)

Mineral dyes. Of the mineral dyes, only lead acetate is commercially available. In the United States, the FDA permits maximal concentrations of 0.6

NATURAL DYES FROM PLANTS USED AS HAIR COLORANTS

Plant	Hair Colorant
Henna (*Lawsonia inermis*)	2-hydroxy-1,4-naphthaquinone
Chamomile	4',5,7trihydroxyflavone
Indigo (*Indogofera* sp.)	CI Pigment Blue 66 - $C_{16}H_{10}N_2O_2$
Logwood - haematein	$C_{16}H_{12}O_6$

Table 2.

Hair dyes and other hair treatments have been popular for centuries, but in recent years have been more chemically sophisticated, taking into account the chemical makeup of hair.

percent; in the United Kingdom, less than 1 percent is allowed. (Kohl or "suma," an eyelash and eyelid cosmetic used in Asian countries, contains up to 80 percent lead and is a known cause of anemia.) In contact with hair, the lead salt is poorly absorbed but interacts with keratin to deposit lead sulfide (at permitted levels [<0.5%] lead is absorbed into the skin without toxic implications). Silver nitrate has been used to color hair brown-black without significant absorption of metal into the circulation; silver is deposited in the hair cortex as silver sulfide. Metallic hair dyes tend to be long-lasting and are lost as hair grows and is shed naturally. Hair coloration is achieved as a gradual process through repeated application of rinses or pastes over several days.

Temporary dyes. Temporary dyes are frequently acidic and provide short-term coloration (i.e., wash out after one shampoo). They are of low penetration and do not involve melanin bleaching or structural changes in the hair fiber. They are commonly identified with a color index (CI) number or as U.S. Certified Colors; they are water-soluble, high-molecular-weight pigments. Temporary dyes are employed in water-thin color rinses, colored hair-setting lotions, colored styling gels, lotions, and shampoos. Hair dyeing is improved when the colors are applied under moderate heat. Hair dyeing and color balance is difficult to control with temporary methods because of the inconsistency of dye delivery systems and instability of the dye-keratin "bonding."

Semipermanent dyes. Semipermanent dyeing systems are designed to last for several weeks. They impart darker colors without the use of oxidizing agents or structural changes in the hair shaft or papillae. Melanin may be partly masked but is not bleached. These dyes diffuse more readily into and out of the hair (aided by solvents and surfactants) and are progressively lost with hair shampooing and normal growth. The method employs dyes that

ESSENTIAL INGREDIENTS OF OXIDATIVE PERMANENT AND SEMIPERMANENT DYEING SYSTEMS

- Surfactant
- Solvent
- Alkalizing Agent
- Oxidant
- Dye

COLORS PRODUCED IN OXIDATIVE DYEING SYSTEMS USING SOME COMMON PRIMARY INTERMEDIATES AND COUPLERS

	p-aminophenol	*p*-phenylenediamine	N,N-*bis*-(2-hydroxyethy)-*p*-phenylenediamine
m-aminophenol	Warm brown	Red-brown	Medium violet
Resourcinol	Yellow green	Greenish brown	Yellow-gray
2-methylresourcinol	Ash brown	Yellow brown	Gray-violet
m-phenylenediamine	Orange-yellow	Blue	Greenish-blue
5-amino-o-cresol	Orange	Purple-red	Purple
a-*naphthol*	Red-orange	Violet	Blue

Table 3.

are already colored, and in general is without the toxic risks associated with semipermanent or permanent methods, which involve de novo color production and strong oxidizing agents. When the dye is lost through shampooing, the hair resumes its natural color.

Oxidative dyes. Oxidative hair dyeing systems involve the use of more toxic **reagents**. They are multistep processes leading to semipermanent or permanent coloration, according to the extent of bleaching involved. Surfactants and solvents influence the penetration of the active constituents; alkalizing agents determine pH. The resulting hair colorations are more stable against normal wearing processes than semi permanent preparations and involve an initial oxidation reaction, a coupling reaction, and production of a color reaction with dyeing of the hair fiber. The process requires a primary intermediate, a *m*-coupler or secondary intermediate (color modifiers), and hydrogen peroxide.

reagent: chemical used to cause a specific chemical reaction

Hydrogen peroxide is commonly used as the oxidizing agent; it has the capacity to bleach melanin but it initiates the first coupling reaction and the ultimate development of the color. Initial oxidation of primary intermediates (e.g., *p*-aminophenol, *p*-phenylenediamine) by hydrogen peroxide is followed by coupling with an agent like resourcinol, phenols, *m*-aminophenols, or *m*-phenylenediamines. Further oxidation of this secondary intermediate leads to the formation of colored indamines, indolanilines, and indophenols. As a general rule, the higher the electron-donating capacity of the coupling agent (especially unsubstituted carbocyclic *m*-couplers), the higher the absorbance maximum of the indo-dye formed. In the presence of couplers, di- and monoimines react to produce indo-dyes.

Many of the organic aromatic amines used in hair dyes are strong sensitizers and oxidative dyes should be used with extreme caution. *P*-phenylenediamine and its derivatives, commonly employed in permanent or semipermanent hair colorings, are strong sensitizing agents and may damage the hair. Although a large number of possible combinations of primary intermediates and couplers leading to the production of exotic hair colors is possible, the cost of conducting regulatory toxicological evaluation is prohibitive in developing many interesting colors.

Bleaches

Lightening or removal of hair color without structurally damaging the hair shaft is a difficult process. Oxidizing agents, including hydrogen peroxide,

COMPOSITION OF TYPICAL STYLING MOUSSE

- Polyoxyethylated fatty alcohol
- Deionized water
- Polyquaternium compound
- Vinyl caprolactam/polyvinylpyrolidone/dimethylaminoethyl methacrylate copolymer
- Ethanol
- Amodimethicone—tallow trimonium chloride
- Additives (perfumes, preservatives, etc.)

can be extremely harmful to hair and will oxidize some cystine to cysteic acid, rendering the fibers less cohesive and susceptible to hydration and swelling under alkaline conditions. Bleached hair shows a loss of melanin granules at the periphery of the hair. Hair color is lost (platinum blond appearance) and the fibers become dry and fragile. Bleaching is inhibited by shampoos or acid rinses.

Hair Conditioners

Hair conditioning includes permanent waving, straightening, and setting. In each case, sequential chemical treatments lead to modifications of the hair shaft with temporary or prolonged changes in disulfide bond distribution and behavioral characteristics. Softening, reshaping, and hardening are integral to permanent waving and involve an initial reduction in disulfide bonds and adhesiveness of adjacent hairs using heat or steam, thioglycollates, or ammonium hydroxide; styling with heated rollers; and setting or neutralizing the reaction. This last event is a reversal of the earlier reduction process with reconstitution of disulfide bonds from adjacent cystine moieties using hydrogen peroxide or a similar oxidizer. Hair straightening is a similar process, but may involve the additional use of hair dressings like gels, sprays, and creams (pomades) to hold the hair in place. Hot comb techniques may be used to disrupt the disulfide bonds followed by application of oils, petroleum jelly, or liquid **paraffin**.

paraffin: saturated aliphatic hydrocarbon (alkane), or hydrocarbon wax

Mousses are designed for hair styling and setting hair in position. Commonly, formulations are based on cationic conditioning polymers with quaternary ammonium salts, alcohols, perfumes, colorants, water, and preservatives. They may be in propellant, foam, or jelly form for direct application to hair after shampoo or cutting. SEE ALSO FIBROUS PROTEIN; FORMULATION CHEMISTRY; PROTEINS.

Alan B. G. Lansdown

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Hall, Charles

AMERICAN CHEMIST
1863–1914

Although aluminum is now widely used as a structural material, this was not always the case. Common in Earth's crust, aluminum is difficult to win from its ore because it is such a reactive **metal**. In the 1850s French chemists interested Napoléon III in this rare and costly metal; he considered using it for soldiers' helmets, and even reserved a set of aluminum tableware for his most honored guests. By the 1880s chemical reduction techniques had been discovered, and the price per pound dropped from over $100,000 to near $100.

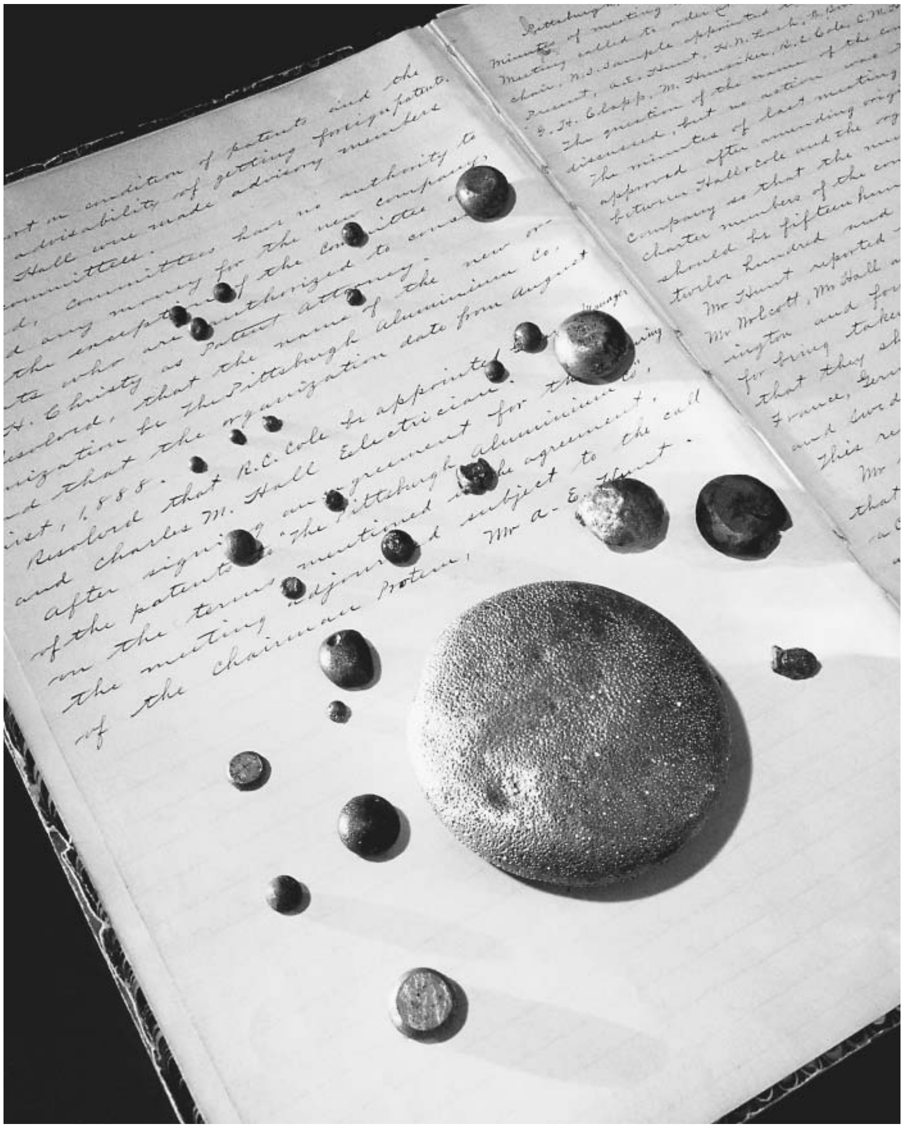
metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Born in Thompson, Oregon, on December 6, 1863, Charles Martin Hall was interested in minerals since the age of twelve. While enrolled at Oberlin College in Ohio, Hall took a class from distinguished professor Frank Fanning Jewett, who had a sample of the precious metal to show the class. After a stirring lecture on the topic, he finished with, "Any person who discovers a process by which aluminum can be made on a commercial scale will bless humanity and make a fortune for himself." Inspired by such a win-win challenge, Hall reportedly said, "I'm going for that metal."

After graduating from Oberlin in June 1885, Hall continued his work in a woodshed behind his family home. There, starting with a blacksmith's forge and **galvanic** cells constructed from fruit jars, he began to investigate mixtures of aluminum and fluorine-containing minerals. Along with help from his sister (an Oberlin student) and continued guidance from Jewett, Hall discovered that alumina (Al_2O_3) and the mineral cryolite (Na_3AlF_6) fuse well and do so at a relatively low temperature (near 1,000°C [1,832°F]), compared to pure alumina. After months of work, Hall and his sister broke open their graphite crucible on February 23, 1886, to find tiny globules of a silvery metal—aluminum. Hall rushed to show them to Jewett, who confirmed his discovery. These same samples are preserved by Alcoa as the company's "crown jewels."

galvanic: relating to direct current electricity especially when produced chemically

Hall's next move in his quest to "bless humanity and make a fortune for himself" was to make aluminum production commercially feasible. Upon receiving the financial backing of local industrialists, the Pittsburgh Reduction Company was formed, and Hall and his employee Arthur Vining Davis



American chemist and inventor Charles Hall coinvented (independently) an inexpensive process for producing aluminum. This photo shows the first aluminum created by Hall in 1886.

produced the first commercial aluminum on Thanksgiving Day, 1888. There still remained complicated patent infringement cases to argue, but eventually Hall was victorious. A more serious challenge came from the independent codiscoverer of the process, Paul Héroult, a French chemist the same age as Hall performing basic research on aluminum-containing compounds. Héroult filed for a patent about the same time that Hall did, but again, Hall won the dispute over patent rights. Nevertheless, the electrolytic reduction of aluminum is rightly named the Hall-Héroult process, honoring both of its discoverers.

Once again, a chemical idea had turned industrial, as the price per pound of aluminum dropped from $4.86 in 1888 to $0.78 in 1893. In 1907 the company was reorganized as the Aluminum Company of America (Alcoa), of which Hall was made a vice-president. In 1911 Hall was awarded the Perkin Medal for his process; Héroult graciously traveled across the Atlantic to congratulate him at the ceremony. Before his death in 1914, Hall donated one-third of his fortune to a grateful Oberlin College, where today stands a life-sized statue of its benefactor, constructed entirely of aluminum. SEE ALSO ALUMINUM; INDUSTRIAL CHEMISTRY, INORGANIC.

Mark A. Pichaj

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Halogens

Chlorine gas belongs to the halogen chemical family.

The halogens are the family of chemical elements that includes fluorine (atomic symbol F), chlorine (Cl), bromine (Br), iodine (I), and astatine (At). The halogens make up Group VIIA of the Periodic Table of the elements. Elemental halogens are diatomic molecules. However, due to their high reactivity, the halogens are never found in nature in native form. The family name means "salt-forming," from the Greek for salt, *halos*, and for generating *genes*. The salinity of the oceans on Earth is due in large part to such halogen salts (halides) as sodium chloride (NaCl) and potassium iodide (KI).

Halogens display physical and chemical properties typical of nonmetals. They have relatively low melting and boiling points that increase steadily down the group. Near room temperature, the halogens span all of the physical states: Fluorine and chlorine are gases, bromine is a liquid, and iodine is a solid. All of the elements are colored, with the color becoming more intense moving down the group. Fluorine gas is pale yellow, and chlorine gas is a yellowish green. Liquid bromine and its vapors are brownish red. Solid iodine appears as shiny, dark gray crystals, and the vapors are a deep purple. The halogens are poor thermal and electrical conductors in all phases, and as solids they are brittle and crumbly. The halogens have distinctive, unpleasant odors, will burn exposed flesh, and are toxic.

The neutral atoms of the halogens possess seven outer electrons. An additional electron can be added to halogen atoms to form singly charged negative ions. These ions have a closed outer-shell configuration. Electronegativity is a measure of the ability of an atom of one element to remove an electron from an atom of another element. As a group, the halogens are among the most **electronegative** elements. Fluorine has the highest electronegativity of all the elements. Halogens are so reactive that all the elements except helium and neon have been found to react with at least one of the halogens. Fluorine is always assigned a formal **oxidation** number of −1, whereas the other halogens can exhibit a range of oxidation numbers.

electronegative: capable of attracting electrons

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

The ability of halogens to form chemical compounds with all metals and most nonmetals has led to a wide variety of uses for these elements. Chlorine is used as a bleach and a disinfectant. Iodine has been used as a topical microbicide. Iodine and bromine are added to halogen lamps to lengthen

isotope: form of an atom that differs by the number of neutrons in the nucleus

the life of the filament and prevent darkening of the bulb. Chloride and iodide are essential dietary minerals for humans. Organic compounds containing halogens are used as fire-retardants (halons), as refrigerants (Freons), and in nonstick coatings (Teflon). Silver bromide and silver iodide have been used in photographic emulsions since the early days of photography. Many halogenated compounds are toxic. A well-known example is DDT (dichlorodiphenyltrichloroethane), once a widely applied pesticide that was banned in the United States after severe environmental effects were discovered. All known **isotopes** of astatine are radioactive, with the longest-lived isotope having a half-life of about eight hours. Relatively little is known of the physical and chemical properties of astatine. However, it is predicted to have properties similar to iodine. SEE ALSO BROMINE; CHLORINE; FLUORINE; IODINE.

John Michael Nicovich

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Heat

Heat is the transfer of energy that results from the difference in temperature between a system and its surroundings. At a molecular level, heat is the transfer of energy that makes use of or stimulates disorderly molecular motion in the surroundings. For instance, when a hydrocarbon fuel burns, the energy released in the reaction stimulates the surrounding atoms and molecules into more vigorous random motion, and we refer to this escape of energy as heat. Heat is not stored: Heat is energy in transit.

The measurement of quantities of energy transferred as heat is called *calorimetry*. Such a measurement is commonly made by observing the rise in temperature caused by the process being studied and interpreting that rise in terms of the heat produced. Calorimetry is used to measure the changes in internal energy and enthalpy that accompany chemical reactions. The field of study is called *thermochemistry*, and it is used to assess the efficacy of fuels, the energy flow in chemical plants, and the strengths of chemical bonds. Measurements of the heat produced or absorbed by chemical reactions are central to thermodynamics, and to assessments of whether or not a particular reaction will tend to occur.

In thermodynamics, the quantity of energy transferred as heat as a result of a chemical reaction is identified with the change in the internal energy of the system if the transfer takes place without change in the system's volume, and with the change in enthalpy of the system if the transfer takes place at constant pressure. The energy or enthalpy change accompanying a chemical reaction that is inaccessible to measurement may be determined by using Hess's law, which states that the enthalpy change accompanying a chemical reaction can be regarded as the sum of the enthalpy changes of the reactions into which the overall reaction may be divided. Hess's law is no more than a special application of the first law of thermodynamics.

The source of heat as a fuel burns is the energy released when the bonds characteristic of the reactants are replaced by the bonds characteristic of the products. Energy is released when hydrocarbons burn because of the great strengths of the oxygen–hydrogen and oxygen–carbon bonds that are formed in the products (water and carbon dioxide), replacing the relatively weak carbon–hydrogen and carbon–carbon bonds of the fuel. Ultimately, the energy of burning fuel is the energy released as the electrons and atomic nuclei settle into more favorable arrangements (just as nucleons do in the much more exothermic processes accompanying **nuclear** rearrangements).

nuclear: having to do with the nucleus of an atom

Although the term "heat energy" is commonly encountered in casual conversation, strictly speaking there is no such entity. The term is commonly used in place of the more precise term "energy of thermal motion," where thermal motion is random molecular motion, as in the motion of molecules in a gas. Nor is heat stored: Only energy is stored, and heat is one of the modes by which it may be increased or extracted. SEE ALSO CHEMISTRY AND ENERGY; ENERGY; EXPLOSIONS; TEMPERATURE; THERMOCHEMISTRY; THERMODYNAMICS.

Peter Atkins

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Heavy Metal Toxins

Even at a very low level, heavy metal ions can cause serious health effects, including reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases, death. The most common heavy metal toxins are aluminum, **arsenic**, cadmium, lead, and mercury. Once emitted from their sources, they have the property of accumulating in the environment for many years. They enter the human body through breathing, drinking, and skin absorption. They also can accumulate in the bodies of animals and humans before they even cause damage.

arsenic: toxic element of the phosphorus group

The sources of heavy metal ions are diverse and specific to each element. Aluminum is mostly found in canned food, cookware, antacids, aluminum foils, and drinking water. Arsenic is encountered through air pollution and in drinking water, meat from commercial farms, and wood preservatives. Cadmium originates mainly from cigarette smoke, air pollution, batteries, fish, paint, and food grown in cadmium-laden soil. The major sources of lead are gasoline, house paints, lead pipes, mines, and batteries. "Silver" dental fillings constitute the most important source of mercury. Other sources of mercury are from gold mining and fish. In general, the increased use of coal favors exposure to major heavy metals. What then is the mode of action of heavy metal ions?

The heavy metal ions form complexes with proteins, in which **carboxylic acid** (–COOH), amine ($–NH_2$), and thiol (–SH) groups are involved. These modified biological molecules lose their ability to function properly and

carboxylic acid: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the $–CO_2H$ functional group

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

catalysis: the action or effect of a substance in increasing the rate of a reaction without itself being converted

toxin: poisonous substance produced during bacterial growth

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

result in the malfunction or death of the cells. When **metals** bind to these groups, they inactivate important enzyme systems, or affect protein structure, which is linked to the **catalytic** properties of enzymes. This type of **toxin** may also cause the formation of radicals, dangerous chemicals that cause the **oxidation** of biological molecules.

Some diseases associated with heavy metal ions are as follows:

- Aluminum has been associated with Alzheimer's and Parkinson's disease, senility, and presenile dementia.
- Arsenic exposure can cause, among other illnesses or symptoms, cancer, abdominal pain, and skin lesions.
- Cadmium exposure produces kidney damage and **hypertension**.
- Lead and mercury may cause the development of autoimmunity, in which a person's immune system attacks its own cells. This can lead to joint diseases and ailments of the kidneys, circulatory system, and neurons. At higher doses, lead and mercury can cause irreversible brain damage.

hypertension: condition in which blood pressure is abnormally high

Heavy metal poisoning or intoxication can be diagnosed through analysis of samples from certain parts of the body. For example, lead poisoning is diagnosed by analyzing blood samples from affected individuals. The maximum allowed concentration of lead is 10 micrograms (3.5×10^{-7} ounces) per deciliter of blood. At exposures above this level, action must be taken to treat the victim.

electronegative: capable of attracting electrons

A common treatment for metal intoxication is the use of chelators. A chelator is a flexible molecule with two or more **electronegative** groups that can form stable complexes with cationic metal atoms. The complexes are then eliminated from the body. The most widely used chelator is ethylenediaminetetraacetic acid (EDTA). It has four binding positions (two nitrogen atoms and two oxygen atoms) that focus on the metal ion. It works very well on many metals, the most notable being calcium, magnesium, and lead. SEE ALSO Enzymes; Proteins; Tertiary Structure; Toxicity.

Joseph Bariyanga

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Heisenberg, Werner

GERMAN PHYSICIST
1901–1976

deterministic: related to the assumption that all events are based on natural laws

Newtonian: based on the physics of Isaac Newton

More so than any other physicist of the twentieth century, Werner Karl Heisenberg challenged our fundamental notions of the surrounding world. It could be argued that as the author of papers on quantum mechanics and the uncertainty principle, he nailed the coffin shut on the **deterministic Newtonian** version of the universe. Heisenberg replaced precision and accuracy with probabilities and uncertainties, and in so doing, he opened up the world of the subatomic to our understanding.

German physicist Werner Karl Heisenberg (fifth from left), recipient of the 1932 Nobel Prize in physics, "for the creation of quantum mechanics, the application of which has, inter alia, led to the discovery of the allotropic forms of hydrogen."

Born the second son of August and Anna Heisenberg, in Würzburg, Germany, Heisenberg demonstrated promise at an early age. At the age of nine, he entered the Maximilian Gymnasium in Munich where his maternal grandfather was headmaster. The curriculum emphasized classical languages and literature, but Heisenberg excelled in the minor subjects of mathematics and physics.

Heisenberg soon outgrew the limited curriculum; he studied Einstein's relativity on his own and taught himself calculus in order to tutor a college student for her final exams. For his final oral exams at the gymnasium, he solved the equations of projectile motion, taking into account air resistance.

His adolescence was set against the backdrop of World War I. Heisenberg participated in various youth movements and even joined a military training unit that helped to bring in the fall harvest before Germany surrendered. Food was scarce. The gymnasium was closed for long periods due to a shortage of coal. With most men serving in the military, Heisenberg and his fellow students were expected to continue their studies independently.

Heisenberg entered the University of Munich in the fall of 1920. His preparation at the gymnasium essentially earned him "junior year" status. The professor of physics at Munich, Arnold Sommerfeld, quickly recognized Heisenberg's potential, and it was not long before he was taking advanced classes. Indeed, he received his doctorate in 1923, at the young age of twenty-two, having studied with Max Born and listened to the Danish physicist Niels Bohr lecture at Göttingen.

A newly minted scientist, Heisenberg returned to Göttingen to serve as Born's assistant until the spring of 1926. It was in 1925 that he achieved his first breakthrough in quantum mechanics. In essence, Heisenberg realized that certain properties do not commute and the law of commutation does not always apply. In normal mathematics, the law of commutation says that $3 \times 2 = 2 \times 3 = 6$ and the order of multiplication does not matter. However, in matrix algebra, commutation is not necessarily observed. The order of multiplication does matter and can produce quite different results. Heisenberg's solution to the problems facing Bohr's quantum model of the atom relied on matrix algebra and provided a different approach in which discontinuities could occur. At almost the same time, Erwin Schrödinger formulated an alternate version of quantum mechanics based on waves. Both competed for center stage, and this resulted in fierce academic debate because Schrödinger's quantum mechanics was more deterministic.

Heisenberg's response was his second major breakthrough: The uncertainty principle that places a limit on the accuracy with which certain properties can be simultaneously known. In particular, the simultaneous measurement of both the position and the momentum of a particle can be known only to $h/4\pi$ (with h as Planck's constant). One can measure the position of a particle to an infinite level of precision, but then its momentum has an infinite uncertainty and vice versa. This sets an absolute limit on human knowledge of the physical world and leads to the idea of **quantum mechanical** probability.

quantum mechanics: theoretical model to describe atoms and molecules by wave functions

Heisenberg went on to say: "If one wants to be clear about what is meant by the 'position of an object,' for example, of an electron . . . , then one has to specify definite experiments by which the 'position of an electron' can be measured; otherwise this term has no meaning at all" (Cassidy, "Werner Heisenberg [1901–1976]"). In effect, reality does not exist until measured. This concept not only reformulated physics, but also had a major impact on Western philosophy.

Heisenberg received, among many other honors, the Nobel Prize in physics in 1932 for his formulation of quantum mechanics and its prediction of observable experimental facts. His work in all aspects of **theoretical physics** kept Heisenberg at the forefront of modern physics until he

theoretical physics: branch of physics dealing with the theories and concepts of matter, especially at the atomic and subatomic levels died of cancer in 1976. see also Bohr, Niels; Quantum Chemistry; Schrödinger, Erwin.

Todd W. Whitcombe

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Helium

MELTING POINT: **−272.2°C—does not solidify under its own vapor**
BOILING POINT: **−268.93°C**
DENSITY: **0.1785 g/L**
MOST COMMON IONS: **None**

2
He
HELIUM
4.0026

Helium, a colorless gas at room temperature, is the first element in the **noble gas** group, and forms few compounds. It is rare in the atmosphere (1 part in 200,000) and recovered on Earth principally by its separation from natural gas obtained in underground wells. Named for the Sun (in Greek, *helios*), helium is a component of the production of energy as well as the basis of the science and technology of cryogenics. Its presence at the surface of the Sun was first confirmed by amateur British astronomer Joseph Norman Lockyer (1868), who observed characteristic lines in the optical spectrum of the Sun, at whose surface helium is produced via theenergy-releasing fusion of hydrogen and deuterium nuclei.

noble gas: element characterized by inert nature; located in the rightmost column in the Periodic Table

Because it is such a light, nonreactive element, helium condenses (at atmospheric pressure) only at 4.2 kelvins. Furthermore, because of **quantum mechanical** effects, helium solidifies (under the application of 25.3 bars of external pressure) only at the lowest temperatures. Liquefied in large compression refrigerators, helium is used to cool cryogenic equipment, in particular the superconducting magnets used in medical magnetic resonance imaging (MRI). At 2.17 kelvins liquid helium transforms into an unusual quantum **phase**, called a superfluid, which has no viscosity and exhibits bizarre flow properties, such as its creeping out of containers.

quantum mechanics: theoretical model to describe atoms and molecules by wave functions

phase: homogeneous state of matter

The gas is also used to fill balloons, in gas discharge lamps, and as an additive in the breathing gases of astronauts and scuba divers. The rarer stable **isotope** of helium (^{3}He) is produced by the decay of radioactive tritium, and is used in resonance imaging and in the attainment of very low temperatures, about 0.010 kelvin, via a process known as dilution refrigeration. see also Noble Gases; Nuclear Fusion.

isotope: form of an atom that differs by the number of neutrons in the nucleus

David G. Haase

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Hemoglobin

Hemoglobin is an iron-containing protein found in the blood of nearly all vertebrates and many **invertebrates**. It transports oxygen from the lungs or gills of an animal to the tissues. Four **polypeptide** chains, each wrapped in a specific way around its own **heme group**, make up the hemoglobin molecule. An iron atom in the **ferrous** state (Fe^{2+}) sits in the middle of the heme. **Ferric** hemoglobin (Fe^{3+}) cannot bind oxygen.

invertebrate: category of animal that has no internal skeleton

polypeptide: compound containing two or more amide units—C(O)NH—produced by the condensation of two or more amino acids

heme group: functional group formed by an iron atom interacting with a heterocyclic ligand called a porphyrin

ferrous: older name for iron in the +2 oxidation state

ferric: older name for iron in the +3 oxidation state

The polypeptide chains of hemoglobin are of two kinds; in the hemoglobin of an adult human, HbA, they are designated as α and β, and the subunit structure of HbA is written $\alpha_2\beta_2$. The α chain contains 141 amino acid residues, the β chain 146. Throughout most of the animal kingdom the subunit structure of hemoglobin remains the same: two polypeptides of one kind with 141 amino acid residues and two of another with 146 residues. The amino acid sequences (the primary structure) of the polypeptides, however, are species dependent. Closely related animals display fewer differences in these amino acid sequences. The α and β chains of human hemoglobin, for example, differ from chicken hemoglobin in 35 and 45 places, respectively. Between human and horse α and β chains these differences drop to 18 and 25. As for chimpanzee and human, their hemoglobins are identical.

Often several kinds of hemoglobin exist in a given animal. In the adult human, for example, HbA ($\alpha_2\beta_2$) makes up 98 percent of the total hemoglobin, and HbA_2 ($\alpha_2\delta_2$), the remaining 2 percent. The polypeptide chain δ has the same number of amino acids as the β chain, but the sequences differ in 10 places. A third kind of human hemoglobin, fetal hemoglobin or HbF ($\alpha_2\gamma_2$), constitutes over 80 percent of the total hemoglobin of a newborn, but vanishes rapidly during the first year of life. The amino acid sequences of the γ and β chains differ in 39 of the 146 residues. Additional types of human hemoglobins exist at embryonic stages of life.

Each polypeptide chain of a hemoglobin molecule coils into several helical segments (the secondary structure of the polypeptide chain) that are linked with nonhelical segments. Intertwining sets of helices wrap tightly around the heme group and produce a compact subunit (the tertiary structure). The four subunits are packed into a nearly spherical package (the quaternary structure) of 55-angstrom (2.17×10^{-7}-inch) diameter.

Each ferrous iron within hemoglobin provides one binding site for O_2. Thus a single hemoglobin molecule has the capacity to combine with four molecules of oxygen. Hemoglobin binds oxygen in a cooperative fashion; occupation of one binding site enhances the affinity of another binding site for oxygen in the molecule. Consequently, the oxygenation curve of hemoglobin (see Figure 1), in which the fractional saturation of hemoglobin with oxygen is displayed as a function of the oxygen pressure in the alveoli of the lungs, rises slowly at first, then more steeply, until it levels off and approaches unity (100% saturation). The steep rise in the oxygenation curve over a relatively small interval of oxygen pressure allows hemoglobin to serve as an efficient transporter of oxygen. SEE ALSO PRIMARY STRUCTURE; QUATERNARY STRUCTURE; SECONDARY STRUCTURE; TERTIARY STRUCTURE; TRANSPORT PROTEIN.

N. M. Senozan

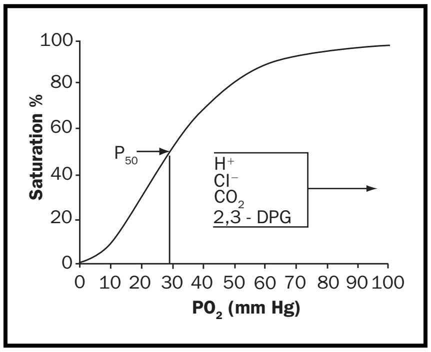

Figure 1. Hemoglobin-oxygen binding curve.

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Herbicides

Herbicides are chemicals used to destroy unwanted plants (terrestrial or aquatic) called weeds. Herbicides fall into two broad categories: inorganic (e.g., copper sulfate, sodium chlorate, and sodium arsenite) and organic (e.g., chlorophenoxy compounds, dinitrophenols, bipyridyl compounds, carbamates, and amide herbicides). Historically, inorganic compounds were the first available and the first used. There has been over a long period a continuous effort to develop herbicide compounds that are more selective—that affect weeds, as opposed to desirable plants.

Historical Developments

The decade 1890 to 1900 saw the introduction of sprays for controlling broad-leaved weeds in cereal crops, and the first efforts by the U.S. Army Corps of Engineers, using sodium arsenite, to control aquatic plants in waterways. In 1925 sodium chlorate (directly applied to soil) was first used for killing weeds. The earliest importation (from France) of sodium nitrocresylate, as the first selective weed killer, was in 1934. The year 1945 witnessed the introduction of organic herbicides and the advent of 2,4-D growth regulator (2,5-dichlorophenoxyacetic acid), subsequently leading to development of 2,4,5-T (2,4,5-trichlorophenoxyacetic acid). During the years 1965 to 1970, U.S. military forces used 2,4,5-T (Silvex) and related materials as defoliants in Vietnam, without knowing that an inevitable by-product of the **synthesis** of 2,4,5-T was a toxic substance, 2,3,7,8-tetrachlorodibenzodioxin (dioxin). There is still debate over the extent of damaging effects sustained by those airmen, soldiers, and civilians who were exposed to this material. Dioxin was present at a level of about 2 ppm (mg/kg sample) in some of the samples of 2,4,5-T (called Agent Orange), but other samples contained more than 30 ppm of the by-product. Dioxin was eventually found to be highly toxic to guinea pigs (the LD_{50} value was 1 ppb, or 1 μg compound/kg of sample), which led to the labeling of dioxin as "the world's most deadly poison," an impressive, if inaccurate, title (inaccurate because of a unique sensitivity of guinea pigs and because some natural toxins are known to be more potent).

synthesis: combination of starting materials to form a desired product

The U.S. federal government's experience with 2,4,5-T demonstrates a significant principle: One must be concerned not only with the safety of the active components of commercial products, but also with the safety of by-products that may be present in those products or that may form during natural degradation. Adherence to this principle is a major and costly challenge to those who develop herbicides, and concern for safety is partly responsible for the (at present) decreasing number of herbicides that are available for treating aquatic weeds.

It is thought that the first water hyacinths were introduced into the United States during an 1884 horticultural exposition in New Orleans, in

Herbicides are being sprayed on this California roadside.

the course of which these plants, imported from Argentina, were given away as souvenirs. It is suspected that they were accidentally put into the St. Johns River in Florida and that they, shortly thereafter, multiplied. The plant grows (under optimal conditions) at the rate of 1.8 daughter plants per parent plant per week, and rapid growth generated dense mats that affected the navigation of boats on this river and others. In 1898 the U.S. Army Corps was given responsibility for maintaining the navigability of rivers, and aquatic plant control became its responsibility as well—a responsibility that has persisted to this day.

Herbicide Toxicity

Because plants and mammals differ in organization and physiology, it might be expected that herbicides would constitute only a slight chemical hazard to mammals. Whereas some herbicides have very low toxicities in mammals, others have considerable. A number of test species are used to appraise toxicity, and their sensitivities are graded as acute (short-term) LD_{50} values.

LD_{50} refers to the amount (LD or lethal dose) that will elicit the deaths of 50 percent of the test species. It is typically expressed as the weight of herbicide per kilogram of body weight. The smaller the LD value, the greater the toxicity.

The chlorophenoxy compounds 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) may be the most familiar herbicides. They have been used in agriculture (to eradicate broadleaf weeds) and to control woody plants in ditches and along highways. They act as growth hormones in many plants, and can evoke active plant growth in areas in which abnormal, twisted, or curtailed growth occurs. Massive doses

CHARACTERISTICS OF REPRESENTATIVE HERBICIDES

Herbicide (type)	Control/Purpose	Acute Toxicity LD$_{50}$ mg/kg
2,4-D (2,4-dichlorophenoxy acetic acid)	Systematic herbicide	300–1,000: rats, guinea pigs, rabbits
Acetochlor	Control of most annual grasses, some broadleaf weeds. Tolerant crops include corn, soybeans, peanuts, sugarcane.	2,953: rat acute oral
Amitrole (triazine)	Broadleaf weeds and grasses in noncrop areas, generally low toxicity.	>5,000: male rats
Arsenic acid (inorganic)	Desiccation of cotton which is to be stripped	48: young rat 100: older rats
Atrazine	Widely used selective herbicide for broadleaf and grassy weeds.	no ill effects in rats, dogs with diet of 25 ppm
Dinosep (dinitrophenol)	Control of seedlings, not established perennial weeds except with repeat treatments. Applicable to variety of crops, except cruciferous crops.	58: rats
Diquat (dipyridyl)	General aquatic herbicide; preharvest top killer or desiccant.	230: rats
Diuron (carbamate)	Low rates—broadleaf and grass weeds in cotton, sugarcane etc. general weedkiller at higher rates	3,400: oral rats
Glyphosate	Broad-spectrum herbicide Used in crop, noncrop, weed control	(Rabbit acute dermal, >5,000 mg/kg)
Metolachlor	Selective herbicide used to control annual grassweeds, yellow nutsedge, some broadleaf in corn, cotton, peanuts, and other crops	2,780: rat acute oral
Paraquat (dipyridyl)	Weed control during establishment of grass seed crops	138: male rats
Propanil (aromatic amide)	Grasses and broadleaf weeds in certain wheat crops (north) and rice (south)	1,870: rats

SOURCE: Weed Science Society of America (1994). *Herbicide Handbook,* 7th edition. Lawrence, KS: Allen Press.

Characteristics of representative herbicides.

of either 2,4-D or 2,4,5-T cause ventricular fibrillation in mammals. Lower doses cause contact dermatitis and chloracne (a kind of severe dermatitis) in workers who have contact with 2,4,5-T (which, as noted, may be mixed with 2,3,7,8-tetrachlorodibenzodioxin, or dioxin).

Dinitrophenols (as alkali salts or aliphatic amine salts) have long been used in weed control. Human exposure to these compounds has led to nausea, gastric upset, rapid breathing, tachycardia (rapid heartbeat), cyanosis, and ultimately coma. Death or recovery occurs within 24 hours.

Paraquat and diquat are the best-known examples of bipyridyl compounds. These compounds appear to act via a free radical mechanism, competing for and depriving plants of an essential **reducing agent**. These compounds are hazardous to human beings. About 200 deaths from accidental poisoning or suicide attempt occurred in the 1960s. The fatalities showed lung, liver, and kidney damage. Paraquat tends to become concentrated in the kidney, with the accumulation of toxic amounts in the lung being secondary to kidney damage.

reducing agent: substance that causes reduction, a process during which electrons are lost (or hydrogen atoms gained)

Propanil is one of a group of amide herbicides (made from aniline treated with organic acids), and is used extensively to control weeds in rice crops. Rice itself contains an enzyme that hydrolyzes propanil to 3,4-dichloroaniline and propionic acid, and so it is resistant to the herbicide. Weeds, lacking this enzyme, are adversely affected by it. (Mammalian liver cells also have an enzyme that causes this hydrolysis.)

The effects of trace contaminants in herbicides are a major concern. For example, the use of Silvex was canceled by the U.S. Environmental Protection Agency in 1979 because the herbicide contained dioxin, a toxic. However, the Army Corps of Engineers argued against the cancellation, noting the overall U.S. waterways navigation benefits. The sum total of benefits of Silvex-based weed control were judged to correspond to approximately $40 million, and the benefit–cost ratio was about 11 to 1. Set against this must be the unknown costs of a toxic substance (dioxin), whose adverse effects are still being evaluated.

The entire world market for crop protection in 2000 was estimated to be $31 billion, and it probably will not grow significantly in the near future. Herbicides are sold as special formulations, and their use in the United States occurs only after extensive testing and governmental approval. Although new chemicals are being developed, the relatively static size of the herbicide market has resulted in a reduction in the number of agrochemical companies (through mergers and acquisitions). The number of new herbicides that will become available in the future will probably be a low one. SEE ALSO Agricultural Chemistry; Gardening; Insecticides; Pesticides.

Dean F. Martin
Barbara B. Martin

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Hess, Germain Henri

RUSSIAN CHEMIST
1802–1850

Germain Henri Hess is noted today for two fundamental principles of thermochemistry: the law of constant summation of heat (known simply as Hess's law) and the law of thermoneutrality. These discoveries were remarkable in that they were postulated without any supporting theoretical framework and took place in a field of study almost totally neglected by his contemporaries. Hess's law is of immense practical importance and is used to this day to determine heats of reaction when their direct measurements are difficult or impossible.

Hess was born on August 8, 1802, in Geneva, Switzerland. At the age of three, he moved with his family to Russia when his father, an artist, became a tutor to a rich family. Hess began his medical studies in 1822 and obtained an M.D. in 1826. While in school, he became interested in chemistry and geology, and upon graduation traveled to Stockholm, Sweden, to study with Jöns Jakob Berzelius, the most renowned chemist of the period. Although he spent barely a month in Berzelius's laboratories, Hess was strongly influenced by him in his later career, and they remained lifelong friends and correspondents. After practicing medicine in Irkutsk for two years, Hess returned to St. Petersburg, where he remained a member of the academic establishment for the remainder of his life.

Although Hess, like most of his colleagues, was involved with the discovery and analysis of new substances, he became interested in the more theoretical aspects of chemistry. His investigations into the nature of chemical affinity—why atoms are attracted to each other—led him to study the amounts of heat generated by chemical reactions. His experiments, carried out on the various hydrates of sulfuric acid, showed that the heat evolved in their formation was always the same, whether the reactions proceeded directly or stepwise through **intermediates**. Although this can be seen in hindsight as a specific example of the law of the conservation of energy, Hess developed it two years before Julius Robert von Mayer elucidated the more general principle in 1842.

intermediate: molecule, often short-lived, that occurs while a chemical reaction progresses but is not present when the reaction is complete

Hess was immediately aware of the significance of his discovery and continued his studies in the same realm. In 1842 he proposed the law of thermoneutrality, which stated that no heat is evolved by the exchange reactions of neutral salts in **aqueous solutions**. He was not able to fully explain these observations, and it was not until forty-five years later that the process of electrolytic dissociation was more completely elucidated by the Swedish physicist and chemist Svante Arrhenius.

aqueous solution: homogenous mixture in which water is the solvent (primary component)

Although his research activity diminished after these two major discoveries, Hess remained influential in the development of chemistry in Russia. His textbook *Fundamentals of Pure Chemistry* saw seven editions and remained the standard Russian text in chemistry until 1861. He remained active in teaching and mentoring younger scientists, until declining health forced his retirement in 1848. He died on December 13, 1850, at the relatively young age of forty-eight. SEE ALSO ARRHENIUS, SVANTE; BERZELIUS, JÖNS JAKOB; THERMOCHEMISTRY.

Bartow Culp

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Heyrovský, Jaroslav

CZECH PHYSICAL CHEMIST
1890–1967

Jaroslav Heyrovský was born on November 20, 1890, in Prague (then part of the Austro-Hungarian Empire), where he also died on March 27, 1967. He began studying chemistry and physics at Prague University in 1909.

Between 1910 and 1914 he studied at University College in London under William Ramsay and Frederick G. Donnan, where he earned a B.Sc. degree in 1913. Following war service in a military hospital during World War I, he earned a Ph.D. degree in Prague in 1918 and a D.Sc. degree in London in 1921. In 1922 Heyrovský was promoted to full professor and head of the Institute of Physical Chemistry at Charles University (in Prague); and in 1950 he became director of the Polarographic Institute of the Czechoslovak Academy of Sciences.

Heyrovský was the discoverer of polarography and the inventor of the polarograph, an instrument that analyzes the composition of solutions electrochemically. His discovery of polarography was a culmination of the work of other scientists in electrochemistry. Other scientists' investigations of electrolysis had demonstrated the dependence of the intensity of a current flowing through a saline solution on the **voltage** applied to electrodes immersed in the solution. They found that at certain voltages, currents began to flow and **metals** were deposited on the electrodes.

voltage: potential difference expressed in volts

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

The second line of research that led to polarography was the investigation of the **interface tension** between mercury and saline solutions. Gabriel Lippmann (1845–1921) found that increasing the voltage applied to mercury in contact with a surrounding saline solution changed the mercury's surface tension in a characteristic manner, which he was able to represent as a **parabolic curve** called an electrocapillary parabola. Professor Bohumil Kučera (1874–1921), Heyrovský's teacher in Prague, made a similar investigation, for which he used a mercury-dropping electrode. The electrode consisted of a capillary tube from which mercury dripped into the solution. Kučera witnessed deviations in the shapes of the curves as he varied the voltages, and proposed that Heyrovský investigate the phenomenon.

interface tension: contractile force at the junction of two liquids

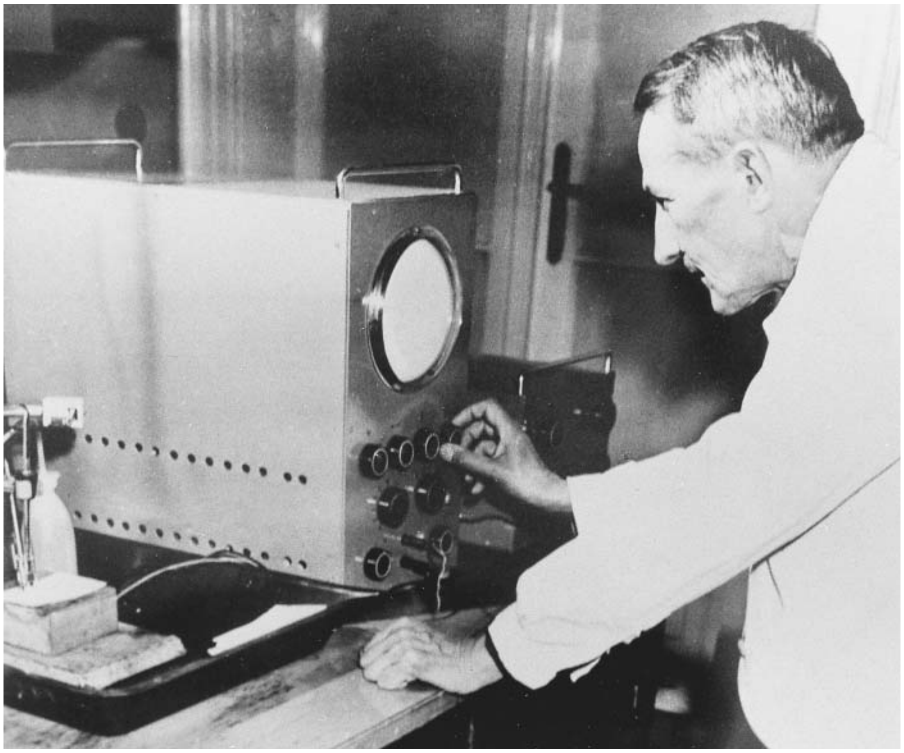
parabolic curve: planar curve each point of which is equidistant from a straight line (axis)

Heyrovský in effect combined the investigations of electrolysis and electrocapillary parabolas. In 1922 Heyrovský constructed an electrical circuit whose voltage from a battery was applied through a **Kohlrausch drum** to a mercury-dropping electrode immersed in a saline solution. The electrical potential of this electrode was then changed incrementally from 0 to 2 volts. A layer of mercury on the bottom of the vessel served as the second electrode. A mirror **galvanometer** would then detect a current flowing through this circuit, and the values of current intensity would be plotted point by point (by hand) as a function of the applied voltage. As the dissolved ions reacted electrochemically with the mercury-dropping electrode, curves with characteristic steps (polarographic waves) at certain voltage values were obtained. The identity of the ion present in the solution was determined by the voltage (expressed in electrochemical potential) at half of the height of the polarographic wave (so-called half-wave potential). The intensity of the current, represented in the graph as the height of the polarographic wave, was found to be directly proportional to the concentration of the ion.

Kohlrausch drum: rotating cylinder used to mount a variable resistance slide wire for a polarograph

galvanometer: instrument used to detect and measure the strength of an electric current

Heyrovský's method, later called polarography, became an excellent analytical tool because it yielded qualitative and quantitative analyses of a solution in a single experiment. With Masuzo Shikata (1895–1964), Heyrovský constructed the first polarograph, an instrument equipped with an electromotor that moved the Kohlrausch drum in accord with photographic paper rotating in a cylindrical cassette. It allowed the potential of the mercury-



Czech chemist Jaroslav Heyerovský, recipient of the 1959 Nobel Prize in chemistry, "for his discovery and development of the polarographic method of analysis."

dropping electrode to change continuously. Light from the mirror galvanometer entered the cassette through a narrow slit (requiring these experiments to be performed in darkness). A continuous polarographic curve appeared upon the development of the photographic paper.

The polarograph was the first fully automatic instrument used in chemistry. For decades polarography was the only precise method for the analysis of inorganic and organic compounds in solution. Polarographic analyses of human blood serum served as a tool for diagnosing cancer during the 1940s and 1950s. Modern polarographs equipped with computers use advanced techniques such as oscillopolarography and square-wave polarography. In 1959 Heyrovský was awarded the Nobel Prize in chemistry "for his discovery and development of the polarographic method of analysis." SEE ALSO ANALYTICAL CHEMISTRY; ELECTROCHEMISTRY.

Vladimir Karpenko

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British chemist Dorothy Crowfoot Hodgkin, recipient of the 1964 Nobel Prize in chemistry, "for her determinations by x-ray techniques of the structures of important biochemical substances."

Hodgkin, Dorothy

ENGLISH CHEMIST
1910–1994

The most powerful technique for determining the structure of a chemical compound is x-ray crystallography. In this technique, a beam of x rays is focused on a crystal of a compound. The diffraction pattern produced enables chemists to determine the location of atoms within the crystals and hence deduce the molecular structure. It was Dorothy Hodgkin who pushed the limits of the technique to determine the structures of some biologically important molecules, including penicillin, **vitamin** B_{12}, and insulin.

vitamins: organic molecules needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

Born in Cairo in 1910 to English parents, Hodgkin became interested in chemistry by the age of ten. At thirteen, she attempted to analyze minerals she had brought back to England from the Sudan. Excelling in high school, in 1927 she was accepted at Oxford University, from which she graduated in 1931. Despite her obvious brilliance, Hodgkin was rejected for several positions. Fortunately, the famous crystallographer John Desmond Bernal at Cambridge University agreed to take her on as a researcher.

Hodgkin enjoyed the sparkling intellectual atmosphere at Cambridge, but financial hardship forced her to take a position as a tutor back at Oxford. It was there that she began her own research career in the lonely basement of the university museum. At that time, women were not permitted to join the chemistry club at Oxford University, so she was in effect barred from sharing in the intellectual life of her colleagues.

Throughout her career, Hodgkin selected projects that were always just beyond the currently accepted limits of feasibility, her initial research on the structure of cholesterol being one such example. In 1942 Hodgkin embarked on the first groundbreaking study of her career—the molecular structure of penicillin. Penicillin was the only effective antibiotic of the time and it had to be obtained from molds. If the structure could be determined, then it would be possible to devise a method of synthesizing it in chemical factories, reducing its cost and dramatically increasing its supply. Hodgkin and her research students determined the molecular structure of penicillin in 1945, in the process devising new crystallographic techniques.

Although Hodgkin had made major contributions to science, she still held the lowly rank of tutor. Deep in debt, she asked a senior professor to help her acquire a better position. With his help, she was appointed university lecturer in 1946. In 1948 she decided to take on the determination of vitamin B_{12}'s structure. This vitamin had been shown to prevent the disease of pernicious anemia but its chemical makeup remained unknown. With ninety-three atoms other than hydrogen, most chemists regarded the task of identifying its structure as impossible. Over the next six years, Hodgkin and her students toiled over the task. Their success in 1956 was the supreme triumph of her career.

Royal Society: The U.K. National Academy of Science, founded in 1660

Not until 1957 was Hodgkin promoted to university reader (approximately the equivalent of a full professor in North America). Even then, she was not provided with modern lab facilities until the following year. Despite her fame, it was the **Royal Society**, not Oxford University, that offered her the pinnacle of academic success, an endowed chair. Worldwide recognition of her work on the determination of the structures of biochemically important molecules came in 1964 when she was awarded the Nobel Prize in chemistry.

Hodgkin's third major project was determining the structure of the protein insulin. It was only technical advances in the 1960s that made the solution finally possible. When the results were published in 1969, the researchers were listed in alphabetical order, showing her willingness to share credit and her egalitarian attitude toward all research workers.

Hodgkin also had a very strong sense of social responsibility. After World War II, she became a member of the Science for Peace organization. Membership in this organization caused her to be denied a visa to attend a meeting in the United States during 1953. For the next twenty-seven years, to attend scientific meetings in the United States, she had to obtain a special entry permit from the U.S. attorney general. Only in 1990, when she was eighty years old, did the U.S. State Department relent and approve a visa application. Hodgkin formally retired in 1977, but she continued to be active in science until her death on July 30, 1994. see also Cholesterol; Insulin; Penicillin.

Marelene Rayner-Canham
Geoffrey W. Rayner-Canham

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Holmium

MELTING POINT: 1,461°C
BOILING POINT: 2,720°C
DENSITY: 8.803 g/cm^3
MOST COMMON IONS: Ho^{3+}

67
Ho
HOLMIUM
164.9303

A member of the **lanthanide**, or rare earth, series of elements, holmium is a gray, somewhat shiny, soft **metal**. It is usually found in minerals containing several of the lanthanides. Because the **rare earths** all have the same outer electron shell configuration ($6s^2$), their chemical properties are very similar, making it difficult to separate them from one another in the minerals in which they are usually complexed. They are best separated via repeated ion-exchange purification, a process developed in the United States during the 1940s. Although several of the rare earths are used in industrial chemical processes and in metal alloying, holmium has few commercial uses.

lanthanides: a family of elements (atomic number 57 through 70) from lanthanum to lutetium having from 1 to 14 4f electrons

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

rare earth elements: older name for the lanthanide series of elements, from lanthanum to lutetium

alloy: mixture of two or more elements, at least one of which is a metal

isotope: form of an atom that differs by the number of neutrons in the nucleus

nuclear: having to do with the nucleus of an atom

Holmium is easily oxidized, forms a wide variety of compounds, especially salts, and forms **alloys** with other metals. The pure metal has unusual magnetic properties that become apparent at low temperatures. In pure holmium the electron spins (which produce the magnetism) are aligned—not in parallel fashion as in iron, but in a manner such that helices are formed. Holmium has been used to make parts for magnets that produce intense magnetic fields. The **isotope** ^{165}Ho has an unusual football-shaped nucleus, which has been the focus of several important experiments investigating the nature of **nuclear** forces. In one atom the holmium electrons interact with the nucleus as if they produce a magnetic field of 740 tesla. This "hyperfine field" is one of the strongest such fields found in nature. SEE ALSO CERIUM; DYSPROSIUM; ERBIUM; EUROPIUM; GADOLINIUM; LUTETIUM; NEODYMIUM; PRASEODYMIUM; PROMETHIUM; SAMARIUM; TERBIUM; THULIUM; YTTERBIUM.

David G. Haase

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Hormones *See Estrogen; Steroids; Testosterone.*

1
H
HYDROGEN
1.0079

Hydrogen

MELTING POINT: **−259.14°C**
BOILING POINT: **−252.87°C**
DENSITY: **0.08988 g/L**
MOST COMMON IONS: **H^+, H^-**

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Hydrogen was first recognized as a gaseous substance in 1766 by English chemist and physicist Henry Cavendish. The abundance of hydrogen in Earth's crust is 1,520 parts per million. The abundance of hydrogen in the universe by weight is 74 percent and by number of atoms is 90 percent. Hence, hydrogen is the major constituent of the universe. Under ordinary conditions (STP) on Earth, hydrogen is a colorless, odorless, tasteless gas that is only slightly soluble in water. It is the least dense gas known (0.08988 grams per liter at STP). Ordinary hydrogen gas (H_2) exists as diatomic molecules. It reacts with oxygen to form its major compound on Earth, water (H_2O). It also reacts with nitrogen, **halogens**, and sulfur, to form ammonia (NH_3), hydrogen monohalide compounds (e.g., HCl) and hydrogen sulfide (H_2S), respectively. It combines with several **metals** to form metal hydrides, and carbon to form a great many organic compounds.

isotope: form of an atom that differs by the number of neutrons in the nucleus

synthesis: combination of starting materials to form a desired product

Hydrogen is a mixture of three **isotopes**: protium (^{1}H; atomic mass 1.007822); deuterium, or heavy hydrogen (^{2}H or D; atomic mass 2.0140; 1 atom of ^{2}H to every 6,700 atoms of ^{1}H); and tritium (^{3}H or T; atomic mass 3.016; has a radioactive nucleus). The fusion of protium nuclei (protons) to form helium is believed to be the major source of the Sun's energy. The extreme heat of reaction in hydrogen-oxygen burning is used in high temperature welding and melting processes. Hydrogen molecule addition reactions (hydrogenation) are widely used in industry, for example, for the hardening of animal fats or vegetable oils, for the **synthesis** of methanol from carbon monoxide, and in petroleum refining. SEE ALSO CAVENDISH, HENRY; EXPLOSIONS; GASES.

Ágúst Kvaran

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Hydrolase

Hydrolases are hydrolytic enzymes, biochemical catalysts that use water to **cleave** chemical bonds, usually dividing a large molecule into two smaller molecules. Examples of common hydrolases include esterases, proteases, glycosidases, nucleosidases, and lipases.

cleave: split

Hydrolases carry out important **degradative** reactions in the body. During digestion, lipases **hydrolyze lipids** and proteases convert protein to amino acids. Hydrolases cleave large molecules into fragments used for **synthesis**, the **excretion** of waste materials, or as sources of carbon for the production of energy. In these reactions, many biopolymers are converted to monomers. Some hydrolases release energy as they act.

degradative: breaking down large molecules such as starch or protein into smaller fragments such as sugars or amino acids

hydrolyze: to react with water

lipid: a nonpolar organic molecule; fatlike; one of a large variety of nonpolar hydrophobic (water hating) molecules that are insoluble in water

synthesis: combination of starting materials to form a desired product

excrete: to eliminate or discharge from a living entity

One of the most important hydrolases is **acetylcholine** esterase (cholinesterase). Acetylcholine is a potent neurotransmitter for voluntary muscle. Nerve impulses travel along neurons to the **synaptic cleft**, where acetylcholine stored in **vesicles** is released, carrying the impulse across the synapse to the **postsynaptic neuron** and **propagating** the nerve impulse. After the nerve impulse moves on, the action of the neurotransmitter molecules must be stopped by cholinesterase, which hydrolyzes acetylcholine to choline and acetic acid. Some dangerous toxins such as the exotoxin of *Clostridium botulinum* and saxitoxin interfere with cholinesterase, and many nerve agents such as tabun and sarin act by blocking the hydrolytic action of cholinesterase. SEE ALSO ENZYMES; HYDROLYSIS.

acetylcholine: neurotransmitter with the chemical formula $C_7H_{17}NO_3$; it assists in communication between nerve cells in the brain and central nervous system

synaptic cleft: tiny space between the terminal button of one neuron and the dendrite or soma of another

vesicle: small compartment in a cell that contains a minimum of one lipid bilayer

postsynaptic neuron: receptor nerve cell

propagating: reproducing; disseminating; increasing; extending

Dan M. Sullivan

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Hydrolysis

Hydrolysis literally means reaction with water. It is a chemical process in which a molecule is cleaved into two parts by the addition of a molecule of water. One fragment of the parent molecule gains a hydrogen ion (H^+) from the additional water molecule. The other group collects the remaining hydroxyl group (OH^-). To illustrate this process, some examples from real life and actual living systems are discussed here.

The most common hydrolysis occurs when a salt of a weak acid or weak base (or both) is dissolved in water. Water autoionizes into negative hydroxyl ions and hydrogen ions. The salt breaks down into positive and negative ions. For example, sodium acetate dissociates in water into sodium and acetate ions. Sodium ions react very little with hydroxyl ions whereas acetate ions combine with hydrogen ions to produce neutral acetic acid, and the net result is a relative excess of hydroxyl ions, causing a basic solution.

catalyst: substance that aids in a reaction while retaining its own chemical identity

However, under normal conditions, only a few reactions between water and organic compounds occur. Generally, strong acids or bases must be added in order to achieve hydrolysis where water has no effect. The acid or base is considered a **catalyst**. They are meant to speed up the reaction, but are recovered at the end of it.

ester: organic species containing a carbon atom attached to three moieties: an O via a double bond, an O attached to another carbon atom or chain, and an H atom or C chain; the R(C=O)OR functional group

carboxylic acid: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the $-CO_2H$ functional group

Acid–base-catalyzed hydrolyses are very common; one example is the hydrolysis of amides or **esters**. Their hydrolysis occurs when the nucleophile (a nucleus-seeking agent, e.g., water or hydroxyl ion) attacks the carbon of the carbonyl group of the ester or amide. In an aqueous base, hydroxyl ions are better nucleophiles than dipoles such as water. In acid, the carbonyl group becomes protonated, and this leads to a much easier nucleophilic attack. The products for both hydrolyses are compounds with **carboxylic acid** groups.

Perhaps the oldest example of ester hydrolysis is the process called saponification. It is the hydrolysis of a triglyceride (fat) with an aqueous base such as sodium hydroxide (NaOH). During the process, glycerol, also commercially named glycerin, is formed, and the fatty acids react with the base, converting them to salts. These salts are called soaps, commonly used in households.

metabolism: the complete range of biochemical processes that take place within living organisms; comprises processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those that break down complex food molecules, thus liberating energy (catabolism)

biosynthesis: formation of a complex molecule from simpler ones

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

adenosine triphosphate (ATP): molecule formed by the condensation of adenine, ribose, and triphosphoric acid, HOP(O)OH–O–(O)OH–OP(O)OH–OH; it is a key compound in the mediation of energy in both plants and animals

Moreover, hydrolysis is an important process in plants and animals, the most significant example being energy **metabolism** and storage. All living cells require a continual supply of energy for two main purposes: for the **biosynthesis** of small and macromolecules, and for the active transport of ions and molecules across cell membranes. The energy derived from the **oxidation** of nutrients is not used directly but, by means of a complex and long sequence of reactions, it is channeled into a special energy-storage molecule, **adenosine triphosphate (ATP)**.

synthesis: combination of starting materials to form a desired product

The ATP molecule contains pyrophosphate linkages (bonds formed when two phosphate units are combined together) that release energy when needed. ATP can be hydrolyzed in two ways: the removal of terminal phosphate to form adenosine diphosphate (ADP) and inorganic phosphate, or the removal of a terminal diphosphate to yield adenosine monophosphate (AMP) and pyrophosphate. The latter is usually cleaved further to yield two phosphates. This results in biosynthesis reactions, which do not occur alone, that can be driven in the direction of **synthesis** when the phosphate bonds are hydrolyzed.

catalysis: the action or effect of a substance in increasing the rate of a reaction without itself being consumed

In addition, in living systems, most biochemical reactions, including ATP hydrolysis, take place during the **catalysis** of enzymes. The catalytic action of enzymes allows the hydrolysis of proteins, fats, oils, and carbohydrates. As an example, one may consider proteases, enzymes that aid digestion by hydrolyzing peptide bonds in proteins. They catalyze the hydrolysis of interior peptide bonds in peptide chains, as opposed to exopeptidases, another class of enzymes, that catalyze the hydrolysis of terminal peptide bonds, liberating one free amino acid at a time.

However, proteases do not catalyze the hydrolysis of all kinds of proteins. Their action is stereo-selective: Only proteins with a certain tertiary structure will be targeted. The reason is that some kind of orienting force is needed to place the amide group in the proper position for catalysis. The necessary contacts between an enzyme and its substrates (proteins) are created because the enzyme folds in such a way as to form a crevice into which the substrate fits; the crevice also contains the catalytic groups. Therefore, proteins that do not fit into the crevice will not be hydrolyzed. This specificity preserves the integrity of other proteins such as hormones, and therefore the biological system continues to function normally. SEE ALSO Enzymes; Tertiary Structure.

Joseph Bariyanga

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Ibuprofen

Ibuprofen is a well-known drug that possesses **analgesic** (pain-relieving) and antipyretic (fever-reducing) properties. It is particularly known for its use in pain relief from arthritis. Ibuprofen was discovered by Dr. Stewart Adams and his colleagues in the United Kingdom in the 1950s, patented in 1961, and first made available in 1969. It became available in the United States in 1974. Ibuprofen tablets are sold under the trade names Advil and Motrin. The chemical name of ibuprofen is 2-(4-isobutylphenyl)propanoic acid.

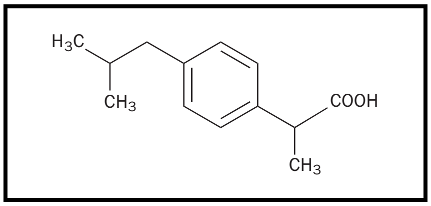
analgesic: compound that relieves pain, e.g., aspirin

Ibuprofen also has anti-inflammatory properties, and it belongs to a class of therapeutic agents known as nonsteroidal anti-inflammatory drugs, or NSAIDs. Like acetylsalicylic acid (aspirin), another NSAID, and acetaminophen, ibuprofen works by inhibiting the activity of a class of enzymes called cyclooxygenases (COX). These enzymes are significant because they catalyze the **synthesis** of prostaglandins, molecules that have both positive and negative effects in the body. Prostaglandins are, for example, protective against the development of stomach ulcers, but they can also **mediate** inflammation (as well as the pain response).

synthesis: combination of starting materials to form a desired product

mediate: to act as an intermediary agent

One of the most interesting things about human COX enzymes is that there is more than one of them—definitely two, and probably at least three. This is important to our understanding of the therapeutic effects of ibuprofen, aspirin, and acetaminophen. It had long been suspected that there was more than one COX enzyme, but it was not until 1991 that evidence for the existence of two forms, COX-1 and COX-2, materialized. It was then recognized that COX-1 is present at near constant levels in the body under all conditions (that is, it is a constitutive enzyme), whereas the levels of COX-2 could increase in response to inflammatory conditions (i.e., it is an inducible enzyme). This led to the idea that the side effects of ibuprofen and aspirin (including stomach ulcers) probably arose from inhibition of the constitutive COX-1 enzyme, whereas the therapeutic benefits arose from inhibition of the inducible COX-2 enzyme.



Structure of ibuprofen.

Ibuprofen and aspirin both inhibit COX-1 and COX-2, but they do it in different ways. Ibuprofen binds noncovalently to a COX enzyme and thus competes with the enzyme's natural substrate. (This is referred to as reversible

covalent bond: bond formed between two atoms that mutually share a pair of electrons

inhibition.) On the other hand, aspirin forms a **covalent bond** to a serine residue in the enzyme, and this bond cannot be broken. (This is called irreversible inhibition.) Acetaminophen does not interact with either COX-1 or COX-2, but it is now understood that it may interact with a newly identified cyclooxygenase, COX-3. Selective targeting of the COX enzymes is an exciting area of pharmacology, in which the challenge continues to be the development of drugs that interact with specific COX enzymes. SEE ALSO ACETYLSALICYLIC ACID; ACETAMINOPHEN; PHARMACEUTICAL CHEMISTRY.

Ian S. Haworth

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49
In
INDIUM
114.818

Indium

MELTING POINT: 156.6°C
BOILING POINT: 2,080°C
DENSITY: 7.31g/cm^3
MOST COMMON IONS: In^{3+}, In^+

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Indium is a soft, silver-white **metal**. It was first isolated in 1863 by German chemists Ferdinand Reich and Hieronymus Theodor Richter. Indium was so named because of an intense blue (indigo) line in its emission spectrum. The element is widely distributed in several ores (often in conjunction with zinc) but in low concentrations, accounting for only 0.05 part per million (ppm) of Earth's crust.

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

The chemical properties of indium are typical of those of Group 13 of the Periodic Table. Most of indium's oxides, salts, and compounds involve the +3 **oxidation** state (e.g., In_2O_3, $In[NO_3]_3$, and $InCl_3$); many of these compounds are electron-pair acceptors, forming addition compounds with donor molecules (e.g., $InBr_3 \cdot py$, py = pyridine). Neutral, cationic, and anionic complexes are also known. Several interesting compounds are derived from the +1 and +2 oxidation states of the element.

alloy: mixture of two or more elements, at least one of which is a metal

isotope: form of an atom that differs by the number of neutrons in the nucleus

Indium was long regarded as rare and uninteresting, but it has found many interesting applications. Its softness results in its use (alone or in **alloys**) as a bearing metal, as a sealant, and in high-temperature solders. The positron-emitting radioactive **isotopes** ^{111}In and ^{113m}In are used in medical diagnostic imaging.

Organoindium substances are important, especially for the production of materials by metal-organic chemical vapor-phase deposition (MOCVD). This technique involves the thermal decomposition of mixtures of an organoindium compound and a compound such as phosphine (PH_3), leading to the deposition of ordered layers of InP. The resulting compound can be used in the formation of semiconductors and solid-state optical devices (similar to silicon). SEE ALSO INORGANIC CHEMISTRY.

Dennis G. Tuck

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Industrial Chemistry, Inorganic

Industrial inorganic chemistry includes subdivisions of the chemical industry that manufacture inorganic products on a large scale such as the heavy inorganics (chlor-alkalis, sulfuric acid, sulfates) and fertilizers (potassium, nitrogen, and phosphorus products) as well as segments of fine chemicals that are used to produce high purity inorganics on a much smaller scale. Among these are **reagents** and raw materials used in high-tech industries, pharmaceuticals or electronics, for example, as well as in the preparation of inorganic specialties such as catalysts, pigments, and propellants.

reagent: chemical used to cause a specific chemical reaction

Metals are chemicals in a certain sense. They are manufactured from ores and purified by many of the same processes as those used in the manufacture of inorganics. However, if they are commercialized as **alloys** or in their pure form such as iron, lead, copper, or tungsten, they are considered products of the metallurgical not chemical industry.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

alloy: mixture of two or more elements, at least one of which is a metal

The Chemical Industry

The chemical industry adds value to raw materials by transforming them into the chemicals required for the manufacture of consumer products. Since there are usually several different processes that can be used for this purpose, the chemical industry is associated with intense competition for new markets. It is made up of companies of different sizes, including several giants that are engaged in the transformation of some very basic raw materials into final products, as well as medium-size or small companies that concentrate on very few of these steps. The closer to the raw material, the larger the scale of operations; such "heavy" inorganic chemicals are usually manufactured by continuous processes. At the other extreme in terms of scale are the firms that manufacture "specialties," mostly in batch processes, from **"intermediates"** that correspond to chemicals which have already gone through several steps of **synthesis** and purification.

intermediate: a substance that is used to prepare a desired product

synthesis: combination of starting materials to form a desired product

Basic chemicals represent the starting point for the manufacture of inorganic industrial chemicals. They are usually one step away from the raw materials listed in Table 1 and are produced on a very large scale employing continuous processes. The unit price of these products is relatively low, and producing them cheaply and efficiently is a major concern for the companies that manufacture them. Sulfur, nitrogen, phosphorus, and chlor-alkali industries are the main producers of basic inorganic chemicals, and they will often sell them to other industries as well as using them in the manufacture of their own end-products. The basic principles for their production and major uses are indicated here for each of these industries.

Inorganic chemicals produced on an industrial scale can be easily identified. Many of today's large companies started as producers of inorganics,

Inorganic chemicals such as chlorine, produced at this plant in Louisiana, are used in the manufacturing of several chlorides, including PVC and hydrochloric acid.

but as coal—and especially petroleum—became important sources of raw materials, they were integrated into the product chain.

Sources of Inorganic Raw Materials

There are many different sources of raw materials for the manufacture of inorganic chemicals (see Table 1). Very few of them are found in their elemental form. Sulfur is a notable exception. It occurs in underground deposits and can be brought to the surface by compressed air after it is melted by superheated steam. However, increasing quantities of sulfur are recovered from petroleum and natural gas (where they occur as impurities).

Air contains molecular nitrogen and oxygen. They may be separated by **liquefaction** and **fractional distillation** along with **inert** gases, especially argon. Salt or **brine** can be used as sources of chlorine and sometimes bromine, sodium hydroxide, and sodium carbonate, whereas metals such as iron, aluminum, copper, or titanium as well as phosphors, potassium, calcium, and fluorine are obtained from mineral ores. **Saltpeter** was once an important source of nitrogen compounds, but today most ammonia and nitrates are produced synthetically from nitrogen gas in the air.

Recovery and recycling provide increasing amounts of some metals. As environmental concerns increase, these operations will probably become an important source of materials used in the manufacture of certain inorganic chemicals.

liquefaction:	process of changing to a liquid form
fractional distillation:	separation of liquid mixtures by collecting separately the distillates at certain temperatures
inert:	incapable of reacting with another substance
brine:	water containing a large concentration of salts, especially sodium chloride (NaCl)
saltpeter:	potassium nitrate; chile saltpeter is sodium nitrate

U.S. PRODUCTION OF MINERALS IN 2001

Source	Thousands of Tons	Examples of Uses
Phosphate rock	37,706	Fertilizers, detergents
Salt	49,723	Chlorine, alkali production
Limestone	20,617	Soda ash, lime
Sulfur	10,144	Sulfuric acid production
Potassium compounds	1,323	Caustic potash, fertilizers
Sodium carbonate	11,356	Caustic soda, cleaning formulations

Table 1. U.S. production of minerals in 2001.

The Beginnings of the Chemical Industry

The origins of the chemical industry can be traced to the **Industrial Revolution**. Sulfuric acid and sodium carbonate were among the first industrial chemicals. “Oil of **vitriol**” (as the former was known) played an important role in the manipulation of metals, but its production on an industrial scale required the development of materials that would resist attack. Sodium carbonate was obtained in its anhydrous form, “soda ash,” from vegetable material until the quantities produced could no longer meet the rapidly expanding needs of manufacturers of glass, soap, and textiles. This led the Royal Academy of Sciences of Paris, in 1775, to establish a contest for the discovery of a process based on an abundant raw material, sodium chloride, and to Nicolas Leblanc’s method for the preparation of soda by converting salt into sulfate

Industrial Revolution: widespread replacement of hand tools by power-driven machines, beginning about 1750 (especially in England)

vitriol: an old term for sulfate of a metal; there are blue (Cu), white (Zn), green (Fe), and rose (Co) vitriols

$$2\ NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2\ HCl$$

followed by conversion of the sulfate to soda with charcoal and chalk

$$Na_2SO_4 + 2\ C + CaCO_3 \rightarrow Na_2CO_3 + CaS + 2\ CO_2$$

Although he did not win the prize, Leblanc’s process is associated with the birth of industrial chemistry.

The industrial production of chemicals was usually based on running reactions that were known to yield the desired products on much larger scales. Success in these endeavors lay much more in the experience and skill of their practitioners than the application of solid chemical principles. This led to serious problems of control and the generation of noxious by-products. The introduction of the Leblanc process in the northwest of England led to a general public outcry against the dark and corrosive smoke that covered the surrounding countryside. The Alkali Act, passed in response in 1863, represents the first legislation that established emission standards.

Sulfuric acid was an essential chemical for dyers, bleachers, and alkali manufacturers. Its production on a large scale required the development of lead-lined chambers that could resist the vapors which were formed when sulfur was burned with nitrates

$$SO_2 + NO_2 + H_2O \rightarrow H_2SO_4 + NO$$

$$NO + 1/2\ O_2 \rightarrow NO_2$$

This process was wasteful and emitted **corrosive gases**. It improved only in the mid-nineteenth century when towers to recycle the gases were finally introduced. The transportation of sulfuric acid was dangerous, and

corrosive gas: gas that causes chemical deterioration alkali manufacturers tended to produce their own as a result. This marked the beginning of the diversification and vertical integration that are characteristic of the chemical industry.

Sulfuric acid was also used in the manufacture of superphosphates, which were produced as fertilizers on a large scale by the mid-nineteenth century. By that time, a solution was found for the complex engineering problems that had hampered the use of the alternative process to produce soda

$$NH_3 + H_2O + CO_2 \rightarrow NH_4HCO_3$$

$$NaCl + NH_4HCO_3 \rightarrow NaHCO_3 + NH_4Cl$$

$$2\ NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$$

Ernest Solvay, a Belgian chemist, designed a tower in which carbon dioxide reacted efficiently with solid salts. The Solvay process had enormous advantages over the Leblanc process: It did not generate as much waste and pollution; its raw materials, brine and ammonia, were readily available (the latter from gasworks); less fuel was used, and no sulfur or nitrate was involved. In spite of its higher capital costs, it was rapidly adopted and soon became the major source of alkali.

Another major process used in the manufacture of inorganic chemicals is the **catalytic conversion** of nitrogen and hydrogen to ammonia. The German chemist Fritz Haber first synthesized ammonia from nitrogen and hydrogen in 1909. Four years later, together with another German, Carl Bosch, he modified the process for the commercial production of ammonia. The Haber (or Haber–Bosch) process represented a technological breakthrough since it required a very specialized plant to handle gases at high pressures and temperatures.

catalytic conversion: catalytic oxidation of carbon monoxide and hydrocarbons in automotive exhaust gas to carbon dioxide and water

Sulfuric Acid and Sulfates

Sulfuric acid has long been the chemical that is manufactured in the largest quantities on a world scale (see Table 2). Its production is often linked to a country's stage of development, owing to the large number of transformation processes in which it is used.

Sulfuric acid is manufactured from elemental sulfur. Mining was the main source for this element, which was obtained from sulfide-containing ores, or in very pure form from underground deposits by the Frasch process (injection of superheated steam and air into drillings and the separation of the mixture that rises to the surface). The large-scale consumption of petroleum and natural gas has changed this scenario since sulfur occurs as an impurity in most fossil fuels and must be removed before the fuels are processed. These fuels are presently the main source of sulfur, and their relative importance tends to increase with more rigorous controls on emissions.

U.S. PRODUCTION OF INORGANIC CHEMICALS IN 2001

Chemical	Thousands of Tons
Sulfuric acid	40,054
Ammonia	13,046
Sodium chloride	12,019
Phosphoric acid	11,605
Sodium hydroxide	10,687
Nitric acid	7,823
Ammonium sulfate	2,556
Titanium dioxide	1,463
Aluminum sulfate	1,165

Table 2. U.S. production of inorganic chemicals in 2001.

Sulfuric acid is manufactured in three stages

$$S + O_2 \xrightarrow{air} SO_2 + \text{heat}$$

$$2\ SO_2 + O_2 \rightarrow 2SO_3$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Since the reaction of sulfur with dry air is exothermic, the sulfur dioxide must be cooled to remove excess heat and avoid reversal of the reaction.

Most plants use reactors with various stages in order to cool the stream for the catalytic step. Conversion by a vanadium pentoxide **catalyst** deposited on a silicate support is the critical step in the process, in which the gaseous stream is passed over successive layers of catalyst. The gas mixture is then passed through an absorption tower. Oleum, the product, is a concentrated solution of sulfuric acid containing excess sulfur trioxide.

catalyst: substance that aids in a reaction while retaining its own chemical identity

As an inexpensive source of acid, a large amount of the sulfuric acid that is produced is used for the manufacture of other mineral acids. It is also used to produce sulfates, such as ammonium sulfate (a low-grade fertilizer), sodium sulfate (used in the production of paper), and aluminum sulfate (used in water treatment), as well as organic sulfates (used as **surfactants**). Sulfuric acid is also a good catalyst for many reactions, including the transformation of ethanol into ethylene or ethyl ether.

surfactants: surface-active agents that lower the surface tension of water; e.g., detergents, wetting agents

Nitrogen Compounds

In general, chemicals containing nitrogen are manufactured from ammonia produced by the Haber process

$$N_2 + 3H_2 \xrightarrow{Fe} 2NH_3$$

Since molecular nitrogen is inert, its reaction with hydrogen requires very severe conditions and a catalyst. An iron catalyst is used. High pressure favors the formation of products, but an increase in temperature will shift the **equilibrium** in the opposite direction. Plants will thus operate under conditions that represent the most favorable balance between operating costs and capital investment.

equilibrium: condition in which two opposite reactions are occurring at the same speed, so that concentrations of products and reactants do not change

Energy consumption is very high, and its cost is an important component along with the starting materials. Nitrogen is easily obtained from air, and hydrogen and can be produced by the shift reaction

$$CO + H_2O \rightarrow CO_2 + H_2$$

or from hydrocarbon reforming

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$$

Further stages are required to assure conversion and to remove carbon dioxide or carbon monoxide from the gas mixture. A mixture of ammonia and synthesis gas ($CO + H_2$) results from the reaction with nitrogen so the two must be separated and the synthesis gas recycled.

Most of the ammonia that is produced is employed as fertilizer or used to manufacture other fertilizers, such as urea, ammonium sulfate, ammonium nitrate, or diammonium hydrogen phosphate. Ammonia is also used in the Solvay process, and it is a starting material for the manufacture of cyanides and nitriles (which are used to make polymers such as nylon and acrylics) as well as aromatic compounds containing nitrogen, such as pyridine and aniline.

The other source of nitrogen compounds in the chemical industry is nitric acid, obtained from the **oxidation** of ammonia

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

$$4\ NH_3 + 5\ O_2 \rightarrow 4\ NO + 6\ H_2O$$

$$3\ NO + 3/2\ O_2 \rightarrow 3\ NO_2$$

$$3\ NO_2 + H_2O \rightarrow 2\ HNO_3 + NO$$

The first reaction is run over platinum-rhodium catalysts at around 900°C (1,652°F). In the second and third stages, a mixture of nitric oxide and air circulates through condensers, where it is partially oxidized. The nitrogen dioxide is absorbed in a tower, and nitric acid sinks to the bottom. Nitric acid is mainly used to make ammonium nitrate, most of it for fertilizer although it also goes into the production of explosives. Nitration is used to manufacture explosives such as nitroglycerine and trinitrotoluene (TNT) as well as many important chemical intermediates used in the pharmaceutical and dyestuff industries.

Phosphorus Compounds

The world's major source of phosphorus is apatite, a class of phosphate minerals. Commercially, the most important is fluoroapatite, a calcium phosphate that contains fluorine. This fluorine must be removed for the manufacture of phosphoric acid, but it also can be used to produce hydrofluoric acid and fluorinated compounds.

Phosphoric acid is the starting material for most of the phosphates that are produced industrially. It is obtained from the reaction of the apatite mineral with sulfuric acid

$$\underbrace{Ca_{10}F_2\,(PO_4)_6}_{\textit{apatite}} + 7H_2SO_4 \rightarrow 3Ca(H_2PO_4)_2 + 7\,CaSO_4 + 2HF$$

Silica is present in the mineral as an impurity, and it reacts with hydrofluoric acid to yield silicon tetrafluoride, which can be converted to fluorosilicic acid, an important source of fluorine. More than half of the phosphoric acid that is produced by the reaction of phosphates with sulfuric acid is converted directly to sodium or ammonium phosphates to be used as fertilizer; thus, purity is not a concern.

For products that require high purity, such as detergents and foodstuffs, phosphoric acid is produced from elemental phosphorus (at about four times the cost). An electric furnace operating at 1,400–1,500°C (2,552–2,732°F) is used to form a molten mass of apatite and silica that reacts with coke and reduces the phosphate mineral

$$2\,Ca_3\,(PO_4)_2 + 6\,SiO_2 + 10\,C \rightarrow P_4 + 6\,CaSiO_3 + 10\,CO$$

Concentrating phosphoric acid leads to polyphosphoric acid, a mixture of several polymeric species, a good catalyst and dehydrating agent. Polyphosphate salts are used as water softeners in detergents or as buffers in food. Small quantities of elemental phosphorus are used to make matches, and phosphorus halides to prepare specialty chemicals for the pharmaceutical and agrochemical industries.

Chlor-Alkali Compounds

Industries producing chlorine, sodium hydroxide (also known as caustic soda), sodium carbonate (or soda ash) and its derivatives and compounds based on calcium oxide (or lime) are usually included under this category. As both sodium hydroxide and chlorine have a common raw material, sodium chloride, they are produced in quantities that reflect their equal molar ratio, irrespective of the market for either product. Since they are produced by electrolysis, they require a cheap source of brine and electricity

$$2\ NaCl + 2\ H_2O \rightarrow 2\ NaOH + Cl_2 + H_2$$

Most processes are based on the electrolysis of a sodium chloride solution, but some plants operate with the molten salt. Three different cell types are used in electrolysis in water: mercury cells, diaphragm cells, and membrane cells. Membrane cells are replacing the other two types in modern units, but it may not be economically feasible to convert older plants.

Sodium hydroxide and sodium carbonate are alternative sources of alkali, and their use has followed the availability of raw materials as well as the efficiency of processes developed for their production. Both require sodium chloride and energy and, if limestone deposits are also available, sodium carbonate may be produced by the Solvay process. Limestone consists mainly of calcium carbonate and can be used to produce calcium oxide (or quicklime) and calcium hydroxide (or slaked lime); the oxide may be obtained by heating (1,200–1,500°C, or 2,192–2,732°F) limestone, while the hydroxide, which is more convenient to handle, is obtained by adding water to the oxide

$$CaCO_3 \xrightarrow{heat} CaO + CO_2$$

$$CaO + H_2O \rightarrow Ca(OH)_2$$

Its principal use is in steelmaking, but it also goes into the manufacture of chemicals, water treatment, and pollution control. In the Solvay process, calcium carbonate and sodium chloride are used to produce calcium chloride and sodium carbonate with ammonia (which is recycled) as a medium for dissolving and carbonating the sodium chloride and calcium hydroxide for precipitating calcium chloride from the solution.

As sodium carbonate may be mined directly, its use may be preferred over a manufactured product. It is used mainly in the glass industry. Sodium silicates may be derived from sodium carbonate and in their finely divided form, silica gel, may be used in detergents and soaps.

Sodium hydroxide has many different uses in the chemical industry. Considerable amounts are used in the manufacture of paper and to make sodium hypochlorite for use in disinfectants and bleaches. Chlorine is also used to produce vinyl chloride, the starting material for the manufacture of polyvinyl chloride (PVC), and in water purification. Hydrochloric acid may be prepared by the direct reaction of chlorine and hydrogen gas or by the reaction of sodium chloride and sulfuric acid. It is used as a chlorinating agent for metals and organic compounds.

In certain regions of the world, there are salt deposits or brines that have been enriched by bromine. Commercially, bromine may be extracted by treating the brines with chlorine and removing it by steam.

$$2\ Br^- + Cl_2 \rightarrow Br_2 + 2Cl^-$$

Bromine is used in water disinfection; bleaching fibers and silk; and in the manufacture of medicinal bromine compounds and dyestuffs.

Titanium Dioxide

Titanium dioxide is by far the most important titanium compound. It can be purified by dissolving in sulfuric acid and precipitating the impurities. The solution is then hydrolyzed, washed, and **calcinated**. Alternatively,

calcine: to heat or roast to produce an oxide (e.g., CaO from calcite)

rutile: common name of TiO_2; also a common structural type for compounds with the general composition AB_2

tetrachloride: term that implies a molecule has four chlorine atoms present

ground **rutile** is chlorinated in the presence of carbon and the resulting titanium **tetrachloride** is burned in oxygen to produce the chloride.

Titanium dioxide is found in nature in three crystal forms: anastase, brookite, and rutile. Its extreme whiteness and brightness and its high index of refraction are responsible for its widespread use as a white pigment in paints, lacquers, paper, floor covering, plastics, rubbers, textiles, ceramics, and cosmetics. SEE ALSO ALUMINUM; CATALYSIS AND CATALYSTS; COPPER; FERTILIZER; HABER, FRITZ; IRON; STEEL.

Peter Rudolf Seidl
Carlos Eduardo da Silva Cortes

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Industrial Chemistry, Organic

Industrial organic chemicals are those 100 or so organic compounds produced in the United States in quantities ranging from millions of pounds to billions of pounds per year. Most of them are derived from petroleum (oil) or natural gas. From organic compounds present in petroleum and natural gas are obtained an amazing variety of products that includes many kinds of plastics, synthetic fibers, elastomers, drugs, surface coatings, solvents, detergents, insecticides, herbicides, explosives, gasoline additives, and countless specialty chemicals.

Historically, most organic chemicals had been obtained as by-products from the coking of coal, e.g., from coal oil. During the twentieth century, however, oil and natural gas became the dominant sources of the world's industrial organic chemicals. By 1950 at least half of U.S. industrial "organics" were being made from oil and gas, and by 2000 more than 90 percent of the organic chemical industry was based on petroleum. In fact, the term "petrochemicals" has almost become synonymous with industrial organic chemistry. Yet, less than 10 percent of the oil and gas we consume each year goes into making organic chemicals and the many billions of pounds of products derived from them. Oil and gas are mainly burned as fuel.

Most industrial organic chemistry falls into one of the following categories:

C-1 chemistry, based on synthesis gas (syn gas)
C-2 chemistry, based on ethylene (ethene)
C-3 chemistry, based on propylene (propene)
C-4 chemistry, based on butanes and butenes
BTX chemistry, based on benzene, toluene, and xylenes

Most organic compounds such as those manufactured at this petrochemical plant, are derived from petroleum.

Synthesis gas or "syn gas" is a variable mixture of CO and H_2 produced by the high temperature reaction of water with coal, oil, or natural gas (mainly natural gas in the United States).

$$CH_4 + H_2O \xrightarrow{\Delta} CO + 3H_2 \tag{1}$$

Alkenes or olefins (ethylene, propylene, butenes, and butadiene) are mainly produced via thermal steam cracking. Here, a petroleum fraction is mixed with water and heated briefly (for about 1 second) at 800 to 900°C (1,472–1,652°F), which breaks C–C bonds to yield shorter chains and splits out adjacent hydrogen atoms to form double bonds. The distribution of products obtained is given in Table 1.

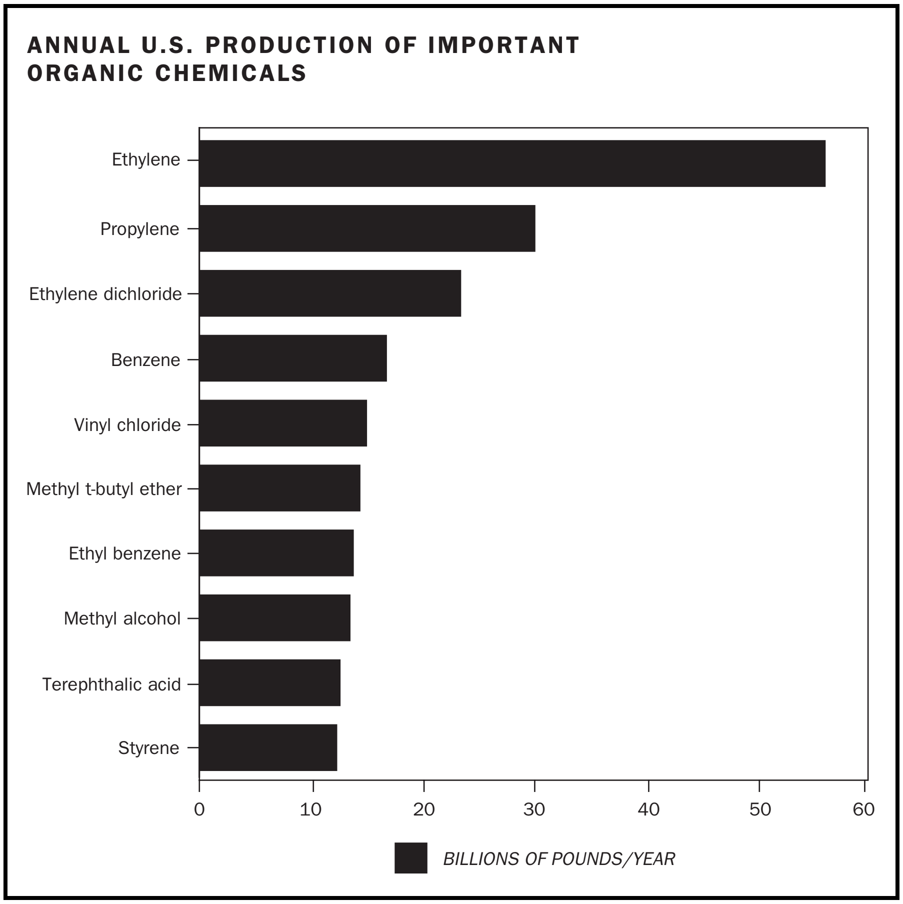
BTX (benzene, toluene, and xylenes), the simplest aromatics, are largely produced during catalytic reforming (platforming). In this process a naphtha rich in C_5 to C_9 alkanes is reacted at about 450°C (842°F) and 20 to 30 atm, over a Pt/SiO_2 catalyst, to yield reaction products that are about 60 percent aromatic hydrocarbons. Typically, the products might contain 3 percent benzene, 12 percent toluene, 18 percent xylenes, and 27 percent of C_9 alkylbenzenes (which have high octane numbers and are blended into gasoline). Because benzene is much more in demand for industrial purposes than toluene, the methyl group of toluene is ofte n removed by hydrogenation.

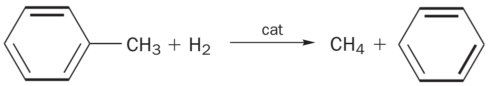
THERMAL STEAM CRACKING PRODUCTS (WEIGHT PERCENT)

Feed	$CH_4 + H_2$	Ethylene	Propylene	Butenes	Gasoline
Ethane	15	80	2	3	trace
Propane	27	42	20	6	5
Butane	25	40	16	10	10
Naphtha ($C_{5–9}$)	16	35	15	9	25

Table 1. Thermal steam cracking products (weight percent).

Figure 1. Annual U.S. production of important organic chemicals.





(2)

Production of Some Important Industrial Organic Chemicals

C-1 Chemistry (Syn Gas). Many important organic chemicals can be produced from the CO and H_2 mixture known as syn gas. They range from simple molecules, such as methanol, to high-grade synthetic crude oil.

The basic reaction for conversion of syn gas to mixtures of hydrocarbons is called the Fischer–Tropsch reaction, used in Germany during World War II to produce fuel mixtures for diesel and gasoline engines. Since the 1950s South Africa has also used this reaction, and currently there is much interest in using it to convert natural gas (methane) to more easily transported liquids.

Ammonia (NH_3), although it is not an organic compound, is often considered as part of C-1 chemistry, since it is produced via a reaction that uses hydrogen gas obtained from methane. It is made by the Haber process

$$N_2 + 3\ H_2 \overset{cat}{\rightleftharpoons} 2\ NH_3 \qquad (3)$$

Ammonia and its derivatives, HNO_3, NH_4NO_3, and $CO(NH_2)_2$, are key fertilizers and ingredients for explosives, and their production consumes nearly 5 percent of the world's natural gas.

Methanol (methyl alcohol, CH_3OH), an important solvent and precursor for many organic chemicals, is made by a process developed in the 1920s

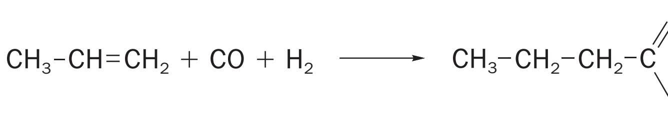
$$CO + 2\ H_2 \rightarrow CH_3OH \tag{4}$$

A major use of methanol is the production of acetic acid via carbonylation.

$$CH_3OH + CO \rightarrow CH_3CO_2H \tag{5}$$

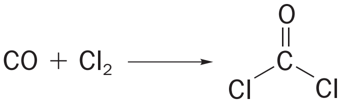
Acetic acid (ethanoic acid, CH_3CO_2H) was for many years made by the simple oxidation of ethanol, but the carbonylation of methanol has now largely displaced this process.

Butanal (butyraldehyde, $CH_3CH_2CH_2CHO$) is made via hydroformylation (the OXO reaction). Although this is a general reaction of syn gas with alkenes to produce aldehydes, the largest poundage reaction of this type (in industry, generating the greatest volume of product) is the reaction of propylene with syn gas to yield butanal.



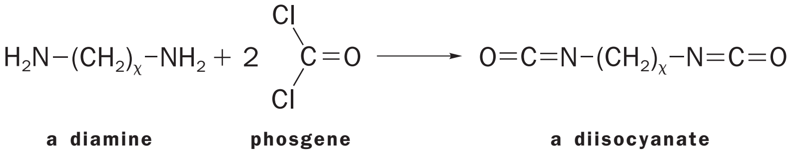
$$CH_3\text{-}CH{=}CH_2 + CO + H_2 \longrightarrow CH_3\text{-}CH_2\text{-}CH_2\text{-}\underset{\diagdown H}{\overset{O /\!/}{C}} \tag{6}$$

Phosgene (Cl_2CO) is made by reacting carbon monoxide from syn gas with chlorine (Cl_2) over activated charcoal at 250°C (482°F).



$$CO + Cl_2 \longrightarrow \underset{Cl \quad Cl}{\overset{\overset{O}{\|}}{C}} \tag{7}$$

Most phosgene is used in the manufacture of polyurethane plastics via diisocyanates.

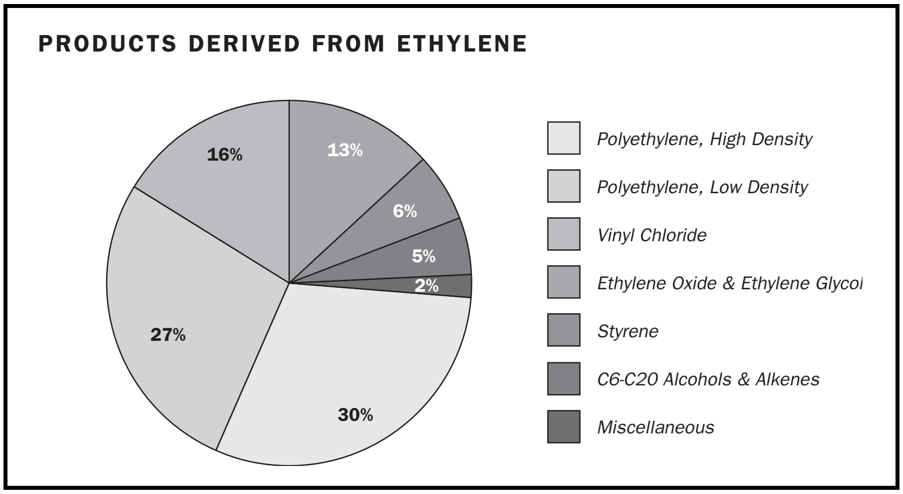


$$H_2N\text{-}(CH_2)_x\text{-}NH_2 + 2\ \underset{Cl}{\overset{Cl}{C}}{=}O \longrightarrow O{=}C{=}N\text{-}(CH_2)_x\text{-}N{=}C{=}O \tag{8}$$

C-2 Chemistry (Ethylene or Ethene). With annual worldwide capacity running over 100 million tons, ethylene is the world's largest volume organic compound. Most of it (almost 60%) is used to make polyethylene, the world's highest poundage plastic.

Polyethylene comes in two basic types: high density and low density. The original polymer was a highly flexible branched product, first prepared in 1932 by a process that required high temperatures and ultrahigh pressures. It is now known as low-density polyethylene (LDPE), to differentiate

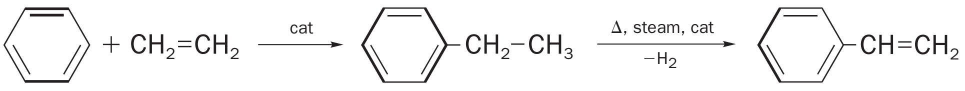
Figure 2. Products derived from ethylene.



it from a linear polymer discovered later and known as high-density polyethylene (HDPE). For many applications the original branched LDPE has now been replaced by linear low-density polyethylene (LLDPE). HDPE is more rigid and less translucent than LDPE or LLDPE, and it has a higher softening point and tensile strength. HDPE is used to make bottles, toys, kitchenware, and so on, whereas LDPE and LLDPE are mainly used for film used in packaging (e.g., plastic bags).

Vinyl chloride ($CH_2{=}CHCl$) is the second-largest-volume chemical made from ethylene. It is made by adding chlorine to ethylene and then thermally cracking out HCl from the intermediate, ethylene dichloride. The vinyl chloride is polymerized to polyvinyl chloride (PVC), also called vinyl, which is used to make pipe, floor covering, wire coating, house siding, imitation leather, and many other products.

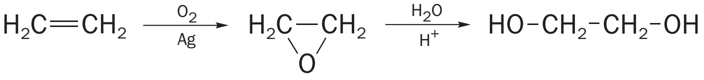
$$CH_2{=}CH_2 + Cl_2 \longrightarrow CH_2Cl{-}CH_2Cl \xrightarrow[-HCl]{\Delta} CH_2{=}CHCl \qquad (9)$$



(10)

Styrene (phenylethylene or vinyl benzene, $C_6H_5\text{-}CH{=}CH_2$) is made from ethylene by reaction with benzene to form ethylbenzene, followed by dehydrogenation. Over 50 percent of manufactured styrene is polymerized to polystyrene for toys, cups, containers, and foamed materials used for insulation and packing. The rest is used to make styrene copolymers, such as styrene-butadiene rubber (SBR).

Ethylene oxide is made by air oxidation of ethylene. Most ethylene oxide (about 60%) is converted to ethylene glycol via acid catalyzed hydrolysis.



$$H_2C{=}CH_2 \xrightarrow[Ag]{O_2} H_2C{-}CH_2\ (\text{O bridge}) \xrightarrow[H^+]{H_2O} HO{-}CH_2{-}CH_2{-}OH \qquad (11)$$

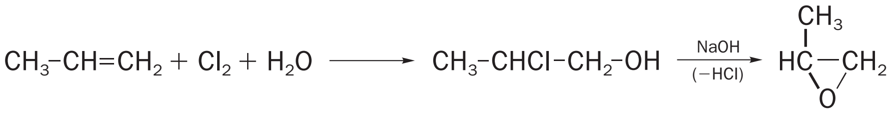
Ethylene glycol ($HOCH_2CH_2OH$) is a toxic dialcohol. Approximately half of what is produced is used as automobile coolant (antifreeze); most of the rest is used to make polyesters for products such as fabrics, rigid films, and bottles.

C-3 Chemistry (Propylene or Propene). Polypropylene manufacture is by far the largest use of propylene. In the late 1950s Karl Ziegler and Giulio Natta developed some special coordination catalysts (aluminum alkyls and titanium salts) that yield very strong addition polymers from propylene. Almost 25 percent of polypropylene is used to make injection-molded articles, such as automotive battery cases, steering wheels, outdoor chairs, toys, and luggage. Another 25 percent is used to make fibers for upholstery, carpets, and special sports clothing. Oligomers (dimers, trimers, and tetramers) of propylene, which are made by acid-catalyzed polymerization, form mixtures known as polygas, used as high-octane motor fuel.

Acrylonitrile ($CH_2{=}CH\text{-}CN$) was made from acetylene and HCN until the 1960s. Today it is made by direct ammoxidation of propylene. Its major use is in making polyacrylonitrile, which is mainly converted to fibers (Orlon). It is also copolymerized with butadiene and styrene to produce high impact plastics.

$$CH_2{=}CH{-}CH_3 + NH_3 + 1/2\ O_2 \xrightarrow{\text{cat}} CH_2{=}CH{-}CN + H_2O \qquad (12)$$

Propylene oxide is made via several methods. The classical one involves treating propylene with chlorine water to produce propylene chlorohydrin, and then using base to split out HCl. The primary use for propylene oxide is its oligomerization (to polypropylene glycols). These products combine with diisocyanates to produce high molecular weight polyurethane foams, which make very good padding for furniture and vehicle seats.



$$CH_3{-}CH{=}CH_2 + Cl_2 + H_2O \longrightarrow CH_3{-}CHCl{-}CH_2{-}OH \xrightarrow[(-HCl)]{NaOH} \text{propylene oxide} \qquad (13)$$

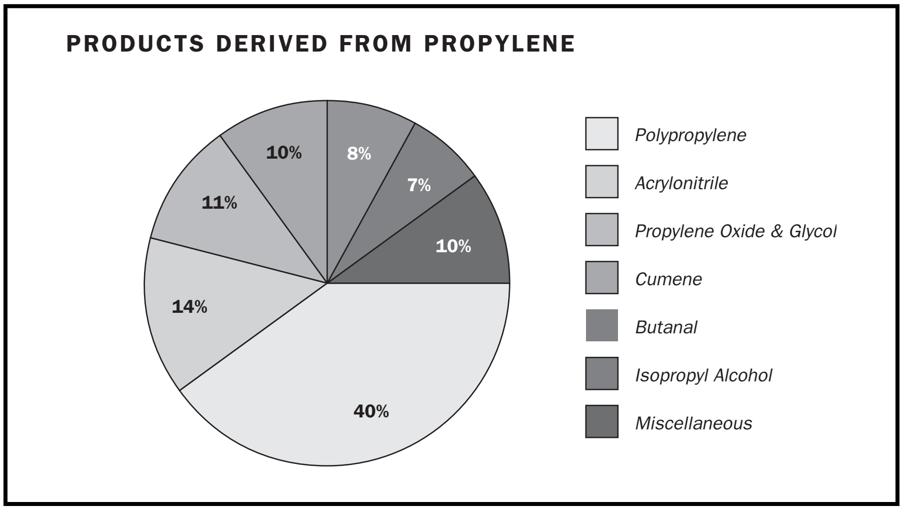
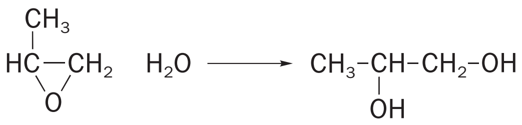


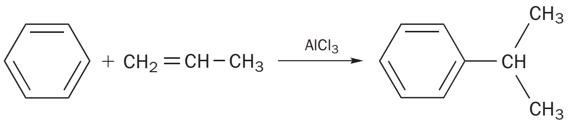
Figure 3. Products derived from propylene.

Manufacture of propylene glycol (CH_3-CHOH-CH_2OH) consumes about 30 percent of the propylene oxide produced. Like ethylene oxide, propylene oxide undergoes hydrolysis to yield the corresponding glycol. Propylene glycol is mainly used to make polyester resins, but it is also used in foods, pharmaceuticals, and cosmetics.



(14)

Cumene (isopropylbenzene) is made by Friedel–Crafts alkylation of benzene with propylene. Although cumene is a high-octane automotive fuel, almost all of the cumene produced is used to make phenol (C_6H_5OH) and acetone [$(CH_3)_2CO$]. Cumene is easily oxidized to the corresponding hydroperoxide, which is readily cleaved in dilute acid, to yield phenol and acetone.



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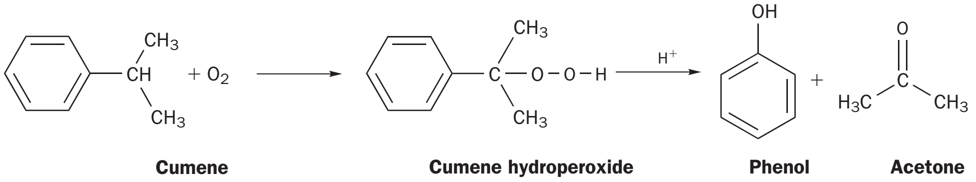
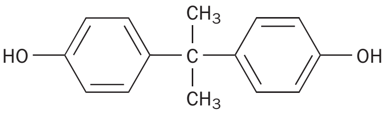


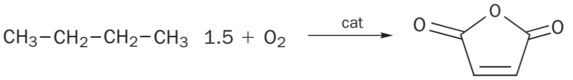
(16)

Phenol and acetone each have a number of important commercial uses, but they also have an important use together. Phenol and acetone can be condensed to form bisphenol A, which is used in the production of polycarbonate and epoxy resins.

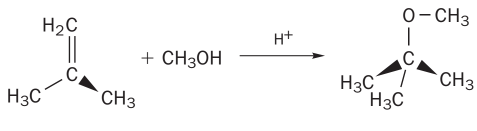


(17)

C-4 Chemistry (Butanes, Butylenes, Butadiene). Maleic anhydride is the main chemical made from *n*-butane. A complex catalyst is used for the oxidation reaction. The major uses for maleic anhydride are the making of unsaturated polyester resins (by reaction with glycol and phthalic anhydride) and tetrahydrofuran (by hydrogenation).



(18)



(19)

Methyl-tertiary-butyl ether (MTBE) is one of the leading chemicals currently being made from isobutylene (methyl propene) via the acid-catalyzed addition of methyl alcohol. MTBE has been added to gasoline as a required "oxygenate." However, it is under attack as a groundwater contaminant and is being phased out.

Polyisobutylenes are easily made via the acid-catalyzed polymerization of isobutylene. The low molecular weight polymers are used as additives for gasoline and lubricating oils, whereas higher molecular weight polymers are used as adhesives, sealants, caulks, and protective insulation.

Butyl rubber is made by polymerizing isobutylene with a small quantity of isoprene. Its main uses are in the making of truck tire inner tubes, inner coatings for tubeless tires, and automobile motor mounts.

Hexamethylenediamine [HMDA, $H_2H\text{-}(CH_2)_6\text{-}NH_2$] is the principal industrial chemical made from butadiene. HMDA is polymerized with adipic acid to make a kind of nylon.

Styrene-butadiene rubber (SBR) accounts for about 40 percent of the total consumption of butadiene. SBR is the material used to make most automobile tires. Other synthetic rubbers, such as polybutadiene and polychloroprene (neoprene), make up another 25 percent of the butadiene market.

ABS resin (acrylonitrile-butadiene-styrene) is a widely used terpolymer that accounts for about 8 percent of the butadiene market.

BTX Chemistry (Benzene, Toluene, Xylene). Styrene, discussed under C-2 chemistry, is one of the main industrial chemicals made from benzene. Most benzene is alkylated with ethylene to form ethylbenzene, which is dehydrogenated to styrene (see Equation 10).

Cumene, discussed under C-3 chemistry, is the second-largest-volume chemical product made from benzene. About 25 percent of manufactured benzene is alkylated with propylene to form cumene. Although its high octane number makes it desirable in gasoline, most cumene is oxidized to the

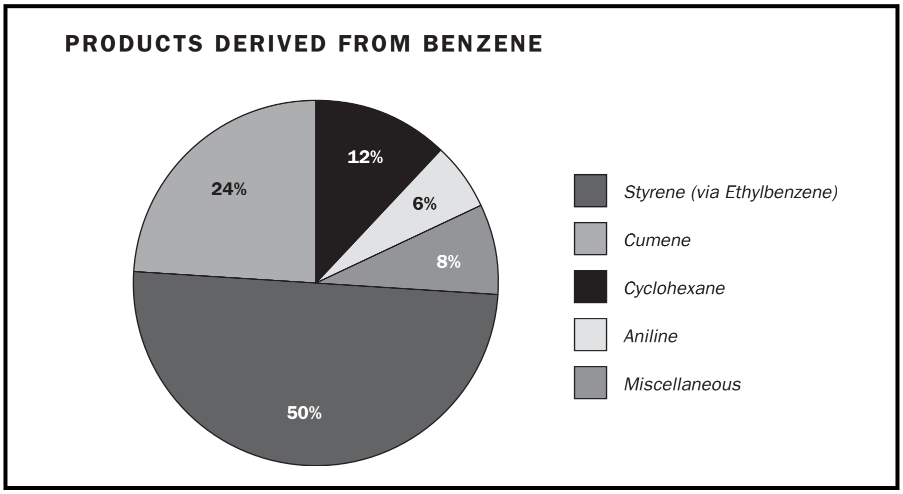
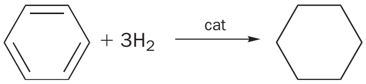


Figure 4. Products derived from benzene.

hydroperoxide, which is readily cleaved to phenol and acetone (see Equation 16).

Cyclohexane (C_6H_{12}) is made by hydrogenation of benzene (over Ni or Pt). Most of it is converted to adipic acid by oxidation, via the intermediaries cyclohexanol and cyclohexanone.

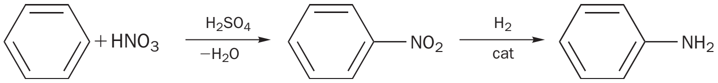


(20)

Adipic acid [$HO_2C(CH_2)_4CO_2H$], the main product of cyclohexane, is reacted with hexamethylene diamine to produce nylon-6,6, a very strong synthetic fiber. Most carpets are made of nylon, as are many silklike garments, some kinds of rope, and many injection-molded articles.

Caprolactam ($C_6H_{11}NO$) is also used to make nylon. Nylon-6 is made by direct polymerization of caprolactam, often obtained by reaction of cyclohexanone with hydroxylamine, followed by rearrangement of the oxime. Although nylon-6,6 is the dominant nylon produced in the United States, nylon-6 is the leading nylon product in Europe.

Aniline ($C_6H_5NH_2$) is made by nitration of benzene to nitrobenzene, followed by hydrogenation over a Cu/SiO_2 catalyst. The major use of aniline is in making diisocyanates, which are used in producing polyurethane materials (e.g., for home insulation).

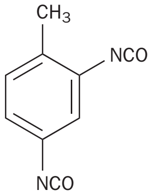


(21)

Alkylbenzene sulfonates ($R\text{-}C_6H_5\text{-}SO_3Na$) are important surfactant compounds used in laundry detergents. Alkylbenzenes (made by the Friedel–Crafts alkylation of benzene using linear olefin molecules that have about twelve carbon atoms) are sulfonated, and the sulfonic acids are then neutralized with NaOH.

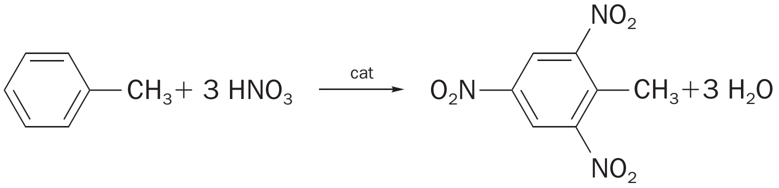
Benzene (C_6H_6), about 40 percent of it, is obtained from toluene by removal of the methyl group (hydrodealkylation, see Equation 2). Benzene production is the primary use of toluene (60%).

Toluene diisocyanate (TDI) is polymerized with diols to produce polyurethanes, which are used to make flexible foam for furniture cushions, mattresses, and carpet pads.

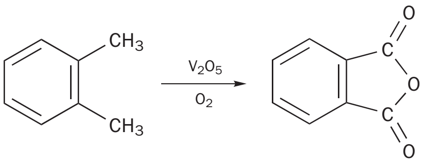


(22)

Trinitrotoluene (TNT) is made via a stepwise nitration of toluene in the 2, 4, and 6 positions. TNT is a high explosive and missile propellant.


(23)

Phthalic anhydride is made by air oxidation of ortho-xylene. About half of phthalic anhydride is used to make plasticizers, especially the compound dioctyl phthalate, for softening polyvinyl chloride plastic. Phthalic anhydride is also used to make unsaturated polyester resins and alkyd paints.


(24)

A Look Toward the Future

Industrial organic chemistry was once based on coal oil. Today it is based mainly on petroleum and natural gas. However, both of these resources are limited in supply and may not last through the twenty-first century.

Because coal reserves are much greater than those of oil and natural gas, perhaps syn gas from coal will become a major source of organic chemicals. However, coal is also a finite raw material, and therefore there is much interest in developing methods for converting renewable resources, such as plants, into industrial organic chemicals. Recently a major chemical company announced its plan to build a small plant for the production of 1,3-propanediol from sugar. This same company has set a goal of producing 25 percent of its feedstocks from renewable resources by 2010. Although this might seem an unrealistic goal, it does indicate current thinking within the chemical industry. SEE ALSO EXPLOSIONS; FERTILIZER; FOSSIL FUELS; ORGANIC CHEMISTRY; PETROLEUM.

Kenneth E. Kolb
Kurt W. Field

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Inert Gases ***See Noble Gases.***

Inhibitors

catalysis: reaction induced by a substance that retains its own chemical identity

An inhibitor is any agent that interferes with the activity of an enzyme. Inhibitors may affect the binding of enzyme to substrate, or **catalysis** (via modification of the enzyme's active site), or both. Researchers use enzyme inhibitors to define metabolic pathways and to understand enzyme reaction mechanisms. Many drugs are designed as inhibitors of target enzymes. Inhibition is also a natural phenomenon. Cells regulate metabolic pathways by specific inhibition of key enzymes.

Enzyme inhibitors are divided into two classes, irreversible and reversible. Irreversible inhibition implies destruction or permanent modification of chemical groups in the enzyme. In contrast, reversible inhibitors form a complex with the enzyme that can dissociate and release the active enzyme. An enzyme E can bind either to substrate S, to form an ES complex (which can go on to products) or to inhibitor I, to form the complex EI.

There are two major types of reversible inhibitors, competitive and noncompetitive. Competitive inhibition can be reversed by increasing substrate concentration, whereas noncompetitive inhibition cannot be reversed by adding more substrate.

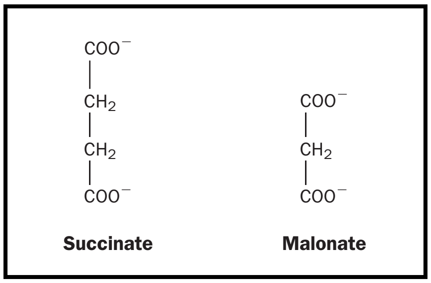
intermediate: molecule, often short-lived, that occurs while a chemical reaction progresses but is not present when the reaction is complete

The classic example of competitive inhibition is inhibition of succinate dehydrogenase, an enzyme, by the compound malonate. Hans Krebs first elucidated the details of the citric acid cycle by adding malonate to minced pigeon muscle tissue and observing which **intermediates** accumulated after incubation of the mixture with various substrates. The structure of malonate is very similar to that of succinate (see Figure 1). The enzyme will bind malonate but cannot act further on it. That is, the enzyme and inhibitor form a nonproductive complex. We call this competitive inhibition, as succinate and malonate appear to compete for the same site on the enzyme. With competitive inhibition, the percent of inhibition is a function of the ratio between inhibitor and substrate, not the absolute concentration of inhibitor.

Noncompetitive inhibition is not reversed by adding more substrate. The inhibitor binds at a site on the enzyme other than the substrate binding site. The inhibitor can bind to either free enzyme, forming EI, or to the ES complex, forming EIS. Both EI and EIS are nonproductive.

synthesis: combination of starting materials to form a desired product

Irreversible inhibitors are those that permanently disable the enzyme. The complex EI or EIS cannot dissociate, so that these are dead-end complexes. When an irreversible inhibitor is added to the enzyme-containing solution, inhibition may not be complete immediately, but increases gradually with time, as more and more enzyme molecules are modified.

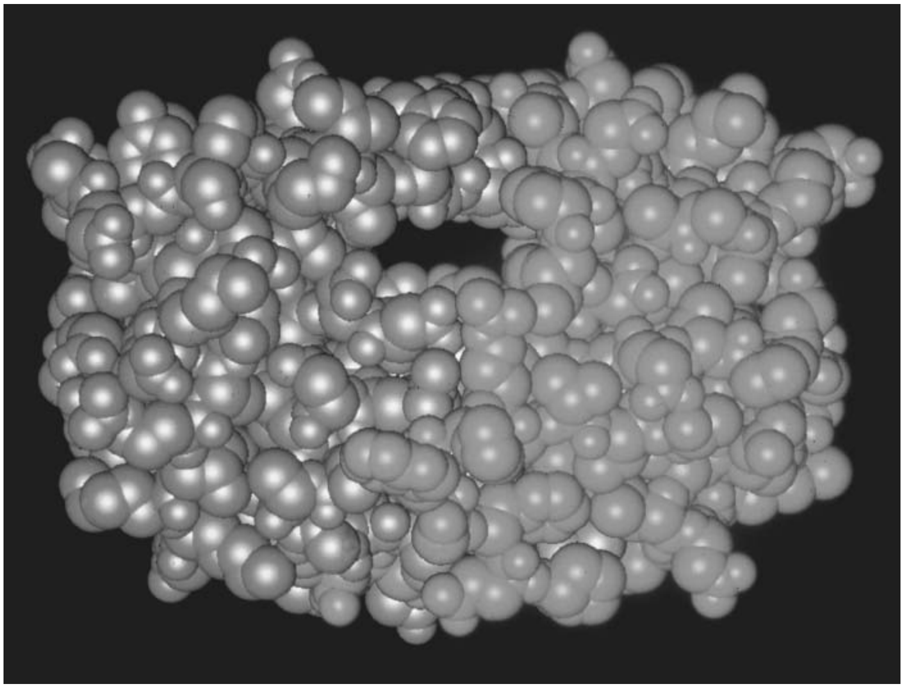


Firuge 1. Structures of succinate and malonate.

Uses of Inhibitors

Among the irreversible inhibitors are organophosphorus compounds, which inhibit the enzyme acetylcholinesterase and similar enzymes. Organophosphorous compounds include nerve gases (such as sarin), that work on the human nervous system, and insecticides like malathion.

Many therapeutic drugs are enzyme inhibitors. Important examples are penicillin, which inhibits an enzyme necessary for bacterial cell wall **syn-**



A computer image of the structure of a protease inhibitor.

thesis, and aspirin, an inhibitor of the synthesis of molecules that **mediate** pain and swelling. More recent examples are drugs used in the treatment of human immunodeficiency virus (HIV) and acquired immunodeficiency syndrome (AIDS) that prevent maturation of the virus by inhibiting the HIV protease, and drugs that lower cholesterol by inhibiting a key step in cholesterol **biosynthesis**. SEE ALSO ACTIVE SITE; ENZYMES; KREBS, HANS ADOLF; NEUROCHEMISTRY.

mediate: to act as an intermediary agent

biosynthesis: formation of a chemical substance by a living organism

Adele J. Wolfson

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Inorganic Chemistry

The scope and boundaries of inorganic chemistry were shaped by the earlier field of organic chemistry in the mid-eighteenth and later centuries. Back in these earlier days of chemistry, all chemicals not classified as organic, in other words all chemicals, including minerals and **alloys**, that do not have an origin in living organisms, were placed in a very large category of "inorganic" substances. Many of the first chemists, therefore, used the describable differences between living and nonliving things to help delineate the boundaries of these two areas. Two common distinctions were that, first, organic compounds contained a unique "vital force" that arose from

alloy: mixture of two or more elements, at least one of which is a metal

their biological origin and second, as a result, organic compounds could not also be synthesized or reproduced in the laboratory. Of course, both of these distinctions were later disproved, but they clearly helped form the divisions by which chemists have labeled themselves. Today a factor commonly used to distinguish between inorganic and organic substances is the presence of the element carbon. Inorganic chemistry, a vast field of study, is usually defined as the study of any compound that does not contain the element carbon, especially as it occurs in chemically bonded chains and rings that have additional chemical bonds to hydrogen atoms.

It should be noted that as chemists move increasingly toward interdisciplinary work, even this arbitrary distinction cannot adequately describe certain chemical compounds. For example, the solid material Sc_3C_4 (three parts scandium, four parts carbon) has ethane- and propanelike organic fragments (without their hydrogen atoms) that are embedded in a solid matrix of inorganic scandium ions. In another broadly diverse field called organometallic chemistry, chains of organic-like carbon atoms form chemical bonds with inorganic **metal** ions such as zirconium, molybdenum, and nickel. Thus chemistry is becoming increasingly integrated and continuous, with no sharp boundary lines, as chemists realize that closely related ideas, such as chemical bonding and acid/base classifications, can be broadly applied to both complex organic substances as well as to inorganic compounds. In a recent example, an expansion of the concept of aromaticity, normally applied strictly to organic molecules such as benzene (C_6H_6), was found by Lai-Sheng Wang and colleagues to explain also the enhanced stability of inorganic, metal-bonded Al_4^{2-} clusters.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Mono- and Polyatomic Ions

Back in the late 1800s many chemists were hard at work categorizing the known elements according to their bond valences and acid/base characteristics. However, the elements are usually not found free and pure in nature. Instead, they are usually found and worked with in the form of ions and complexes that also contain other elements. When elements combine with each other, ions tend to form, as electrons are transferred to the most **electronegative** elements and partially shared to form chemical bonds. An element that has gained electrons, such as O^{2-}, is called an **anion**, and one that has lost electrons, such as Al^{3+}, is called a cation. In an **aqueous solution**, these ions will interact electrostatically with the solvent, as well as with each other. For example, ions will interact with the partially charged negative and positive regions of H_2O, the most common solvent on Earth. Cations will be surrounded more closely by the oxygen atoms, the more negative region of the H_2O molecules, while an anion will be more closely surrounded by the hydrogen atoms, or the more positive region of the H_2O molecules. The product of this interaction is called a hydrated ion, shown in the following equation, and it is one of the simplest chemical species in solution (e.g., Na^+, K^+, F^-, Cl^-):

electronegative: capable of attracting electrons

anion: negatively charged chemical unit, like Cl^-, CO_3^{2-}, or NO_3^-

aqueous solution: homogenous mixture in which water is the solvent (primary component)

$$M^{n+/-} + H_2O \rightarrow M(H_2O)_x^{n+/-} \ (x \sim 4-6)$$

As the charges of the ions increase across the Periodic Table such as from Na^+ to Sc^{3+} to V^{5+}, or from F^- to O^{2-} to N^{3-}, the bond formed between the ions and the water molecules grows strong enough to weaken and ultimately break the O–H bond. This kind of reaction with water is called hydrolysis. Products of this reaction with cations will yield hydroxides and oxides, such as Sc_2O_3 and V_2O_5, and the solutions will become acidic due to the released hydrogen ions. On the other hand, the reaction with highly charged anions will tend to result in hydrides, NH_3, and the solution will become basic due to the released hydroxide ions. Using this simple picture, which is based on the **electrostatic interaction** of oppositely charged ions, the principle forms of almost all the elements in nature can be qualitatively predicted (see Figure 1).

electrostatic interaction: force that arises between electrically charged particles or regions of particles

"Polyoxocations" and "-anions" are the names given to ions that exist in solution bonded to multiple oxygen atoms, such as ReO_4^{-} and SO_4^{2-}, and occurs only with the highest charged ions, such as Re^{7+} and S^{6+}. These high formal **oxidation** states prevent a large charge buildup on the ion and therefore dramatically lower the basicity of the anion and further association with H^+. The sizes of many polyoxoanions may range up to the nanometer scale, with extremely large clusters, more than 100 atoms, existing in molybdenum-containing solutions. Many other types of complex ions exist in different, and less common, solvents. Among the many possible examples are fluorides, TiF_6^{2-} or SiF_6^{2-}; cyanides, [C d(CN)$_4$]$^{2-}$; chlorides, $PtCl_6^{2-}$; and some organic-bonded ions, $ZrCl_2(Cp)_2$ (Cp = C_5H_5; cyclopentadienyl). To understand these compounds, it is first necessary to expand our acid/base definitions.

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

Complex Transition-Metal Ions and Compounds

Many reactions and properties that are characteristic of typical acids (H^+ donors) and bases (OH^- donors) occur in chemical compounds that lack any hydrogen or hydroxide ions, such as in nonaqueous solvents. For example, the nitrogen group on a pyridine molecule can donate an electron pair to acidic **metal cations**, such as Zn^{2+} or Cu^{2+}, as well as to H^+-containing acids such as HCl. The Zn–N, Cu–N or H–N bond formed neutralizes the acidic character of cations (H^+ and M^{n+}, discussed above), and thus the pyridine molecule functions much like a base. An expanded definition of bases is necessary to include all chemical species that can donate a pair of electrons. These are commonly called Lewis bases, after Gilbert N. Lewis, who was among the first to note this similarity in solid salts such as $[C_5H_5NH]^+Cl^-$ or $[Cd(C_5H_5N)_2Cl_2]$. Conversely, any chemical species that can accept a pair of electrons is called a Lewis acid.

metal cation: positively charged ion resulting from the loss of one or more valence electrons

The bond formed between Lewis acids and bases is termed a **coordinate covalent bond**, and the acid/base pair is called a coordination compound. In coordination compounds, the **ligands** directly bonded to the central metal atom are included within the brackets, as in $[Co(NH_3)_6]^{3+}$, while the nonbonded ions that balance the cation charge, the counter-ions, are located outside the brackets, as in Cl^- for $[Co(NH_3)_6]Cl_3$. The subscripts indicate that six ammonia molecules form coordinate **covalent bonds** to Co^{3+}. In other words, the coordination number is six. In the compound $Sn(C_5H_5N)Cl_2$, tin is bonded to one pyridine molecule and to two chloride anions, for a total coordination number of three. The charge on Sn can be calculated by knowing the charges on the ligand species, so that if each pyridine is uncharged and the charge on each Cl is 1–, the net positive charge on Sn must be 2+ to give a neutral molecule. There are hundreds if not

coordinate covalent bond: covalent bond in which both of the shared electrons originate on only one of the bonding atoms

ligand: molecule or ion capable of donating one or more electron pairs to a Lewis acid

covalent bond: bond formed between two atoms that mutually share a pair of electrons

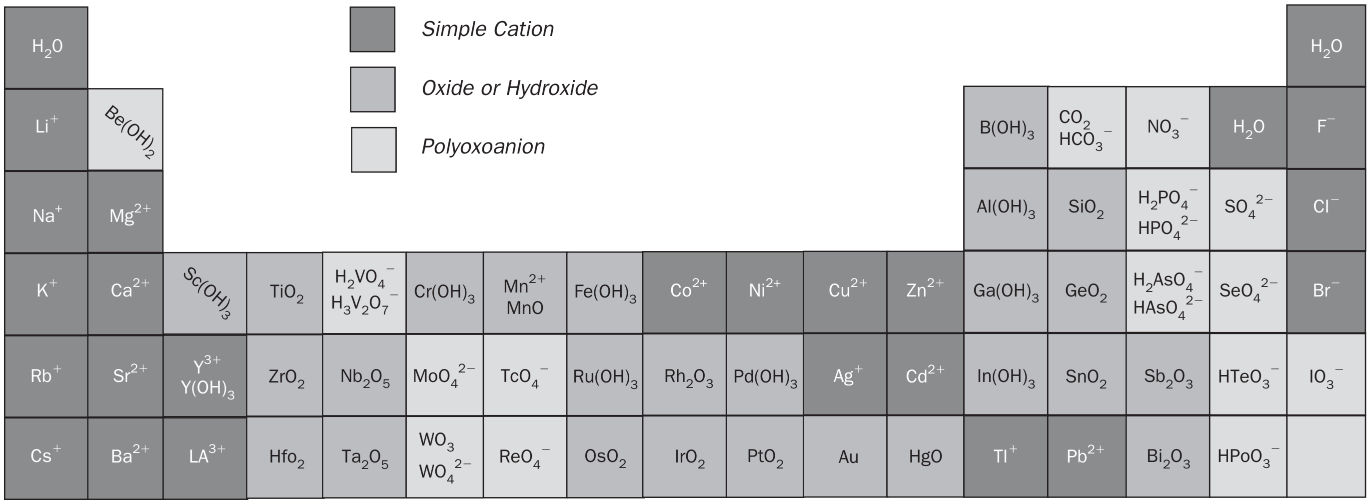

Figure 1. Main form of the ions at a pH = 5.5–7 in a moderately aerated solution. (Redrawn from Wulfsberg, Gary. *Inorganic Chemistry,* p. 127.)

thousands of possible ligands that can attach to the more than forty metal cations, so an almost unlimited number of coordination compounds may be formed. At this point, it is very useful to describe the principles that determine which metal-ligand combinations are preferred.

HSAB Classification

The question of which metal ions prefer to form complex ions with which ligands was answered partly by Ralph G. Pearson during a critical review of hundreds of naturally occurring minerals and synthetic coordination compounds. The general rule of thumb is that hard (Lewis) acids tend to combine with hard (Lewis) bases, and soft acids with soft bases. This is known as the hard-soft acid/base (HSAB) principle. The closer on the Periodic Table that a metal ion is to gold, the softest element, the softer that metal ion is, such as the soft Ag^+ or Cd^{2+} ions. The farther from gold, the harder the metal cation, such as the hard Ca^{2+} ion. For inorganic anions, the hardest is the fluoride anion. The farther away on the Periodic Table, the softer the anion, such as the soft I^- anion. For complex anions, such as $PO_4{}^{3-}$, $SO_4{}^{2-}$, or $CO_3{}^{2-}$, the electron donor groups are the oxygen atoms, and thus these are hard anions.

This concept can explain many of the toxicological effects and the biochemistry of ions and ligands in the body. For example, soft metal cations that are soluble in the digestive tract, such as CH_3Hg^+ and certain Pb salts, are extremely poisonous, as they deactivate key biological enzymes by disrupting their S–H (soft element) bonds. However, many hard metal ions, such as K^+ or Na^+, are essential elements in the body. Examples of toxic soft bases include carbon monoxide, :CO, and the cyanide ion, $:CN^-$, which compete with O_2 for binding to Fe^{2+} in hemoglobin. Representative examples of this concept in major mineral sources include limestone, $CaCO_3$ (hard–hard), fluorite, CaF_2 (hard–hard), sphalerite, ZnS (soft–soft), and argentite, Ag_2S (soft–soft).

Ligand Types

There are further properties of ligands beyond their HSAB characteristics that determine their bonding preferences to metal ions. The simplest ligands, such as pyridine or ammonia, have only a single lone pair of electrons to donate and are called **monodentate** ligands. However, if there are multiple unshared electron pairs, as in pyrazine or thiocyanate, these can be donated to two different metal centers to form a bridge. Alternatively, if these multiple lone pairs are situated at a distance of four to five atoms from each other, the ligand can then "wrap" itself around and donate multiple electron pairs to the same metal cation. These types of ligands are known as chelating ligands, such as in EDTA (ethylenediaminetetraacetate), which has six binding sites. Competition for binding to a metal cation will favor the chelating ligands rather than the monodentate ligands, due to the increased entropy (increased number of particles) of the products:

monodentate: capable of donating one electron pair; literally, one-toothed

$$\mathrm{Co(NH_3)_6}^{3+} + \mathrm{EDTA}^{4-} \rightarrow \mathrm{Co(EDTA)}^{1-} + 6\mathrm{NH_3}$$

In both the reactants and products, cobalt retains a coordination number of six, but the number of individual chemical species increases from two to seven. In another type of ligand, a macrocycle, multiple electron donation sites are held in a rigid conformation for metal binding. This type is best illustrated by many biologically related ligands, such as **chlorophyll**, heme, and **vitamin** B_{12}, which are all tetradentate macrocyclic ligands with nitrogen atom electron donors. These are used in living organisms as moving platforms with photo- and redox-active metal centers, and also as transports for certain ligands such as O_2. Competition for binding to a metal ion between a chelating and macrocyclic ligand will favor the latter, due to entropy gains again, as the more flexible chelating ligand has greater degrees of freedom when unbound. These ligands are highly favorable architectures that transport key ions around the body.

chlorophyll: active molecules in plants undergoing photosynthesis

vitamins: organic molecules needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

Additional Areas

There is a great and never-ending story to the many types of complex ions, ligands, compounds, and bonding types that are known and rapidly being discovered by inorganic chemists. Some of these areas include organometallics, metal–metal bonded molecules and solids, multiply bonded main group elements, and intermetallics. SEE ALSO ALKALI METALS; ALKALINE EARTH METALS; CHALCOGENS; HALOGENS; INDUSTRIAL CHEMISTRY, INORGANIC; LEWIS, GILBERT N.; SEMICONDUCTORS.

Paul A. Maggard Jr.

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Insecticides

Insecticides are natural or synthetic chemicals used to manage insects pests; they are important for disease control and providing food and fiber for a growing world population. Insect control with chemicals began about 2,000 years ago with the use of natural products, whereas the age of synthetic insecticides began with the introduction of dichlorodiphenyl trichloroethane (DDT) in the 1940s. Here the major classes of insecticides are covered, and important example compounds provided. The discussion is organized topically by mode of action/target tissue. In addition to synthetic materials, natural products are addressed because their use is increasing in "organic farming." This entry then explores the development of plants or viruses genetically engineered to produce insect-selective **toxins**. The harmful effects of insecticides on humans will also be discussed, as well as some nonchemical control techniques.

toxin: poisonous substance produced during bacterial growth

Compounds Affecting Nerves

The pyrethroids are composed of natural pyrethrins, which are isolated from chrysanthemum flowers, as well as newer synthetic materials. Older pyrethroids (e.g., pyrethrins and tetramethrin) **degrade** too rapidly in the environment to be used in agriculture. They are used in buildings, and because of their general safety, they are even applied to humans to control lice. Newer pyrethroids have greater chemical stability (e.g., permethrin and deltamethrin), which allows their use on many types of field crops. Another important use of permethrin is application to mosquito netting. Intoxication by pyrethroids develops rapidly (in 1 to 2 minutes), and involves a rapid loss of normal posture and movement called "knockdown." Pyrethroids affect nerve impulse generation throughout the entire nervous system. Multiple nerve impulses occur when only a single one was expected, and there is an increased release of chemical neurotransmitters as well. These actions result in convulsions, prostration, and death.

degrade: to decompose or reduce to complexity of a chemical

Sabadilla, an extract from the seeds of a tropical lily, is used in home gardens and organic farming operations. It degrades rapidly in the environment, and causes signs of intoxication, and has a mode of action similar to that of pyrethroids. Sabadilla extract has low toxicity to mammals.

The tobacco compound nicotine has been used as an insecticide for over 200 years. It is especially effective against sucking insects, such as aphids, and has excellent **contact activity**. Related compounds are neonicotinoids (e.g., imidacloprid), which have similar insecticidal activity, but are less toxic to mammals. Nicotine and imidacloprid mimic the action of **acetylcholine**, which is the major **excitatory neurotransmitter** in an insect's central nervous system. The action of acetylcholine is stopped by the enzyme acetylcholinesterase, which rapidly breaks down acetylcholine. Nicotine and imidacloprid are also neuroexcitatory, but do so persistently, since they are not affected by acetylcholinesterase. Overstimulation of the nervous system often leads to convulsions, paralysis, and death.

contact activity: process involving the touching of different surfaces

acetylcholine: neurotransmitter with the chemical formula $C_7H_{17}NO_3$; it assists in communication between nerve cells in the brain and central nervous system

excitatory neurotransmitter: molecule that stimulates postsynaptic neurons to transmit impulses

The organophosphorus (OP) and carbamate insecticides are used to control a wide variety of insect pests. The acute toxicity of the OPs and carbamates varies, and many of them have high **mammalian toxicity**. These compounds react chemically with the active site of acetylcholinesterase, producing a blocked enzyme that cannot degrade acetylcholine. The concentration of acetylcholine then builds up and hyperexcitation occurs. The signs of intoxication include restlessness, tremors, convulsions, and paralysis. Blockage of acetylcholinesterase by OPs is persistent, and recovery of the enzyme takes many hours or even days. The mode of action of the carba-

mammalian toxicity: poisonous effect on humans and other mammals

Tent caterpillars on a cocoon, Glacier North Park, Montana. Insecticides are used to eradicate populations of such species where they are not desirable.

mates is similar, except that enzyme blockage is less stable and recovers in a matter of minutes. Among insects, carbamates are particularly toxic to hymenoptera, such as honeybees.

Organochlorines represent one of the oldest groups of synthetic insecticides, with only biodegradable materials such as lindane and endosulfan still used in pest control. High mammalian toxicity was common with organochlorines, but a newer compound, fipronil, has improved selective toxicity toward a variety of insect pests. These insecticides cause hyperexcitability and convulsions by blocking the **inhibitory** neurotransmitter γ-aminobutyric acid (GABA). Normally, GABA has a dampening effect that maintains normal nerve activity. Blocking the effects of GABA removes inhibition, leading to hyperexcitation of the nervous system and convulsions.

inhibitory: relating to the prevention of an action that would normally occur

Deet is an important insect repellant. This compound is applied to skin or clothing, and repels biting flies (e.g., blackflies and mosquitoes). Deet acts on the sensory nerves, causing insects to avoid treated surfaces.

Compounds Affecting Muscles

Ryania consists of the powdered stem of the tropical shrub, *Ryania speciosa*. The extract contains ryanodine and related compounds, and has a low toxicity to mammals. The powder is used as a stomach poison on vegetables and fruit. Ryanodine induces paralysis in insects by direct action on the muscles, resulting in sustained **contraction** and paralysis.

contraction: the shortening and thickening of a functioning muscle or muscle fiber

Avermectins are a group of closely related compounds isolated from the fungus *Streptomyces avermitilis* that are used to control the parasites of humans and animals, as well as arthropod pests in crops. They have fairly high mammalian toxicity, but their movement into treated leaves, oral activity against insect pests, and rapid breakdown in sunlight are all favorable properties. In insects and worms poisoned by avermectin, inactivity and flaccid paralysis occur from its relaxing effect on muscles.

Compounds Disrupting Energy Metabolism

These compounds vary, from the natural product rotenone (from *Derris* or *Lonchocarpus* root, used to control vegetable and fruit insects) to the synthetics sulfluramid and hydramethylnon (used to control mites and cockroaches). Interestingly, the highest acute toxicity to mammals is caused by the natural product rotenone. These compounds affect the production of **adenosine triphosphate (ATP)**, the energy storage molecule of the cell that is produced by mitochondria, the "powerhouse" of the cell. The disruption of energy metabolism and the subsequent loss of ATP result in a slowly developing toxicity, and the effects of all these compounds include inactivity, paralysis, and death.

adenosine triphosphate (ATP): molecule formed by the condensation of adenine, ribose, and triphosphoric acid, HOP(O)OH–O–(O)OH–OP(O)OH–OH; it is a key compound in the mediation of energy in both plants and animals

Insect Growth Regulators

Insects exposed to diflubenzuron and related compounds are unable to form normal cuticle (skin) because their ability to synthesize it is lost. Thus, the cuticle becomes thin and brittle, and is unable to support the insect or to withstand molting, a process requiring the shedding of the old cuticle, as in metamorphosis. Diflubenzuron and other chitin **synthesis** inhibitors have extremely low mammalian toxicity and are used against termites.

synthesis: combination of starting materials to form a desired product

Methoprene and fenoxycarb mimic the action of insect juvenile hormone in molting and reproduction, and have low toxicity to mammals. Exposure at molting produces deformed insects having mixed larval/pupal or larval/adult morphologies, and they disrupt reproductive physiology in adults to effectively serve as a method of birth control.

Tebufenozide acts by mimicking the effects of the insect hormone ecdysone, which along with juvenile hormone, controls the initiation of a molt. Exposure to tebufenozide induces a premature molt that traps the insect in its old cuticle. This compound is especially effective against caterpillars.

Toxins from *Bacillus thuringiensis*

The bacterium *Bacillus thuringiensis* forms an internal crystal that contains a number of insecticidal protein toxins. When eaten by the insect, the crystal dissolves in the midgut, the **toxin** mixture is released, and the proteins are **cleaved** into active forms. The toxins bind specifically to midgut cells and assemble a pore that leads to disintegration of the cells, gut paralysis, and death. *B. thuringiensis* strains have toxins specific for caterpillars, beetles, or flies. They have little or no effect on mammals.

toxin: poisonous substance produced during bacterial growth

cleave: split

Human Toxicity of Insecticides

In mammals DDT and related organochlorines have effects on the endocrine system, including the disruption of thyroid hormone synthesis and mimicking of the effects of **estrogen**. Liver cancer has also been observed in mice exposed to these substances, and there has been one claimed association between exposure to DDT and breast cancer. Epidemiological studies show a consistent connection between exposure to pesticides and the occurrence of Parkinson's disease in rural populations. A well-documented effect of some OPs is organophosphorus-induced delayed **neuropathy**, a slowly developing degeneration of the leg nerves that results in irreversible limping. A spe-

estrogen: female sex hormone

neuropathy: degenerative state of the nerves or nervous system cific hazard of pyrethroids is paresthesia, a tingling or burning sensation in exposed skin.

Ladybugs are natural predators of aphids, mealy bugs, and leaf hoppers and may be introduced into a garden environment as a nonchemical pest-control method.

Nonchemical Control Methods

There is considerable interest in developing genetically enhanced, insect-specific viruses or crop plants that would replace conventional chemical insecticides. Corn, cotton, and potatoes have been engineered to express *B. thuringiensis* toxins to control chewing insects. Although this approach has worked effectively for controlling some pests, others not targeted by the *B. thuringiensis* toxin must be controlled by other means.

Sex pheromones, chemicals that attract one sex of an insect to the other, also have uses in pest control. They are often utilized with traps to monitor the number of pest insects in an area, and when applied in the field at higher levels, they can disrupt reproduction or egg laying.

Biological control involves the introduction of predators and parasitoids to attack pests. The extent of control using this technique varies and can be quite good in some cases, but unforeseen ecological impacts occur when imported species attack nontarget organisms.

Chemical insecticides remain an important tool for managing insect pests of humans, animals, and food and fiber crops. Compounds that are persistent in the environment are no longer used, and the amounts sprayed have dropped from kilograms per acre to grams per acre of active ingredient. Future compounds and technologies will seek to maintain high levels of effectiveness with a reduced impact on the environment and human health. SEE ALSO Agricultural Chemistry; Herbicides; Pesticides.

Jeffrey R. Bloomquist

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Insect Repellents ***See Insecticides.***

Insulin

Insulin is a small peptide (protein) consisting of fifty-one amino acids synthesized and stored within the pancreas, an organ situated behind the stomach. The protein itself consists of two chains, denoted A and B, linked by disulfide (sulfur-sulfur) bridges between cysteine residues (see Figure 1).

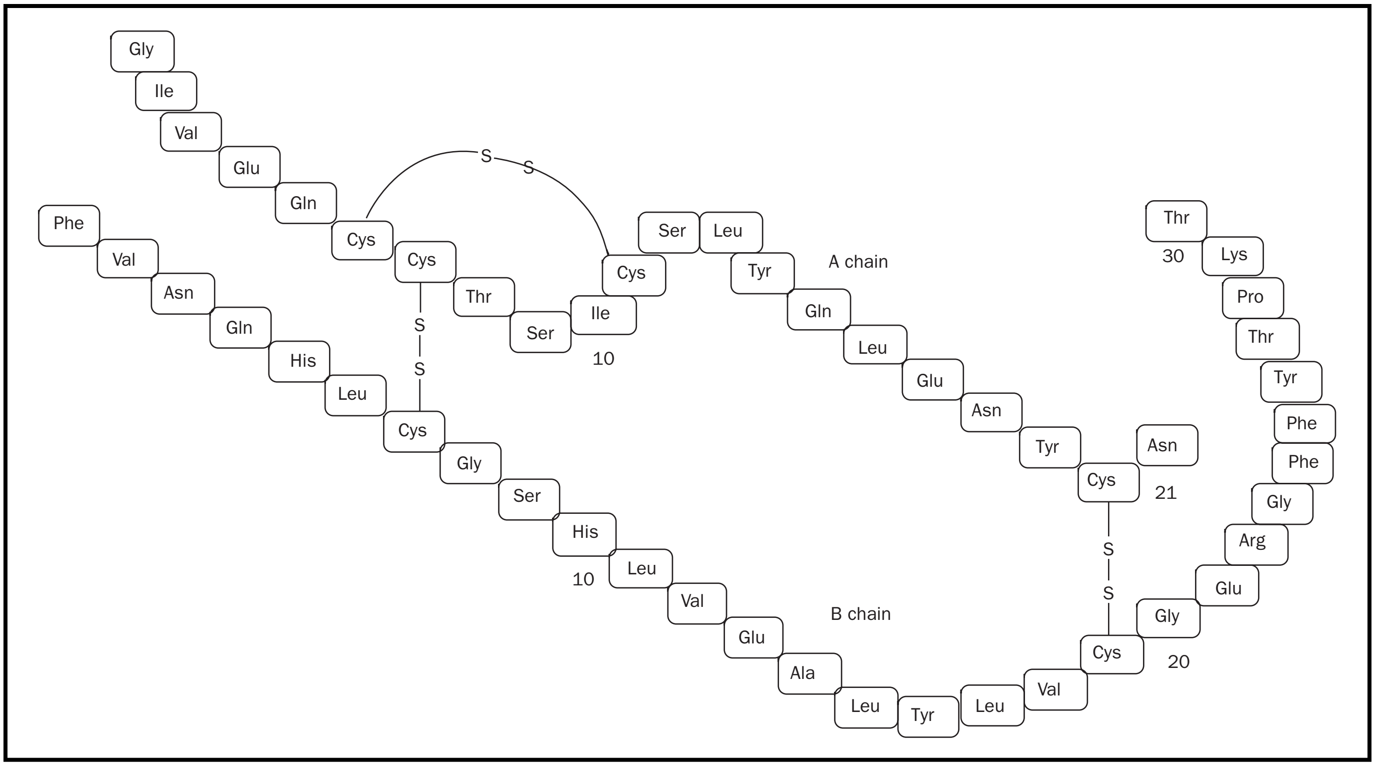

Figure 1. Structure of human insulin.

Insulin is a hormone, a chemical transported in the blood that controls and regulates the activity of certain cells or organs in the body. When blood sugar levels rise following a meal, the pancreas is stimulated to release insulin into the bloodstream. In order for tissues to absorb **glucose** from the blood, they must first bind insulin. Glucose **metabolism** is necessary for cell growth and energy needs associated with cell function. When insulin binds to **receptors** on cell membranes, glucose transporter proteins are released from within the cell to the surface of the cell membrane. Once on the exterior surface of cells, glucose transporters can carry sugar from the blood into the tissue where it is metabolized. Without insulin, cells cannot absorb glucose and effectively starve.

A deficiency in insulin production results in a condition called diabetes mellitus. Approximately 6.2 percent of the population in the United States is affected with diabetes. Type 1 diabetics account for 10 percent of those individuals suffering from diabetes mellitus. It is also known as juvenile diabetes and generally develops in young people, typically between the ages of ten and fifteen years, as a result of an autoimmune disorder. Why the body's immune system turns on itself, attacking and destroying beta cells, the pancreatic cells in which insulin is synthesized, is not clear. The unfortunate consequence is insulin deficiency.

The majority of individuals afflicted with diabetes mellitus suffer from type 2 diabetes. The onset of type 2 diabetes occurs much later than for type 1 and typically in people over the age of fifty. The pancreas of type 2 diabetics continues to produce and release insulin. However, cells do not respond appropriately to insulin levels in the blood. This condition is known as insulin-resistance and is associated with obesity and high blood pressure. Children who are obese can also develop type 2 diabetes.

glucose: common hexose monosaccharide; monomer of starch and cellulose; also called grape sugar, blood sugar, or dextrose

metabolism: the complete range of biochemical processes that take place within living organisms; comprises processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those which break down complex food molecules, thus liberating energy (catabolism)

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

Gestational diabetes affects 3 to 5 percent of pregnant women. Onset generally occurs in the fifth or sixth month of pregnancy. In pregnant women, the placenta produces hormones to support the growing fetus. Some of these hormones (e.g., **estrogen** and cortisol) interfere with the actions of insulin. Insulin-resistance develops despite adequate blood insulin levels. Gestational diabetes does not last beyond pregnancy and the condition disappears after delivery.

estrogen: female sex hormone

Before the discovery of insulin, type 1 diabetics usually died within a few years of onset of the disease. During the early 1920s, a young Canadian physician, Frederick Grant Banting, working with John James Rickard Macleod, professor of physiology at the University of Toronto, and Charles Best, a medical student, discovered insulin while performing investigations on extracts acquired from dog pancreas. Soon after, Banting and Macleod were awarded the 1923 Nobel Prize in physiology or medicine for their discovery (Banting reportedly split his share of the prize money with Best).

Insulin was rapidly put into clinical use, chiefly through the efforts of August Krogh, a Danish scientist who cofounded the Nordic Insulin Laboratory in Copenhagen, Denmark, for the production of insulin. Large quantities of insulin were initially acquired from the pancreatic tissues of slaughtered animals, typically cows and pigs. Although bovine (cow) and porcine (pig) insulin are still the major components of commercially available insulin in the United States, the use of human insulin preparations is rapidly growing. Since the 1980s, recombinant **DNA** techniques have made human insulin available for clinical use. Genetically modified strains of *Escherichia coli* bacteria or *Saccharomyces cerevisiae* (baker's yeast) containing human genes coding for insulin have been developed for the mass production of human insulin.

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

Insulin is not a cure for diabetes. It does, however, allow diabetics, especially those with type 1 diabetes, to gain some control over their condition. Insulin is typically administered by subcutaneous (under the skin) injection. There are four principal types of insulin preparations commercially available. Insulin lispro (ultra-short-acting insulin) is rapidly absorbed into the blood and lasts only 3 to 4 hours. Regular insulin, on the other hand, takes 30 minutes to become effective, and lasts 5 to 7 hours. Lente and NPH (neutral protamine Hagedorn) insulin preparations are longer-acting formulations typically administered every 12 hours. Finally, mixtures of insulin preparations are also commercially available. Typical mixtures consist of 70 percent NPH and 30 percent insulin lispro. SEE ALSO Genetic Engineering; Glycolysis.

Nanette M. Wachter

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Interferon

Interferon, a small protein containing fewer than two hundred amino acids, is an interesting example of a biologically active polypeptide. There are three classes of interferon, labeled by the first three letters of the Greek alphabet. Interferon-α is used to treat leukemia, hepatitis B and C, and Kaposi's sarcoma. Interferon-β finds use as a treatment for multiple sclerosis and interferon-γ has applications in treating a rare genetic disorder called granulomatous disease.

Cells within the body synthesize interferon when experiencing stress from incidents such as viral attack. When interferon is released into the bloodstream by an infected cell, it helps signal an immune response to the invader. Other mechanisms that interferon activates in the fight against viral infections are less understood. It is hypothesized that in addition to signaling the immune system they somehow inhibit the ability of viruses and tumor cells to reproduce. Research to further the understanding of how interferon works is inhibited by the fact that, aside from humans, only a few other animals have cells that make interferon. Many studies of how drug molecules work are carried out first with animals, but for interferon, this type of study is less productive.

Dr. Alick Isaacs and Dr. Jean Lindenmann discovered interferon in 1957 in Great Britain. In an experiment, they mixed live viruses with egg membranes and unexpectedly found that the viruses did not grow. They did not know what caused this observation and simply indicated something interfered with the virus, so the term "interferon" was coined. They eventually identified the polypeptide and were able to isolate it from various cells, including those taken from calves, monkeys, and humans.

Interferon is produced naturally in very small quantities. When it originally was introduced as a form of medical treatment, the expense associated with isolating the compound from sources such as blood made it prohibitively expensive. Interferon became viable as a medical intervention only through the application of genetic engineering. The gene that tells a cell how to construct interferon is introduced into *Escherichia coli* bacteria. These bacteria are grown in culture and they produce the interferon. Because the bacteria can be grown relatively quickly, large quantities of interferon can be generated with this method. While many people tend to react to the phrase "genetic engineering" with some fear, interferon represents an excellent example of how advances in medical treatment were made possible only by its application. SEE ALSO AMINO ACID; PROTEIN.

Thomas A. Holme

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International System of Units

The International System of Units (SI), which began as the decimal metric system during the French Revolution, deals with the definitions, terminology, proper usage, and modifications of scientific units. The metric system was established officially in France on June 22, 1799, and consisted of two standard measures: the meter for length and the kilogram for mass. The German mathematician and astronomer Carl Friedrich Gauss (1777–1855) promoted the use of the metric system and in 1832 added the second as the unit of time. The British Association for the Advancement of Science (BAAS) in 1874 introduced an alternative system, known as the CGS system, whose units of measure were the centimeter, gram, and second. Until 1889 the scientific community had two metric standards for length, mass, and time.

The first General Conference on Weights and Measures (Conférence Générale des Poids et Mesures, or CGPM) in 1889 sanctioned a new system, the MKS system, that included the international prototypes for the meter and kilogram and the astronomical second as the unit of time. Fifty years later, in 1939, the International Committee for Weights and Measures (Comité International des Poids et Mesures, or CIPM), under authority of the CGPM, proposed a four-unit MKS system with the addition of the ampere for electric current. Official recognition of the ampere had to wait until 1946, after World War II had ended.

The tenth CGPM in 1954 added two more standards when it officially approved both the kelvin for thermodynamic temperature and the candela for luminous intensity. In 1960 the eleventh CGPM renamed its MKS system of units the International System of Units, and in 1971 the fourteenth CGPM completed the seven-unit system in use today, with the addition of the mole as the unit for the amount of a substance, setting it equal to the gram-molecular weight of a substance.

SI units fall into two groups: basic units and derived units. The basic units are the seven mutually independent units (see Table 1) and include the meter, kilogram, second, ampere, kelvin, mole, and candela. They represent,

SI BASIC UNITS

Base Quantity	Base Unit	Symbol
Length	meter	m
Mass	kilogram	kg
Time	second	s
Electric current	ampere	A
Thermodynamic temperature	kelvin	K
Amount of substance	mole	mol
Luminous intensity	candela	cd

SOURCE: Taylor, Barry N., ed., and National Institute of Standards and Technology (1995). *Guide for the Use of the International System of Units (SI).* Special Publication 811. Washington, DC: U.S. Government Printing Office.

Table 1. SI basic units.

Table 2. SI-derived units.

SI-DERIVED UNITS

Derived Quantity	Name	Symbol
Area	square meter	m^2
Volume	cubic meter	m^3
Velocity	meter per second	m/s
Acceleration	meter per second squared	m/s^2
Wave number	reciprocal meter	m^{-1}
Mass density	kilogram per cubic meter	kg/m^3
Specific volume	cubic meter per kilogram	m^3/kg
Current density	ampere per square meter	A/m^2
Magnetic field strength	ampere per meter	A/m
Amount-of-substance concentration	mole per cubic meter	mol/m^3
Luminance	candela per square meter	cd/m^2
Mass fraction	kilogram per kilogram, which may be represented by the number 1	kg/kg = 1

SOURCE: Taylor, Barry N., ed., and National Institute of Standards and Technology (1995). *Guide for the Use of the International System of Units (SI).* Special Publication 811. Washington, DC: U.S. Government Printing Office.

respectively, length, mass, time, electric current, thermodynamic temperature, amount of substance, and luminous intensity. Derived units, as the name indicates, are units obtained algebraically from the seven basic units (see Table 2).

The CIPM has approved twenty prefixes for SI units (see Table 3) and permits the use of any SI prefix with an SI unit, with one exception. The SI unit for mass, the kilogram, already has a prefix in its name and can have no other SI prefix. To use prefixes with a unit for mass, the rule is to remove the "kilo" prefix and add the new prefix to "gram" (unit symbol g), as in milligram and its abbreviation mg.

The CIPM has developed several rules to ensure the proper use of SI units and to eliminate ambiguity from scientific communications. The National Institute of Standards and Technology in Washington, D.C., makes available a complete detailed list of the rules.

SI units, or those the CIPM recognizes, express quantity values. Other units, if used, may appear in parentheses after the appropriate SI or recognized units. The CIPM uses no abbreviations for names and only accepted unit symbols, unit names, prefix symbols, and prefix names. It makes no differentiation in symbol use for a plural, and the only time a period follows a unit symbol is at the end of a sentence. The addition of subscripts does not change a unit name or symbol.

Mathematical operations have specific rules for the use of mathematical symbols with SI units. A space or a half-high dot represents the multiplication of units; a negative exponent, horizontal line, or slash represents the division of units, and if these mathematical symbols appear in the same line, parentheses must differentiate them. The percent sign (%) denotes the number 0.01 or 1/100, so that 1%= 0.01, 30% = 0.30, and so forth. Arabic numerals with the appropriate SI or recognized unit indicate the values of quantities. Commas are not used to separate numbers into groups of three. If more than four digits appear on either side of the decimal point, a space separates the groups of three.

PREFIXES

Factor	Name	Symbol
10^{24}	yotta	Y
10^{21}	zetta	Z
10^{18}	exa	E
10^{15}	peta	P
10^{12}	tera	T
10^{9}	giga	G
10^{6}	mega	M
10^{3}	kilo	k
10^{2}	hecto	h
10^{1}	deka	da
10^{-1}	deci	d
10^{-2}	centi	c
10^{-3}	milli	m
10^{-6}	micro	μ
10^{-9}	nano	n
10^{-12}	pico	p
10^{-15}	femto	f
10^{-18}	atto	a
10^{-21}	zepto	z
10^{-24}	yocto	y

SOURCE: Taylor, Barry N., ed., and National Institute of Standards and Technology (1995). *Guide for the Use of the International System of Units (SI).* Special Publication 811. Washington, DC: U.S. Government Printing Office.

Table 3. Prefixes.

Table 4. Non-SI units accepted for use.

NON-SI UNITS ACCEPTED FOR USE

Name	Symbol	Value in SI units
Minute (time)	min	1 min = 60 s
Hour	h	1 h = 60 min = 3,600 s
Day	d	1 d = 24 h = 86,400 s
Degree (angle)	°	1° = (PI/180) rad
Minute (angle)	'	1' = (1/60)° = (PI/10,800) rad
Second (angle)	''	1'' = (1/60)' = (PI/648,000) rad
Liter	L	1 L = 1 dm^3 = 10^{-3} m^3
Metric ton	t	1 t = 10^3 kg
Neper	Np	1 Np = 1
Bel	B	1 B = (1/2) ln 10 Np
Electronvolt	eV	1 eV = 1.602 18 x 10^{-9} J, approximately
Unified atomic mass unit	u	1 u = 1.660 54 x 10^{-27} kg, approximately
Astronomical unit	ua	1 ua = 1.495 98 x 10^{11} m, approximately

SOURCE: Taylor, Barry N., ed., and National Institute of Standards and Technology (1995). *Guide for the Use of the International System of Units (SI).* Special Publication 811. Washington, DC: U.S. Government Printing Office

Numbers, unit symbols, and names have set rules for mixing and differentiation for clarity of text and mathematical operations. These include a space between a numerical value and its unit symbol, indicating clearly the number a symbol belongs to in a given mathematical calculation, and no mixing of unit symbols and names nor making calculations on unit names. Different symbols represent values and units and the unit symbol should follow the value symbol separated by a slash. SI requires the use of standardized mathematical symbols and the explicit writing of a quotient quantity.

SI units and their symbols have distinctive type styles. Items given in italic type are variables, quantity symbols, superscripts and subscripts if they represent variables, quantities, or running numbers. Items given in roman type are unit symbols, superscripts, and subscripts that are descriptive. The typeface used in the surrounding text of the document does not change these rules.

Several terms used in vernacular science are not appropriate for scientific communication. The CIPM does not use such terms as parts per million, parts per billion, or parts per trillion or their abbreviations as expressions of quantities. The word “weight” is a force with the SI unit of newton, not a synonym for mass with the SI unit of kilogram. Terms for an object and quantities describing the object require a clear different action. Normality, molarity, and molal are obsolete terms no longer used.

Several important and widely used units are not officially part of the SI, but the CIPM has accepted them for use with SI units (see Table 4). They include the liter, day, hour, minute, electronvolt, and degree. Although the CIPM adopted the liter in 1879, it is not a current SI unit. Its symbol (L in the United States, l everywhere else) causes some confusion, but the CIPM has approved neither.

In the United States, the National Institute of Standards and Technology (NIST) also has compiled a list of units outside the SI that it has approved for domestic use (see Table 5). It recommends defining them in terms of accepted SI units. The CIPM does not encourage the use of units on the NIST list but accepts all of them, excluding the curie, roentgen, rad,

Table 5. Non-SI units approved by the NIST.

NON-SI UNITS APPROVED BY THE NIST

Name	Symbol	Value in SI units
Nautical mile	n/a	1 nautical mile = 1,852 m
Knot	n/a	1 nautical mile per hour = (1,852/3,600) m/s
Are	a	1 a = 1 dam^2 = 10^2 m^2
Hectare	ha	1 ha = 1 hm^2 = 10^4 m^2
Bar	bar	1 bar = 0.1 MPa = 100 kPa = 1,000 hPa = 10^5 Pa
Angstrom	Å . . .	1 Å . . . = 0.1 nm = 10^{-10} m
Barn	b	1 b = 100 fm^2 = 10^{-28} m2
Curie	Ci	1 Ci = 3.7 x 10^{10} Bq
Roentgen	R	1 R = 2.58 x 10^{-4} C/kg
Rad	rad	1 rad = 1 cGy = 10^{-2} Gy
Rem	rem	1 rem = 1 cSv = 10^{-2} Sv

SOURCE: Taylor, Barry N., ed., and National Institute of Standards and Technology (1995). *Guide for the Use of the International System of Units (SI).* Special Publication 811. Washington, DC: U.S. Government Printing Office.

and rem, which American scientists have nonetheless continued to use. SEE ALSO MEASUREMENT; MOLE CONCEPT.

Anthony N. Stranges
Sean McMaughan

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53
I
IODINE
126.9

Iodine

MELTING POINT: 113.7°C
BOILING POINT: 184.3°C
DENSITY: 4.94 g/cm^3
MOST COMMON IONS: IO^-, IO_3^-, IO_6^{5+}

Iodine is the heaviest of the **halogen** family of elements, excluding the radioactive element astatine. It was discovered in 1811 by French chemist Bernard Courtois, who isolated the element from seaweed. The element is named for its color in the gas **phase** (the Greek word *iodes* means "violet").

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

phase: homogeneous state of matter

At normal temperatures and pressures, iodine is a shiny, purplish-black or gray solid. Near room temperature, iodine sublimes (i.e., it does not melt to form a liquid but goes directly from the solid to the gas phase). It is found at a level of about 60 parts per billion (ppb) by weight in seawater but its concentration is enhanced in marine organisms.

As with the other halogens, iodine is a diatomic molecule. It is always found in nature in a combined state, often as iodide salts where it has a −1 **oxidation** number. Compounds in which iodine is found to have oxidation numbers of 7, 3, 5, and 1 are also well known. Iodine is prepared commercially by treatment of natural salt solutions (seawater or brines) with chlorine (a more reactive halogen), according to the reaction:

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

$$2\ I^- + Cl_2 \rightarrow I_2 + 2\ Cl^-$$

Iodine is necessary for the proper function of the thyroid gland in humans. Dietary deficiencies can be avoided by the occasional consumption of seafood or by using iodized salt, which combines common table salt (NaCl) with potassium iodide (KI). Iodine is a useful antiseptic, either as tincture of iodine (an alcohol solution of I_2), or as an **aqueous solution** of providone iodine (Betadine). SEE ALSO Halogens; Inorganic Chemistry.

aqueous solution: homogenous mixture in which water is the solvent (primary component)

John Michael Nicovich

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Ion Channels

Ion channels play a fundamental role in the way cells communicate. They generate the electrical signals that make hearts beat and muscles contract, and allow brains to receive and process information. This communication between cells allows for the orchestration of physical and mental activities in humans. Many diseases result from ion channels that do not function properly.

Ion channels are transmembrane proteins that span the cell membrane and are formed from one or more protein subunits. The channels are shaped like tunnels, which form pores through the plasma membrane. The pores have gates that open and close to allow ions to diffuse down their chemical gradient and move in or out of a cell. Ion channels are specific for certain types (and combinations of types) of ions, such as chloride, sodium, potassium, and calcium.

Ions are atoms or molecules that have gained or lost one or more electrons to give them either a net positive or negative electrical charge. They are unequally distributed, creating a separation of charge across a membrane, resulting in an electrical potential. When an ion channel is open, a million ions can flow in or out of the cell per second. This causes an electrical signal or current, which allows cells to communicate very quickly.

There are two major classes of ion channels defined by the way the channel opens: ligand-gated and voltage-gated. Ligand-gated ion channels open when a specific chemical signal called a neurotransmitter is released from one cell, diffuses through a gap known as a synapse, and binds to **receptors** on ion channels of a second cell. The binding of the neurotransmitter causes the ion channel gate to open. Voltage-gated ion channels have sensors for the electrical potential across the membrane. They open when the cell is at a specific membrane potential. Some other channels can open due to mechanical stress or the levels of signaling molecules inside the cell.

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

An important function of ion channels is to regulate when cells are at rest and when they are communicating. When a neuron is at its resting potential, it is not sending a signal to any other cells. The inside of a neuron at rest is more negative than the outside. If a neuron is stimulated to communicate with other cells, ion channels open to make the inside of the cell more positive than the resting potential. The neuron will reach a threshold and fire an action potential, where voltage-gated ions channels open, allowing sodium ions to rush in and potassium ions to rush out of the cell. Action potentials propagate and repeat many times to carry a signal the length of a nerve cell. This cell can then continue to communicate by releasing neurotransmitter to bind ligand-gated ion channels on another cell.

A number of diseases occur when ion channels do not function properly. Some examples are epilepsy, cystic fibrosis, heart arrhythmia, and high blood pressure. Ion channels are also the target of many types of drugs and toxins, which can alter the fundamental communication between cells. SEE ALSO CONCENTRATION GRADIENT; MEMBRANE; NEUROTRANSMITTERS; TRANSMEMBRANE PROTEIN.

Ingrid A. Lobo
R. Adron Harris

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Iridium

77
Ir
IRIDIUM
192.22

MELTING POINT: 2,454°C
BOILING POINT: 3,590°C
DENSITY: 22.6 g/cm^3 (at 25°C)
MOST COMMON IONS: Ir^{3+}

Iridium was discovered by English chemist Smithson Tenant. It was named after the Greek goddess Iris (a goddess related to the rainbow) because of the variety of color in its compounds. A very rare element (0.0001 ppm of Earth's crust), iridium is found in the naturally occurring **alloys** osmiridium (approximately 50% iridium) and iridiosmium (approximately 70% iridium) in Alaska and South Africa. It is obtained by igniting ammonium chloroiridate, $(NH_4)_3IrCl_6$, in hydrogen atmosphere. Its ground state electronic configuration is $[Xe]4p^{14}5d^76s^2$.

alloy: mixture of two or more elements, at least one of which is a metal

Iridium is the densest of all elements and its **metal** is lustrous, silvery, and very hard. The metal has the face-centered cubic crystal structure. Iridium has two stable **isotopes**: ^{191}Ir (37.3%) and ^{193}Ir (62.7%).

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

isotope: form of an atom that differs by the number of neutrons in the nucleus

IRIDIUM COMPLEXES WITH EXAMPLES

Oxidation States	Examples
(−I)	$K[Ir(PF_3)_4]$
(0)	$[Ir(NH_3)_5Br]Br$ (yellow)
(I)	$Ir(CO)Cl(PPh_3)_2$
(II)	$Ir(NO)Br_3(PPh_3)_2$ (μB = 1.34 BM)
(III)	$K_3[IrCl_6]$ (olive-green) diamagnetic
(IV)	$K_2[IrF_6]$ (red)
(V)	$K[IrF_6]$

Table 1. Iridium complexes with examples.

Iridium is extremely **inert** to acids, but reacts slowly with oxygen and **halogens** at high temperatures. It forms the fluoride compounds IrF_6, $(IrF_5)_4$, and IrF_4. There is some doubt of the existence of other halides with the composition IrX_4. The most stable halides are the trihalides. Compounds that have the composition $[IrX_6]^{2-}$ are strongly colored.

inert: incapable of reacting with another substance

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

$Ir_2O_3 \cdot nH_2O$ (a brown solid) is obtained via the addition of alkali to $IrCl_6^{2-}$ in the presence of H_2O_2. This hydrated oxide is oxidized in air to $IrO_2 \cdot nH_2O$. IrO_2 (black), with **rutile** structure, is the product of the reaction of Ir with O_2 at approximately 1,100°C (2,012°F); it dissociates at higher temperatures (>1,100°C, or >2,012°F).

rutile: common name of titanium dioxide; also a common structural type for compounds with the general composition AB_2

Iridium may form complexes in its several **oxidation** states. Table 1 contains some examples of these complexes.

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

Iridium oxide, IrO_2, is used in the fabrication of thin films for stable electrochromic materials and as an electrode material. Iridium metal is used in the manufacture of fountain pen points, airplane spark plugs, and hypodermic needles. SEE ALSO Inorganic Chemistry.

Lea B. Zinner

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Iron

MELTING POINT: 1,535°C
BOILING POINT: 2,750°C
DENSITY: 7.874 g/cm^3 (at 20°C)
MOST COMMON IONS: Fe^{2+}, Fe^{3+}

26
Fe
IRON
55.847

Iron, believed to have been introduced on Earth by meteors, was found in Egyptian tombs dating from 3500 B.C.E. The Hittites (in the area known today as Turkey) smelted iron from ore around 1500 B.C.E. From ancient times to the present, the major use of iron has been in the production of steel.

Elemental iron, the major element in Earth's core, is the fourth most abundant element in Earth's crust (about 5.0% by mass overall, 0.5%–5% in soils, and approximately 2.5 parts per billion in seawater.) In the crust, iron is found mainly as the oxide minerals hematite, Fe_2O_3, and magnetite, Fe_3O_4. Other common mineral forms are siderite, $FeCO_3$, and various forms of FeO(OH). Iron is an essential element in almost all living organisms. In the human body, its concentration ranges between 3 and 380 parts per million (ppm) in bone, 380–450 ppm in blood, and 20–1,400 ppm in tissue.

isotope: form of an atom that differs by the number of neutrons in the nucleus

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

ferrous: older name for iron in the +2 oxidation state

ferric: older name for iron in the +3 oxidation state

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

Iron has a very stable nucleus and has fourteen known **isotopes**. Four isotopes, ^{54}Fe (5.9%), ^{56}Fe (91.72%), ^{57}Fe (2.1%), and ^{58}Fe (0.28%) make up essentially 100 percent of naturally occurring iron. Pure iron is a soft, white, lustrous **metal**. Elemental iron oxidizes in moist air but is stable in dry air. Finely divided elemental iron is pyrophoric. Iron dissolves in dilute mineral acid and in hot sodium hydroxide solution. Iron has seven **oxidation** states (–2, 0, +1, +2, +3, +4, and +6) with the +2, **ferrous** or Fe(II), and +3, **ferric** or Fe(III), states being the most common. With mild heating, iron reacts with the **halogens** and with sulfur, phosphorus, boron, carbon, and silicon to form a variety of compounds. SEE ALSO Hemoglobin; Industrial chemistry, Inorganic.

Douglas Cameron

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Irradiated Foods

isotope: form of an atom that differs by the number of neutrons in the nucleus

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Gray: unit of radiation dose per second; 1 Gray = 1 J/kg

Irradiation is the process of exposing a material to ionizing radiation whose source is photons (γ-rays, x rays), or high energy electrons. Commonly, γ-rays are produced by radioactive **isotopes** such as cobalt-60 and cesium-137. These isotopes have been approved for use in food because the γ-rays they produce have insufficient energy to induce radioactivity in foods. Conversely, electron beams are produced by electron accelerators, such as Van de Graaff generators or linear accelerators. The power limits for these machines are also regulated to no more than 10 million EV, to assure that they cannot induce radioactivity in foods. Finally, x rays are produced by the collision of high energy electrons, produced by linear accelerators, with a **metal** target. The amount of ionizing energy absorbed by a material is the dose, and this dose is measured in Grays (1 **Gray**, abbreviated Gy, equals 1 J/kg) or kiloGrays (kGy).

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

photon: a quantum of electromagnetic energy

Irradiation destroys bacteria primarily by disrupting the chromosomal **DNA** in individual cells. A second mode of action is the "near-miss" theory, where a **photon** of energy passes very close to the DNA and forms a peroxide radical (from oxygen in the air) in the cell cytoplasm. The peroxide radical then oxidizes part of the DNA.

Purposes of Food Irradiation

The purpose of food irradiation is to improve the quality of the food being irradiated, either from a microbiological, physical, or **organoleptic** perspective. Very low doses (<1 kGy) are used to prevent sprouting in potatoes or delay the ripening of fruits. These doses can also be used to disinfect foods by killing insects in grains and fruits or inactivating parasites (trichinae) in meat. Slightly higher doses (1–5 kGy) can be used to pasteurize foods. Radiation **pasteurization**, or radurization, significantly reduces or eliminates bacteria of public health significance in the food while also decreasing the total number of bacteria in the food. As with pasteurization by heating, this reduction in the total number of bacteria in a food also results in an increase in the shelf life of the food. Finally, very high doses, on the order of 25 kGy or greater, can be used to sterilize foods. In practice, most of the current interest and research has focused on the low doses commonly used in pasteurization.

organoleptic: effect of a substance on the five senses

pasteurization: process of heating foods such as milk to destroy bacteria

One of the main interests in food irradiation is that it can be used as a "cold" pasteurization technique. Many food-borne disease bacteria, including *Salmonella*, *Escherichia coli* O157:H7, and *Listeria monocytogenes*, are very sensitive to irradiation. Although there are some variations in sensitivity among the previously listed bacteria, a dose range of 1.5–3.0 kGy is sufficient to eliminate all these bacteria as they naturally occur in foods.

An advantage of irradiation is that it can penetrate packaging material. Foods can be prepackaged and then irradiated, eliminating the potential for contamination during packaging. In addition, irradiation can be used as a replacement for many food additives that are used to inhibit bacterial growth. Irradiation can also be used as a quarantine treatment for imported fruits and vegetables, which eliminates the need for the use of toxic fumigants.

Irradiation can kill many disease-causing bacteria, including *E. coli, Listeria,* and salmonella. Irradiation can penetrate packaging, eliminating contamination introduced during the packaging process.

Consumer Concerns

vitamins: organic molecules needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

Consumer concerns about food irradiation fall into two broad categories: the first relating to the technology and the second relating to the quality of the food. The terms "radiation" and "radioactivity" have negative connotations to many individuals. There is still lingering doubt in the mind of some consumers regarding induced radiation. The radiation sources that the U.S. Food and Drug Administration (FDA) has approved for food irradiation cannot make the food radioactive. Another consumer concern relating to the quality of the irradiated food is that of nutrient loss. Irradiation does, in fact, reduce the levels of **vitamins** in foods, especially the B vitamins. Thiamine is particularly sensitive to irradiation, and substantial losses of this vitamin can occur in irradiated foods at high doses. However, vitamin losses occur with many food processes, including cooking and canning. There is no question that an irradiated food which is cooked will have a slightly lower vitamin content than an identical food which has not been irradiated prior to cooking. However, it is not anticipated that every food will be irradiated, and even if an individual specifically limited his or her consumption to irradiated products, there would still be sufficient vitamins in that individual's diet. The American Dietetics Association (ADA) has reviewed the nutritional changes caused by food irradiation and is on record as supporting the technology.

Toxicity

The ultimate consumer concern with any new food process is, "Is the food safe to eat?" A joint committee of the Food and Agriculture Organization (FAO), the International Atomic Energy Agency, and the World Health Organization (WHO) evaluated all available studies on the wholesomeness of irradiated food. The final report concluded that the irradiation of any food commodity causes no toxicological hazard and hence toxicological testing of foods treated in this manner is no longer required. Many toxicological studies have been conducted over the years, but one of the most comprehensive was a multigenerational study conducted in the United States during the 1970s, in which five different species of animals and insects were fed irradiation-sterilized (58 kGy) chicken as a major component in their diet. The results of these studies, including all the original histology slides, were completely reevaluated by the FDA during its consideration of the petition to irradiate poultry. After more than two years of evaluation, the FDA concurred with the conclusions of the original study and issued regulations on poultry irradiation. In addition, during this same time period the American Medical Association (AMA) reviewed the toxicological data; it has publicly supported food irradiation. SEE ALSO AGRICULTURAL CHEMISTRY; RADIATION; RADIOACTIVITY; TOXICITY.

James S. Dickson

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Isomerism

The term **"isomer"** (*iso* from the Greek meaning same and *meros* meaning part) describes the relationship between molecular arrangements that, although differing in chemical or physical properties, have a level of commonality (have the "same parts"). There are two distinct levels of commonality used to describe molecular structure: one that excludes and one that includes three-dimensional considerations. The level of comparison that excludes three-dimensionality is comprised of substances having the same set of atoms but differing in how they are connected. These substances are known as **constitutional isomers**. The constitution of molecules (number, kind, and connectivity of atoms) may be represented by a two-dimensional "map" in which the interatomic linkages are indicated. There are two constitutional isomers for the molecular formula C_2H_6O: ethanol and dimethyl ether. The difference in connectivity, which is not evident in the empirical formula C_2H_6O, can be represented by typographical line formulas, CH_3CH_2OH for ethanol and CH_3OCH_3 for dimethyl ether, or in structural representations (see Figure 1). As the number and kind of atoms in substances increases, the number of constitutional isomers increases.

isomer: molecules with identical compositions but different structural formulas

constitutional isomer: form of a substance that differs by the arrangement of atoms along a molecular backbone

Chemical reactions in which one isomer is converted to another are called isomerizations. An intramolecular Diels–Alder reaction (see Figure 2) is an example of an isomerization reaction in which the level of difference is that of connectivity. An isomerization that involves a rapid **equilibrium** between connectivities that cannot be easily isolated from one another is called a tautomerization (see Figure 3). Note that the number and kind of atoms remains the same on both sides of the chemical equation, and that there is only one compound involved.

equilibrium: condition in which two opposite reactions are occurring at the same speed, so that concentrations of products and reactants do not change

History

The concept of constitutional isomerism was a significant advance in the history of modern chemistry, and especially in the development of organic chemistry. By the late 1700s only a few pure substances had been isolated via the study of "animal" and "vegetable" chemistry, and many of these by a single individual, Carl Wilhelm Scheele (1742–1786). Due to the extensive variety in organic compounds, each new substance presented a new elemental composition, which matched the generalized observation from "mineral" chemistry. As the number of isolated organic compounds increased during the early 1800s, the identification of different substances

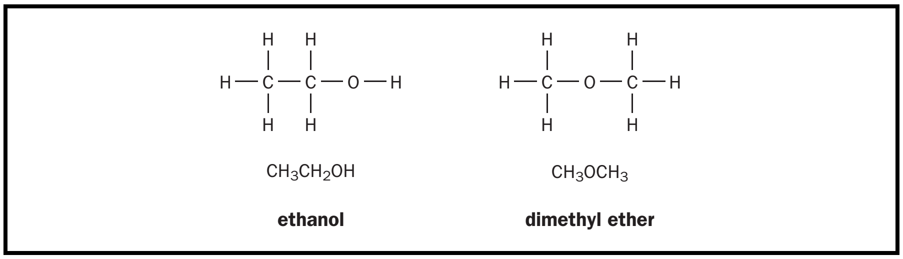
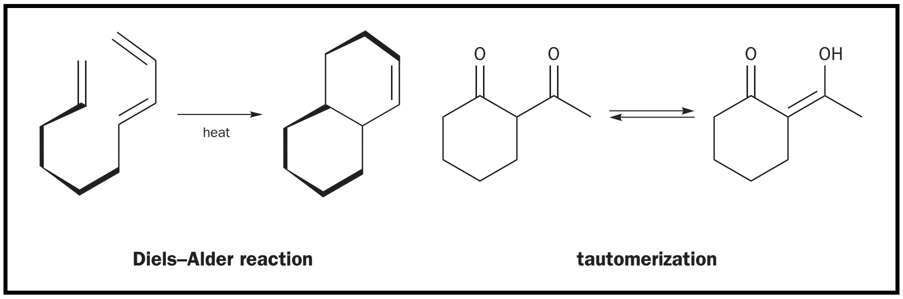


Figure 1.

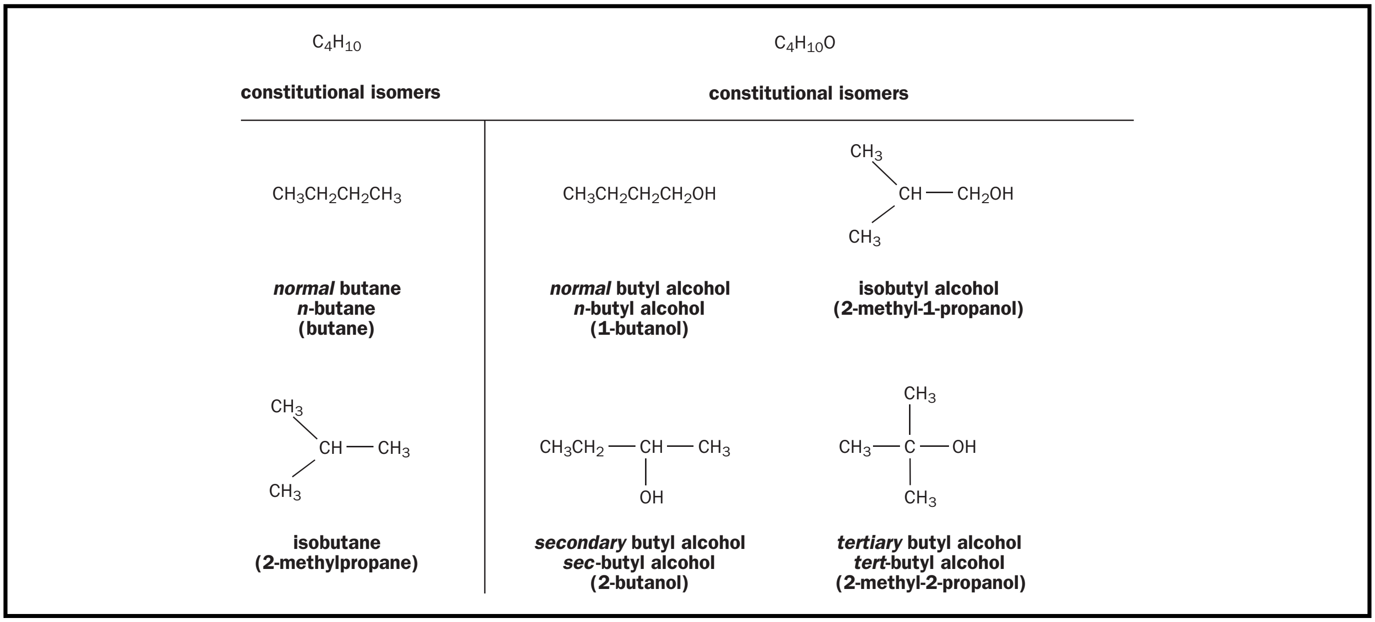
Figures 2–3.



having the same elemental composition was inevitable. In his 1830 *History of Chemistry*, Thomas Thomson wrote (p. 302) that “[Berzelius] applied the [atomic] theory also to the vegetable kingdom by analyzing several of the vegetable acids, and showing their atomic constitution. But here a difficulty occurs, which in the present state of our knowledge, we are unable to surmount. There are two acids . . . that are composed of exactly the same kind of atoms. . . . Now how are we to account for this [striking difference in properties]? Undoubtably by the different ways in which the atoms are arranged in each.” Thomson then drew different arrangements (on paper) of the atomic symbols used at the time (those of John Dalton), as a way to explain why two acids with the same elemental composition could have different physical and chemical properties.

Up until the early nineteenth century, it was generally believed that those chemical substances found in living organisms possessed a particular vital force associated with living things, and that these substances required living systems in order to be produced. The belief was that nowhere else in nature except in living systems could one find these compounds. Friedrich Wöhler (1800–1882) is universally credited with the observation of isomerization that led to the decline of the idea of vitalism. In 1828 Wöhler synthesized a sample of urea, $(NH_2)_2C{=}O$ (also CH_4N_2O), that was

Figure 4. Constitutional isomers for C_4H_{10} and $C_4H_{10}O$.



indistinguishable from the urea isolated from urine. He prepared this "animal" substance from the clearly inorganic (mineralogical) starting material ammonium cyanate, NH_4 (+) NCO(−) (also CH_4N_2O), which results from combining ammonium chloride and silver cyanate. In *The Development of Modern Chemistry*, Aaron J. Ihde (p. 165) points out that the preparation of urea from inorganic starting materials had been conducted earlier, by both Wöhler, in 1824, and Humphry Davy, in 1811, but that their achievements were not recognized for what they were at the time. The concept of isomerism is central to structural chemistry, and this concept is beautifully encapsulated in the title of a book by Nobel laureate Roald Hoffmann, *The Same and Not the Same.*

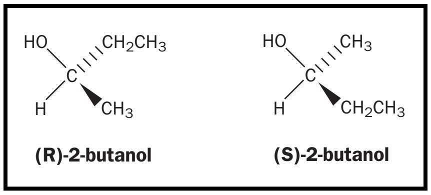


Figure 5.

Nomenclature

The early development of a systematic nomenclature for organic compounds reflected structural isomeric relationships. A few of the terms have persisted: "normal" or "n-" to indicate a straight chain of atoms; "iso" as a prefix derived from the word "isomer" to indicate the attachment of a methyl group on the penultimate carbon of a straight chain; "tertiary," "tert-," or "t-" to indicate an arrangement in which three alkyl groups are attached to a common site; and "secondary" or "sec-" to indicate that there are two alkyl groups. Examples of common usage are provided in Figure 4 (the contemporary standard usage is included parenthetically).

Stereoisomerism

The second level of isomeric comparison includes substances that have the same connectivity but differ in their three-dimensional geometrical arrangements. The study of the resulting relationships is called stereochemistry. Two categories exist for comparing different three-dimensional geometries: configuration and conformation. Because there is an empirical component to these terms, a universally unambiguous distinction between configurational stereoisomers (sometimes simply referred to as stereoisomers) and conformational stereoisomers (sometimes simply referred to as conformations or conformers) has not emerged. There is a general understanding, however, that stereoisomers are geometrical forms that are distinct enough to be isolated under normal conditions, whereas conformers are geometrical forms that interconvert under the same conditions. Some examples will help to clarify this distinction. Tetravalent atoms bearing four different atoms or atomic groupings can occur in two different geometrical forms. The carbon atom with the OH group in 2-butanol (see Figure 4) demonstrates this. The two (and only two) different arrangements of 2-butanol are shown in Figure 5. Both of these molecules have the 2-butanol connectivity, but their three-dimensionality must be additionally labeled in order to give these two different molecules different names. Using a system that is based on assigning

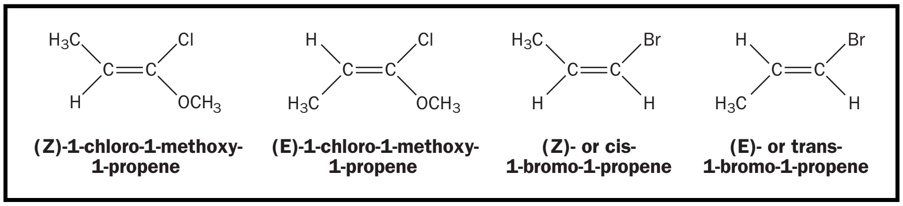
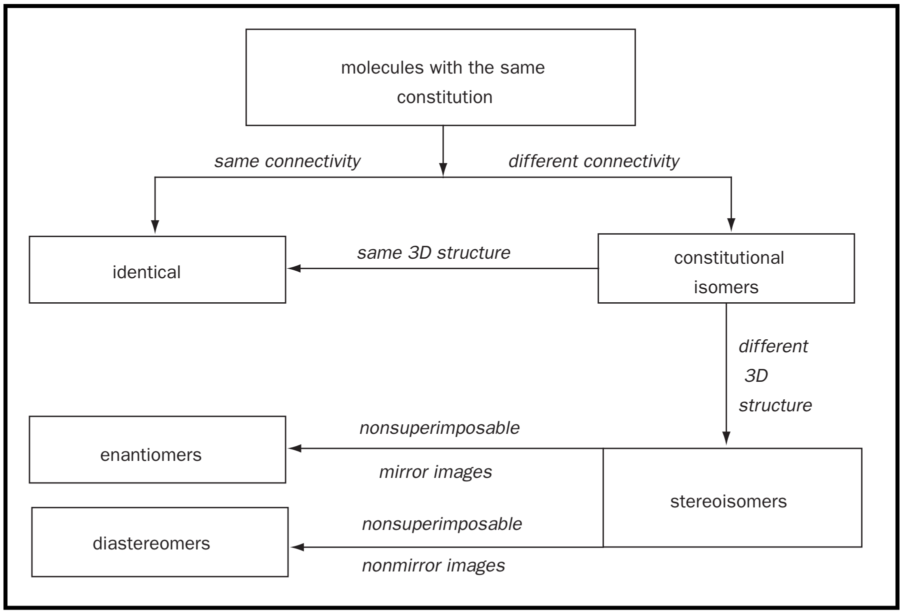


Figure 6.

Figure 7. Schematic relationship between isomers.



priorities to the four different groups, called the Cahn–Ingold–Prelog rules, one of two unique geometrical labels, namely "R" or "S," can be assigned to the three-dimensional geometry of such an atom. "R" and "S" come from the Latin terms *rectus* and *sinester*, meaning "to the right" and "to the left," respectively.

The greater the number of these tetrahedral centers with four different groups that there are in a molecule, the greater the number of stereoisomers. For the most part, this is a simple exercise in probability and statistics. With two such centers, there are four stereoisomers possible (2 geometries at the one center × 2 at the second = 4), and with three such centers there are eight stereoisomers (2 × 2 × 2 = 8).

There are other molecular subunits that can give rise to stereoisomers. Double bonds that bear different groups at both ends, for example, give rise to two distinctly different stereoisomers that do not easily interconvert under normal conditions. Using the Cahn–Ingold–Prelog rules once again, geometrical labels of "E" and "Z" can be assigned to these geometrical arrangements. "E" and "Z" come from the German terms *entgegen* and *zusammen*, meaning "apart" and "together," respect ively. In some cases, in which there is one hydrogen atom at each end, the labels "cis" and "trans" may also be used (see Figure 6).

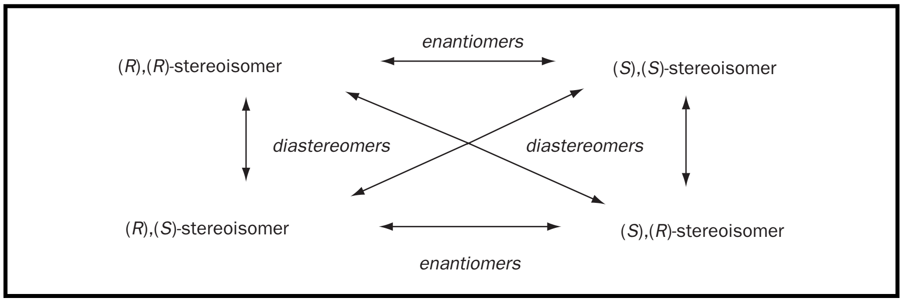
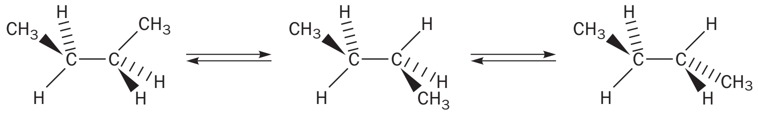


Figure 8.

Conformational changes in butane result in the formation of stereochemically related molecular geometries (conformational stereoisomers) that are not easily separated from one another.



A conformational change results in the formation of the 2 configurational stereoisomers for this biphenyl derivative (the rotational energy barrier is high enough to allow easy separation).

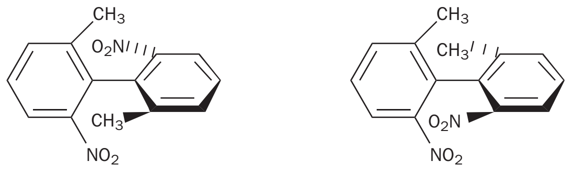


Figure 9. Conformational changes.

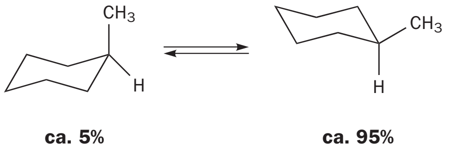
Stereoisomers: Enantiomers and Diastereomers

The two categories into which stereoisomers can be placed are absolutely distinctive in definition. Two stereoisomers that are nonsuperimposable mirror images are called enantiomers. The only other category is defined negatively. Stereoisomers that are not enantiomers are called diastereomers. (See Figure 7.)

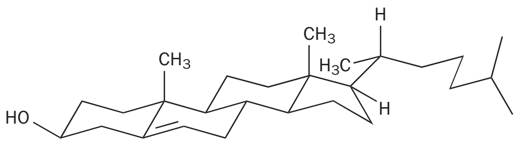
Molecules with a single stereocenter as the only source of configurational stereoisomerism can exist as one of two enantiomers; no configurational diastereomers are possible. Molecules with two dissimilar stereocenters can exist as one of four stereoisomers. Figure 8 outlines the relationships among these four stereoisomers.

Conformers

According to Ernest L. Eliel and Samuel H. Wilen in *Stereochemistry of Organic Compounds* (1994, p. 102), configurational stereoisomers result from "arrangments of atoms in space of a molecule with a defined constitution without regard to arrangements that differ only by rotation about one or

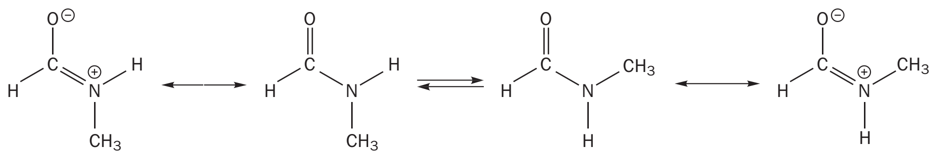


chair-chair conformational interconversion of 1-methylcyclohexane

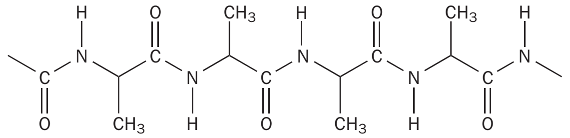


naturally occuring cholesterol

Figure 10.



two planar conformations for N-methylformamide based on C-N bond resonance



a segment of polyalanine, a protein made up of amino acids joined through amide (peptide) bonds

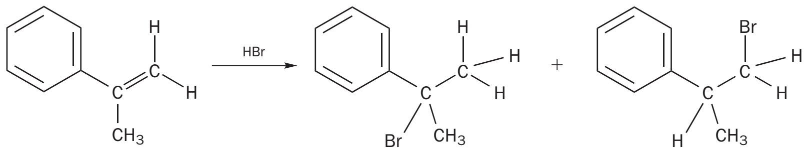
Figure 11. The chemistry of amide bonds involves restricted rotation.

more single bonds, providing that such a rotation is so fast as not to allow isolation of the species so differing." Conformational stereoisomers are then taken to be the result of such single bond rotations. Every single bond that has atoms with some identifiable geometry exists in a full range of molecular geometrical shapes based on rotation around that bond. Some examples are shown in Figure 9. In the first example, the bond rotation of the central bond of butane creates a series of molecular geometries that cannot be isolated or separated from each other. On the other hand, the Eliel and Wilen definition is well illustrated by the second example. The single bond between the two benzene rings has undergone only a 180° rotation in defining the relationship between the two structures (a conformational change), yet this creates two different molecules (stereoisomers), because under normal conditions these two molecular geometries are not easily interconverted, and these two represent separable molecules. It is not easy to predict when two separable molecules are going to be possible; it is determined empirically.

The effects of the overall molecular geometry of a molecule were recognized as contributing to chemical reactivity in the 1950s. Substituted cyclohexanes were among the first systems that could be explained by conformational analysis. These structural units appear in many different (and biologically significant) molecules. Methylcyclohexane, for example, exists as a roughly 95:5 mixture of two forms differing in stability based on the bad collisional interaction that exists for the methyl group when it lies closer to the rest of the ring. Notice how this molecular shape, called a **chair**

chair conformation: arrangement of atoms in a cycle structure (usually a six-membered ring) that appears to be arranged like a chair (as opposed to the other conformation which is described as a "boat")

two regioisomeric products



major product (Markovnikov selectivity)

minor product

Figure 12.

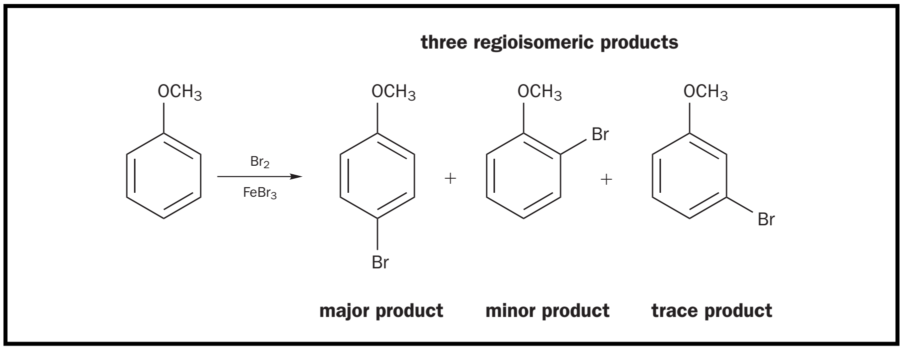


Figure 13.

conformation, recurs in the more complex cholesterol molecule (see Figure 10).

Rotamers

In general, single bonds can undergo free rotation, while double bonds cannot. Because of the resonance phenomenon, some bonds have character that puts them partially between single and double bonding. Sometimes the partial double bond is strong enough to prevent fast bond rotation but weak enough to permit both possible geometrical isomers to be present. The amide **functional group**, which in biochemistry is called the peptide bond in proteins, demonstrates this property (see Figure 11).

functional group: portion of a compound with characteristic atoms acting as a group

Regioisomers

Another type of isomerism is produced as a result of the different outcomes of chemical reactions in which there are different orientations or sites to choose from. For example, when addition reactions between unsymmetrical **reagents** and unsymmetrical double or triple bonds occur, two outcomes are possible. As part of the original observations of this chemistry, wherein one of the atoms added was a hydrogen and the other was some distinctive, nonhydrogen atom, the placement of this distinctive atom was said to occur at one region or other of the molecule, hence the formation of regioisomers (see Figure 12). Based on the mechanism of the chemical reaction, the selectivity for one of these regioisomers forming faster than the other can be predicted. With the addition of simple mineral acids, for example, the product derived from a faster protonation giving a more stable **intermediate** is referred to as the Markovnikov regioselectivity, after the nineteenth-century Russian chemist who made the observations (see Figure 12).

reagent: chemical used to cause a specific chemical reaction

intermediate: molecule, often short-lived, that occurs while a chemical reaction progresses but is not present when the reaction is complete

Regioselectivity in the formation of regioisomers is also observed in electrophilic aromatic substitution reactions. In the case of monosubstituted benzene derivatives, there are three possible regiosomeric products that form at different rates, based on the mechanism of the reaction (see Figure 13). SEE ALSO BERZELIUS, JÖNS JAKOB; CHIRALITY; DALTON, JOHN; DAVY, HUMPHRY; MOLECULAR STRUCTURE; SCHEELE, CARL; WÖHLER, FRIEDRICH.

Brian P. Coppola

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Julian, Percy

AMERICAN CHEMIST
1899–1975

Percy Lavon Julian, the grandson of slaves, developed many useful products from soybeans, including cortisone. He was born in Montgomery, Alabama, on April 11, 1899. His father, James Sumner Julian, was a railway clerk, and his mother, Elizabeth Lena (Adams) Julian, a schoolteacher.

Julian attended public schools in Montgomery. After he was admitted to DePauw University, his family moved with him to Greencastle, Indiana, to enable them to give him their full support. At DePauw his interest in science evolved into a desire to become a research organic chemist. Julian graduated at the top of his class with a bachelor's degree in chemistry in 1920. He was class valedictorian and was elected to Phi Beta Kappa.

Julian taught organic chemistry for two years at Fisk University in Nashville, Tennessee. He then, with the help of Professor William M. Blanchard at DePauw, obtained a graduate research fellowship at Harvard University. He earned a master's degree there in one year, again finishing at the top of his class. He remained at Harvard three more years, as a research assistant, supporting himself with minor fellowship positions and odd jobs outside the university. His application for a teaching assistantship at Harvard was repeatedly rejected on the grounds that the students would not respect a "Negro" instructor.

In 1926 Julian joined the faculty of the West Virginia School for Negroes (later West Virginia State College) at Institute, West Virginia. A year later he became an associate professor of chemistry at Howard University in Washington, D.C., where he quickly rose to the positions of full professor and department head.

Julian had become interested in the chemistry of natural substances and was very eager to do original research in that field. Frustrated in his efforts to pursue doctoral studies in the United States, he obtained a fellowship for graduate study at the University of Vienna, Austria, where he worked and studied indole **alkaloids** under the tutelage of Professor Ernst Spaeth. He earned a Ph.D. from the University of Vienna in 1931.

Upon Julian's return to the United States, DePauw University offered him a faculty position and research support. His first project was the total **synthesis** of **physostigmine**, an indole alkaloid extracted from the Calabar bean, used in the treatment of glaucoma. Sir Robert Robinson at Oxford University in England was also working on this synthesis. Julian achieved the synthesis of physostigmine, and showed that Robinson's hypotheses about its structure were wrong.

Having also found **stigmasterol** among the substances in the Calabar bean, Julian directed his research efforts toward using this **sterol** as the start-

alkaloid: alkaline nitrogen-based compound extracted from plants

synthesis: combination of starting materials to form a desired product

physostigmine: alkaloid derived from the leaves of the Calabar bean, formula $C_{15}H_{12}N_3O_2$; salts are used for anticholinesterase activity

stigmasterol: sterol found in soybeans, $C_{29}H_{48}O$

sterol: steroid containing an alcohol group; derived from plants or animals; e.g., cholesterol ing point for the synthesis of the sex hormones. Because stigmasterol is readily available from soybean oil, Julian wrote to the Glidden Company, a major manufacturer of soybean oil products, to request a 5-gallon sample of the oil to use as his starting point. The request elicited a telephone call from Glidden, offering Julian the position of director of research of Glidden's Soya Products Division in Chicago.

Julian worked for Glidden for seventeen years, developing several new products from soybeans. He mapped out commercially viable syntheses of **progesterone**, testosterone, and cortisone from soya sterols. From soya protein he developed "Aero-Foam," a fire extinguishing foam for oil and gasoline fires, which saw use by the U.S. armed forces during World War II.

progesterone: steroid found in the female reproductive system: formula $C_{21}H_{30}O_2$

In 1953 Julian resigned from Glidden to establish his own laboratory in Franklin Park, Illinois. As director of the Julian Research Institute and president of Julian Associates, Inc., he continued work on steroid chemistry and returned to his studies of indole alkaloids. In 1974 Julian became ill, and it was necessary for him to scale back his activities. He died on April 19, 1975.

Julian's scientific work generated about 100 technical papers and more than 200 patents. He received nineteen honorary degrees, was a trustee at six colleges and universities, and was active in the Chicago Urban League, the National Association for the Advancement of Colored People (NAACP), and the Mental Health Association of Greater Chicago.

The man who had stoked furnaces to support himself at Harvard was the first African American to serve as a faculty member of a non-Negro college and to achieve a supervisory research position within a major American corporation. When, in 1950, Julian became the first African American to purchase a home in all-white Oak Park, Illinois, he and his family became the objects of racist threats and even attacks. As in his professional career, Julian stood firm, and won the respect of his new neighbors.

Julian attributed his success in life and in his professional career to the motivation he received from his father, who taught him that he should not be satisfied with being merely good, when he had the ability to be the very best. SEE ALSO CORTISONE; MEDICINAL CHEMISTRY.

Lyman R. Caswell

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Volume 2

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Market. Reproduced by permission; p. 92: Carpet trader in Sarajevo. Photograph. David Reed/Corbis. Reproduced by permission; p. 94: Dacron polyester fibers, photograph. © Science Photo Library, The National Audubon Society Collection/Photo Researchers, Inc. Reproduced with permission; p. 95: Colored scanning electron micrograph of eyelashes growing from the surface of human skin, photograph. Photo Researchers, Inc. Reproduced by permission; p. 100: Torchlight parade, photograph by Byron Hertzler. AP/Wide World Photos. Reproduced by permission; p. 103: Fleming, Sir Alexander, photograph. Corbis-Bettmann. Reproduced with permission; p. 107: Supermarket deli worker waiting on a customer, photograph by Jeff Zaruba. Corbis. Reproduced by permission; p. 109: Forensic scientist, removing a fragment of material from a bloodstained garment recovered from a crime scene for DNA testing, photograph by Dr. Jurgen Scriba. Photo Researchers, Inc. Reproduced by permission; p. 111: Lab Agent Kathy Dressel works on DNA evidence in the murder of JonBenet Ramsey at the Colorado Bureau of Investigation, Boulder, Colorado, photograph. AP/Wide World Photos. Reproduced by permission; p. 118: Motorist filling up his automobile gas tank at a Union 76 gas station in San Francisco, California, photograph. © Reuters Newsmedia Inc./Corbis. Reproduced by permission; p. 124: Franklin, Rosalind, British X-ray Crystallographer, photographer. Photo Researchers, Inc. Reproduced by permission; p. 127: Goddard Space Flight Center, National Aeronautics and Space Administration; p. 129: Buckminsterfullerene, photograph by Laguna Design. Photo Researchers, Inc. Reproduced by permission; p. 132: Open microwave oven on kitchen counter, photograph by Robert J. Huffman. FieldMark Publications. Reproduced by permission; p. 137: Photograph by Kelly A. Quin. Copyright © 2003 Kelly A. Quin. Reproduced by permission; p. 138: Soil tilth test using compost (open palm with dirt), photograph by Robert J. Huffman/Field Mark Publications. Reproduced by permission; p. 149: Gay-Lussac, Joseph Louis, photograph. Archive Photos, Inc. Reproduced by permission; p. 153: Diamonds, a mixture of natural and synthetic, shapes and sizes, photograph by Sinclair Stammers. Photo Researchers, Inc. Reproduced by permission; p. 154: Handful of gems that were found in a bucket of dirt at a mine near Franklin, North Carolina, photograph by Raymond Gehman. Corbis. Reproduced by permission; p. 158: Lab technician removes corn embryos to be grown in controlled conditions for desired genetic traits at the Sungene Technologies Lab, Palo Alto, CA, photograph. © Lowell Georgia/Corbis. Reproduced by permission; p. 161: Gibbs, Josiah Willard (three-quarter view from his right, wide bow tie), engraving. The Library of Congress; p. 167: The Artsgarden (glass vault), Indianapolis, Indiana, photograph by Shawn Spence. The Indianapolis Project. Reproduced by permission; p. 177: Goodyear, Charles, sketch. The Library of Congress; p. 179: Zion National Park, Utah, photograph by Robert J. Huffman. Field Mark Publications. Reproduced by permission; p. 183: Haber, Fritz, photograph. © Austrian Archives/Corbis. Reproduced by permission; p. 188: Karen getting hair highlighted by stylist Patti (unseen), sheet of foil under lock of hair, at Maximillian's Salon, photograph by Kelly A. Quin. Reproduced by permission; p. 192: The first blobs of isolated aluminum, photograph. © James L. Amos/Corbis. Reproduced by permission; p. 193: Chlorine gas, in a clear jar, photograph by Martyn F. Chillmaid. Photo Researchers, Inc. Reproduced by permission; p. 197: Heisenberg, W., (second from left) discussing with the staff of the Russian Stand, the adiabatic trap "Ogra", photograph. © Bettmann/Corbis. Reproduced by permission; p. 202: Worker with the California Transportation Department riding on the front of a truck and spraying herbicide, photograph by Ed Young. Corbis. Reproduced by permission; p. 207: Heyrovsky, Jaroslav, portrait. The Library of Congress; p. 208: Hodgkin, Dorothy, photograph. Archive Photos, Inc./Express Newspapers. Reproduced by permission; p. 216: Chlorine plant in Louisiana, photograph.

© Royalty Free/Corbis. Reproduced by permission; p. 223: Petrochemical plant at dusk, photograph by Jeremy Walker. Photo Researchers, Inc. Reproduced by permission; p. 233: Protease inhibitor, photograph by Leonard Lessin. Photo Researchers, Inc. Reproduced by permission; p. 239: Tent caterpillars, (making cocoon), photograph by Edward S. Ross. Copyright E. S. Ross. Reproduced by permission; p. 241: Ladybug on a green stalk, photograph by Robert J. Huffman. Field Mark Publications. Reproduced by permission; p. 253: Sandwich meats in a supermarket, photograph by Todd Gipstein. Corbis. Reproduced by permission.

Volume 3

p. 1: Kekule, Friedrich, photograph. Photo Researchers, Inc. Reproduced by permission; p. 3: Kelsey, Frances Oldham, photograph. The Library of Congress; p. 5: Khorana, Har Gobind, photograph. AP/Wide World Photos. Reproduced by permission; p. 8: Acid dehydration of sugar, photograph by David Taylor. Science Photo Library, National Audubon Society Collection/Photo Researchers, Inc. Reproduced by permission; p. 10: Krebs, Hans Adolf, photograph. The Library of Congress; p. 16: Lavoisier, Antoine-Laurent, photograph. The Library of Congress; p. 17: Instruments from Lavoisier's lab, portrait. The Library of Congress; p. 18: Lawrence, Ernest (with atom smasher), photograph. Corbis-Bettmann. Reproduced by permission; p. 23: Le Bel, Joseph Achille, photograph. Photo Researchers, Inc. Reproduced by permission; p. 24: Leblanc, Nicholas, photograph. Bettmann/Corbis. Reproduced by permission; p. 28: Leloir, Luis F., photograph. UPI/Corbis-Bettmann. Reproduced by permission; p. 29: Lewis, Gilbert N., photograph. Corbis-Bettmann. Reproduced by permission; p. 34: Liebig, Justes von, portrait. The Library of Congress; p. 40: Transmission electron micrograph of lipid droplets in a rat fat cell, magnified x 90,000, photograph by David M. Phillips, The Population Council/Photo Researchers, Inc. Reproduced by permission; p. 41: Woman holding a digital fishfinder, photograph. © AFP/Corbis. Reproduced by permission; p. 45: Waterstrider bug, photograph. © Hermann Eisenbeiss, National Audubon Society Collection/Photo Researchers, Inc. Reproduced by permission; p. 46: Liquids, viscosity, photograph. © Yoav Levy/Phototake NYC. Reproduced by permission; p. 48: Lister, Joseph, photograph. © Bettmann/Corbis. Reproduced by permission; p. 50: Lonsdale, Kathleen, photograph. AP/Wide World Photos. Reproduced by permission; p. 52: False-color angiogram showing stenosis in the carotid artery, photograph by Alfred Pasteka. © CNRI/ Science Photo Library, National Audubon Society Collection/Photo Researchers, Inc. Reproduced by permission. p. 56: Bar magnet with iron filings showing field of force (bright blue background), photograph. Grantpix/Photo Researchers, Inc. Reproduced by permission; p. 60: Oppenheimer, J. Robert, 1946, photograph. © Bettmann/Corbis. Reproduced by permission; p. 62: Martin, Archer, photograph by Nick Sinclair. Photo Researchers, Inc. Reproduced by permission; p. 63: Red sports car, photograph. © Royalty Free/Corbis. Reproduced by permission; p. 67: Maxwell, James Clerk, engraving. The Library of Congress; p. 69: Post-mounted sundial in a Bolivian town, photograph. © John Slater/Corbis. Reproduced by permission; p. 72: Teenage girl being weighed on large scale, photograph by Robert J. Huffman. Field Mark Publications. Reproduced by permission; p. 74: Hahn, Otto, standing with Lise Meitner, photograph. Photo Researchers, Inc. Reproduced by permission; p. 77: Mendeleev, Dmitri Ivanovich, in the chemical factory of the University of St. Petersburg, photograph. © Bettmann/Corbis. Reproduced by permission; p. 82: Landfill with aluminum drum for mercury waste, photograph. Recio/Greenpeace. Reproduced by permission; p. 83: Ritalin tablets, photograph. © Photo Researchers, Inc. Reproduced by permission; p. 85: Lothar von Meyer, Julius, photograph. Photo Researchers, Inc. Reproduced by permission; p. 86: Millikan, Robert A., photograph. The Library of Congress; p. 88: Stratas of banded liassic limestone and shale on a seacliff by

Chinch Gryniewicz. Ecoscene/Corbis. Reproduced by permission; p. 89: Matrix of diamond, photograph. U. S. National Aeronautics and Space Administration (NASA); p. 104: Chaney, Michael wearing special 3-D glasses to view a computer model of Fluoxetine, or Prozac. Lilly Research Labs, Indianapolis, February 22, 1994, photograph. Corbis. Reproduced by permission; p. 115: Three-dimensional computer model of a protein molecule of matrix porin found in the E. Coli bacteria, photograph. © Corbis. Reproduced by permission; p. 118: Two models which represent the arrangement of atoms in a chemical molecule, illustration. Tek Image/Science Photo Library. Photo Researcher, Inc. Reproduced by permission; p. 122: Moseley, Henry, photograph. Photo Researchers, Inc. Reproduced by permission; p. 124: Six-legged frog, photograph. JLM Visuals. Reproduced by permission; p. 130: Coffee shop sign at the Pike Place Public Market, Seattle, Washington, ca. 1990, photograph by Stuart Westmorland. CORBIS/Stuart Westmorland. Reproduced by permission; p. 132: Professor Walther Nernst of Berlin University, Nobel Prize winner for physics, in his laboratory, photograph. © Bettmann/Corbis. Reproduced by permission; p. 137: Diagram showing transmitting and receiving neurons and the role of serotonin in communication between one neuron and the next, illustration by Frank Forney; p. 143: Photovoltaic cell powered desalination system, Saudi Arabia, photograph. Mobil Solar Energy Corporation/Phototake NYC. Reproduced by permission; p. 144: Newton, Sir Isaac (oval frame, allegorical elements surrounding), engraving. The Library of Congress; p. 153: Hand pouring liquid nitrogen into beaker, photograph. © David Taylor/Photo Researchers. Reproduced by permission; p. 155: Nobel, Alfred (wearing suit, checked bow tie), drawing. The Library of Congress; p. 158: Scientist from University of California—Berkley studying helium gas being released from a hot spring in Yellowstone National Park, photograph. © James L. Amos/Corbis. Reproduced by permission; p. 168: Lasers focus on a small pellet of fuel in attempt to create nuclear fusion reaction, photograph. © Roger Ressmeyer/Corbis. Reproduced by permission; p. 169: Seaborg, Glenn, photograph by Lawrence Berkeley. Photo Researchers, Inc. Reproduced by permission; p. 172: Nuclear reactors, interior of the containment building, photograph by Mark Marten. Photo Researchers, Inc. Reproduced by permission; p. 174: Nuclear fusion, computer simulation, photograph by Jens Konopka and Henning Weber. Photo Researchers, Inc. Reproduced by permission; p. 178: Magnetic Resonance Imaging System (room with equipment and viewing machine), photograph by Mason Morfit. FPG International Corp. Reproduced by permission; p. 181: Colored positron emission tomography (PET) scans comparing the brain of a depressed person (top) with the brain of a healthy person, illustration. © Photo Researchers, Inc. Reproduced by permission; p. 192: Oppenheimer, Dr. J. Robert, atomic physicist and head of the Manhattan Project, photograph. National Archives and Records Administration; p. 209: Ostwald, Friedrich Wilhelm, portrait. The Library of Congress; p. 211: Doctor communicating with a patient lying in a pressure chamber and undergoing hyperbaric oxygen therapy, photograph by James King-Holmes/Science Photo Library. Reproduced by permission; p. 214: Woodcut from “Works”, of Paracelsus ca. 1580 edition, of Mercury in its alchemical form as Azoth, photograph. Fortean Picture Library. Reproduced by permission; p. 218: © Kevin Fleming/Corbis. Reproduced by permission; p. 220: Pasteur, Louis, photograph. Hulton-Deutsch Collection/Corbis. Reproduced by permission; p. 222: Pauli, Wolfgang, photograph by Zurich Bettina. Courtesy of CERN-European Organization for Nuclear Research. Reproduced by permission; p. 223: Pauling, Linus, proponent of heavy vitamin C use, tossing an orange, photograph. © Roger Ressmeyer/Corbis. Reproduced by permission; p. 225: Penicillin, photograph by Andrew McClenaghan, photograph. Photo Researchers, Inc. Reproduced by permission; p. 229: Early Periodic Table, portrait. The Library of Congress; p. 234: Worker in

protective photograph by Ed Young. Corbis. Reproduced by permission; p. 238: Smith, Billy, Drilling Foreman, seated at Drake Well, photograph. AP/Wide World. Reproduced by permission; p. 241: Man in red hardhat standing on bluish oil refinery equipment, yellow flames from burning natural gas at top right, photograph. © Lowell Georgia/Corbis. Reproduced by permission; p. 249: The first known photograph of a courtyard outside Niepce's room, photograph. The Bettmann Archive/Corbis. Reproduced by permission; p. 256: Hot water vaporizing as it is thrown into air during minus 35-degree Fahrenheit temperature, Boundary Waters Canoe Area Wilderness, Minnesota, USA, photograph © Layne Kennedy/Corbis. Reproduced by permission; p. 258: X-ray diffraction crystallography, photograph by James King-Holmes. OCMS/Science Photo Library/ Photo Researchers, Inc. Reproduced by permission; p. 259: Several open cans of paint in an assortment of colors, photograph by Matthias Kulka. Corbis. Reproduced by permission; p. 262: Planck, Max, photograph. © Bettmann/Corbis. Reproduced by permission.

Volume 4

p. 5: Travolta, John, with Karen Lynn Gorney in a scene from "Saturday Night Fever," photograph. The Kobal Collection. Reproduced by permission; p. 12: Ghost crab walking among a sandy shoreline, photograph. Sapelo Island National Estuarine Research Reserve. Reproduced by permission; p. 30: Priestley, Joseph, engraving. International Portrait Gallery; p. 38: Scientist adjusts equipment used in fast protein liquid chromatography, photograph. Photo Researchers, Inc. Reproduced by permission; p. 50: Spectrum of electromagnetic radiation, (chart) illustrations by Robert L. Wolke. Reproduced by permission; p. 52: Radioactive emission of alpha particles from radium, yellow sunburst, dark blue background, photograph. Photo Researchers, Inc. Reproduced by permission; p. 58: International mobile radiological radiologists measuring soil radioactivity levels near Ukraine's Chernobyl Nuclear Plant, wearing protective clothing, from International Mobile Radiological Laboratories, near Chernobyl, Ukraine, photograph. © Reuters NewsMedia Inc./Corbis. Reproduced by permission; p. 60: Radon test kit and carbon monoxide detector, photograph by Robert J. Huffman.
Field Mark Publications. Reproduced by permission; p. 63: Ramsay, William, portrait. The Library of Congress; p. 65: Reaction rate, illustration. GALE Group. Studio: EIG; p. 74: Bragg, Kevin, photograph. © James A. Sugar/Corbis. Reproduced by permission; p. 80: Open electric oven showing the glowing red heating element, photograph by Robert J. Huffman. FieldMark Publications. Reproduced by permission; p. 86: Robinson, Robert, portrait. The Library of Congress; p. 89: Captured German V-2 rocket cuts through the clouds during experiment, 1947, photograph. AP/Wide World Photos. Reproduced by permission; p. 90: Full-scale operational model of the Mars Viking Lander, photograph by Lowell Georgia/Corbis. Reproduced by permission; p. 97: Rubidium, photograph. © Russ Lappa/Science Source, National Audubon Society Collection/Photo Researchers, Inc. Reproduced by permission; p. 99: Rutherford, Ernest, Walton (left to right), Ernest Rutherford, and J.D. Cockcroft, standing together outside, photograph. © Hulton-Deutsch Collection/Corbis; p. 103: Large pile of salt at a salt mine, October 29, 1996, Upington, South Africa, photograph. © Charles O'Rear/Corbis; p. 106: Sanger, Frederick looking up at model of DNA molecule, photograph. © Bettmann/Corbis. Reproduced by Corbis Corporation; p. 108: Scheele, Carl Wilhelm, portrait. The Library of Congress; p. 110: Schrodinger, Professor Erwin of Magdalen College, Oxford, winner of the 1933 Nobel Prize in Physics along with Professor P.H.M. Dirac of Cambridge University, England, November 18, 1933, photograph. © Bettmann/Corbis. Reproduced by permission; p. 111: Seaborg, Glenn T., photograph. © Roger Ressmeyer/Corbis. Reproduced by permission; p. 115: Seibert, Florence, photograph. AP/Wide World Photos. Reproduced by permission; p. 116: Dish of selenium, photograph. © Rich

Treptow, National Audubon Society Collection/Photo Researchers, Inc. Reproduced by permission; p. 117: Person holding a conventional tub amplifier, photograph. © Bettmann/Corbis. Reproduced by permission; p. 120: Micro wires, silicon chip, photograph by Andrew Syred. The National Audubon Society Collection/ Photo Researchers, Inc. Reproduced by permission; p. 122: Worker testing silicon wafers at the Matsushita Semiconductor plant in Puyallup, Washington, c. 1994, photograph. © Kevin R. Morris/Corbis. Reproduced by permission; p. 131: Soddy, Frederick, drawing. The Library of Congress; p. 132: Sodium acetate hot pack reacting, photograph by Charles D. Winters. Photo Researchers, Inc. Reproduced by permission; p. 149: Solution of water and oil, droplets are exposed to polarized light, magnification, photograph by David Spears. © Science Pictures Limited/Corbis; p. 154: Electron spectroscopy, chemical analysis, photograph by Joseph Nettis. Photo Researchers, Inc. Reproduced by permission; p. 157: Stanley, Wendell Meredith, photograph. The Library of Congress; p. 159: Staudinger, Hermann, portrait. The Library of Congress; p. 161: Steel worker sampling molten metal, photograph by John Olson. Stock Market. Reproduced by permission; p. 164: Steel Bridge, Portland, Oregon, photograph by James Blank. © James Blank. Reproduced by permission; p. 167: Hand holding 50 mg bottle of the injectable anabolic steroid Durabolin, photograph. Custom Medical Stock Photo. Reproduced by permission; p. 169: Razor blade cutting powder form of the drug Speed into lines for snorting, photograph. Science Photo Library. Reproduced by permission; p. 174: Germinating garden pea Pisum Sativum, showing embryonic root growing downward, macrophotograph, photograph. © J. Burgess/Photo Researchers. Reproduced by permission; p. 176: Rayleigh, 3rd Baron (John W. Strut, III), drawing. The Library of Congress; p. 179: Vat of sulfur, photograph by Farrell Grehan. Corbis. Reproduced by permission; p. 180: Sumner, James B., portrait. The Library of Congress; p. 182: Meissner effect, cube floating above a superconductor, photograph by Yoav Levy. Phototake NYC. Reproduced by permission; p. 187: Scanning tunneling microscope image of sulfur atoms on rhodium surface, photograph by Dr. James Batteas. National Institute of Standards and Technology; p. 187: Topographic image of a reconstructed silicon surface showing outermost atomic positions, photograph of Dr. James Batteas. National Institute of Standards and Technology. Reproduced by permission; p. 189: Infrared near-field scanning optical microscope (NSOM) image of blended polystyrene/polyethylacrylate film on silicon, photograph by f Dr. Chris Michaels and Dr. Stephan Stranick, National Institute of Standards and Technology. Reproduced by permission; p. 189: Nanowriting of a mercaptbenzoic acid layer into a background layer of dodecanethiol using nanografting, photograph by Dr. Jayne Gerano, National Institute of Standards and Technology. Reproduced by permission; p. 191: Tractor riding past wind generators, photograph. © AP/Wide World Photos. Reproduced by permission; p. 192: Cutaway of the ITER tokamak device, photograph. Photo Researchers, Inc. Reproduced by permission; p. 193: Svedberg, Theodor, portrait. The Library of Congress; p. 195: Synge, Richard L.M., photograph. The Library of Congress; p. 198: Organic chemist synthesizing chemotherapy agent, photograph by Geoff Tompkinson. Photo Researchers, Inc. Reproduced by permission; p. 200: Szent-Gyorgyi, Dr. Albert, Nobel Prize winner, discoverer of Vitamin C and bioflavinoids, photograph. © Bettmann/CORBIS. Reproduced by permission; p. 205: Photocopier in office, photograph by Robert J. Huffman. FieldMark Publications. Reproduced by permission; p. 207: © Royalty-Free/Corbis. Reproduced by permission; p. 209: Yendell, Thomas, a Thalidomide baby, picks up a toy with his feet, photograph. AP/Wide World Photos. Reproduced by permission; p. 215: Thallium heart scan, photograph by Peter Berndt, M.D. Custom Medical Stock Photo. Reproduced by permission; p. 226: Thomson, Sir Joseph John, photograph. UPI/Corbis-Bettmann.

Reproduced by permission; p. 227: Man, writing, being flanked by two other men watching. AP/Wide World Photos. Reproduced by permission; p. 228: Army medic, taking an x-ray of a fellow soldier simulating an injury, photograph. © Bettmann/Corbis. Reproduced by permission; p. 236: Stanford Linear Accelerator Center, photograph by David Parler. National Audubon Society Collection/Photo Researchers Inc. Reproduced by permission; p. 241: Alchemist (seated left wearing eyeglasses) and his assistants, engraving. The Granger Collection, New York. Reproduced by permission; p. 244: Computer generated graphic of a molecule of hemoglobin-carrier of oxygen in the blood, photograph. © Science Photo Library. Photo Researchers. Reproduced by permission; p. 249: Urey, Harold, photograph. The Library of Congress; p. 253: Van Der Waals, Johannes Diderik, photograph. Science Photo Library. Photo Researchers, Inc. Reproduced by permission; p. 255: Helmont, Jan (Baptise) Van (standing), print; p. 256: Hoff, Jacobus Henricus vant, photograph. Photo Researchers, Inc. Reproduced by permission; p. 258: Banded gila monster, photograph by Renee Lynn. The National Audubon Society Collection/Photo Researchers, Inc. Reproduced by permission; p. 261: Allesandro Volta, standing, body turned slightly to his left, painting. UPI/Corbis-Bettmann. Reproduced by permission; p. 263: Waksman, Selman A.(in laboratory), photograph. The Library of Congress.; p. 265: Molecular graphic of water molecules evaporating from a solution, photograph. © K. Eward/Photo Researchers. Reproduced by permission; p. 270: Dead fish, killed from water pollution, photograph. © U.S. Fish & Wildlife Service; p. 273: Newly treated water in the Orange County Water Treatment Works, Florida, photograph by Alan Towse. © Ecoscene/CORBIS. Reproduced by permission; p. 275: Watson, Dr. James Dewey, with DNA model, 1962, photograph. UPI/Corbis-Bettmann. Reproduced by permission; p. 277: Werner, Alfred, portrait. The Library of Congress; p. 279: Willstatter, Richard, photograph. Photo Researchers, Inc. Reproduced by permission; p. 280: Wohler, Friedrich, portrait. The Library of Congress; p. 282: Woodward, Robert Burns (standing with unknown man, viewing book), photograph. The Library of Congress; p. 284: Cylindrical map of the eastern half of the surface of Venus, as viewed from the spacecraft Magellan, photograph. NASA/JPL/CALTECH. Reproduced by permission; p. 285: Yalow, Rosalyn, 1978, photograph. Corbis-Bettmann. Reproduced by permission; p. 288: Yukawa, Hideki (holding chalk, pointing to writing on board), photograph. The Library of Congress; p. 293: Kangaroo on the beach in Australia, photograph. © Australian Picture Library/Corbis. Reproduced by permission; p. 294: Zsigmondy, Richard, portrait. The Library of Congress.

Glossary

acetylcholine: neurotransmitter with the chemical formula $C_7H_{17}NO_3$; it assists in communication between nerve cells in the brain and central nervous system

acid rain: precipitation that has a pH lower than 5.6; term coined by R. A. Smith during the 1870s

activation analysis: technique that identifies elements present in a sample by inducing radioactivity through absorbtion of neutrons

adenine: one of the purine bases found in nucleic acids, $C_5H_5N_5$

adenosine triphosphate (ATP): molecule formed by the condensation of adenine, ribose, and triphosphoric acid, HOP(O)OH–O–(O)OH–OP(O)OH–OH; it is a key compound in the mediation of energy in both plants and animals

adrenalin: chemical secreted in the body in response to stress

alchemy: medieval chemical philosophy having among its asserted aims the transmutation of base metals into gold

aldehyde: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the RC(O)H functional group

aliphatic: having carbon atoms in an open chain structure (as an alkane)

aliquot: specific volume of a liquid used in analysis

alkaloid: alkaline nitrogen-based compound extracted from plants

alloy: mixture of two or more elements, at least one of which is a metal

α subunit: subunit that exists in proteins that are composed of several chains of amino acids, the first unit in the "counting" of the units

α-particle: subatomic particle with 2+ charge and mass of 4; a He nucleus

amalgam: metallic alloy of mercury and one or more metals

amine functional group: group in which nitrogen is bound to carbon in an organic molecule in which two other groups or hydrogen atoms are bound to nitrogen; major component of amino acids

amino acid residue: in a protein, which is a polymer composed of many amino acids, that portion of the amino acid that remains to become part of the protein

amino acid sequence: twenty of the more than five hundred amino acids that are known to occur in nature are incorporated into a variety of proteins that are required for life processes; the sequence or order of the amino acids present determines the nature of the protein

amphetamine: class of compounds used to stimulate the central nervous system

anabolism: metabolic process involving building of complex substances from simpler ones, using energy

analgesic: compound that relieves pain, e.g., aspirin

androgen: group of steroids that act as male sex hormones

angiotensin: chemical that causes a narrowing of blood vessels

anhydrous compound: compound with no water associated with it

anion: negatively charged chemical unit, like Cl−, CO_{32}−, or NO_3−

anthcyanin: antioxidant flavanoid that makes raspberries red and blueberries blue

antibody: protein molecule that recognizes external agents in the body and binds to them as part of the immune response of the body

anticoagulant: molecule that helps prevent the clotting of blood cells

antiscorbutic: substance that has an effect on scurvy

apoenzyme: the protein part of an enzyme that requires a covalently bound coenzyme (a low molecular weight organic compound) or a cofactor (such as a metal ion) for activity

aqueous solution: homogenous mixture in which water is the solvent (primary component)

aromatic: having a double-bonded carbon ring (typified by benzene)

asparagine residue: amino acid asparagine unit as it occurs in a polypeptide chain

atomic mass units: unit used to measure atomic mass; 1/12 of the mass of a carbon-12 atom

atomic number: the number of protons in an atomic nucleus, expressed in terms of electric charge; it is usually denoted by the symbol Z

atomic orbital: mathematical description of the probability of finding an electron around an atom

atomic spectrum: electromagnetic array resulting from excitement of a gaseous atom

atomic theory: concept that asserts that matter is composed of tiny particles called atoms

atomic weight: weight of a single atom of an element in atomic mass units (amu)

attraction: force that brings two bodies together, such as two oppositely charged bodies

axial bond: covalent bond pointing along a molecular axis

azo dye: synthetic organic dye containing a –N=N– group

bacteriophage multiplication: process by which immune system cells responsible for battling bacterial infections reproduce

basal metabolism: the process by which the energy to carry out involuntary, life-sustaining processes is generated.

β subunit: subunit that exists when two or more polypeptide chains associate to form a complex functional protein, the chains are referred to as "subunits"; these subunits are often identified as α, β, etc.

biological stain: dye used to provide contrast among and between cellular moieties

biomass: collection of living matter

biosynthesis: formation of a chemical substance by a living organism

boat conformation: the arrangement of carbon atoms in cyclohexane, C_6H_{12}. In which the spatial placement of the carbon atoms resembles a boat with a bow and a stern

brine: water containing a large amount of salts, especially sodium chloride (NaCl)

Brownian motion: random motion of small particles, such as dust or smoke particles, suspended in a gas or liquid; it is caused by collisions of the particle with gas or solvent molecules which transfer momentum to the particle and cause it to move

calc: calcium carbonate

calcine: to heat or roast to produce an oxide (e.g., CaO from calcite)

capacitor plate: one of several conducting plates, or foils, in a capacitor, separated by thin layers of dielectric constant, an insulating material

carboxylate: structure incorporating the –COO– group

carboxyl group: an organic functional group, –C(O), found in aldehydes, ketones, and carboxyl acids.

carboxylic acid: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the $–CO_2H$ functional group

catabolism: metabolic process involving breakdown of a molecule into smaller ones resulting in a release of energy

catalysis: the action or effect of a substance in increasing the rate of a reaction without itself being converted

catalyst: substance that aids in a reaction while retaining its own chemical identity

catalytic conversion: catalytic oxidation of carbon monoxide and hydrocarbons in automotive exhaust gas to carbon dioxide and water

cell culture: artificially maintained population of cells, grown in a nutrient medium and reproducing by asexual division

cephalosporin C: family of antibiotics obtained from a fungus acting in a manner similar to penicillin

chain of custody: sequence of possession through which evidentiary materials are processed

chair conformation: arrangement of atoms in a cycle structure (usually a six-membered ring) that appears to be arranged like a chair (as opposed to the other conformation which is described as a "boat")

chemical-gated: of a membrane protein whose action to open a pore in the membrane occurs only after a substrate has been binded to the protein or a cofactor

chlorofluorocarbon (CFC): compound containing carbon, chlorine, and fluorine atoms that remove ozone in the upper atmosphere

chlorophyll: active molecules in plants undergoing photosynthesis

chromatography: the separation of the components of a mixture in one phase (the mobile phase) by passing in through another phase (the stationary phase) making use of the extent to which the components are absorbed by the stationary phase

chromophore: part of the molecule that yields characteristic colors

cladding: protective material surrounding a second material, which is frequently tubes filled with uranium dioxide pellets in a nuclear reactor

cleave: split

cobrotoxin: polypeptide toxin containing sixty-two residues that is found in the venom of cobras

code: mechanism to convey information on genes and genetic sequence

cofactor: inorganic component that combines with an apoenzyme to form a complete functioning enzyme

coherent mass: mass of particles that stick together

color fastness: condition characterized by retention of colored moieties from a base material

combustion: burning, the reaction with oxygen

competitive inhibitor: species or substance that slows or stops a chemical reaction

complementarity: basis for copying the genetic information, where each nucleotide base has a complementary partner with which it forms a base-pair

congener: an element or compound belonging to the same class

constitutional isomer: form of a substance that differs by the arrangement of atoms along a molecular backbone

contact activity: process involving the touching of different surfaces

contraction: the shortening of a normal trend of a quantity

coordinate covalent bond: covalent bond in which both of the shared electrons originate on only one of the bonding atoms

coordination chemistry: chemistry involving complexes of metal ions surrounded by covalently bonded ligands

corrosive gas: gas that causes chemical deterioration

covalent bond: bond formed between two atoms that mutually share a pair of electrons

crystal lattice: three-dimensional structure of a crystaline solid

crystallization: process of producing crystals of a substance when a saturated solution in an appropriate solvent is either cooled or some solvent removed by evaporation

culture: living material developed in prepared nutrient media

cyanobacterium: eubacterium sometimes called "the blue-green alga"; it contains chlorophyll (the pigment most abundant in plants), has very strong cell walls, and is capable of photosynthesis

cyclopentadienyl ring: five-membered carbon ring containing two C–C double bonds; formula C_5H_6

cysteine residue: sulfhydryl-containing cysteine unit in a protein molecule

cytosine: heterocyclic, pyrimidine, amine base found in DNA

dedifferentiation: the opposite of the biological process of differentiation by which a relatively unspecialized cell undergoes a progressive change to a more specialized form or function

degradative: relating to or tending to cause decomposition

degrade: to decompose or reduce the complexity of a chemical

delocalized: of a type of electron that can be shared by more than one orbital or atom

denitrification: process of removing nitrogen

density-functional theory: quantum mechanical method to determine ground states

depolarization: process of decreasing the separation of charge in nerve cells; the opposite of hyperpolarization

deterministic: related to the assumption that all events are based on natural laws

deuteron: nucleus containing one proton and one neutron, as is found in the isotope deuterium

dialcohol: organic molecule containing two covalently-bonded –OH groups

diamagnetic: property of a substance that causes it to be repelled by a magnetic field

diamine: compound, the molecules of which incorporate two amino groups ($-NH_2$) in their structure, such as 1,2 diamino ethane (sometimes called ethylenediamine) and the three diamine benzene compounds

dibasic acid: acidic substance that incorporates two or more acidic hydrogen atoms in one molecule, such as sulfuric (H_2SO_4) and phosphoric (H_3PO_4) acids

dihydroxy compound: compound with molecules that incorporate two hydroxyl groups (–OH) in their structure, such as 1,2 dihydroxy ethane (sometimes called glycol) and the three dihydroxy benzene compounds

directing effect: ability of a functional group to influence the site of chemical reaction, such as substitution, for a molecule

discharge display tube: glass tube containing gas at low pressure through which a beam of electrons is passed

disperse system: two-phase system in which one phase, the disperse phase, is distributed in the second phase, the dispersion medium

disulfide bond: bond in a complex substance that involves two bonding sulfur atoms, –S–S–

disulfide bridge: covalent –S–S– linkage that provides cross-links in protein molecules

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

dope: to add a controlled amount of an impurity to a very pure sample of a substance, which can radically change the properties of a substance

drug resistance: ability to prevent the action of a particular chemical substance

ductile: property of a substance that permits it to be drawn into wires

Eighteen Electron Rule: rule noting that coordination complexes with eighteen electrons are stable; electrons from both metal species and ligand donor species are counted

electrolyte solution: a liquid mixture containing dissolved ions

electron correlation error: quantum mechanical method for studying atoms, ions, or molecules

electronegative: capable of attracting electrons

electrophoresis: migration of charged particles under the influence of an electric field, usually in solution; cations, the positively charged species, will move toward the negative pole and anions, the negatively charged species, will move toward the positive pole

electrostatic interaction: force that arises between electrically charged particles or regions of particles

elemental analysis: determination of the percent of each atom in a specific molecule

emulsifier: substance that stabilizes the formation of an emulsion—normally it contains molecules with both polar and non-polar functional groups

emulsion: immiscible two-phase mixture in which one phase is dispersed (as small droplets) in the other phase

enantiomorphic shape: mixture of molecules with the same molecular formulas but different optical characteristics

endohedral: descriptive term for a point within a three-dimensional figure

endoplasmic reticulum: internal membrane system that forms a net-like array of channels and interconnections of organelles within the cytoplasm of eukaryotic cells

Equation of State for Ideal Gases: mathematical statement relating conditions of pressure, volume, absolute temperature, and amount of substance; $PV = nRT$

equatorial bond: covalent bond perpendicular to a molecular axis

equilibrium: condition in which two opposite reactions are occurring at the same speed, so that concentrations of products and reactants do not change

erythromycin: antibiotic used to treat infections

ester: organic species containing a carbon atom attached to three moieties: an O via a double bond, an O attached to another carbon atom or chain, and an H atom or C chain; the R(C=O)OR functional group

esterification: chemical reaction in which esters (RCO_2R_1) are formed from alcohols (R_1OH) and carboxylic acids (RCO_2R')

estrogen: female sex hormone

eukaryotic cell: cell characterized by membrane-bound organelles, most notably the nucleus, and that possesses chromosomes whose DNA is associated with proteins

excitatory: phenomenon causing cells to become active

excitatory neurotransmitter: molecule that stimulates postsynaptic neurons to transmit impulses

exclusion principle: principle that states that no two electrons can have the same four quantum numbers

excrete: to eliminate or discharge from a living entity

expressed: made to appear; in biochemistry—copied

extracellular matrix: entity surrounding mammalian tissue cells, also called connective tissue; composed of structural proteins, specialized proteins, and proteoglycans

face centered cubic structure: close-packed crystal structure having a cubic unit cell with atoms at the center of each of its six faces

feedstock: mixture of raw materials necessary to carry out chemical reactions

Fermi conduction level: vacant or partially occupied electronic energy level resulting from an array of a large number of atoms in which electrons can freely move

ferric: older name for iron in the +3 oxidation state

ferrous: older name for iron in the +2 oxidation state

fibril: slender fiber or filament

fission: process of splitting of an atom into smaller pieces

fissionable: of or pertaining to unstable nuclei that decay to produce smaller nuclei

5′ end: situation in nucleic acids in which the phosphate group is attached at the fifth carbon atom from where the base is attached

folic acid: pteroylglutamic acid; one of the B complex vitamins

formaldehyde: name given to the simplest aldehyde HC(O)H, incorporating the –C(O)H functional group

fractional distillation: separation of liquid mixtures by collecting separately the distillates at certain temperatures

fulcrum: prop or support to an item as in a lever

functional group: portion of a compound with characteristic atoms acting as a group

galactose: six-carbon sugar

galvanic: relating to direct current electricity, especially when produced chemically

galvanometer: instrument used to detect and measure the strength of an electric current

gas density: weight in grams of a liter of gas

glucocorticoid: class of hormones that promotes the breakdown of proteins to make amino acids available for gluconeogenesis; this elevates the blood sugar level and leads to glycogen synthesis in the liver

glucose: common hexose monosaccharide; monomer of starch and cellulose; also called grape sugar, blood sugar, or dextrose

golgi apparatus: collection of flattened stacks of membranes in the cytoplasm of eukaryotic cells that function in the collection, packaging, and distribution of molecules synthesized in the cell

gram negative: bacteria that do not retain their color when exposed to basic dyes such as crystal violet and then exposed to organic solvents; named after Danish bacteriologist Hans Christian Joachim Gram

gram positive: bacteria that retain their color when exposed to basic dyes such as crystal violet and then exposed to organic solvents; named after Danish bacteriologist Hans Christian Joachim Gram

Gray: unit of radiation dose per second; 1 Gray = 1 J/kg

greenhouse effect: presence of carbon dioxide in the atmosphere prevents heat from escaping, thereby raising Earth's temperature

Griess reagent: solution of sulfanilic acid and a-naphthylamine in acetic acid; reagent for nitrites

guanine: heterocyclic, purine, amine base found in DNA

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

heavy metal: by convention, a metal with a density greater than 5 g/cm^3; 70 elements are thus classified as heavy metals

helix: in the shape of a spiral or coil, such as a corkscrew

heme group: functional group formed by an iron atom interacting with a heterocyclic ligand called a porphyrin

hemiacetal: relating to organic compounds formed from an alcohol and a carbonyl-containing molecule

hemlock: poisonous herb of the genus Conium

Hippocrates: Greek physician of fifth century B.C.E. known as the "father of medicine"

homogeneous: relating to a mixture of the same materials

homogeneous solution: mixture of molecules that forms a single phase (solid, liquid, or gas)

hormonal signaling: collective processes by which hormones circulate in the blood stream to their target organs and trigger the desired responses

hydrogen bonding: intermolecular force between the H of an N–H, O–H or F–H bond and a lone pair on O, N or F of an adjacent molecule

hydrolyze: to react with water

hydrophilic: having an affinity with water

hydrophobic: water repelling

hyperbolic relationship: a geometric system in which two or more lines can be drawn through any point in a plane and not intersect a given line in that plane

hyperpolarization: process of causing an increase in charge separation in nerve cells; opposite of depolarization

hypertension: condition in which blood pressure is abnormally high

Ibn Sina: given name of an Islamic scientist known in the West as Avicenna (979–1037); reputed to be the author of more than 100 books that were Europe's most important medical texts from the 12th century until the 16th century

inert: incapable of reacting with another substance

inhibitory: preventing an action that would normally occur

integro-differential: complex mathematical model used to calculate a phase transition

interface tension: contractile force at the junction of two liquids

intermediate: molecule, often short-lived, that occurs while a chemical reaction progresses but is not present when the reaction is complete

intermolecular force: force that arises between molecules, generally it is at least one order of magnitude weaker than the chemical bonding force

internuclear: distance between two nuclei

intestinal epithelium: layer of cells in the intestines that allows the passage of water and solutes

intramolecular force: force that arises within molecules—essentially the force associated with chemical bonds

invertebrate: category of animal that has no internal skeleton

in vitro: Latin, meaning “in glass” and applied to experiments done under artificial conditions, that is, in a test tube

in vivo: Latin, meaning “in life” and applied to experiments conducted in a living cell or organism

ion exchange chromatography: form of liquid-solid chromatography based on the reversible formation of bonds between the fixed ions bound to an insoluble matrix of an ion exchanger and mobile counter ions present in the liquid phase passing over the insoluble matrix

ionization: dissociation of a molecule into ions carrying + or − charges

isolate: part of a reaction mixture that is separated and contains the material of interest

isomer: molecules with identical compositions but different structural formulas

isoprene: common name for 2-methyl-1,3butadiene, the monomer of the natural rubber polymer

isostructural: relating to an arrangement of atomic constituents that is geometrically the same although different atoms are present

isotope: form of an atom that differs by the number of neutrons in the nucleus

ketone: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the RC(O)R functional group

kinetic theory: theory of molecular motion

Kohlrausch drum: rotating cylinder used to mount a variable resistance slide wire for a polarograph

lanthanides: a family of elements (atomic number 57 through 70) from lanthanum to lutetium having from 1 to 14 4f electrons

lattice: systematic geometrical arrangement of atomic-sized units that describe the structure of a solid

ligand: molecule or ion capable of donating one or more electron pairs to a Lewis acid

lipid: a nonpolar organic molecule; fatlike; one of a large variety of nonpolar hydrophobic (water-hating) molecules that are insoluble in water

lipophilic: a molecule that tends to congregate in solution with lipids—it will be a nonpolar molecule or the nonpolar portion of a molecule

liposome: sac formed from one or more lipid layers that can be used for drug transport to cells in the body

liquefaction: process of changing to a liquid form

locomotor: able to move from place to place

Lucretius: Roman poet of first century B.C.E., also known as Titus Carus; author of *De Rerum Natura*

lysergic acid: one of the Ergot series of alkaloids, which constrict blood vessels so that the victim develops burning sensations in the limbs, gangrene, and, ultimately, convulsions; the diethylamide of this substance (LSD) induces visual perception disorders, delusion

lysis: breakdown of cells; also the favorable termination of a disease

macrolide: substance with a large ring lactone structure

macronutrient: one of a number of substances, needed in relatively large amounts, that provide nourishment for living organisms

macroscopic phenomena: events observed with human vision unassisted by instrumentation

mammalian toxicity: poisonous effect on humans and other mammals

Manhattan Project: government project dedicated to creation of an atomic weapon; directed by General Leslie Groves

manifold of ensemble states: a set of quantum states that meet the specific requirements (such as total energy) being considered in a calculation

mechanical energy: energy of an object due to its position or motion

mediate: to act as an intermediary agent

melting point: temperature at which a substance in the solid state undergoes a phase change to the liquid state

mentorship: the process by which a wise and trusted teacher guides a novice in the development of his/her abilities

metabolism: the complete range of biochemical processes that take place within living organisms; comprises processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those that break down complex food molecules, thus liberating energy (catabolism)

metabolites: products of biological activity that are important in metabolism

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

metal cation: positively charged ion resulting from the loss of one or more valence electrons

metalloenzyme: a protein enzyme that contains at least one metal atom, often in an active site of the protein

metalloid: elements that exhibit properties that are between those of metals and nonmetals; generally considered to include boron, silicon, germanium, arsensic, antimony, tellurium, and polonium

metallothionein: class of low molecular weight proteins and polypeptides with very high metal and sulfur content; thought to play a role in concentration and flow of essential elements, e.g., Cu and Zn, and in ameliorating the influence of toxic elements, e.g., Hg and Cd, in the body

metallurgy: the science and technology of metals

microchemistry: chemical investigation carried out on a microscopic level

microcrystalline: relating to the structure of crystals of very small size, typically a micron (μm) in dimension

micromolar: relating to a solution of a substance that is in the concentration range of micromoles per liter, or 10^{-6} moles per liter

mitochondrial matrix: soluble phase inside the inner mitochondrial membrane containing most of its enzymes

mitosis: process by which cells divide, particularly the division of the cell nucleus

molecular identity: “fingerprint” of a molecule describing the structure

monoclinic: one of several arrangements of atoms found in crystalline solids; characterized by a unit cell of three axes each of a differing length; two axes are mutually perpendicular while the third is at an oblique angle

monodentate: capable of donating one electron pair; literally, one-toothed

monosaccharide: one class of the natural products called carbohydrates with the general formula $C_x(H_2O)_y$; monosaccharides have a weak sweet taste, are readily soluble in water, and are called sugars

mordant dye: dye substance containing an acidic moiety, e.g., a carboxyl group, which binds metallic compounds, forming insoluble colored compounds

natural philosophy: study of nature and the physical universe

nesosilicate: any silicate in which the SiO_4 tetrahedra are not interlinked

net charge: total overall charge

neurologic: of or pertaining to the nervous system

neuropathy: degenerative state of the nerves or nervous system

neuropeptide: neurotransmitter released into the blood stream via nerve cells

neutron activation analysis: method for detecting traces of elements by bombardment with high-flux neutrons and then measuring the decay rate of the radioactive products

Newtonian: based on the physics of Isaac Newton

nicotine adenine dinucleotide (NAD): one compound of a group of coenzymes found in hydrogen-transferring enzymes

nitric oxide: compound, NO, which is involved in many biological processes; the drug Viagra enhances NO-stimulation of pathways to counteract impotence; may be involved in killing tumors

nitrotoluic acid: benzoic acid molecule with methyl and nitro groups attached

noble gas: element characterized by inert nature; located in the rightmost column in the Periodic Table

noncovalent: having a structure in which atoms are not held together by sharing pairs of electrons

noncovalent aggregation: non-specific interaction leading to the association of molecules

nonpolar: molecule, or portion of a molecule, that does not have a permanent, electric dipole

nuclear: (a) having to do with the nucleus of an atom; (b) having to do with the nucleus of a cell

nucleosynthesis: creation of heavier elements from lighter elements via fusion reactions in stars

octahedral: relating to a geometric arrangement of six ligands equally distributed around a Lewis acid; literally, eight faces

odd chain fatty acid: long chain carboxylic acid with an odd number of carbon atoms

oligomeric chain: chain that contains a few repeating units of a growing polymeric species

opioid: naturally produced opium-like substance found in the brain

optically active: capable of rotating the plane of plane-polarized light

organoleptic: effect of a substance on the five senses

organometallic compound: compound containing both a metal (transition) and one or more organic moieties

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

oxidation state zero: condition characterized by an atom having neither lost nor gained electrons

oxidation–reduction reaction: reaction, sometimes called redox, that involves the movement of electrons between reactants to form products

oxide ion conductor: series of oxides of various compounds in perovskite structure—especially of interest in high-temperature fuel cells

parabolic curve: planar curve each point of which is equidistant from a straight line (axis)

paraffin: saturated aliphatic hydrocarbon (alkane), or hydrocarbon wax

partial pressure: portion of a total pressure of a gas mixture contributed by a single type of gas in the sample

passive diffusion: mechanism of transporting solutes across membranes

pasteurization: process of heating foods such as milk to destroy bacteria

peerage: a body of peers; dignitaries of equal standing

perpendicular: condition in which two lines (or linear entities like chemical bonds) intersect at a 90-degree angle

pH effect: effect caused by a change in the concentration of hydrogen ions

phase: homogenous state of matter

phenol: common name for hydroxybenzene (C_6H_5OH)

phosphorylation: the addition of phosphates into biological molecules

photodiode assembly: grouping of electronic devices which includes a photodiode—a photodetector; useful in medical diagnostics, bar code readers, and guidance systems

photon: a quantum of electromagnetic energy

photosynthesis: process by which plants convert carbon dioxide and water to glucose

physostigmine: alkaloid derived from the leaves of the Calabar bean, formula $C_{15}H_{12}N_3O_2$; salts used for anticholinesterase activity

pilot plant: intermediate stage of testing for chemical process, between bench-top and production scale

planar complex: arrangement of atoms in which all atoms lie within a common two-dimensional plane

plane polorized light: electromagnetic radiation (light) in which the electric (or magnetic) vectors are all vibrating in the same plane

platelet: smallest noncellular component of human blood

pneumatic chemist: early chemist who studied primarily the properties of gases

polynucleotide synthesis: formation of DNA or RNA

polypeptide: compound containing two or more amide units—C(O)NH—produced by the condensation of two or more amino acids

porphyrin: common type of heterocyclic ligand that has four five-member rings with a nitrogen, all of which lie in a plane; nitrogen atom lone pairs are available for coordinate covelent bonds

postsynaptic neuron: receptor nerve cell

potash: the compound potassium oxide, K_2O

precipitation: process of separating a solid substance out of a solution

precursor molecule: molecule that is the chosen starting point for the preparation of another molecule; a starting molecule in a chemical synthesis; a reactant molecule

primary electrochemical cell: voltaic cell based on an irreversible chemical reaction

principal oxidation state: oxidation state that is most important

prism: triangular-shaped material made from quartz or glass used to diffract light

prodrug: precursor of a drug that is converted into an active form by a metabolic process

progesterone: steroid found in the female reproductive system; formula $C_{21}H_{30}O_2$

prokaryotic: relating to very simple cells of the type found in bacteria

propagating: reproducing; disseminating; increasing; extending

protecting group: substance added to a functional group of a molecule preventing further reaction until the substance is removed by subsequent reactions

proximate percent: nearest percent of a population (e.g. people, substances)

purine base: one of two types of nitrogen bases found in nucleic acids

putative: commonly believed or hypothesized

pyramidal: relating to a geometric arrangement of four electron-donating groups at the four vertices of a pyramid

pyrimidine base: one of two types of nitrogen bases found in nucleic acids

pyruvate: anion of pyruvic acid produced by the reaction of oxygen with lactic acid after strenuous exercise

quantum: smallest amount of a physical quantity that can exist independently, especially a discrete amount of electromagnetic energy

quantum mechanical: theoretical model to describe atoms and molecules by wave functions

quantum physics: physics based on the fact that the energy of an electron is equal to its frequency times Planck's constant

radioactive decay: process involving emission of subatomic particles from a nucleus, typically accompanied by emission of very short wavelength electromagnetic radiation

radioelement: a radioactive element; one in which the nucleus spontaneously decomposes (decays) producing α (alpha) and β (beta) particles and γ (gamma) rays

rare earth elements: older name for the lanthanide series of elements, from lanthanum to lutetium

rate-limiting step: slowest step in a complex reaction; it determines the rate of the overall reaction; sometimes called the rate-determining step

reagent: chemical used to cause a specific chemical reaction

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

reducing agent: substance that causes reduction, a process during which electrons are lost (or hydrogen atoms gained)

reducing potential: stored energy capable of making a chemical reduction occur

relativistic calculation: quantum mechanical model that includes the effects of relativity, particularly for core electrons

repulsive force: force that repels two bodies; charges of the same sign repel each other

reserpine: one of a group of alkaloids found naturally in the shrub *Rarewolfia serpentina*; has been used for centuries to treat hypertension, insomnia, and mental disorders; more recently it has been used to reduce blood pressure

retardation: to slow down a chemical reaction

retrosynthetic analysis: method of analyzing chemical reactions that starts with the product and works backward to determine the initial reactants

reverberator furnace: furnace or kiln used in smelting that heats material indirectly by deflecting a nearby flame downward from the roof

ribosome: large complex of proteins used to convert amino acids into proteins

RNA: ribonucleic acid, a natural polymer used to translate genetic information in the nucleus into a template for the construction of proteins

RNA polymerase: enzyme used to make RNA using DNA as a template

rough endoplasmic reticulum: regions of endoplasmic reticulum the outer surfaces of which are heavily studded with ribosomes, which make proteins for activities within membrane-bounded organelles

Royal Society: The U.K. National Academy of Science, founded in 1660

rutile: common name of TiO_2; also a common structural type for compounds with the general composition AB_2

saltpeter: potassium nitrate; chile saltpeter is sodium nitrate

screen: process of comparing multiple reagents simultaneously to provide information on reaction of one reagent with another

seed germination: beginning of the process by which a seed produces a new plant

selenium toxicity: condition created by intake of excess selenium (Se) from plants or seleniferous water; acute and chronic toxicity are known

semisynthetic: produced by synthesis from natural starting materials

serology: the study of serum and reactions taking place within it

sigma plus pi bonding: formation of a double bond within a molecule or ion

single Slater determinant: wave function used to describe atoms and molecules

size of the basis set: number of relatively simple mathematical functions (called the basis set) used to represent a more complicated mathematical function such as an atomic orbital

smelting: process by which ores are reduced in the production of metals

Socrates: Greek philosopher, c.470–399 B.C.E.

somatic cell: cells of the body with the exception of germ cells

spectral line: line in a spectrum representing radiation of a single wavelength

spectroscopy: use of electromagnetic radiation to analyze the chemical composition of materials

spinel: name given to a group of minerals that are double oxides of divalent and trivalent metals, for example, $MgO \cdot Al_2O_3$ or $MgAl_2O_4$; this mineral is called spinel; also a structural type

stacking interactions: one type of interaction that affects conformation of double-stranded DNA; caused by van der Waals forces

stereospecific: yielding one product when reacted with a given compound but the opposite product when reacted with its stereoisomer

steric repulsion: repulsive force that exists when two atoms or groups get too close together

sterol: steroid containing an alcohol group; derived from plants or animals; e.g., cholesterol

stigmasterol: sterol found in soybeans, $C_{29}H_{48}O$

stratosphere: layer of the atmosphere where ozone is found; starts about 6.2 mi (10 km) above ground

streptomycin: antibiotic produced by soil bacteria of genus *Streptomyces*

subcritical: mass of nuclear materials below the amount necessary to cause a chain reaction

subshell: electron energy sublevel, of which there are four: *s*, *p*, *d*, and *f*

sulfonamides: first of a series of drugs used for the prevention and cure of bacterial infections in humans; sulfanomides are amides of sulfuric acids and contain the $–SO_2NRR_1$ group

super-heavy elements: elements of atomic number greater than 103

superhelix: helical-shaped molecule synthesized by another helical-shaped molecule

surfactants: surface-active agents that lower the surface tension of water; e.g., detergents, wetting agents

synaptic cleft: tiny space between the terminal button of one neuron and the dendrite or soma of another

synthesis: combination of starting materials to form a desired product

synthon: in retrosynthesis, molecules are broken into characteristic sections called synthons

tetrachloride: term that implies a molecule has four chlorine atoms present

tetravalent oxidation state: bonding state of an atom that can form four bonds

theoretical physics: branch of physics dealing with the theories and concepts of matter, especially at the atomic and subatomic levels

3′ end: situation in nucleic acids in which the phosphate group is attached at the third carbon atom from where the base is attached

thykaloid membrane: part of a plant that absorbs light and passes the energy on to where it is needed

thymine: one of the four bases that make up a DNA molecule

toluic acids: methylbenzoic acids

torsion balance: instrument used to measure small forces (weights), based upon the resistance of a wire to be twisted

toxicology: division of pharmacology dealing with poisons, their identification, detection, effects on the body, and remedies

toxin: poisonous substance produced during bacterial growth

trace element: element occurring only in a minute amount

transcription: enzyme-catalyzed assembly of an RNA molecule complementary to a strand of DNA

transition metal complex: species formed when a transition metal reacts with ions or molecules, including water

transition metals: elements with valence electrons in d-sublevels; frequently characterized as metals having the ability to form more than one cation

translational process: transfer of information from codon on mRNA to anticodon on tRNA; used in protein synthesis

trigonal bipyramidal: geometric arrangement of five ligands around a central Lewis acid, with ligands occupying the vertices of two trigonal pyramids that share a common face; three ligands share an equatorial plane with the central atom, two ligands occupy an axial position

tropocollagen: fibers, or fibrils, consisting of three polypeptide sequences arranged in a helix

tyrosine: one of the common amino acids

ultraviolet radiation: portion of the electromagnetic spectrum with wavelengths shorter than visible but longer than x rays

uracil: heterocyclic, pyrimidine, amine base found in RNA

valence: combining capacity

vertabrates: animals that have a skeleton

vesicle: small compartment in a cell that contains a minimum of one lipid bilayer

vitamins: organic molecules needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

vitriol: sulfate of a metal; there are blue (Cu), white (Zn), green (Fe), and rose (Co) vitriols

volatile: low boiling, readily vaporized

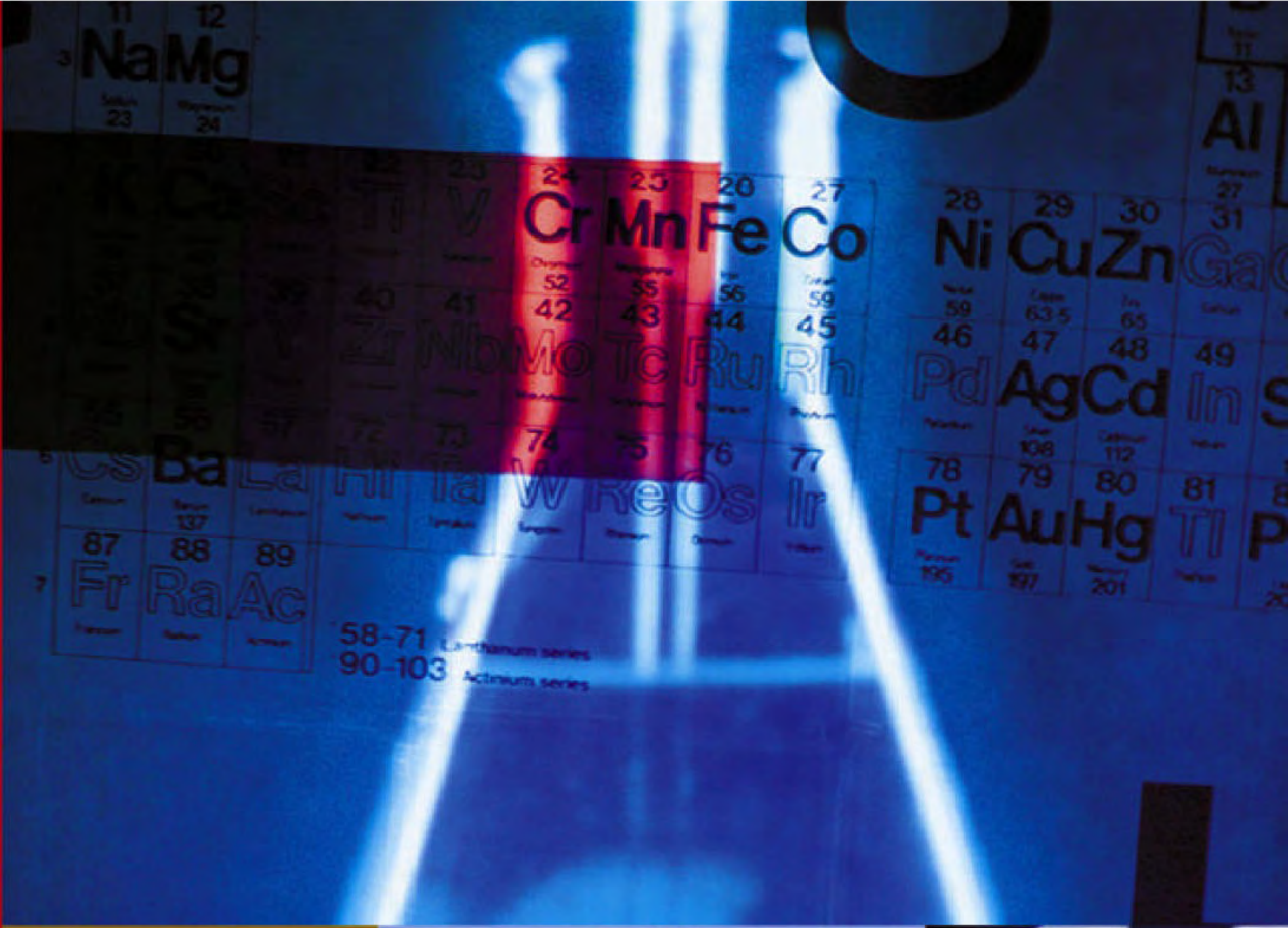
voltage: potential difference expressed in volts

vulcanized rubber: chemical process of mixing rubber with other materials like sulfur; it strengthens rubber so it can be used under hot or cold conditions; discovered by Charles Goodyear

wetting agent: molecule that, when added to a liquid, facillitates the spread of the liquid across a surface

zoology: branch of biology concerned with the animal kingdom

zwitterion: molecule that simultaneously contains a positive and a negative charge



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Chemistry: Foundations and Applications

J. J. Lagowski, Editor in Chief

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Table of Contents

Volume 1

Volume 2

Volume 3

Volume 4

Preface

Chemistry. The word conjures up mystery—perhaps magic—smoke, fireworks, explosions, unpleasant odors. But it could evoke "smokeless burning," which would be invisible, fluorescent lights, "neon" signs, the quiet crumbling of rocks under the pressure of freezing water, the slow and quiet formation of caves in limestone, and the delightful scents of perfumes or fruit aromas. There is no magic, only knowledge and understanding. We offer this *Encyclopedia* as a contribution to help readers gain knowledge and understanding of chemistry.

Chemistry was manifested as an art at the beginnings of civilization. The early decorative chemical arts included the preparation of pigments such as the Egyptian blue applied to King Tutankhamen's golden death mask; the various bronze alloys that were used to make vases in the ancient world of the Middle East as well as in China; and the glass objects that have been found in Mesopotamia (now known as Iraq). Those chemical arts became a science in the eighteenth century when Antoine Laurent Lavoisier (1743–1794) led what has been called "the chemical revolution." Using accurate measurements of primarily mass, early chemists began to make order out of the myriad of substances that are found in the natural world. This order was eventually expressed in a number of chemical concepts that include the laws of chemical composition (constant composition, mass conservation, multiple proportions), periodicity, the nature of atoms, chemical bonding, and a variety of concepts involving chemical structures. The early symbiosis of chemistry with civilization remains. Chemistry is still a useful science in the advancement of civilization. Chemists have developed and refined the core concepts of chemistry to the point where they have become powerful tools to assist humankind in the acquisition of materials of practical use to extend and preserve civilization. Humans now have available a broader array of substances with a remarkable spectrum of properties than was available before chemistry became a science. Light emitting diodes (LEDs) produce more light than the individual torches, candles, and oil lamps of the distant past—indeed, than the incandescent light bulbs of the immediate past—more efficiently and with less pollution. Polymeric materials or composites can be produced with virtually any property desired—from stretching clingy Saran Wrap to Kevlar used in bullet proof vests; from nonstick Teflon to optical fibers; from rubber objects that are impervious to oil and gasoline to tires that can be used for 100,000 miles before needing replacement; from fibers that compete with (in some cases

surpass) natural materials to plastics that have more desirable optical properties than glass. In a word, chemistry is *everywhere.*

There is no magic, only knowledge and understanding.

These volumes are a contribution to assist readers in their understanding of chemistry and chemical ideas and concepts. The 509 articles have been carefully chosen to provide basic information on a broad range of topics. For those readers who desire to expand their knowledge of a topic, we have included bibliographic references to readily accessible sources.

The continual evolution of the discipline of chemistry is reflected in our treatment of the elements. The careful reader will note that we have included articles for the first 104 elements; the remainder of the elements are "recently" discovered or exist only as short-lived species and, accordingly, are not readily available for the usual chemical studies that reveal, for example, their bulk properties or reactivity and much of the "standard chemistry" that is of interest. Much of what little we know about the elements beyond 104 permits us to place these elements in their appropriate places in the periodic table, which nevertheless still turns out to be quite insightful from a chemical point of view.

Entries in the *Encyclopedia* are in alphabetic sequence. Cross-references appear in small capitals at the ends of the articles to help readers locate related discussions. Articles range from brief, but concise, definitions to extensive overviews that treat key concepts in larger contexts. A list of common abbreviations and symbols, and a list of the known elements, as well as a modern version of the periodic table are included in the For Your Reference section at the beginning of each volume. A glossary and a comprehensive index appear at the end of each volume. Contributors are listed alphabetically, together with their academic and professional affiliations, at the beginning of each volume.

Following this preface, we offer a topical arrangement of the articles in the *Encyclopedia.* This outline provides a general overview of the principal parts of the subject of chemistry and is arranged in alphabetical order.

Many individuals have contributed greatly and in many ways to this *Encyclopedia.* The associate editors—Alton J. Banks, Thomas Holme, Doris Kolb, and Herbert Silber—carried the major responsibility in shaping the intellectual content of the *Encyclopedia.* The authors of the articles executed that plan admirably and we thank them for that effort.

The staff at Macmillan Reference USA—Marie-Claire Antoine, Hélène Potter, Ray Abruzzi, Gloria Lam, and Christine Slovey—have been outstanding in their dedication and contributions to bring this *Encyclopedia* from its initial concept to the current reality. Without their considerable input, insightful guidance, and effort this *Encyclopedia* would never have seen the light of day. I take this opportunity to thank them personally and publicly. I am particularly grateful to Rita Wilkinson, my administrative assistant for her persistent and careful attention to details that kept the editorial office and my office connected for the smooth transmission of numerous critical details. I am especially grateful to Christine Slovey who, through her determined efforts and dedication, made a potentially difficult and tedious task far less onerous and, indeed, enjoyable.

J. J. Lagowski

Topical Outline

Analytical Chemistry Applications

Adhesives
Agricultural Chemistry
Analytical Chemistry
Bleaches
Ceramics
Chemical Engineering
Chemical Informatics
Coal
Cosmetics
Cryogenics
Detergents
Disposable Diapers
Dyes
Explosions
Fertilizer
Fibers
Food Preservatives
Forensic Chemistry
Formulation Chemistry
Freons
Gardening
Gasoline
Gemstones
Genetic Engineering
Glass
Hair Dyes and Hair Treatments
Herbicides
Industrial Chemistry, Inorganic
Industrial Chemistry, Organic
Insecticides
Irradiated Foods
Materials Science
Nanochemistry
Nylon
Pesticides
Pigments
Polymers, Synthetic
Recycling
Rocketry
Superconductors
Zeolites

Aqueous Chemistry

Acid-Base Chemistry
Bases
Bleaches
Chemical Reactions
Colloids
Corrosion
Equilibrium
Solution Chemistry
Water

Astrochemistry

Astrochemistry

Biochemistry

Acetylcholine
Active Site
Allosteric Enzymes
Amino Acid
Antibiotics
Artificial Sweeteners
Base Pairing
Bioluminescence
Caffeine
Carbohydrates
Cellulose
Chemiluminescence
Cholecalciferol
Cholesterol
Chromosome
Clones
Codon
Coenzyme
Cofactor
Collagen
Cortisone
Denaturation
Deoxyribonucleic Acid
Disaccharides
DNA Replication
Dopamine
Double Helix
Endorphins
Enzymes
Epinephrine
Estrogen
Fats and Fatty Acids
Fibrous Protein
Genes
Genetic Engineering
Genome
Globular Protein
Glycolysis
Glycoprotein
Hemoglobin
Hydrolase
Hydrolysis
Ion Channels
Kinase
Krebs Cycle
Lipid Bilayers
Lipids
Low Density Lipoprotein (LDL)
Membrane
Methylphenidate
Mutagen
Mutation
Neurochemistry
Neurotoxins
Neurotransmitters
Nicotinamide
Nicotinamide Adenine Dinucleotide (NAD)
Nicotine
Norepinephrine
Nucleic Acids
Nucleotide
Peptide Bond
Phospholipids

Photosynthesis
Polymerase Chain Reaction (PCR)
Polymers, Natural
Polysaccharides
Proteins
Primary Structure
Protein Solubility
Protein Synthesis
Protein Translation
Quaternary Structure
Residue
Restriction Enzymes
Retinol
Rhodium
Ribonucleic Acid
RNA Synthesis
Secondary Structure
Starch
Steroids
Stimulants
Storage Protein
Substrate
Taste Receptors
Teratogen
Tertiary Structure
Testosterone
Thiamin
Toxicity
Transmembrane Protein
Transport Protein
Triglycerides
Venom
Zwitterion

Biographies

Al Razi, Abu Bakr Muhammed ibn Zakariya
Anfinsen, Christian
Arrhenius, Svante
Avery, Oswald
Avogadro, Amedeo
Baekeland, Leo
Balmer, Johann Jakob
Bardeen, John
Becquerel, Antoine-Henri
Berg, Paul
Berthollet, Claude-Louis
Berzelius, Jöns Jakob
Black, Joseph
Bohr, Niels
Boltzmann, Ludwig
Boyle, Robert
Bragg, William Henry
Bragg, William Lawrence
Brønsted, Johannes Nicolaus
Bunsen, Robert
Caldwell, Mary
Calvin, Melvin
Cannizzaro, Stanislao
Carnot, Sadi
Carothers, Wallace
Carver, George Washington
Cavendish, Henry
Chadwick, James
Chappelle, Emmett
Chardonnet, Hilaire
Charles, Jacques
Chevreul, Michel
Cleve, Per Theodor
Cori, Carl and Gerty
Cottrell, Frederick
Coulomb, Charles
Curie, Marie Sklodowska
Dalton, John
Davy, Humphry
de Broglie, Louis
Dewar, James
du Pont, Éleuthère Irénée
Ehrlich, Paul
Einstein, Albert
Elion, Gertrude Belle
Fahrenheit, Gabriel
Faraday, Michael
Fermi, Enrico
Fischer, Emil Hermann
Fleming, Alexander
Franklin, Rosalind
Gadolin, Johan
Gay-Lussac, Joseph-Louis
Gibbs, Josiah Willard
Goodyear, Charles
Haber, Fritz
Hall, Charles
Heisenberg, Werner
Hess, Germain Henri
Heyrovsky, Jaroslav
Hodgkin, Dorothy
Julian, Percy
Kekulé, Friedrich August
Kelsey, Frances Kathleen Oldham
Khorana, Har Gobind
Krebs, Hans Adolf
Lavoisier, Antoine
Lawrence, Ernest
Le Bel, Joseph-Achille
Leblanc, Nicolas
LeChâtelier, Henri
Leclanché, Georges
Leloir, Luis
Lewis, Gilbert N.
Liebig, Justus von
Lister, Joseph
Lonsdale, Kathleen
Lucretius
Marsden, Ernest
Martin, Archer John Porter
Maxwell, James Clerk
Meitner, Lise
Mendeleev, Dimitri
Menten, Maud
Meyer, Lothar
Millikan, Robert
Morgan, Agnes Fay
Moseley, Henry
Nernst, Walther Hermann
Newton, Isaac
Nobel, Alfred Bernhard
Northrop, John
Oppenheimer, Robert
Ostwald, Friedrich Wilhelm
Paracelsus
Pasteur, Louis
Pauli, Wolfgang
Pauling, Linus
Perkin, William Henry
Planck, Max
Priestley, Joseph
Raman, Chandrasekhara
Ramsay, William
Remsen, Ira
Robinson, Robert
Röntgen, Wilhelm
Rutherford, Ernest
Rydberg, Johannes
Sanger, Frederick
Scheele, Carl
Schrödinger, Erwin
Seaborg, Glenn Theodore
Seibert, Florence
Soddy, Frederick
Stanley, Wendell
Staudinger, Hermann
Strutt, John (Lord Rayleigh)
Sumner, James
Svedberg, Theodor
Synge, Richard Laurence Millington
Szent-Györgyi, Albert
Thomson, Joseph John
Todd, Alexander
Travers, Morris
Urey, Harold
van der Waals, Johannes
Van Helmont, Johann Baptista
Van't Hoff, Jacobus Hendricus
Volta, Alessandro
Waksman, Selman
Watson, James Dewey
Weizmann, Chaim

Werner, Alfred
Willstätter, Richard
Wöhler, Friedrich
Woodward, Robert
Yalow, Rosalyn
Yukawa, Hideki
Zsigmondy, Richard

Chemical Substances

Coordination Compounds
Materials Science
Minerals
Nanochemistry
Nylon
Plastics
Rubber
Rydberg, Johannes
Silicone
Soap
Starch
Steel
Water

Computing

Chemical Informatics
Computational Chemistry
Digital X Ray
Molecular Modeling

Elements

Actinides
Actinium
Alkali Metals
Alkaline Earth Metals
Allotropes
Aluminum
Americium
Antimony
Argon
Arsenic
Astatine
Barium
Berkelium
Beryllium
Bismuth
Boron
Bromine
Cadmium
Calcium
Californium
Carbon
Cerium
Cesium
Chalcogens
Chlorine
Chromium
Cobalt
Copper
Curium
Dysprosium
Einsteinium
Erbium
Europium
Fermium
Fluorine
Francium
Fullerenes
Gadolinium
Germanium
Gold
Hafnium
Halogens
Helium
Holmium
Hydrogen
Indium
Iodine
Iridium
Iron
Lanthanides
Lanthanum
Lawrencium
Lead
Lithium
Lutetium
Magnesium
Manganese
Mendelevium
Mercury
Molybdenum
Neodymium
Neon
Neptunium
Nickel
Niobium
Nitrogen
Nobelium
Noble Gases
Osmium
Oxygen
Ozone
Palladium
Platinum
Plutonium
Polonium
Potassium
Praseodymium
Promethium
Protactinium
Radium
Radon
Rhenium
Rhodium
Rubidium
Ruthenium
Rutherfordium
Samarium
Scandium
Selenium
Silicon
Silver
Sodium
Sulfur
Tantalum
Technetium
Tellurium
Terbium
Thallium
Thorium
Thulium
Tin
Titanium
Transactinides
Tungsten
Uranium
Vanadium
Xenon
Ytterbium
Yttrium
Zinc
Zirconium

Energy

Chemistry and Energy
Energy
Energy Sources and Production
Explosions
Fire, Fuels, Power Plants
Fossil Fuels
Heat
Manhattan Project
New Battery Technology
Nuclear Fission
Nuclear Fusion
Petroleum
Solar Cells
Solid-State Devices
Storage Protein
Sustainable Energy Use
Temperature
Thermochemistry
Thermodynamics

Environmental Chemistry

Air Pollution
Atmospheric Chemistry
Environmental Pollution
Fertilizer

History

Inorganic Chemistry

Medicine

Organic Chemistry

Physical Chemistry

Radiation

Reactions

States of Matter

Structure

For Your Reference

TABLE 1. SELECTED METRIC CONVERSIONS

WHEN YOU KNOW	MULTIPLY BY	TO FIND
Temperature		
Celsius (˚C)	1.8 (˚C) +32	Fahrenheit (˚F)
Celsius (˚C)	˚C +273.15	Kelvin (K)
degree change (Celsius)	1.8	degree change (Fahrenheit)
Fahrenheit (˚F)	[(˚F) −32] / 1.8	Celsius (˚C)
Fahrenheit (˚F)	[(˚F −32) / 1.8] +273.15	Kelvin (K)
Kelvin (K)	K −273.15	Celsius (˚C)
Kelvin (K)	1.8(K −273.15) +32	Fahrenheit (˚F)

WHEN YOU KNOW	MULTIPLY BY	TO FIND
Distance/Length		
centimeters	0.3937	inches
kilometers	0.6214	miles
meters	3.281	feet
meters	39.37	inches
meters	0.0006214	miles
microns	0.000001	meters
millimeters	0.03937	inches

WHEN YOU KNOW	MULTIPLY BY	TO FIND
Capacity/Volume		
cubic kilometers	0.2399	cubic miles
cubic meters	35.31	cubic feet
cubic meters	1.308	cubic yards
cubic meters	8.107×10^{-4}	acre-feet
liters	0.2642	gallons
liters	33.81	fluid ounces

WHEN YOU KNOW	MULTIPLY BY	TO FIND
Area		
hectares (10,000 square meters)	2.471	acres
hectares (10,000 square meters)	107,600	square feet
square meters	10.76	square feet
square kilometers	247.1	acres
square kilometers	0.3861	square miles

WHEN YOU KNOW	MULTIPLY BY	TO FIND
Weight/Mass		
kilograms	2.205	pounds
metric tons	2205	pounds
micrograms (µg)	10^{-6}	grams
milligrams (mg)	10^{-3}	grams
nanograms (ng)	10^{-9}	grams

TABLE 2. ALPHABETIC TABLE OF THE ELEMENTS

Symbol	Element	Atomic Number	Atomic Mass*	Symbol	Element	Atomic Number	Atomic Mass*
Ac	Actinium	89	(227)	Mt	Meitnerium	109	(266)
Al	Aluminum	13	26.982	Md	Mendelevium	101	(258)
Am	Americium	95	(243)	Hg	Mercury	80	200.59
Sb	Antimony	51	121.75	Mo	Molybdenum	42	95.94
Ar	Argon	18	39.948	Nd	Neodymium	60	144.24
As	Arsenic	33	74.922	Ne	Neon	10	20.180
At	Astatine	85	(210)	Np	Neptunium	93	237.048
Ba	Barium	56	137.33	Ni	Nickel	28	58.69
Bk	Berkelium	97	(247)	Nb	Niobium	41	92.908
Be	Beryllium	4	9.012	N	Nitrogen	7	14.007
Bi	Bismuth	83	208.980	No	Nobelium	102	(259)
Bh	Bohrium	107	(262)	Os	Osmium	76	190.2
B	Boron	5	10.811	O	Oxygen	8	15.999
Br	Bromine	35	79.904	Pd	Palladium	46	106.42
Cd	Cadmium	48	112.411	P	Phosphorus	15	30.974
Ca	Calcium	20	40.08	Pt	Platinum	78	195.08
Cf	Californium	98	(251)	Pu	Plutonium	94	(244)
C	Carbon	6	12.011	Po	Polonium	84	(209)
Ce	Cerium	58	140.115	K	Potassium	19	39.1
Cs	Cesium	55	132.90	Pr	Praseodymium	59	140.908
Cl	Chlorine	17	35.453	Pm	Promethium	61	(145)
Cr	Chromium	24	51.996	Pa	Protactinium	91	231.036
Co	Cobalt	27	58.933	Ra	Radium	88	226.025
Cu	Copper	29	63.546	Rn	Radon	86	(222)
Cm	Curium	96	(247)	Re	Rhenium	75	186.207
Ds	Darmastadtium	110	(269)	Rh	Rhodium	45	102.906
Db	Dubnium	105	(262)	Rb	Rubidium	37	85.47
Dy	Dysprosium	66	162.50	Ru	Ruthenium	44	101.07
Es	Einsteinium	99	(252)	Rf	Rutherfordium	104	(261)
Er	Erbium	68	167.26	Sm	Samarium	62	150.36
Eu	Europium	63	151.965	Sc	Scandium	21	44.966
Fm	Fermium	100	(257)	Sg	Seaborgium	106	(263)
F	Fluorine	9	18.998	Se	Selenium	34	78.96
Fr	Francium	87	(223)	Si	Silicon	14	28.086
Gd	Gadolinium	64	157.25	Ag	Silver	47	107.868
Ga	Gallium	31	69.723	Na	Sodium	11	22.990
Ge	Germanium	32	72.61	Sr	Strontium	38	87.62
Au	Gold	79	196.967	S	Sulfur	16	32.066
Hf	Hafnium	72	178.49	Ta	Tantalum	73	180.948
Hs	Hassium	108	(265)	Tc	Technetium	43	(98)
He	Helium	2	4.003	Te	Tellurium	52	127.60
Ho	Holmium	67	164.93	Tb	Terbium	65	158.925
H	Hydrogen	1	1.008	Tl	Thallium	81	204.383
In	Indium	49	114.82	Th	Thorium	90	232.038
I	Iodine	53	126.905	Tm	Thulium	69	168.934
Ir	Iridium	77	192.22	Sn	Tin	50	118.71
Fe	Iron	26	55.847	Ti	Titanium	22	47.88
Kr	Krypton	36	83.80	W	Tungsten	74	183.85
La	Lanthanum	57	138.906	U	Uranium	92	238.029
Lr	Lawrencium	103	(260)	V	Vanadium	23	50.942
Pb	Lead	82	207.2	Xe	Xenon	54	131.29
Li	Lithium	3	6.941	Yb	Ytterbium	70	173.04
Lu	Lutetium	71	174.967	Y	Yttrium	39	88.906
Mg	Magnesium	12	24.305	Zn	Zinc	30	65.38
Mn	Manganese	25	54.938	Zr	Zirconium	40	91.224

*Atomic masses are based on the relative atomic mass of ^{12}C=12. These values apply to the elements as they exist in materials of terrestrial origin and to certain artificial elements. Values in parenthesis are the mass number of the isotope of the longest half-life.

TABLE 3. COMMON ABBREVIATIONS, SYMBOLS, AND ACRONYMS

’	minute (of arc); single prime
”	second (of arc); double prime
+	plus
$^+$	positive charge
−	minus
$^-$	negative charge
±	plus-or-minus
∓	minus-or-plus
×	multiplied by
·	multiplied by
÷	divided by
=	equals
≠	not equal to
∽	about, approximately
≅	congruent to; approximately equal to
≈	approximately equal to
≡	identical to; equivalent to
<	less than
≤	less than or equal to
>	greater than
≥	greater than or equal to
%	percent
°	degree (temperature; angle of arc)
@	at
—	single bond
═	double bond
: :	double bond
≡	triple bond
: : :	triple bond
∞	infinity
∝	variation
∂	partial derivative or differential
α	proportional to, alpha
√	square root
Δ	delta; increment of a variable
ϵ_0	dielectric constant; permittivity
θ	plane angle
λ	wavelength
μ	magnetic moment; micro
μA	microampere
μC	microcoulomb
μF	microfarad
μg	microgram
μg/ml	microgram per milliliter
μK	microkelvin
μm	micrometer (also called micron)
μmol;	micromole
μs, μsec	microsecond
ν	frequency
υ	velocity
π or pi	ratio of the circumference of a circle to its diameter; double as in double bond
σ	single as in single bond; Stefan-Boltzmann constant
Σ	summation
ϕ	null set
ψ	amplitude of a wave (as in *wave,* or *psi, function)*
→	reaction to right
←	reaction to left
↔	connecting resonance forms
⇆	equilibrium reaction beginning at right
⇄	equilibrium reaction beginning at left
⇌	reversible reaction beginning at left
⇋	reversible reaction beginning at right
↑	elimination
⇓	absorption
a	acceleration
A	area
a_o	Bohr Unit
AAS	atomic absorption spectroscopy
ABS	alkylbenzene sulfate
ACS	American Chemical Society
ADH	alcohol dehydrogenase
ADP	adenosine diphosphate
AEC	Atomic Energy Commission
AES	atomic emission spectroscopy
AFM	atomic force microscope; atomic force microscopy
AFS	atomic fluorescence spectroscopy
ALDH	aldehyde dehydronase
amp	ampere
AMS	accelerator mass spectrometry
AMU	atomic mass unit
atm.	standard atmosphere (unit of pressure)
ATP	adenosine triphosphate
β	beta
b.p.	boiling point
Btu	British thermal unit
c	centi-; speed of light
C	carbon; Celsius; centigrade; coulomb
C	heat capacity; electric capacitance

TABLE 3. COMMON ABBREVIATIONS, SYMBOLS, AND ACRONYMS [continued]

Ci	Curies
cm	centimeter
CT	computed tomography
d	d-orbital
D	dipole moment
DC	direct current
deg	degree
dr	diastereomer ratio
e	elementary charge
E	electric field strength; energy
$\mathrm{E_a}$	activation energy
$\mathrm{E_g}$	bandgap energy
EA	electron affinity
er	enantiomer ratio
eV	electron volts
f	f-orbital
F	Fahrenheit; Faraday's constant; fluorine
F	force
g	gram
g	g-orbital; gas
h	hour
h	Planck's constant
Hz	hertz
i	i-orbital
IUPAC	International Union of Pure and Applied Chemistry
J	joule
J	electric current density
k	k-orbital
K	degrees Kelvin; Kelvin; potassium
$\mathrm{K_a}$	acidity constant for the dissociation of weak acid (the weaker the acid, the lower the $\mathrm{K_a}$ value
$\mathrm{k_B}$	Boltzmann's constant
Kg	kilogram
kHz	kilohertz
kJ	kilojoule
kJ mol	kilojoule mole
km	kilometer
$\mathrm{K_m}$	Michaelis constant
l	length; liquid
L	lambert; liter
L	length; Avogadro's constant
LD	lethal dose
L/mole	liters per mole
ln	natural logarithm
log	logarithm

m	meter; milli-; molal (concentration)
m	mass
M	molar (concentration)
m_e	electron mass
mA	milliamperes
mg	milligram
mg/L	milligrams per liter
MHz	megahertz
min	minute
ml	milliliter
MO	molecular orbital
p	p-orbital
ω	omega
ppb	parts per billion
ppm	parts per million
ppt	parts per trillion
psi	per square inch; English for ψ
q	quantity
REM	Roentgen Equivalent Man (radiation-dose unit of measure)
s	solid; s-orbital
S	entropy
sec	second; secant
SEM	scanning electron microscope
SI	Système Internationale (International System of Measurements)
SPM	scanning probe microscope
STM	scanning tunneling microscope
STP	standard temperature and pressue (˚C, 1 atm)
Sv	sievert unit (1 Sv = 100 REM; used to measure radiation dose)
t	time
T	moment of force, thermodynamic temperature (in degrees Kelvin); torque
$\mathrm{T_c}$	critical temperature
TEM	transmission electron microscope
u	unified atomic mass unit
U	electric potential
V	electric potential; vanadium; volume
V	volt
vap.	vaporization
VB	valence bond
vel.	velocity
VSEPR	valence shell electron pair repulsion
Z	atomic number

PERIODIC TABLE OF THE ELEMENTS*†

	I	II													III	IV	V	VI	VII	VIII
																				2 HELIUM **He** 4.003
5	3 LITHIUM **Li** 6.941	4 BERYLLIUM **Be** 9.012						1 HYDROGEN **H** 1.008						p	5 BORON **B** 10.811	6 CARBOM **C** 12.011	7 NITROGEN **N** 14.007	8 OXYGEN **O** 15.999	9 FLUORINE **F** 18.998	10 NEON **Ne** 20.180
	11 SODIUM **Na** 22.990	12 MAGNESIUM **Mg** 24.305													13 ALUMINUM **Al** 26.982	14 SILICON **Si** 28.086	15 PHOSPHORIUS **P** 30.974	16 SULFUR **S** 32.066	17 CHLORINE **Cl** 35.453	18 ARGON **Ar** 39.948
	19 POTASSIUM **K** 39.1	20 CALCIUM **Ca** 40.08	d	21 SCANDIUM **Sc** 44.966	22 TITANIUM **Ti** 47.88	23 VANADIUM **V** 50.942	24 CHROMIUM **Cr** 51.996	25 MANGANESE **Mn** 54.938	26 IRON **Fe** 55.847	27 COBALT **Co** 58.933	28 NICKEL **Ni** 58.69	29 COPPER **Cu** 63.546	30 ZINC **Zn** 65.38		31 GALLIUM **Ga** 69.73	32 GERMANIUM **Ge** 72.61	33 ARSENIC **As** 74.922	34 SELENIUM **Se** 78.96	35 BROMINE **Br** 79.904	36 KRYPTON **Kr** 83.80
	37 RUBIDIUM **Rb** 85.47	38 STRONTIUM **Sr** 87.62		39 YTTRIUM **Y** 88.906	40 ZIRCONIUM **Zr** 91.224	41 NIOBIUM **Nb** 92.908	42 MOLYBDENIUM **Mo** 95.94	43 TECHNETIUM **Tc** (98)	44 RUTHENIUM **Ru** 101.07	45 RHODIUM **Rh** 102.906	46 PALLADIUM **Pd** 106.42	47 SILVER **Ag** 107.868	48 CADMIUM **Cd** 112.411		49 INDIUM **In** 114.82	50 TIN **Sn** 118.71	51 ANTIMONY **Sb** 121.75	52 TELLURIUM **Te** 127.60	53 IODINE **I** 126.905	54 XENON **Xe** 131.29
	55 CESIUM **Cs** 132.90	56 BARIUM **Ba** 137.33		71 LUTETIUM **Lu** 174.967	72 HAFNIUM **Hf** 178.49	73 TANTALUM **Ta** 180.948	74 TUNGSTEN **W** 183.85	75 RHENIUM **Re** 186.207	76 OSMIUM **Os** 190.2	77 IRIDIUM **Ir** 192.22	78 PLATINUM **Pt** 195.08	79 GOLD **Au** 196.967	80 MERCURY **Hg** 200.59		81 THALLIUM **Tl** 204.383	82 LEAD **Pb** 207.2	83 BISMUTH **Bi** 208.980	84 POLONIUM **Po** (209)	85 ASTATINE **At** (210)	86 RADON **Rn** (222)
	87 FRANCIUM **Fr** (223)	88 RADIUM **Ra** 226.025		103 LAWRENCIUM **Lr** (260)	104 RUTHERFORDIUM **Rf** (261)	105 DUBNIUM **Db** (262)	106 SEABORGIUM **Sg** (263)	107 BOHRIUM **Bh** (262)	108 HASSIUM **Hs** (265)	109 MEITNERIUM **Mt** (266)	110 DARMASTADTIUM **Ds** (269)	111 UNUNUNIUM **Uuu** (272)	112 (?)							

f	57 LANTHANUM **La** 138.906	58 CERIUM **Ce** 140.15	59 PRAESEODYMIUM **Pr** 140.908	60 NEODYMIUM **Nd** 144.24	61 NEODYMIUM **Pm** (145)	62 SAMARIUM **Sm** 150.36	63 EUROPIUM **Eu** 151.965	64 GADOLINIUM **Gd** 157.25	65 TERBIUM **Tb** 158.925	66 DYSPROSIUM **Dy** 162.50	67 HOLMIUM **Ho** 164.93	68 ERBIUM **Er** 167.26	69 THULIUM **Tm** 168.934	70 YTTERBIUM **Yb** 173.04
	89 ACTINIUM **Ac** 227.03	90 THORIUM **Th** 232.038	91 PROTACTINIUM **Pa** 231.036	92 URANIUM **U** 238.029	93 NEPTUNIUM **Np** 237.048	94 PLUTONIUM **Pu** (244)	95 AMERICIUM **Am** (243)	96 CURIUM **Cm** (247)	97 BERKELIUM **Bk** (247)	98 CALIFORNIUM **Cf** (251)	99 EINSTEINIUM **Es** (252)	100 FERMIUM **Fm** (257)	101 MENDELEVIUM **Md** (258)	102 NOBELIUM **No** (259)

*Each element in the table is listed with (from top to bottom) its atomic number, its name, its symbol, and its atomic mass. Atomic mass numbers in parentheses are the mass numbers of the longest-lived isotope. Other atomic mass numbers are the average mass number of the naturally occurring isotopes.

†The names and labels for elements beyond number 103 are controversial. IUPAC initially ruled in favor of Latin names based on atomic number, but in 1994 a set of specific names and symbols was suggested. After considerable debate, a revised final list of names for elements 104-109 was issued on August 30, 1997. Temporary names were also assigned for elements 110 and 111. Various groups have suggested alternatives names for some of these elements. Additional elements continue to be synthesized, though with increasing difficulty, with no definite upper atomic-number limit yet established.

Contributors

Catalina Achim
Carnegie Mellon University
Pittsburgh, Pennsylvania

David T. Allen
University of Texas at Austin
Austin, Texas

Carolyn J. Anderson
Washington University School of Medicine
St. Louis, Missouri

Ronald D. Archer
Professor Emeritus
University of Massachusetts, Amherst
Amherst, Massachusetts

D. Eric Aston
University of Idaho
Moscow, Idaho

Peter Atkins
University of Oxford
Oxford, United Kingdom

Cynthia Atterholt
Western Carolina University
Cullowhee, North Carolina

Michèle Auger
Laval University
Quebec, Quebec, Canada

Karl W. Böer
Professor Emeritus
University of Delaware
Newark, Delaware

Catherine H. Banks
Peace College
Raleigh, North Carolina

Joseph Bariyanga
University of Wisconsin
Milwaukee, Wisconsin

Nathan J. Barrows
University of Northern Colorado
Greeley, Colorado

David A. Bassett
Brockton, Massachusetts

James D. Batteas
CUNY - College of Staten Island
Staten Island, New York

Bruce Beaver
Duquesne University
Pittsburgh, Pennsylvania

C. Larry Bering
Clarion University
Clarion, Pennsylvania

Bill Bertoldi
Kingsford, Michigan

W. E. Billups
Rice University
Houston, Texas

Koen Binnemans
Catholic University of Leuven
Leuven, Belgium

James P. Birk
Arizona State University
Tempe, Arizona

Jeffrey R. Bloomquist
Virginia Polytechnic Institute and State University
Blacksburg, VA

John E. Bloor
University of Tennessee
Knoxville, Tennessee

George Bodner
Purdue University
West Lafayette, Indiana

Paul W. Bohn
University of Illinois
Urbana, Illinois

Valerie Borek
Boothwyn, Pennsylvania

Erwin Boschmann
Indiana University
Indianapolis, Indiana

Wayne B. Bosma
Bradley University
Peoria, Illinois

Ole Bostrup
The Danish Society of The History of Chemistry
Fredensborg, Denmark

F. Javier Botana
University of Cadiz
Cadiz, Spain

Lawrence H. Brannigan
Southwestern Illinois College
Bellville, Illinois

Ronald Brecher
GlobalTox International Consultants Inc.
Guelph, Ontario, Canada

Jeffrey C. Bryan
University of Wisconsin-La Crosse
La Crosse, Wisconsin

Robert A. Bulman
National Radiological Protection Board
Oxfordshire, England

Jean-Claude Bunzli
Swiss Federal Institute of Technology
Lausanne, Switzerland

Douglas Cameron
Montana Tech of the University of Montana
Butte, Montana

Michael C. Cann
University of Scranton
Scranton, Pennsylvania

Charles E. Carraher Jr.
Florida Atlantic University
Boca Raton, Florida

Henry A. Carter
Augustana University College
Camrose, Alberta, Canada

John Castro
Huntington Station, New York

Lyman R. Caswell
Texas Woman's University
Denton, Texas

Raymond Chang
Williams College
Williamstown, Massachusetts

Philip J. Chenier
University of Wisconsin
Eau Claire, Wisconsin

Peter E. Childs
University of Limerick
Limerick, Ireland

Gregory R. Choppin
Florida State University
Tallahassee, Florida

Abraham Clearfield
Texas A&M University
College Station, Texas

Brian P. Coppola
University of Michigan
Ann Arbor, Michigan

Eugene C. Cordero
San José State University
San José, California

Paul A. Craig
Rochester Institute of Technology
Rochester, New York

M. J. Crawford
Ludwig-Maximilians-Universtät-München
Munich, Germany

Mary R. S. Creese
University of Kansas
Lawrence, Kansas
(retired)

Bartow Culp
Purdue University
West Lafayette, Indiana

Carlos Eduardo da Silva Cortes
Universidade Federal Fluminense
Rio de Janeiro, Brazil

G. Brent Dawson
University of North Carolina at Greensboro
Greensboro, North Carolina

Stephanie E. Dew
Centre College
Danville, Kentucky

Anthony Diaz
Central Washington University
Ellensburg, Washington

Diego J. Diaz
University of Illinois at Urbana-Champaign
Urbana, Illinois

James S. Dickson
Iowa State University
Ames, Iowa

David A. Dobberpuhl
Creighton University
Omaha, Nebraska

Daryl J. Doyle
Kettering University
Flint, Michigan

Michael Eastman
Northern Arizona University
Flagstaff, Arizona

Andrew Ede
University of Alberta
Edmonton, Canada

Edward M. Eyring
University of Utah
Salt Lake City, Utah

Scott E. Feller
Wabash College
Crawfordsville, Indiana

Kurt W. Field
Bradley University
Peoria, Illinois

Matthew A. Fisher
St. Vincent College
Latrobe, Pennsylvania

George Fleck
Smith College
Northampton, Massachusetts

Michael J. Fosmire
Purdue University
West Lafayette, Indiana

Mark Freilich
The University of Memphis
Memphis, Tennessee

Ken Geremia
Copper Development Association, Inc.
New York, New York

Gregory S. Girolami
University of Illinois, Champaign-Urbana
Urbana, Illinois

Carmen Giunta
Le Moyne College
Syracuse, New York

Harold Goldwhite
California State University, Los Angeles
Los Angeles, California

Barbara E. Goodman
University of South Dakota
Vermillion, South Dakota

Gordon W. Gribble
Dartmouth College
Hanover, New Hampshire

Robert K. Griffith
West Virginia University
Morgantown, West Virginia

Neena Grover
Colorado College
Colorado Springs, Colorado

William G. Gutheil
University of Missouri-Kansas City
Kansas City, Missouri

David G. Haase
North Carolina State University
Raleigh, North Carolina

Arthur M. Halpern
Indiana State University
Terre Haute, Indiana

R. Adron Harris
The University of Texas at Austin
Austin, Texas

John Harwood
Tennessee Technological University
Cookeville, Tennessee

Ian S. Haworth
University of Southern California
Los Angeles, California

James M. Helt
CUNY- College of Staten Island
Staten Island, New York

J. Carver Hill
Cary, North Carolina

Darleane C. Hoffman
Lawrence Berkeley National Laboratory, University of California
Berkeley, California

Thomas A. Holme
University of Wisconsin-Milwaukee
Milwaukee, Wisconsin

Chaim T. Horovitz
Emeritus Professor
Rehovot , Israel

John D. Hostettler
San José State University
San José, California

Brian R. James
University of British Columbia
Vancouver, British Columbia, Canada

Frank A. J. L. James
The Royal Institution
London, England

Mark Jensen
Argonne National Laboratory
Argonne, Illinois

Melvin D. Joesten
Vanderbilt University
Nashville, Tennessee

W. L. Jolly
University of California, Berkeley
Berkeley, California

Loretta L. Jones
University of Northern Colorado
Greeley, Colorado

David A. Juckett
Michigan State University
Lansing, Michigan
Barros Research Institute
Holt, Michigan

Paul J. Karol
Carnegie Mellon University
Pittsburgh, Pennsylvania

Vladimir Karpenko
Charles University
Prague, Czech Republic

George B. Kauffman
California State University, Fresno
Fresno, California

W. Frank Kinard
College of Charleston
Charleston, SC

Thomas M. Klapotke
Ludwig-Maximillians-Universität München
Munich, Germany

Kyle Knight
University of Tennessee at Chattanooga
Chattanooga, Tennessee

Paul E. Koch
Penn State, Behrend College
Erie, Pennsylvania

Doris K. Kolb
Bradley University
Peoria, Illinois

Kenneth E. Kolb
Bradley University
Peoria, Illinois

Daniel P. Kramer
Kramer & Asscociates, Ltd.
Centerville, Ohio

Ágúst Kvaran
University of Iceland
Reykjavik, Iceland

J. J. Lagowski
The University of Texas
Austin, Texas

Michael Laing
Professor Emeritus
University of Natal
Durban, South Africa

Rattan Lal
The Ohio State University
Columbus, Ohio

Thomas H. Lane
Dow Corning Coporation
Midland, Michigan

Alan B. G. Lansdown
Imperial College School of Medicine
London, United Kingdom

Amanda Lawrence
University of Illinois, Champaign-Urbana
Urbana, Illinois

Peter B. Leavens
University of Delaware
Newark, Delaware

G. J. Leigh
University of Sussex
Brighton, United Kingdom

H. Eugene LeMay, Jr.
University of Nevada
Reno, Nevada

Kenneth B. Lipkowitz
North Dakota State University
Fargo, North Dakota

Ingrid A. Lobo
University of Texas at Austin
Austin, Texas

Walter Loveland
Oregon State University
Corvallis, Oregon

Phyllis A. Lyday
U.S. Geological Survey
Reston, Virginia

Paul A. Maggard Jr.
North Carolina State University
Raleigh, North Carolina

Michael E. Maguire
Case Western Reserve University
Cleveland, Ohio

Keith L. Manchester
University of the Witwatersrand, Johannesburg
South Africa

Dean F. Martin
University of South Florida
Tampa, Florida

Barbara B. Martin
University of South Florida
Tampa, Florida

James D. Martin
North Carolina State University
Raleigh, North Carolina

Anthony F. Masters
University of Sydney
New South Wales, Australia

Seymour Mauskopf
Duke University
Durham, North Carolina

Sean McMaughan
Texas A&M University
College Station, Texas

Paul F. McMillan
University College London, Christopher Ingold Laboratories
London, United Kingdom

Edward A. Meighen
McGill University
Montreal, Canada

Louis Messerle
University of Iowa
Iowa City, Iowa

Donald E. Moreland
Professor Emeritus
North Carolina State University
Raleigh, North Carolina

Matthew J. Morra
University of Idaho, Soil & Land Resources Division
Moscow, Idaho

Richard Mowat
North Carolina State University
Raleigh, North Carolina

Frank Mucciardi
McGill University
Montreal, Quebec, Canada

Kathleen L. Neeley
University of Kansas
Lawrence, Kansas

John Michael Nicovich
Georgia Institute of Technology
Atlanta, Georgia

Robert Noiva
University of South Dakota School of Medicine
Vermillion, South Dakota

Charles E. Ophardt
Elmhurst College
Elmhurst, Illinois

Richard Pagni
University of Tennessee
Knoxville, Tennessee

Gus J. Palenik
University of Florida
Gainsville, Florida

Robert P. Patterson
North Carolina State University, Crop Science Department
Raleigh, North Carolina

Harry E. Pence
State University of New York, College at Oneonta
Oneonta, New York

Mark A. Pichaj
Biola University
La Marada, California

John Pickering
San José State University
Nuclear Science Facility
San José, California

Tanja Pietraß
New Mexico Tech
Socorro, New Mexico

A. G. Pinkus
Baylor University
Waco, Texas

Jennifer L. Powers
Kennesaw State University
Kennesaw, Georgia

Suzanne T. Purrington
North Carolina State University
Raleigh, North Carolina

Ray Radebaugh
National Institute of Standards and Technology, Cryogenics Technologies Group
Boulder, Colorada

Thomas B. Rauchfuss
University of Illinois, Champaign-Urbana
Urbana, Illinois

Geoffrey W. Rayner-Canham
Sir Wilfred Grenfell College

Corner Brook, Newfoundland, Canada

Marelene Rayner-Canham
Sir Wilfred Grenfell College
Corner Brook, Newfoundland, Canada

Jeffrey C. Reid
North Carolina Geological Survey
Raleigh, North Carolina

Richard E. Rice
Florence, Montana

D. Paul Rillema
Wichita State University
Wichita, Kansas

Frank Rioux
St. John's University
College of St. Benedict
St. Joseph, Minnesota

Robert Rittenhouse
Walla Walla College
College Place, Washington

Elizabeth S. Roberts-Kirchhoff
University of Detroit Mercy
Detroit, Michigan

Brett Robinson
Horticultural and Food Research Institute of New Zealand
Palmerston North, New Zealand

Herbert W. Roesky
University of Göttingen
Göttingen, Germany

Hiranya S. Roychowdhury
New Mexico State University
Las Cruces, New Mexico

Gordon Rutter
Royal Botanic Garden Edinburgh
Edinburgh, United Kingdom

Martin D. Saltzman
Providence College
Providence, Rhode Island

Jerry L. Sarquis
Miami University
Oxford, Ohio

Nancy N. Sauer
Los Alamos National Laboratory
Los Alamos, New Mexico

Wolf-Dieter Schubert
Vienna University of Technology
Vienna, Austria

Joachim Schummer
University of South Carolina
Columbia, South Carolina

Alan Schwabacher
University of Wisconsin-Milwaukee
Milwaukee, Wisconsin

A. Truman Schwartz
Macalester College
Saint Paul, Minnesota

William M. Scovell
Bowling Green State University
Bowling Green, Ohio

Lydia S. Scratch
Ottawa, Ontario, Canada

Peter Rudolf Seidl
Universidade Federal do Rio de Janeiro
Rio de Janeiro, Brazil

N. M. Senozan
California State University
Long Beach, California

James F. Shackelford
University of California at Davis
Davis, California

Stephanie Dionne Sherk
Westland, Michigan

Ben Shoulders
The University of Texas at Austin
Austin, Texas

David B. Sicilia
University of Maryland
College Park, Maryland

Herbert B. Silber
San José State University
San José, California

Robert J. Silva
Lawrence Berkeley National Laboratory, University of California
Berkeley, California

Sharron W. Smith
Hood College
Frederick, Maryland

C. Graham Smith
Penicuik, United Kingdom

Mary L. Sohn
Florida Institute of Technology
Melbourne, Florida

David Speckhard
Loras College
Dubuque, Iowa

Jonathan N. Stack
North Dakota State University
Fargo, North Dakota

Conrad L. Stanitski
University of Central Arkansas
Conway, Arkansas

Donald H. Stedman
University of Denver
Denver, Colorado

Anthony N. Stranges
Texas A&M University
College Station, Texas

Dan M. Sullivan
University of Nebraska at Omaha
Omaha, Nebraska

Tammy P. Taylor
Los Alamos National Laboratory
Los Alamos, New Mexico

Ann T. S. Taylor
Wabash College
Crawfordsville, Indiana

Sidney Toby
Rutgers University
Piscataway, New Jersey

Reginald P. T. Tomkins
New Jersey Institute of Technology
Newark, New Jersey

Anthony S. Travis
The Hebrew University
Jerusalem, Israel

Donald G. Truhlar
University of Minnesota
Minneapolis, Minnesota

Georgios Tsaparlis
University of Ioannina
Ioannina, Greece

Dennis G. Tuck
University of Windsor
Windsor, Ontario, Canada
(deceased)

Geraldo Vicentini
Instituto de Quimíca, University of São Paulo
São Paulo, Brazil

Nanette M. Wachter
Hofstra University
Hempstead, New York

George H. Wahl Jr.
North Carolina State University
Raleigh, North Carolina

Helen R. Webb
Monash University
Clayton, Victoria, Australia

Laurence E. Welch
Knox College
Galesburg, Illinois

J. Reed Welker
University of Arkansas
Fayetteville, Arkansas
(retired)

Guang Wen
Tottori University
Tottori, Japan

Todd W. Whitcombe
University of Northern British Columbia
Prince George, British Columbia, Canada

Vivienne A. Whitworth
Ryerson University
Toronto, Ontario, Canada

David A. Williams
University College London
London, United Kingdom

Robert K. Wismer
Millersville University
Millersville, Pennsylvania

Ronni Wolf
Kaplan Medical Center
Rechovot, Israel

Adele J. Wolfson
Wellesley College
Wellesley, Massachusetts

Burghard Zeiler
Wolfram Bergbau und Hüttenges m.b.H.
Austria, Germany

Lea B. Zinner
Departamento de Química
São Paulo, Brazil

Cynthia G. Zoski
Georgia State University
Atlanta, Georgia

Thomas M. Zydowsky
FMC Corporation
Princeton, New York

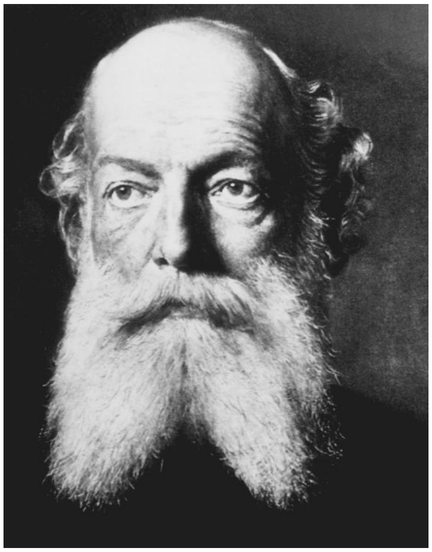
Kekulé, Friedrich August

GERMAN CHEMIST
1829–1896

Friedrich August Kekulé was born on September 7, 1829, in Darmstadt, Hesse (later part of Germany). He showed an early aptitude for both languages and drawing and wanted to be an architect. He began his architecture studies at the University of Geissen in 1847, but after attending the lectures of the famous chemist Justus von Liebig he switched to chemistry. Kekulé had great interest in the theoretical aspects of chemistry, and less in the more practical applications that so interested von Liebig. On von Liebig's advice Kekulé went to Paris in 1851 to further his chemical studies.

Paris during the 1850s was an ideal place for a young scientist, as there was a great deal of interest in that city in theoretical chemistry, particularly in the structure of molecules. Preexisting ideas (such as the dualism of Swedish chemist Jöns J. Berzelius) stressed that molecules formed because of the inherent electrical charges that individual elements possessed (which were sometimes opposing and therefore attractive). Organic molecules were not in keeping with the dualism concept, but some scientists proposed that they could be derived from a number of simple inorganic molecules.

Kekulé returned to Germany in 1852, obtained his doctoral degree at Geissen in that year, and then spent a year working in Switzerland. This was followed by two years in London (1853–1855), where he met the chemist Alexander Williamson. Williamson had extended Charles Gerhardt's "type theories" to explain how ethers could be derived from the water type. Kekulé, with Williamson's encouragement, extended type theory further and introduced a new type—the methane or marsh gas type. This led to the development of the tetravalent model of carbon and the understanding that carbon forms rings and chains.



German chemist Friedrich Kekulé, known for his work and theories in molecular structure, such as the tetravalent structure of carbon.

Kekulé's principal insight was to realize that type theory did not take into account the specific combining power (or valences) of specific atoms. In 1857 Kekulé suggested that carbon was tetravalent, his suggestion based on the specific chemistries of the compounds that carbon formed with elements such as hydrogen (CH_4) and chlorine (CCl_4). Kekulé extended his ideas in the following year by suggesting that two carbon atoms bonded together in the formation of hydrocarbons such as ethane ($C_2 H_6$). Similarly, additional carbon and hydrogen units could be added, extending the carbon atom chain and forming an ordered series. A similar structural theory was developed independently at around the same time by the Scottish chemist Archibald Scott Couper, working in the laboratory of Adolphe Wurtz in Paris. Publication of Couper's paper was delayed by Wurtz (until Kekulé's had appeared) and the structural theory of organic chemistry is really a culmination of the efforts of Kekulé and Couper.

Kekulé was offered the position of professor of chemistry at the University of Ghent in Belgium in 1858. There his linguistic abilities stood him in good stead, as he had to lecture in French. In 1867 Kekulé was called to the University of Bonn and remained there until his death, on July 13, 1896.

In 1859 Kekulé started to use graphical representations of organic molecules, in part to emphasize the tetravalent nature of carbon atoms and their ability to form chains. He then turned his attention to the structure of benzene (C_6H_6), a compound with unusual properties that could not be explained by any theories of the day.

JOSEF LOSCHMIDT (1821–1895)

Before Kekulé dreamed of his structure for benzene, Josef Loschmidt proposed the ring structure of the molecule. Unfortunately, Loschmidt did not publish his theory in a widely read scientific journal. As a result, the credit for this revolutionary theory is hotly debated today.

—***Valerie Borek***

Kekulé proposed in 1865 that benzene had a structure in which six carbon atoms formed a ring, with alternating single and double bonds. However, the chemistry of benzene was not always consistent with this structural formula. (All of the carbon atoms in a benzene molecule were equal and equivalent in terms of the reactions of benzene.) To overcome this problem, Kekulé suggested in 1872 that there were two forms of benzene, in dynamic **equilibrium**. Kekulé's dynamical theory proved to be only partially correct. In 1933 Linus Pauling used quantum mechanics to explain more fully the nature of benzene.

equilibrium: condition in which two opposite reactions are occurring at the same speed, so that concentrations of products and reactants do not change

On March 11, 1890, on the occasion of the twenty-fifth anniversary of his announcement of his benzene theory, Kekulé gave a speech in Berlin in which he revealed that both his structural theories and the structure of benzene were revealed to him in dreams. Scholars have tended to dismiss his account of his own creative processes and have placed more stock in the early training that Kekulé received in architecture as the key to his inspiration. SEE ALSO BERZELIUS, JÖNS JAKOB; LIEBIG, JUSTUS VON; ORGANIC CHEMISTRY; PAULING, LINUS.

Martin D. Saltzman

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Kelsey, Frances Kathleen Oldham

CANADIAN-AMERICAN PHARMACOLOGIST AND PHYSICIAN
1914–

Born Frances Kathleen Oldham in Cobble Hill, Vancouver Island, Canada, on July 24, 1914, Oldham grew up in the country and always wanted to be a scientist. She earned B.S., M.S., and Ph.D. degrees in pharmacology. During the 1930s Oldham and fellow pharmacologist Fremont Ellis Kelsey studied the effects of the drug quinine on pregnant rabbits and their embryos at the University of Chicago. They discovered that the adult rabbits could

Pharmacologist Frances Oldham Kelsey, who rejected the use of the sedative thalidomide in the United States.

metabolize the drug, due to the presence of an enzyme in their bodies, but that the embryos died, because they had not yet acquired this enzyme. They were among the first scientists to verify that some drugs that are safe for adult humans are dangerous to human embryos. Oldham and Kelsey married in 1943. Frances Kelsey earned an M.D. degree in 1950; the Kelseys then moved to South Dakota, where Frances practiced medicine part time, taught pharmacology, and reviewed scientific articles.

In 1960 the Kelseys moved to Washington, D.C., where Frances was offered a job at the Food and Drug Administration (FDA). Her job was to evaluate applications from drug companies that wished to market new drugs. She had sixty days to evaluate each application. The first drug she was asked to evaluate was thalidomide, a sedative prescribed to pregnant women for relief from morning sickness. The drug had been marketed to the masses in West Germany, where it had first been developed, and in many other countries, including Canada.

metabolize: performing metabolism—the processes that produce complex substances from simpler components, with a consequent use of energy (anabolism) and those that break down complex food molecules, thus liberating energy (catabolism)

Frances Kelsey and the pharmacologist and chemist who assisted her in the review of thalidomide were immediately concerned that the information that had been provided by the drug firm did not prove the drug's safety. The company was asked to resubmit their application. At around this time, Kelsey began to read reports that some patients who had taken thalidomide had developed peripheral neuritis, a disease whose symptoms included a painful tingling in the arms and feet. Kelsey rejected a second application. Remembering her earlier research with quinine, Kelsey wondered what thalidomide might do to the developing fetuses of pregnant women. The drug company continued to pressure Kelsey to approve its application, even contacting her superiors at the FDA. She continued to reject their applications. In 1961 European pediatricians began reporting an epidemic of phocomelia among newborns, a developmental anomaly characterized by short limbs, toes attached to hips, and flipperlike arms. By November 1961 a German pediatrician had determined that the teratogen (a substance causing one or more developmental abnormalities in fetuses) was thalidomide. From 1957 to 1962, more than 10,000 children in forty-six countries were estimated to have deformities owing to their mothers' use of thalidomide during early pregnancy. By her insistence on getting thorough, all-sided information on drug safety before drug application approval, Kelsey had prevented the use of thalidomide in the United States.

On August 17, 1962, President John F. Kennedy presented Kelsey with the President's Award for Distinguished Federal Civilian Service, in recognition of her having prevented (almost single-handedly) a national tragedy. In late 1962 the U.S. Congress passed the Kefauver–Harris Amendments to the Food, Drug, and Cosmetics Act (named after the senator and congressman who sponsored the bills in Congress), which gave medical officers at the FDA more power. The amendments outlawed drug testing on humans without informed consent, and mandated that a new drug could not be approved until scientific evidence had established that the drug was safe and effective. As of 2001 Kelsey still worked at the FDA as one of their leading compliance officers. In 2000 she was inducted into the National Women's Hall of Fame, whose Web site states: "Kelsey is both a woman of courage and one of reason—demanding of herself and others in her profession high standards of science and integrity." SEE ALSO ENZYMES; TERATOGEN.

Kathleen L. Neeley

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Khorana, Har Gobind

AMERICAN BIOCHEMIST
1922–

Har Gobind Khorana was born in a small village in British India, in which his family was among the few literate residents. He received his M.S. from the University of Lahore, and in 1945 he was awarded a grant to study for a Ph.D. at the University of Liverpool. He then went on to complete postdoctoral work in Switzerland and at Cambridge. It was there, while working with Alexander Todd, that Khorana became interested in both nucleic acids and proteins, the study of which became his life's work.

In 1952 G. M. Shrum, head of the British Research Council on the campus of the University of British Columbia, Vancouver, Canada, offered Khorana the opportunity to form his own research group on whatever topic he wished. His group became very successful in developing methods for synthesizing phosphate **ester** derivatives of nucleic acids, and in 1959 he and John G. Moffatt announced the **synthesis** of acetyl coenzyme A (acetyl CoA), a molecule essential to the biochemical processing of proteins fats and carbohydrates. Prior to this work, the coenzyme had to be extracted from yeast by a very laborious and expensive process, so this discovery led to Khorana's international recognition within the scientific community and he received many job offers as a result. He accepted the position of codirector of the Institute for Enzyme Research at the University of Wisconsin.

In the early 1960s it had been recognized that **DNA** and **RNA** (in the form of messenger RNA [mRNA]) were somehow involved in the synthesis of proteins in living cells. Whereas the basic building blocks of DNA are the four nucleotides adenosine (A), **cytosine** (C), **guanine** (G), and **thymine** (T)—in RNA, **uracil** (U) is substituted for thiamine—the basic building blocks of all proteins are twenty amino acids strung together in different sequences to produce individual proteins. In 1961, Marshall W. Nirenberg, and Heinrich J. Matthaei announced that they had created a synthetic mRNA, which, when inserted into *E. coli* bacteria, always caused the addition of one amino acid phenylalanine to a growing strand of linked amino acid. They also determined that if they synthesized RNA with three units of uracil joined together, it caused an amino acid chain consisting entirely of phenylalanine to be produced.

These experiments, which proved that mRNA transmits the genetic information from DNA, thus directing the creation of specific complex proteins, stimulated Khorana to use his expertise in **polynucleotide synthesis** to uncover the exact mechanisms involved. The results were spectacular. Within a few short years his research group was able to establish which serial combinations of nucleotides form which specific amino acids; that nucleotide instructions (genetic **code**) are always transmitted to the cell in groups of three called codons; and that some of the codons direct the cell to start or stop the manufacture of proteins. For this work Khorana, along with Nirenberg and biochemist Robert W. Holley, was awarded the Nobel Prize in physiology in 1968.

In 1970 Khorana announced the creation of the first artificial DNA gene of yeast. At the same time, he and most of his research team moved to the Massachusetts Institute of Technology (MIT) because, as he explained, "You stay intellectually alive longer if you change your environment every so often" (McMurray, p. 1089). Since going to MIT, Khorana has reported major advances concerning how rhodopsin, the photo**receptor** in the human eye, functions. SEE ALSO Codon; Nucleic Acids; Todd, Alexander.

John E. Bloor

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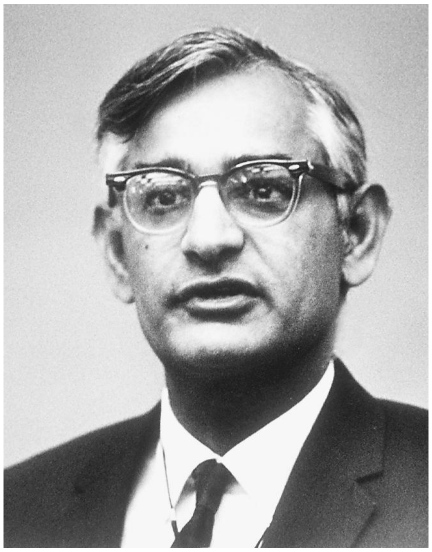

American chemist Har Gobind Khorana, corecipient, with Robert W. Holley and Marshall W. Nirenberg, of the 1968 Nobel Prize in physiology or medicine, "for their interpretation of the genetic code and its function in protein synthesis."

ester: organic species containing a carbon atom attached to three moieties: an O via a double bond, an O attached to another carbon atom or chain, and an H atom or C chain; the R(C═O)OR functional group

synthesis: combination of starting materials to form a desired product

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

RNA: ribonucleic acid—a natural polymer used to translate genetic information in the nucleus into a template for the construction of proteins

cytosine: heterocyclic, pyrimidine, amine base found in DNA

guanine: heterocyclic, purine, amine base found in DNA

thymine: one of the four bases that make up a DNA molecule

uracil: heterocyclic, pyrimidine, amine base found in RNA

polynucleotide synthesis: formation of DNA or RNA

code: mechanism to convey information on genes and genetic sequence

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

Kinase

adenosine triphosphate (ATP): molecule formed by the condensation of adenine, ribose, and triphosphoric acid, HOP(O)OH–O–(O)OH–OP(O)OH–OH; it is a key compound in the mediation of energy in both plants and animals

phosphorylation: the process of addition of phosphates into biological molecules

glucose: common hexose monosaccharide; monomer of starch and cellulose; also called grape sugar, blood sugar, or dextrose

metabolism: the complete range of biochemical processes that take place within living organisms; comprises processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those that break down complex food molecules, thus liberating energy (catabolism)

code: mechanism to convey information on genes and genetic sequence

Kinases are enzymes that transfer a phosphate group from **adenosine triphosphate (ATP)**, or other trinucleotide, to a number of biological substrates, such as sugars or proteins. They are part of a larger family of enzymes known as group transferases, but are limited to phosphate transfers. A typical reaction catalyzed by a kinase (e.g., hexokinase) is the **phosphorylation** of **glucose** upon its entry into a cell

$$\text{Glucose} + \text{ATP} \rightarrow \text{Glucose-6-phosphate} + \text{ADP}$$

This reaction sets the stage for the subsequent **metabolism** of glucose via a number of metabolic pathways. Creatine kinase (CK), which transfers a phosphate from ATP to creatine, acts to store some of the energy of ATP in the muscle molecule creatine. CK levels in blood are measured in blood tests to diagnose heart attacks, as damaged heart muscle cells release CK into the bloodstream. Recently there has been great interest in the phosphorylation of specific amino acids in proteins. This modification acts as a regulation of the protein's activity. Hormonal signals outside a cell initiate a cascade of biochemical events inside the cell that include activation of a number of protein kinases. Of further interest in kinase regulation is the fact that several cancer-causing genes (oncogenes) **code** for kinases. The lack of regulation of these genes may be important in the etiology of cancer. SEE ALSO Amino Acid; Enzymes.

C. Larry Bering

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Kinetics

Chemical kinetics is the study of the rates of chemical reactions. Such reaction rates range from the almost instantaneous, as in an explosion, to the almost unnoticeably slow, as in corrosion. The aim of chemical kinetics is to make predictions about the composition of reaction mixtures as a function of time, to understand the processes that occur during a reaction, and to identify what controls its rate.

Rates and Rate Laws

spectroscopy: use of electromagnetic radiation to analyze the chemical composition of materials

The rate of a chemical reaction is defined as the rate of change of the concentration of one of its components, either a reactant or a product. The experimental investigation of reaction rates therefore depends on being able to monitor the change of concentration with time. Classical procedures for reactions that take place in hours or minutes make use of a variety of techniques for determining concentration, such as **spectroscopy** and electrochemistry. Very fast reactions are studied spectroscopically. Spectroscopic procedures are available for monitoring reactions that are initiated by a rapid pulse of electromagnetic radiation and are over in a few femtoseconds (1 fs $= 10^{-15}$ s).

The analysis of kinetic data commonly proceeds by establishing a *rate law*, a mathematical expression for the rate in terms of the concentrations of the reactants (and sometimes products) at each stage of the reaction. For instance, it may be found that the rate of consumption of a reactant is proportional to the concentration of the reactant, in which case the rate law is

$$\text{Rate} = k[\text{Reactant}]$$

where [Reactant] denotes the concentration of the reactant and k is called the rate constant. The rate constant is independent of the concentrations of any species in the reaction mixture but depends on the temperature. A reaction with a rate law of this form is classified as a *first-order rate law*. More generally, a reaction with a rate law of the form

$$\text{Rate} = k[\text{Reactant A}]^a[\text{Reactant B}]^b\ldots$$

is said to be of order a in A, of order b in B, and to have an overall order of $a + \mathrm{b} + \ldots$. Some rate laws are far more complex than these two simple examples and many involve the concentrations of the products.

The advantage of identifying the reaction order is that all reactions with the same rate law (but different characteristic rate constants) behave similarly. For example, the concentration of a reactant in a first-order reaction decays exponentially with time at a rate determined by the rate constant

$$[\text{Reactant}] = [\text{Reactant}]_0 e^{-kt}$$

where $[\text{Reactant}]_0$ is the initial concentration of the reactant. On the other hand, all second-order reactions lead to the following time-dependence of the concentration:

$$[\text{Reactant}] = \frac{[\text{Reactant}]_0}{1 + kt[\text{Reactant}]_0}$$

Figure 1 shows the time-dependence predicted by these expressions. It is common to report the time-dependence of first-order reactions in terms of the *half-life*, $t_{1/2}$, of the reactant, the time needed for its concentration to fall to half its initial value. For a first-order reaction (but not for other orders)

$$t_{1/2} = \frac{\ln 2}{k}$$

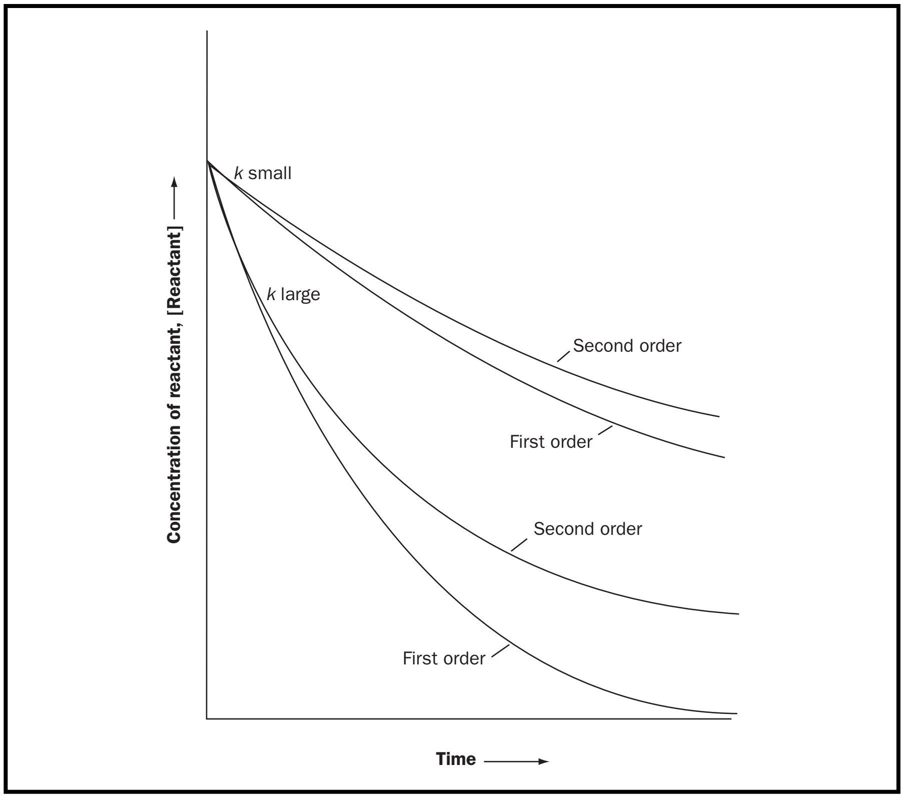
Thus, reactions with large rate constants have short half-lives.

Reaction Mechanisms

The identification of a rate law provides valuable insight into the reaction mechanism, the sequence of elementary steps by which a reaction takes place. The aim is to identify the reaction mechanism by constructing the rate law that it implies. This procedure may be simplified by identifying the *rate-determining step* of a reaction, the slowest step in a sequence that determines the overall rate. Thus, if the proposed mechanism is $A \rightarrow B$ followed by $B \rightarrow C$, and the former is much faster than the latter, then the overall rate of the reaction will be equal to the rate of $A \rightarrow B$, for once B is formed, it immediately converts into C.

In general, for a mechanism of many steps (including their reverse), the construction of the overall rate law is quite difficult, requiring an approximation or a computer for a numerical analysis. One common approximation

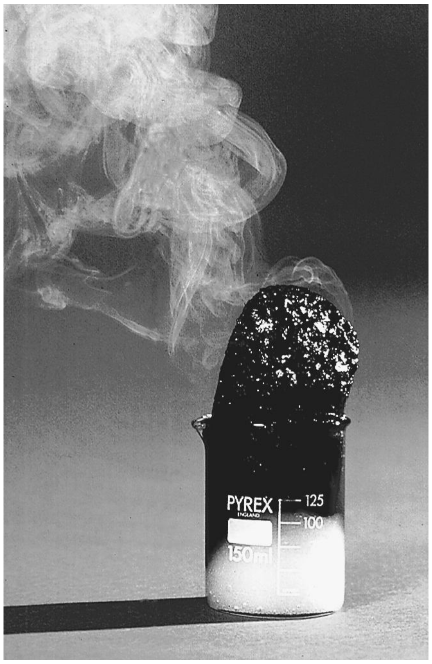
Figure 1. The time-dependence of the concentration of the reactant in first-order and second-order reactions. The two reactions have the same initial rate. Note how the reactant takes longer to disappear in a second-order reaction.



intermediate: molecule, often short-lived, that occurs while a chemical reaction progresses but is not present when the reaction is complete

phase: homogeneous state of matter

is the *steady-state assumption*, in which the net rate of formation of any **intermediate** (B in the present example) is set equal to zero. A hazard of using kinetic information to identify a reaction mechanism, however, is that more than one mechanism might result in the same rate law, especially when approximate solutions are derived. For this reason, proposed reaction mechanism must be supported by additional evidence.



Kinetics is the study of the rate of chemical reactions, such as the acid dehydration of sugar, shown in this photograph.

The Origin of Reaction Rates

Once a reaction mechanism has been identified, attention turns to the molecular properties that govern the values of the rate constants that occur in the individual elementary steps. A clue to the factors involved is provided by the experimental observation that the rate constants of many reactions depend on temperature according to the Arrhenius expression

$$\ln k = A - \frac{E_a}{RT}$$

where E_a is called the *activation energy*.

The simplest model that accounts for the Arrhenius expression is the *collision theory* of gas-**phase** reaction rates, in which it is supposed that reaction occurs when two reactant molecules collide with at least a minimum kinetic energy (which is identified with the activation energy, Figure 2). A more sophisticated theory is the *activated complex theory* (also known as the *transition state theory*), in which it is supposed that the reactants encounter each other, form a loosened cluster of atoms, then decompose into products.

Reactions in solution require more detailed consideration than reactions in gases. It is necessary to distinguish between "diffusion-controlled" and

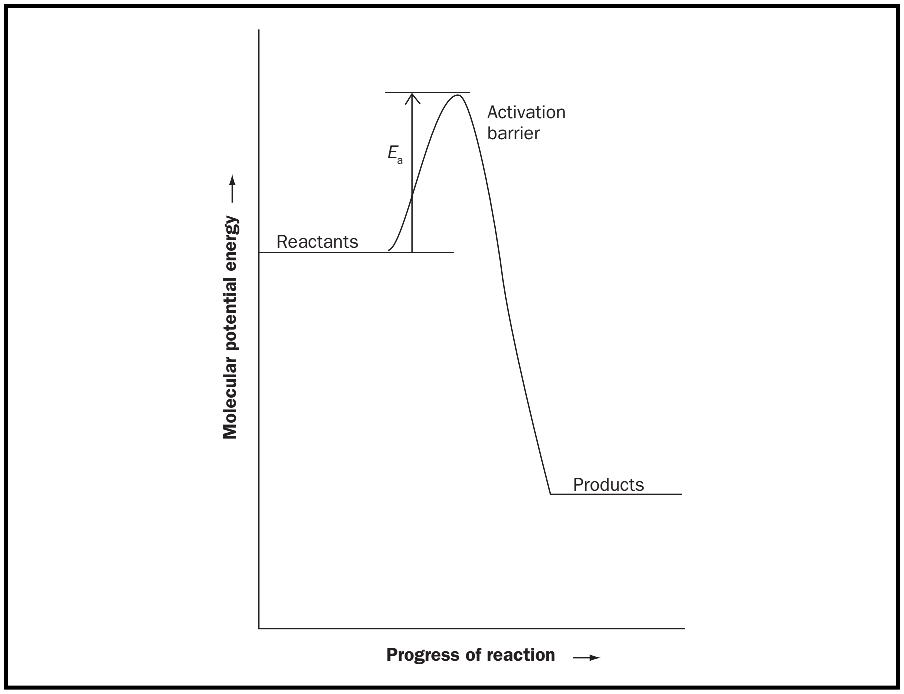


Figure 2. A "reaction profile" showing how molecular potential energy varies as reactants change into products. Only reactants that encounter each other with a kinetic energy equal to the height of the activation barrier can go on to form products. The height of the activation barrier is the activation energy of the reaction.

"activation-controlled" reactions. In a diffusion-controlled reaction, the rate is controlled by the ability of the reactants to migrate through the solvent and encounter each other. In an activation-controlled reaction, the rate is controlled by the ability of the reactants that have met each other to acquire enough energy to react.

The rate of a reaction may also be increased by finding a **catalyst**, a substance that takes part in a reaction by providing an alternative pathway with a lower activation energy but is regenerated in the process and is therefore not consumed. **Catalysis** is the foundation of the chemical industry and a great effort is made to discover or fabricate efficient, economical catalysts. It is also the foundation of life, because the biological catalysts known as enzymes (elaborate protein molecules) control almost every aspect of an organism's function. SEE ALSO CATALYSIS AND CATALYSTS; ENZYMES; PHYSICAL CHEMISTRY.

catalyst: substance that aids in a reaction while retaining its own chemical identity

catalysis: the action or effect of a substance in increasing the rate of a reaction without itself being converted

Peter Atkins

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Krebs, Hans Adolf

BRITISH BIOCHEMIST
1900–1981

Hans Krebs was born into a prosperous and well-educated family in Hildesheim, Germany. His father was a physician who specialized in otolaryngology, and it was Hans's intention to follow in his father's footsteps and

British biochemist Sir Hans Adolf Krebs, corecipient of the 1953 Nobel Prize in physiology or medicine, “for his discovery of co-enzyme A and its importance for intermediary metabolism.”

become a physician. Krebs was educated at the Gymnasium Andreanum, and after World War I, he went on to study medicine at the Universities of Göttingen, Freiburg, and Berlin. In 1925 he earned an M.D. degree at the University of Hamburg. He was at this point passionately attracted to medical research, and he did not enter medical practice. In 1926, Krebs became an assistant to Professor Otto Warburg at the prestigious Kaiser Wilhelm Institute for Biology in Berlin, a post he held until 1930. Warburg (who later won the 1931 Nobel Prize in medicine) encouraged Krebs to pursue a career in research.

In 1931 Krebs moved to Freiburg to teach medicine. It was there that he authored (with Kurt Henseleit) his first important paper, which examined liver function in mammals and described how ammonia was converted to urea in liver cells. Krebs also studied the syntheses of uric acid and purines in birds. However, Krebs’s research was cut short when the Nazis came to power in 1933. Krebs was Jewish, and he was therefore summarily fired from his post. He left Germany for England, taking a position at the School of Biochemistry at Cambridge University at the invitation of Sir Frederick Gowland Hopkins (who had won the 1929 Nobel Prize in medicine). In 1935 Krebs moved to the University of Sheffield to become a lecturer in pharmacology.

At Sheffield Krebs embarked upon the work that would elucidate some of the complex reactions of cell **metabolism** (the processes that extract energy from food). This extraction of energy is achieved via a series of chemical transformations that remove energy-rich electrons from molecules obtained from food. These electrons pass along a chain of molecular carriers in a way that ultimately gives rise to water and **adenosine triphosphate (ATP)**, which is the primary source of chemical energy that powers cellular activity.

metabolism: the complete range of biochemical processes that take place within living organisms; comprises processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those that break down complex food molecules, thus liberating energy (catabolism)

adenosine triphosphate (ATP): molecule formed by the condensation of adenine, ribose, and triphosphoric acid, HOP(O)OH–O–(O)OH–OP(O)OH–OH; it is a key compound in the mediation of energy in both plants and animals

Krebs found that the pivotal mechanism of cell metabolism was a cycle. The cycle starts with glycolysis, which produces acetyl coenzyme A (acetyl CoA) from food molecules—carbohydrates, fats, and certain amino acids. The acetyl CoA reacts with oxaloacetate to form citric acid. The citric acid then goes through seven reactions that reconvert it back to oxaloacetate, and the cycle repeats. There is a net gain of twelve molecules of ATP per cycle. Not only does this cycle (known as the Krebs cycle, and also as the tri**carboxylic acid** cycle and the citric acid cycle) generate the chemical energy to run the cell, it is also a central component of the syntheses of other biomolecules.

carboxylic acid: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the $-CO_2H$ functional group

Krebs published his groundbreaking paper on this cyclic component of cell metabolism in the journal *Enzymologia* in 1937, and it quickly became a foundational concept in biochemistry and cell biology. It was for this research that Krebs won the Nobel Prize in medicine in 1953. (He remains one of the most often cited scientists in cell biology, with his work being noted more than 11,000 times since 1961, when the citation records of original articles in cell biology began being counted.)

Krebs worked in both research and applied science in the area of cell metabolism and nutrition. During World War II he developed a bread that helped to keep the British people nourished at a time of food shortages. He developed new analytical techniques for research in cell biology and investigated other metabolic reactions, such as the **synthesis** of glutamic acid.

synthesis: combination of starting materials to form a desired product

He was also an energetic instructor. His students went on to become directors of laboratories and to win many prizes.

In 1954 Krebs was appointed the Whitley Chair of Biochemistry at Oxford University. That same year he received the Royal Medal of the **Royal Society** of London. In 1958, for his scientific work and his contributions to the lives of British people, Krebs was knighted. Even after his retirement in 1967, he continued to do research on liver disease, the genetic bases of metabolic diseases, and the link between poor nutrition and juvenile delinquency. In addition to his Nobel Prize and Royal Medal, he received honorary degrees from nine universities. SEE ALSO GLYCOLYSIS; KREBS CYCLE.

Royal Society: The U.K. National Academy of Science, founded in 1660

Andrew Ede

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More information available from <www.nobel.se/medicine/laureates/1953/>.

Krebs Cycle

The Krebs cycle is a series of enzymatic reactions that catalyzes the aerobic **metabolism** of fuel molecules to carbon dioxide and water, thereby generating energy for the production of **adenosine triphosphate (ATP)** molecules. The Krebs cycle is so named because much of its elucidation was the work of the British biochemist Hans Krebs. Many types of fuel molecules can be drawn into and utilized by the cycle, including acetyl coenzyme A (acetyl CoA), derived from glycolysis or fatty acid **oxidation**. Some amino acids are metabolized via the enzymatic reactions of the Krebs cycle. In **eukaryotic cells**, all but one of the enzymes catalyzing the reactions of the Krebs cycle are found in the mitochondrial matrixes.

The sequence of events known as the Krebs cycle is indeed a cycle; oxaloacetate is both the first reactant and the final product of the metabolic pathway (creating a loop). Because the Krebs cycle is responsible for the ultimate oxidation of metabolic **intermediates** produced during the metabolism of fats, proteins, and carbohydrates, it is the central mechanism for metabolism in the cell. In the first reaction of the cycle, acetyl CoA condenses with oxaloacetate to form citric acid. Acetyl CoA utilized in this way by the cycle has been produced either via the oxidation of fatty acids, the breakdown of certain amino acids, or the oxidative decarboxylation of **pyruvate** (a product of glycolysis). The citric acid produced by the condensation of acetyl CoA and oxaloacetate is a tri**carboxylic acid** containing three **carboxylate** groups. (Hence, the Krebs cycle is also referred to as the citric acid cycle or tricarboxylic acid cycle.)

After citrate has been formed, the cycle machinery continues through seven distinct enzyme-catalyzed reactions that produce, in order, isocitrate, α-ketoglutarate, succinyl coenzyme A, succinate, fumarate, malate, and

metabolism: the complete range of biochemical processes that take place within living organisms; comprises processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those that break down complex food molecules, thus liberating energy (catabolism)

adenosine triphosphate (ATP): molecule formed by the condensation of adenine, ribose, and triphosphoric acid, HOP(O)OH–O–(O)OH–OP(O)OH–OH; it is a key compound in the mediation of energy in both plants and animals

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

eukaryotic cell: cell characterized by membrane-bound organelles, most notably the nucleus, and that possesses chromosomes whose DNA is associated with proteins

intermediate: molecule, often short-lived, that occurs while a chemical reaction progresses but is not present when the reaction is complete

pyruvate: anion of pyruvic acid produced by the reaction of oxygen with lactic acid after strenuous exercise

carboxylic acid: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the $–CO_2H$ functional group

carboxylate: structure incorporating the –COO– group

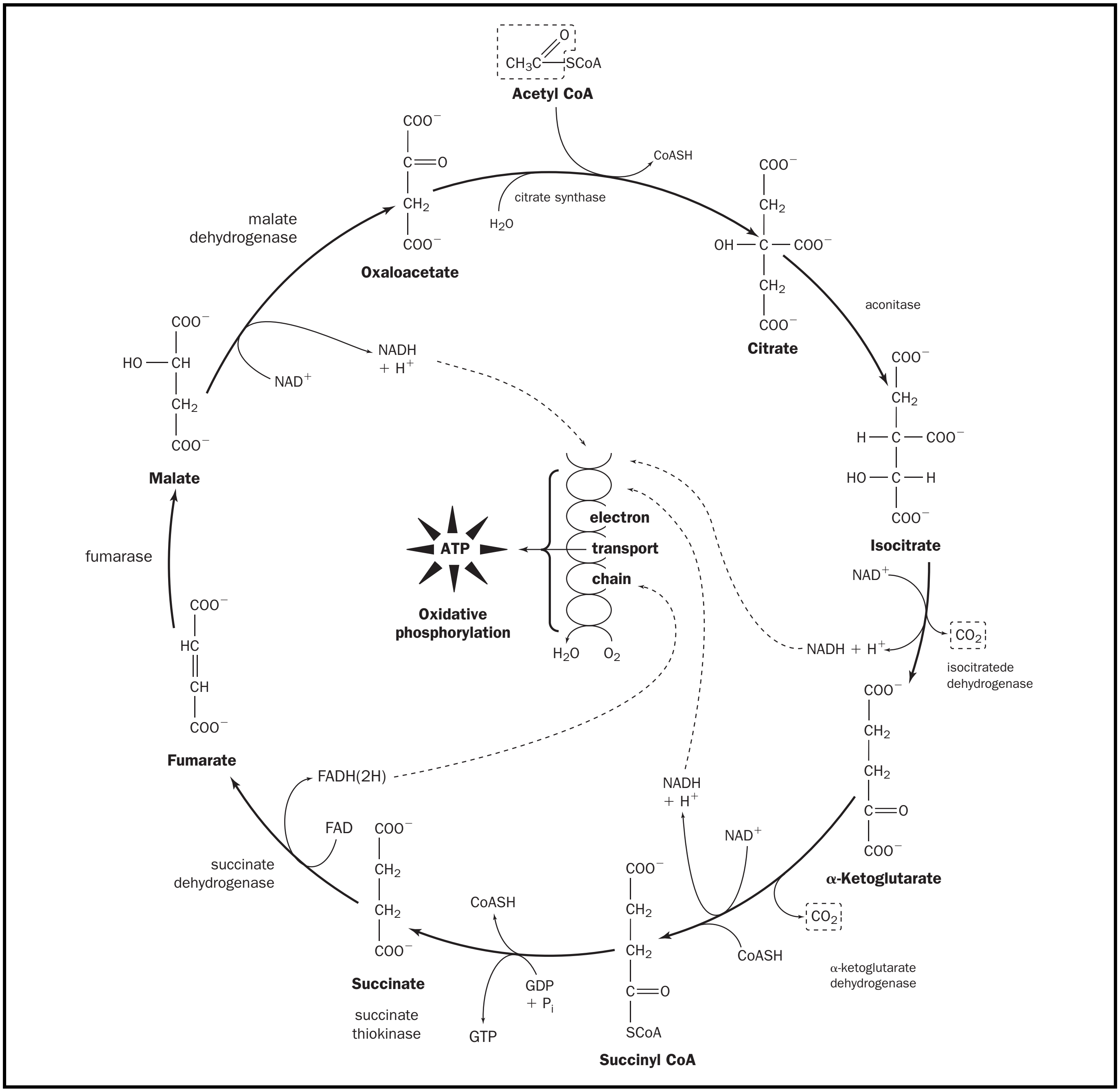

Figure 1. Krebs Cycle.

oxidation–reduction reaction: reaction, sometimes called redox, that involves the movement of electrons between reactants to form products

oxaloacetate. The freshly produced oxaloacetate, in turn, reacts with yet another molecule of acetyl CoA, and the cycle begins again. Each turn of the Krebs cycle produces two molecules of carbon dioxide, one guanosine triphosphate molecule (GTP), and enough electrons to generate three molecules of NADH and one molecule of $FADH_2$.

The Krebs cycle is present in virtually all eukaryotic cells that contain mitochondria, but functions only as part of aerobic metabolism (when oxygen is available). This oxygen requirement is owing to the close relationship between the mitochondrial electron transport chain and the Krebs cycle. In the Krebs cycle, four **oxidation–reduction reactions** occur. A high energy phosphate bond in the form of GTP is also generated. (This high energy phosphate bond is later transferred to adenosine diphosphate [ADP] to form adenosine triphosphate [ATP].) As the enzymes of the Krebs cycle oxidize fuel molecules to carbon dioxide, the coenzymes NAD^+, FAD, and coenzyme Q (also known as ubiquinone) are reduced. In order for the cycle to continue, these reduced coenzymes must become reoxidized by transferring their electrons to oxygen, thus producing water. Therefore, the final acceptor of the electrons produced by the oxidation of fuel molecules as part of the Krebs cycle is oxygen. In the absence of oxygen, the Krebs cycle is inhibited.

The citric acid cycle is an amphibolic pathway, meaning that it can be used for both the **synthesis** and degradation of biomolecules. Besides acetyl CoA (generated from **glucose**, fatty acids, or ketogenic amino acids), other biomolecules are metabolized by the cycle. Several amino acids are degraded to become what are intermediates of the cycle. Likewise, odd-chain fatty acids are metabolized to form succinyl coenzyme A, another intermediate of the cycle. Krebs cycle intermediates are also used by many organisms for the synthesis of other important biomolecules. Some organisms use the Krebs cycle intermediates α-ketoglutarate and oxaloacetate in the synthesis of several amino acids. Succinyl coenzyme A is utilized in the synthesis of **porphyrin** rings, used in heme manufacture and **chlorophyll biosynthesis**. Oxaloacetate and malate are utilized in the synthesis of glucose, in a process known as gluconeogenesis. SEE ALSO Glycolysis; Krebs, Hans Adolf.

Robert Noiva

synthesis: combination of starting materials to form a desired product

glucose: common hexose monosaccharide; monomer of starch and cellulose; also called grape sugar, blood sugar, or dextrose

porphyrin: common type of heterocyclic ligand that has four five-member rings with a nitrogen, all of which lie in a plane; nitrogen atom lone pairs are available for coordinate covalent bonds

chlorophyll: active molecules in plants undergoing photosynthesis

biosynthesis: formation of a chemical substance by a living organism

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Krypton

MELTING POINT: −157.36°C
BOILING POINT: −153.22°C
DENSITY: 2.818 g/cm^3
MOST COMMON IONS: None

36
Kr
KRYPTON
83.798

Krypton (from the Greek word *kryptos*, meaning "hidden"), is the second heaviest of the **noble gases**. It was discovered in 1898 by Sir William Ramsay and Morris Travers during their experiments with liquid air, air that has been liquefied by cooling. It has a concentration of 1.14 ppm by volume in Earth's atmosphere. It is present in the Sun and in the atmosphere of Mars.

noble gas: element characterized by inert nature; located in the rightmost column in the Periodic Table

At room temperature krypton is a colorless, odorless gas. Upon freezing it forms a white crystal with a face-centered cubic structure. In a vacuum discharge tube, it emits primarily a mixture of green and yellow light. During the late twentieth century the wavelength of light corresponding to krypton's 605.78-nanometer (2.4×10^{-5}-inch) **spectral line** was the internationally adopted definition of the meter. Krypton gas is used in the manufacture of fluorescence lights and flashlamps used in high-speed photography.

spectral line: line in a spectrum representing radiation of a single wavelength

Krypton is produced deep within stars during **nucleosynthesis**. It has six naturally occurring (i.e., stable) **isotopes**, the most abundant of which is krypton-84 (57%). Some long-lived radioactive isotopes exist as well.

nucleosynthesis: creation of heavier elements from lighter elements via fusion reactions in stars

isotope: form of an atom that differs by the number of neutrons in the nucleus

fission: process of splitting an atom into smaller pieces

Two of them, krypton-85 (half-life = 10.7 y) and krypton-81 (half-life = 210,000 y) have been used to date well water. Radioactive krypton is produced in **fission** reactions of heavy elements. Thus, radioactive isotopes of krypton have always formed part of the natural radiation background of Earth's atmosphere.

Although a noble gas, krypton is not entirely unreactive. One krypton compound, krypton difluoride (KrF_2), is commercially available in small quantities. SEE ALSO GASES; NOBLE GASES; RAMSAY, WILLIAM; TRAVERS, MORRIS.

Richard Mowat

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Lanthanides

rare earth elements: older name for the lanthanide series of elements, from lanthanum to lutetium

atomic number: the number assigned to an atom of an element that indicates the number of protons in the nucleus of that atom

The lanthanide or **rare earth elements** (atomic numbers 57 through 71) typically add electrons to the 4f orbitals as the **atomic number** increases, but lanthanum ($4f^0$) is usually considered a lanthanide. Scandium and yttrium are also chemically similar to lanthanides. Lanthanide chemistry is typically that of +3 cations, and as the atomic number increases, there is a decrease in radius for each lanthanide, known as the "lanthanide contraction." Because bonding within the lanthanide series is usually predominantly ionic, the lanthanide contraction often determines the differences in properties of lanthanide compounds and ions. Lanthanide compounds often have high coordination numbers between 6 and 12. SEE ALSO CERIUM; DYSPROSIUM; ERBIUM; EUROPIUM; GADOLINIUM; HOLMIUM; LANTHANUM; LUTETIUM; PRASEODYMIUM; PROMETHIUM; SAMARIUM; TERBIUM; THULIUM; YTTERBIUM.

Herbert B. Silber

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57
La
LANTHANUM
138.9055

Lanthanum

MELTING POINT: **920°C**
BOILING POINT: **3,469°C**
DENSITY: **6.16 g/cm^3**
MOST COMMON IONS: **La^{3+}**

isotope: form of an atom that differs by the number of neutrons in the nucleus

rare earth elements: older name for the lanthanide series of elements, from lanthanum to lutetium

lanthanides: a family of elements (atomic number 57 through 70) from lanthanum to lutetium having from 1 to 14 4f electrons

Elemental lanthanum has a ground state (electronic configuration) of $[Xe]5d6s^2$. Naturally occurring lanthanum is a mixture of two stable **isotopes**, ^{138}La and ^{139}La. The element was discovered in 1839 by Carl Gustaf Mosander in the form of the lanthanum oxide, at that time called "lanthana." The name is derived from the Greek *lanthanein* ("to lie hidden"), as the element had been overlooked due to its similarity to the earlier discovered cerium.

Monazite and bastnasite are the principal lanthanum ores, in which lanthanum occurs together with other members of the **rare earth elements** or the **lanthanides**. It can be separated from the other rare earths by ion exchange or solvent extraction techniques. Lanthanum is a silver-white, malleable, and **ductile metal**. It is soft enough to be cut with a knife. The metal is rapidly oxidized when exposed to air. Cold water attacks lanthanum only slowly, but reaction with hot water is fast.

ductile: property of a substance that permits it to be drawn into wires

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Lanthanum chemistry is dominated by the trivalent lanthanum(III) ion, La^{3+}. This ion forms ionic bonds with **ligands** containing an oxygen or nitrogen donor atom. The ground state electronic configuration of La^{3+} is $[Xe]4f^0$. Due to the absence of unpaired 4f electrons, lanthanum(III) compounds are colorless, both in solution and in the solid state. Lanthanum(III) oxide is added to optical glass to increase its refractive index and alkali resistance. Lanthanum-nickel **alloys** are being used in the storage of hydrogen gas. Thulium(III)-**doped** lanthanum oxybromide ($LaOBr:Tm^{3+}$) is a blue-emitting phosphor used in x-ray intensifying screens. SEE ALSO CERIUM; DYSPROSIUM; ERBIUM; EUROPIUM; GADOLINIUM; HOLMIUM; LANTHANIDES; LUTETIUM; NEODYMIUM; PRASEODYMIUM; PROMETHIUM; SAMARIUM; TERBIUM; YTTERBIUM.

ligand: molecule or ion capable of donating one or more electron pairs to a Lewis acid

alloy: mixture of two or more elements, at least one of which is a metal

dope: to add a controlled amount of an impurity to a very pure sample of a substance, which can radically change the properties of a substance

Koen Binnemans

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Lavoisier, Antoine

FRENCH CHEMIST
1743–1794

Antoine-Laurent Lavoisier, born in Paris, France, is considered the father of modern chemistry. During the course of his career, Lavoisier managed to transform just about every aspect of chemistry. But Lavoisier was not just a scientist. He was involved in French taxation politics during a turbulent time in the country's history—the French Revolution (the first major social revolution proclaiming the liberty of the individual [ca. 1789–1799]). Because of his involvement with the ruling class, he was executed during the revolutionary days known as the Terror, at the height of his scientific career.

Just before and during the French Revolution, another revolution was taking place. In any study of the history of chemistry, the period between 1770 and 1790 is commonly regarded as the "Chemical Revolution." This revolution, which marked the beginnings of modern chemistry, occurred in large part as a result of Lavoisier's scientific excellence and brilliant experimental capabilities. He played a role in many aspects of the Chemical Revolution, including the abandonment of the phlogiston theory of **combustion**, the evolution of the concept of an element, and the development of a new chemical nomenclature.

combustion: burning, the reaction with oxygen

Perhaps Lavoisier's most important accomplishment was his role in the dismantling of the phlogiston theory of combustion. Phlogiston was a substance believed to be emitted during combustion and the **calcination** of **metals**. Earlier chemists, such as the Germans Johann Becher (1635–1682) and George Stahl (1660–1734), supposed that a metal was composed of calx and phlogiston, and that burning resulted from the loss of phlogiston. The fact that metals actually gained weight during combustion was usually

calcine: to heat or roast to produce an oxide (e.g., CaO from calcite)

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

French chemist Antoine-Laurent Lavoisier, considered to be the founder of modern chemistry.

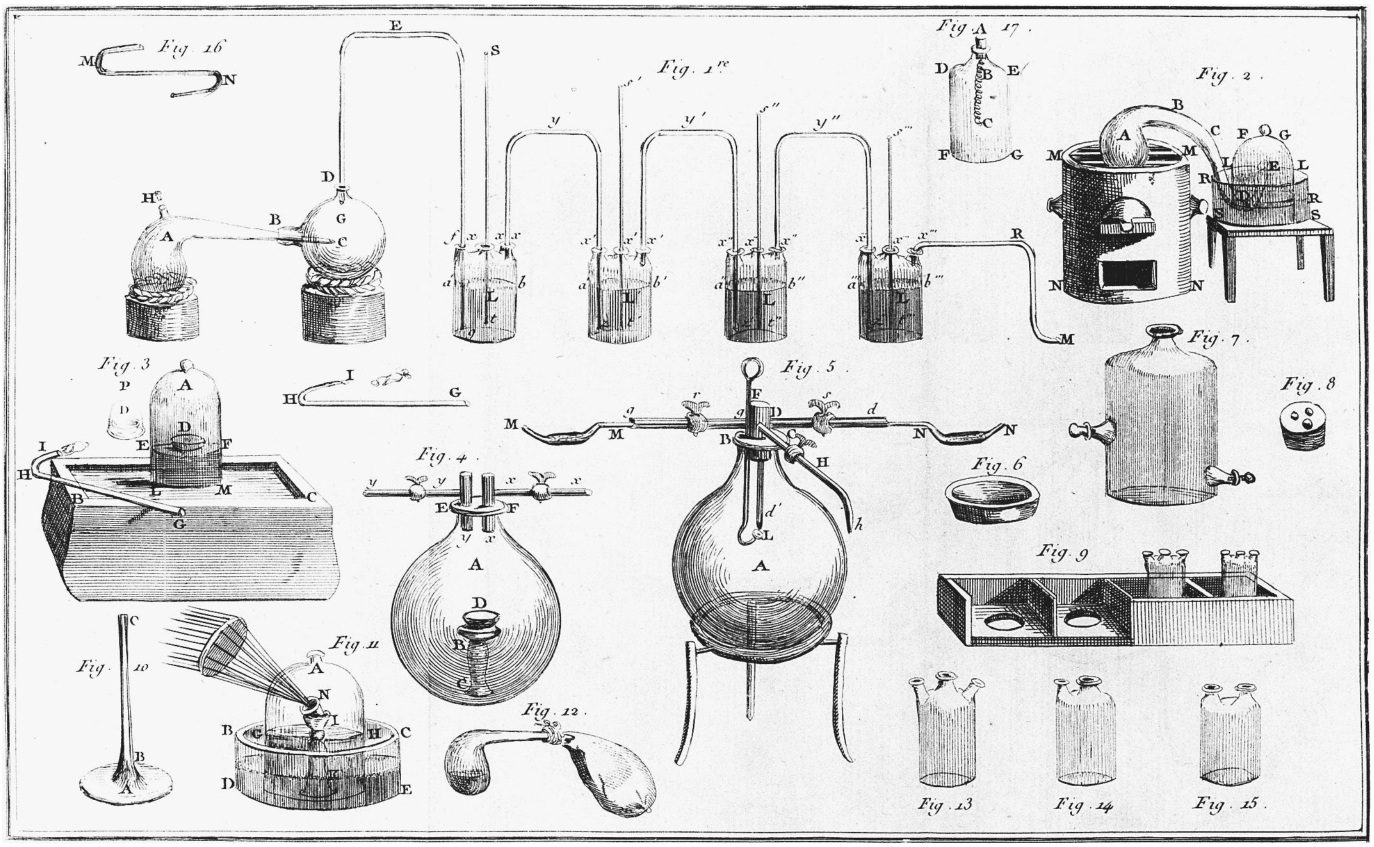
explained away by the theory that phlogiston had negative weight. Lavoisier, like some others, saw that it was illogical for anything to have negative weight.

To prove his supposition that phlogiston did not exist, Lavoisier introduced quantitative measurement to the laboratory. Using precise weighing, he showed that in all cases of combustion where an increase in weight was observed, air was absorbed, and that when a calx was burned with charcoal, air was liberated. In addition to showing by precise measurement that phlogiston did not exist, Lavoisier's findings also implied that the total weight of the substances taking part in a chemical reaction remains the same before and after the reaction—an early statement of the law of conservation of mass. By ridding the chemical world of the phlogiston theory of combustion using quantitative analysis, Lavoisier was able to push chemistry toward its modern state. No longer would counterintuitive notions such as a substance having negative weight occupy the minds of chemists.

Likewise, Lavoisier's work was also able to refute the theory that the world was composed of either one, two, three, or four elements. Lavoisier defined an element as the "last point which analysis is capable of reaching," or in modern terms, a substance that cannot be broken down any further into its components. This break from the theories of the ancient world allowed chemists to pursue the study of chemistry with a different outlook of the world. By defining elements as the last points of analysis, Lavoisier opened up new investigative possibilities. In his classic textbook *Elements of Chemistry* (generally acknowledged to be the first modern chemistry textbook), he compiled a list of all the substances he could not break down into simpler substances, that is, he created the first table of elements (although not the Periodic Table of later years). By acknowledging that there could be more elements than his preliminary list provided, Lavoisier left the search for more elements to his successors.

Lavoisier's dismantling of the phlogiston theory and his systematic definition of an element caused many chemists to view basic concepts differently and to embrace the principles of Lavoisier's new chemistry. One of the methods Lavoisier used to spread his ideas was to construct a new and logical system for naming chemicals. Working with Claude Berthollet and Antoine Fourcroy, Lavoisier developed a new nomenclature based on three general principles: (1) Substances should have one fixed name, (2) names ought to reflect composition when known, and (3) names should generally be chosen from Greek or Latin roots. This new nomenclature was published in 1787, and it swayed even more chemists to adopt the new chemistry.

Nevertheless, Lavoisier did not always hit on the right theories for the right reasons. For example, he believed that acidity was caused by the presence of oxygen in a compound. Lavoisier concluded in 1776 that oxygen was the part of a compound that was responsible for the property of acidity because he had isolated it from so many acids. In fact, oxygen means "acid former." According to Lavoisier, the other portion of the compound combined with the oxygen was called an "acidifiable base" and it was responsible for the specific properties of the compound. Although these concepts turned out to be wrong, the thinking behind them is important since it represented the first systematic attempt to chemically characterize acids and bases.



A rendering of instruments in Lavoisier's laboratory.

Lavoisier was not only interested in the theoretical aspects of chemistry. He also devoted much of his time to studying more practical topics, such as the best ways of lighting streets in a large town. In addition, Lavoisier took part in the development of what was to become the metric system and he was involved in improving the manufacture of gunpowder.

Although Lavoisier was independently wealthy, thanks to a considerable fortune inherited from his mother, he sought to increase his wealth in order to pursue his scientific career on a larger scale. For this reason, he entered the Ferme, a private company whose members purchased the privilege of collecting national taxes. During the French Revolution, the tax collectors of the Ferme were the subject of popular hatred. Although he carried out his duties honestly, Lavoisier was associated with the perceived corruption of the tax collection system. At the height of the Revolution, Lavoisier was arrested and executed by beheading in 1794.

Lavoisier's untimely death ended an era in the history of chemistry. With his contributions to chemistry ranging from developing the modern concept of combustion to establishing the language of chemistry, Lavoisier provided the foundation for the study of chemistry as a modern science. SEE ALSO BERTHOLLET, CLAUDE-LOUIS.

Lydia S. Scratch

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Lawrence, Ernest

AMERICAN PHYSICIST
1901–1958

isotope: form of an atom that differs by the number of neutrons in the nucleus

Ernest Orlando Lawrence was a pioneer of "big science," the use of complicated and expensive instrumentation by large teams of researchers. He is best known for inventing the cyclotron, one of the first and most successful "atom smashers." With this particle accelerator, Lawrence and his colleagues were able to make new radioactive **isotopes**, synthesize transuranium

American physicist Ernest Orlando Lawrence, recipient of the 1939 Nobel Prize in physics, "for the invention and development of the cyclotron and for results obtained with it, especially with regard to artificial radioactive elements."

elements that do not occur in nature, and advance knowledge of the atomic nucleus.

Youth and Education

According to his mother, Lawrence was "born grown up" on August 8, 1901, in Canton, South Dakota, a rural town of less than one thousand inhabitants. Ernest's father, Carl, was superintendent of the Canton public schools when his eldest son was born. A second son, John, was born in 1904. Both boys demonstrated early interest in science and technology and they eventually worked together on medical applications of the cyclotron.

Lawrence graduated from the University of South Dakota in 1922 with a bachelor of arts in chemistry. His original intention had been to become a physician, but as a sophomore he met Lewis Akeley, the university's lone physics professor. Akeley soon recognized the young man's talent and transformed him into a physicist. Although it was at the time impossible to major in that discipline at the university, Akeley provided special tutorials for his prize student and thus prepared him for graduate study.

In 1922 Lawrence entered the University of Minnesota, where he became a research student of W. F. G. Swann and was awarded a master of science in physics. His thesis became the basis for his first publication. When Swann moved to the University of Chicago and then to Yale, Lawrence followed him, earning his Ph.D. from the latter institution in 1925. After his degree he remained at Yale, first as a research fellow and soon thereafter as a faculty member.

The Atomic Nucleus and the Cyclotron

Ernest Lawrence's experimental skill, hard work, and professional ambition were soon common knowledge among many physicists, and offers of employment came from a number of universities. The most attractive was from the University of California in Berkeley, an institution that was eager to build a reputation as a world-class center for scientific research and education. In 1928 Lawrence moved across the country to assume an associate professorship at Berkeley. Two years later he was a full professor, the youngest in the history of the university.

The first quarter of the twentieth century was a time of great intellectual ferment in the physical sciences. Experimental discoveries such as x rays, cathode rays (electrons), and radioactivity demanded drastic revisions in the prevailing concept of atomic structure. There was convincing evidence, largely obtained in European laboratories, that atoms consisted of minuscule, incredibly dense, positively charged nuclei surrounded by negative electrons. The new quantum or wave mechanics, developed by German physicist Max Planck, Danish physicist Niels Bohr, German physicist Werner Heisenberg, Austrian physicist Erwin Schrödinger, and others, appeared to provide the theoretical and mathematical tools to explain this structure. But what was the nature of the nucleus and the forces that held together the positively charged protons that, according to classical electrostatic arguments, should be repelling each other?

It was to such problems that Lawrence soon applied his experimental genius. He was confident that nuclei could be probed by bombarding atoms with protons and other subatomic particles. What was needed was a machine to accelerate these tiny projectiles to high velocities and energies. The design for such a device came to him in the spring of 1929, while reading a paper by Norwegian engineer Rolf Wideröe. The prototype for the "magnetic-resonance accelerator" was built by Niels Edlefsen, Lawrence's first Ph.D. student, in early 1930.

The first "cyclotron," as it came to be known, consisted of a flat glass cylinder containing two semicircular D-shaped electrodes. These electrodes (called "dees") were attached to a radio-frequency oscillator that would cause them to alternate polarity rapidly between positive and negative charges. A strong electromagnet, with 4-inch pole faces above and below the apparatus, created a magnetic field **perpendicular** to the plane of the electrodes. In operation, the glass chamber was pumped down to a near vacuum and protons (hydrogen ions) were injected into the center of the device. As the dees changed polarity, the positive protons would be alternatively pulled and pushed in a circular orbit of increasing diameter. As the orbit increased, so did the velocity and energy of the particles. When the stream of protons reached the desired energy, they were deflected and directed at the intended target.

perpendicular: condition in which two lines (or linear entities like chemical bonds) intersect at a 90-degree angle

The first model cyclotron, a leaky gadget coated with sealing wax that cost about $25, was soon replaced with a brass box. Before long, the size of the device began to grow. The 4-inch version was succeeded by a 9-inch model, followed by cyclotrons 11, 27, 34, 60, and finally 184 inches in diameter. Each increase in size required larger electromagnets, more electric power, and more money. The energy of the accelerated particles also increased, and that was the point of the enterprise—to obtain more powerful probes. At the 11-inch stage, Lawrence and his team "split" their first atom, and the 184-inch cyclotron attained his goal of particles with energies of 100 million electron volts. In all this research, significant contributions were made by Lawrence's students and collaborators at the Radiation Laboratory, especially M. Stanley Livingston and Edwin M. McMillan.

Applications, Issues, and Analysis

In 1939 Ernest Lawrence was awarded the Nobel Prize in physics for his invention of the cyclotron. That same year Austrian physicists Lise Meitner and Otto Frisch correctly concluded that the experimental results of German chemists Otto Hahn and Fritz Strassmann indicated that neutrons cause uranium atoms to split (undergo **fission**) into smaller fragments, with the release of great quantities of energy. It was also in 1939 that the German army invaded Poland, launching World War II (1939–1945). With the latter two events, the study of the atomic nucleus and atomic energy literally became a matter of life and death.

fission: process of splitting an atom into smaller pieces

Lawrence's 184-inch cyclotron was soon modified to separate uranium isotopes and became the prototype for the **calutrons** used for similar purposes in the **Manhattan Project**. Both during and after the war, Lawrence was one of the most politically influential American scientists; he served on many key committees, including the Scientific Panel that advised on the first use of the atomic bomb.

calutron: electromagnetic device that separates isotopes based on their masses

Manhattan Project: government project dedicated to creation of an atomic weapon; directed by General Leslie Groves

Ernest Lawrence died on August 27, 1958, in Palo Alto, California. Never a gifted mathematician or theoretician, he was a brilliant experimentalist with the entrepreneurial skills to enthusiastically promote his vision of "big science." Thanks to the cyclotron and other accelerators there are hundreds of radioactive isotopes that have applications in medicine and elsewhere, dozens of subatomic particles, and at least seventeen artificial elements that stretch beyond uranium in the Periodic Table. Lawrence's legacy is commemorated in the Lawrence Berkeley Laboratory, the Lawrence Hall of Science, the Lawrence Livermore Laboratory, and, most appropriately, in element number 103 (which concludes the actinide series). Lawrencium (Lr) was the first element named for an American. **see also** Bohr, Niels; Heisenberg, Werner; Meitner, Lise; Planck, Max; Radioactivity; Schrödinger, Erwin; Transactinides.

A. Truman Schwartz

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Lawrencium

MELTING POINT: **Unknown**
BOILING POINT: **Unknown**
DENSITY: **Unknown**
MOST COMMON IONS: **Lw^{3+}**

103
Lr
LAWRENCIUM
262

Lawrencium is a synthetic radioactive element and the last member of the actinide series. It was discovered in 1961 by Albert Ghiorso and his coworkers, who bombarded a target of **isotopes** of californium (^{249}Cf–^{252}Cf) with boron projectiles (either ^{10}B or ^{11}B) using the Heavy Ion Linear Accelerator (HILAC) at the University of California, Berkeley, producing isotopes of unknown element 103 of masses 257 and 258. The atoms recoiling after the **nuclear** reaction were caught on metalized Mylar tape, which was then moved past a series of α-detectors, and the decays of a few new atoms of element 103 (^{257}103 and ^{258}103), having half-lives of seconds or less, were recorded. The element is named after Ernest O. Lawrence, the inventor of the cyclotron and the founder of the Berkeley Radiation Laboratory. "Lawrencium" was suggested and accepted by the International Union of Pure and Applied Chemistry, but the originally suggested symbol of Lw was changed to Lr. In 1965 Evgeni D. Donets at the Joint Institutes of Nuclear Research in Dubna, Russia, using a double-recoil technique, confirmed the **atomic number** of element 103 by linking its decay, via either electron capture followed by α-decay, or α-decay followed by electron capture, to its known granddaughter, an isotope of fermium (^{252}Fm).

isotope: form of an atom that differs by the number of neutrons in the nucleus

nuclear: having to do with the nucleus of an atom

atomic number: the number assigned to an atom of an element that indicates the number of protons in the nucleus of that atom

α-particle: subatomic particle with 2+ charge and mass of 4; a He nucleus

fission: process of splitting an atom into smaller pieces

lanthanides: a family of elements (atomic number 57 through 70) from lanthanum to lutetium having from 1 to 14 4f electrons

aqueous solution: homogenous mixture in which water is the solvent (primary component)

All Lr isotopes are radioactive, decaying by **α-particle** emission, electron capture, and/or spontaneous **fission**, and have half-lives ranging from a few tenths of a second for the isotope of mass 252, the lightest isotope, to 3.6 hours for the isotope of mass 262, the heaviest. The ground state electronic configuration of the gaseous Lr atom is believed to be [Rn]5f^{14}6d7s^{2}, by analogy to its **lanthanide** homologue, lutetium (element 71). Its most stable ion in **aqueous solution** is Lr^{3+}, and attempts to reduce it to Lr^{2+}

or Lr^{1+} in aqueous solution have been unsuccessful. see also Actinium; Berkelium; Einsteinium; Fermium; Lawrence, Ernest; Mendelevium; Neptunium; Nobelium; Plutonium; Protactinium; Radioactivity; Rutherfordium; Thorium; Transmutation; Uranium.

Darleane C. Hoffman

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82
Pb
LEAD
207.2

Lead

MELTING POINT: 327.5°C
BOILING POINT: 1,740.0°C
DENSITY: 11.34 g/cm^3
MOST COMMON IONS: Pb^{2+}, Pb^{4+}

Lead makes up only about 0.0013 percent of Earth's crust but was well known in the ancient world and was even mentioned in the Book of Exodus. The word "lead" is derived from the Anglo-Saxon word *laedan.* Lead's symbol, Pb, comes from the Latin word for lead, *plumbum.* Because of lead's long use in piping, the word "plumber" comes from that same root. Lead is an extremely dense but malleable **metal** that is very resistant to corrosion.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Lead is sometimes found free in nature but is usually obtained from ores such as galena (PbS) or cerussite ($PbCO_3$), from which it is easily mined and refined. Most lead is obtained by simply roasting galena in hot air. About one-third of the lead used in the United States is obtained through recycling efforts.

Lead has seen many uses over the ages. As a constituent of pewter (an **alloy** of tin and lead), lead was a component of Roman eating and drinking utensils. It has been suggested that the decline of the Roman Empire may have been tied to this use, since acidic foodstuffs extract small amounts of lead, a cumulative human poison. Lead's use as a pottery glaze has been banned for the same reason—the danger of lead ingestion via the extraction of the lead by food and drink. During the twentieth century, a **volatile** form of lead—tetraethyl lead [$Pb(CH_2CH_3)_4$]—was developed and widely used to improve the octane level of gasoline. That use has also been banned for health and environmental reasons.

alloy: mixture of two or more elements, at least one of which is a metal

volatile: low boiling, readily vaporized

Lead remains in wide use in electrical cable sheathing, automobile batteries, lead crystal, radiation protection, and some solders. see also Inorganic Chemistry; Radioactivity.

George H. Wahl Jr.

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Le Bel, Joseph-Achille

FRENCH CHEMIST
1847–1930

French chemist Joseph-Achille Le Bel, who, with Jacobus van't Hoff, was the founder of modern stereochemistry.

Joseph-Achille Le Bel, born in Pechelbronn, France, was, with Dutch physical chemist Jacobus Hendricus van't Hoff, the cofounder of modern stereochemistry. They independently established the relation between optical activity and asymmetric carbon compounds.

Le Bel was born into a wealthy family that controlled the petroleum industry in Pechelbronn, Alsace. In 1865 he was sent to the École Polytechnique in Paris to obtain a chemical education and spent most of his time there doing chemical research. After graduation, he worked with the French chemists Antoine Balard and Adolphe Wurtz in Paris, in between intermediate periods of refinery construction at home. Finally in 1889, he sold his shares in the family business and established a private laboratory in Paris where he devoted himself to organic chemistry and, in his later years, paleontology, botany, and philosophy. An independent thinker who never held an academic appointment, Le Bel did manage to achieve general recognition as a chemist and even became president of the French Chemical Society in 1892.

In 1874, at the age of twenty seven, Le Bel presented a brief paper to the Paris Chemical Society that led to his scientific fame, although it may be regarded as his only outstanding contribution to the field of chemistry. By the late 1840s the great chemist and microbiologist Louis Pasteur had separated two sorts of tartrate crystals of the same composition, each crystal shape being the mirror image of the other. These crystals in solution not only rotated the plane of polarized light to a certain angle (optical activity), the rotation also occurred in opposite directions. Pasteur called such pairs of substances optical **isomers**, and because they showed no difference in chemical properties, they were represented by the same constitutional structural formula in the new chemical structure theory. Le Bel then extended the structure theory, from constitutional structural to configurational representations in three-dimensional space, to account for the difference in optical isomers. He argued that if a tetravalent carbon atom combined with four different groups, as in tartrate, the carbon must be asymmetric in three-dimensional space (i.e., without a symmetry plane or center). Furthermore, for each such asymmetric carbon there were exactly two different structures (stereoisomers), each being the mirror image of the other, just like the crystal shapes of Pasteur. Le Bel's structure theory could not explain optical activity, but it explained and predicted which compounds had stereoisomers and which did not, an approach that he also extended to nitrogen compounds.

isomer: molecules with identical compositions but different structural formulas

Oddly enough, van't Hoff, with whom Le Bel had worked in Wurtz's laboratory shortly beforehand, independently arrived at the same theory from a different starting point at virtually the same time. SEE ALSO CHIRALITY; PASTEUR, LOUIS; VAN'T HOFF, JACOBUS.

Joachim Schummer

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French chemist Nicolas Leblanc, inventor of the process for transforming sodium chloride (NaCL, or common salt) into soda ash.

Leblanc, Nicolas

FRENCH CHEMIST AND SURGEON
1742–1806

Nicolas Leblanc invented a method of making alkali soda from salt that became one of the most important chemical processes of the nineteenth century. Leblanc was born in Issoudun, France; his father managed an ironworks. After completing his medical education in about 1780, Leblanc became a private physician in the house of Philippe Égalité, duc d'Orléans (1747–1793). France had been suffering from an acute shortage of alkali from traditional vegetable sources. Alkali was critical in the manufacture of glass, textiles, paper, soap, and other products. In 1775 the French Royal Academy offered a prize to anyone who could develop a process for transforming common salt (sodium chloride) into soda ash. With Égalité's support, Leblanc achieved the goal by 1789 and opened a small factory at Saint Denis that began production in 1791.

What became known as the Leblanc process was actually several interrelated processes. Salt was first reacted with sulphuric acid in a cast-iron pan, then in a **reverberator furnace** (in which heat was applied from a flame blown from a separate chamber, not in direct contact with the salt), to produce saltcake (sodium sulphate), with hydrochloric acid released as a waste gas. Saltcake was used to make sodium carbonate, or roasted with limestone (calcium carbonate) and coal or coke to produce "black ash." This mixture of sodium carbonate, calcium sulphide, sodium sulphide, lime, salt, carbon, and ash could be treated further with hot water to produce impure sodium carbonate in solution, evaporated into soda crystals (washing soda), or heated to yield anhydrous sodium carbonate. The latter, in turn, could be reacted with lime to made caustic soda (sodium hydroxide), the strongest commercial alkali then available.

reverberator furnace: furnace or kiln used in smelting that heats material indirectly by deflecting a nearby flame downward from the roof

Leblanc personally benefited little from his innovation. The National Assembly granted him a fifteen-year patent in September 1791, but three years later the revolutionary government sequestered his factory and made his patents public, giving Leblanc only meager compensation for his assets. Napoléon Bonaparte returned the plant to him in 1802, but by then Leblanc was too poor to resume production and, in 1806 he took his own life. (In 1855 Napoléon III gave Leblanc's heirs a payment in lieu of the 1775 prize.)

Leblanc's process—by greatly reducing the cost and boosting the efficiency of alkali for the key industries that depended on it—boosted European industrialization for two generations. The year of Leblanc's suicide, the Saint Gobain Company opened a soda ash factory; by 1818 French producers were turning about roughly 10,000 to 15,000 tons of Leblanc soda ash per year. British producers, discouraged until a prohibitive tax on salt was repealed in 1823, embraced the new process and surpassed the French by the middle of the century. U.S. alkali makers remained wedded to **potash** but imported Leblanc soda ash after 1850. Germany took the lead in Leblanc soda production in the 1870s.

potash: the compound potassium oxide, K_2O

By that time the Leblanc process was facing competition from the newer Solvay (ammonia soda) alkali. The dominance of Leblanc soda was extended by improvements, most notably the Deacon process (1868), which converted the wasteful and harmful hydrochloric acid gases into chlorine, and the

Chance process (1882), which recovered waste sulphur. By the turn of the twentieth century, however, the Leblanc and Solvay processes were eclipsed by new electrolytic methods for making chlorine and caustic soda. SEE ALSO Alkali Metals; Industrial Chemistry, Inorganic; Sodium.

David B. Sicilia

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Le Châtelier, Henri

FRENCH CHEMIST
1850–1936

Henri-Louis Le Châtelier was born into a family of architects, engineers, and scientists in Paris. His family home was like a drop-in center for France's leading chemists. Le Châtelier became a well-known industrial chemist himself, interested in **metallurgy**, cements, glasses, fuels, explosives, and, most famously, chemical **equilibrium**. By mixing theoretical work with practical applications, Le Châtelier became one of France's most valuable and productive chemists.

metallurgy: the science and technology of metals

equilibrium: condition in which two opposite reactions are occurring at the same speed, so that concentrations of products and reactants do not change

Le Châtelier served as an army lieutenant during the Franco–Prussian War in 1870, after which he returned to school to finish his degree. His intention was to become a mining engineer, but he changed his mind when he was offered a professorship in chemistry at the École des Mines in Paris.

Le Châtelier's first area of investigation was the chemistry of cements. By repeating the experiments of Antoine Lavoisier on the preparation of plaster of paris, Le Châtelier learned that when a cement comes into contact with water, a solution is formed that yields an interlaced, **coherent mass** of minute crystals.

coherent mass: mass of particles that stick together

Through his studies on cements, Le Châtelier became interested in the applications of thermodynamics to chemistry. It was while working with thermodynamics that Le Châtelier devised what became known as Le Châtelier's principle in 1884. This principle states that if a system is in a state of equilibrium and one of the conditions is changed, such as the pressure or temperature, the equilibrium will shift in such a way as to try to restore the original equilibrium condition. Using Le Châtelier's principle as a guide the efficiency of chemical processes can be improved by shifting a system to yield more of the desired product. For example, the German chemist Fritz Haber employed the principle in his development of a process for synthesizing ammonia. Le Châtelier considered missing this practical application of his principle to be the greatest blunder in his scientific career.

In addition to his work on equilibrium, Le Châtelier was involved in many other areas of chemistry and science in general. For instance, he investigated the cause and prevention of mining disasters. He helped produce safer explosives and conducted research that was used to develop the torch now used in cutting and welding steel. He also designed instruments when none existed to suit his purposes, such as the thermocouple to measure very high temperatures.

Le Châtelier was additionally involved in other areas of research. He wrote numerous biographies and spent much time working on articles on social welfare, the relationship of science to economics, and the relationship between pure and applied science. Le Châtelier was also devoted to teaching, working at the École des Mines until he retired at the age of sixty-nine. He advised his students to be content with adding to the structure of science, but to pay attention to anything unusual they observed.

Le Châtelier contributed much to chemistry. He bridged the gaps between theory and practice by choosing research problems that looked as if they would have industrial applications. For this reason, he became one of the most successful researchers in combining theoretical science with practical applications. SEE ALSO Equilibrium; Haber, Fritz; Lavoisier, Antoine; Thermodynamics.

Lydia S. Scratch

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Leclanché, Georges

FRENCH ENGINEER AND INVENTOR
1839–1882

primary electrochemical cell: voltaic cell based on an irreversible chemical reaction

In 1866 Georges-Lionel Leclanché was granted French patent no. 71,865, which described a remarkable advancement in the technology of the **primary electrochemical cell**. Typically called a battery, an electrochemical cell generates electrical current by chemical reactions at the two electrodes of the cell, the cathode and the anode. In early batteries the current was originally carried through an electrically conductive liquid; later improvements substituted a conductive paste for the liquid. Although Leclanché did not invent this type of battery, commonly called a dry cell, his version, only slightly modified since then, is used today to power millions of devices from toys to portable computers.

metallurgy: the science and technology of metals

Leclanché was born on October 9, 1839, in Paris, France. His father was a cultured and politically active lawyer in the French government during a tempestuous time in that country's history. Because of shifting political winds, young Georges and his father spent the better part of eighteen years away from Paris. Upon his return in 1856, Leclanché enrolled in the École Centrale Imperiale des Arts et Manufactures, where he majored in **metallurgy**. He was far more interested in analytical and industrial chemistry, however, and after graduating in 1860, he became a laboratory manager in a company that manufactured lead salts.

Politically active like his father, Leclanché was forced to flee to Belgium in 1863 because of his opposition to France's involvement in Mexico. While there, he became interested in electrochemical research. He returned to Paris the following year and became a chemist in the materials laboratory of a railroad company, where he further developed his cell. After his cell was patented, he started a company for its manufacture and continued to perfect its design until his untimely death from throat cancer in 1882, at the age of forty-three.

Although electrochemical cells had been developed and used since the beginning of the nineteenth century, they suffered several practical disadvantages: They generally contained costly or dangerous ingredients (such as platinum or mercury), and they were composed of delicate components in liquid solutions, which limited their portability. Leclanché's original cell used a manganese dioxide/carbon cathode, a zinc anode, and ammonium chloride as the **electrolyte solution**. Although this was technically a "wet" cell, later advances in design replaced the electrolyte solution with a conductive paste. The main advantages of the Leclanché cell were the low cost of its components and the cell's robust construction, which allowed it to be manufactured cheaply and utilized widely at a time when batteries were the only source of electricity. SEE ALSO ELECTROCHEMISTRY; NEW BATTERY TECHNOLOGY.

electrolyte solution: a liquid mixture containing dissolved ions

Bartow Culp

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Leloir, Luis

ARGENTINE CHEMIST
1906–1987

Luis Leloir was born in Paris in 1906. His parents were Argentine, and he resided in Buenos Aires from the age of two and for most of his career until his death in 1987. Leloir received his M.D. from the University of Buenos Aires in 1932, after which he worked at the Institute of Physiology with Professor Bernardo Houssay on the action of **adrenalin** in carbohydrate **metabolism**. In 1936 he collaborated with Sir F. G. Hopkins at the Biochemical Laboratory in Cambridge, England. He returned to Buenos Aires to study the **oxidation** of fatty acids in the liver and on the formation of **angiotensin**. He was forced to leave Argentina in 1943 when Houssay's laboratory was closed by the government of Juan Perón in response to Houssay's public criticism of the dictatorship. During the next few years Leloir worked in the United States in the laboratory of Carl and Gerty Cori at Washington University in St. Louis, Missouri, and D. E. Green at Columbia University in New York City.

adrenalin: chemical secreted in the body in response to stress

metabolism: the complete range of biochemical processes that take place within living organisms; comprises processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those that break down complex food molecules, thus liberating energy (catabolism)

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

angiotensin: chemical that causes a narrowing of blood vessels

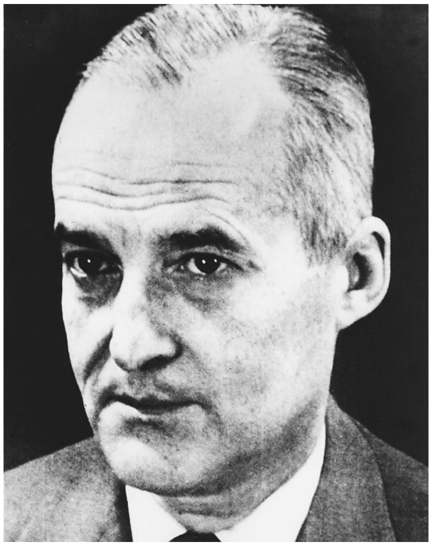
Leloir returned to Argentina in 1945 to take part in the founding of the Instituto de Investigaciones Bioquimicas supported by the Jaime Campomar Foundation. He became the institute's first director. Most of the research at the institute was conducted on a shoestring budget, and some of the complex equipment there was ingeniously built by Leloir or his colleagues

R. Caputto, C. E. Cardini, R. Trucco, and A. C. Paladini from everyday objects. For instance, a fraction-collecting device for column **chromatography** was built with a Meccano set (a toy from Leloir's childhood that was similar to an erector set); its collection bottles moved about with a toy railroad train.

In spite of inadequate funding and the resulting limitations, work began at the new institute on the metabolism of the sugar **galactose**; it led to the discovery of **glucose** 1,6-diphosphate and uridine diphosphate glucose (UDPG). The latter substance was the first sugar nucleotide discovered. Leloir continued his work in this sector of research and discovered several other sugar nucleotides. He and his coworkers determined that UDPG is the nucleotide that provides the glucose units in the **biosynthesis** of glycogen. Glycogen is the form of polymeric carbohydrate in which energy is stored inside an animal cell, while starch is the form in which energy is stored in plants. Further work demonstrated that the donor of the glucose units for the biosynthesis of starch is adenosine diphosphate glucose (ADPG.) This work was quite important in improving scientists' understanding of the processes by which carbohydrates are converted to energy and the glycogen storage diseases. Leloir received the Nobel Prize in chemistry in 1970; his was the first Nobel Prize in chemistry ever awarded to an Argentine.

Leloir is best remembered for producing Nobel Prize–quality research under very difficult conditions and for contributing significantly to the development of scientific analysis and discovery in Argentina. SEE ALSO CARBOHYDRATES; CORI, CARL AND GERTY; NUCLEOTIDE.

Lawrence H. Brannigan



Argentine chemist Luis Leloir, recipient of the 1970 Nobel Prize in chemistry, "for his discovery of sugar nucleotides and their role in the biosynthesis of carbohydrates."

chromatography: the separation of the components of a mixture in one phase (the mobile phase) by passing it through another phase (the stationary phase) making use of the extent to which the components are absorbed by the stationary phase

galactose: six-carbon sugar

glucose: common hexose monosaccharide; monomer of starch and cellulose; also called grape sugar, blood sugar, or dextrose

biosynthesis: formation of a chemical substance by a living organism

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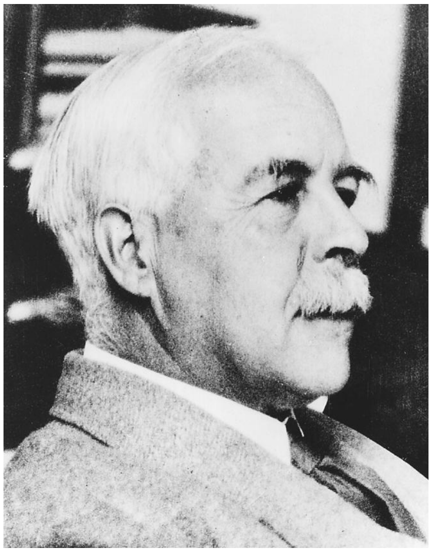
Lewis, Gilbert N.

AMERICAN PHYSICAL CHEMIST
1875–1946

Gilbert Newton Lewis was born on October 25, 1875, in West Newton, Massachusetts. A precocious child, he received his early education at home and learned to read by the age of three. When Lewis was nine, his family moved to Lincoln, Nebraska. He attended the University of Nebraska for two years and in 1893 transferred to Harvard University, from which he received his B.S. in 1896.

After a brief stint as a teacher at Phillips Academy in Andover, Massachusetts, Lewis returned to Harvard, where he obtained his M.A. in 1898 and Ph.D. in 1899. He subsequently studied at the universities at Göttingen and Leipzig in Germany (1900–1901) and then returned to Harvard as an instructor (1901–1906). In 1907 Lewis became an assistant professor at the Massachusetts Institute of Technology, where he soon rose to the rank of full professor.

In 1912 Lewis accepted a position as dean and chairman of the College of Chemistry at the University of California, Berkeley. He remained at Berkeley for the rest of his life and transformed the chemistry department there into a world-class center for research and teaching. His reforms in the way chemistry was taught, a **catalyst** for the modernization of chemical education, were widely adopted throughout the United States. Lewis introduced thermodynamics to the curriculum, and his book on the same subject became a classic. He also brought to the study of physical chemistry such concepts as fugacity, activity and the activity coefficient, and ionic strength.



American chemist Gilbert N. Lewis, a theorist of chemical bonds, or valence.

catalyst: substance that aids in a reaction while retaining its own chemical identity

attraction: force that brings two bodies together, such as two oppositely charged bodies

valence: combining capacity

noble gas: element characterized by inert nature; located in the rightmost column in the Periodic Table

At the beginning of the twentieth century physicists tried to relate the electronic structure of atoms to two basic chemical phenomena: the chemical bond (the **attraction** between atoms in a molecule) and **valence** (the quality that determines the number of atoms and groups with which any single atom or group will unite chemically and also expresses this ability to combine relative to the hydrogen atom). German chemist Richard Abegg was the first to recognize in print the stability of the group of eight electrons, the arrangement of outer electrons that occurs in **noble gases** and is often attained when atoms lose or gain electrons to form ions. Lewis called this the "group of eight," and American chemist and physicist Irving Langmuir labeled it an "octet."

In 1902, while explaining the laws of valence to his students at Harvard, Lewis conceived a concrete model for this process, something Abegg had not done. He proposed that atoms were composed of a concentric series of cubes with electrons at each of the resulting eight corners. This "cubic atom" explained the cycle of eight elements in the Periodic Table and corresponded to the idea that chemical bonds were formed by the transfer of electrons so each atom had a complete set of eight electrons. Lewis did not publish his theory, but fourteen years later it became an important part of his theory on the shared electron-pair bond.

In 1913 Lewis and Berkeley colleague William C. Bray proposed a theory of valence that differentiated two different types of bond: a polar bond formed by the transfer of electrons and a **nonpolar** bond not involving electron transfer. In 1916 Lewis published his seminal article suggesting that the chemical bond is a pair of electrons shared or held jointly by two atoms. He depicted a single bond by two cubes sharing an edge, or more simply by double dots in what has become known as Lewis dot structure.

nonpolar: molecule, or portion of a molecule, that does not have a permanent, electric dipole

According to Lewis's octet rule, each atom should be surrounded by four pairs of electrons, either shared or free pairs. Lewis derived structures for **halogen** molecules, the ammonium ion, and oxy acids, inexplicable according to previous valence theories. He viewed polar bonds as unequally shared electron pairs. Because the complete transfer of electrons was only an extreme case of polarity, he abandoned his earlier dualistic view; the polar theory was just a special case of his more general theory.

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

Lewis's shared electron-pair theory languished until Langmuir revived and elaborated it beginning in 1919. It was soon accepted as the Lewis–Langmuir theory, one of the most fundamental concepts in the history of chemistry.

Lewis's acid-base concept is also well known to introductory-level chemistry students. A Lewis acid, for example, BF_3, $AlCl_3$, or SO_3, is a substance

coordination chemistry: chemistry involving complexes of metal ions surrounded by covalently bonded ligands

ligand: molecule or ion capable of donating one or more electron pairs to a Lewis acid

coordinate covalent bond: covalent bond in which both of the shared electrons originate on only one of the bonding atoms

isotope: form of an atom that differs by the number of neutrons in the nucleus

that can accept a pair of electrons from a Lewis base, for example, NH_3 or OH^-, which is a substance that can donate a pair of electrons. It can be applied to various areas, for example, **coordination chemistry**: The metal ion is a Lewis acid, the **ligand** is a Lewis base, and the resulting formation of a **coordinate covalent bond** corresponds to a Lewis acid–base reaction.

Lewis made additional valuable contributions to the theory of colored substances, radiation, relativity, the separation of **isotopes**, heavy water, photochemistry, phosphorescence, and fluorescence. As a major in the U.S. Army Chemical Warfare Service during World War I, he worked on defense systems against poison gases. From 1922 to 1935 he was nominated numerous times for the Nobel Prize in chemistry. Lewis's death, while measuring the dielectric constant of hydrogen cyanide on March 23, 1946, precluded his receiving the prize, which is not awarded posthumously. SEE ALSO Acid-Base Chemistry; Lewis Structures.

George B. Kauffman

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Lewis Acids ***See Acid-Base Chemistry.***

Lewis Structures

In 1902, while trying to find a way to explain the Periodic Table to his students, the chemist Gilbert Newton Lewis discovered that the chemistry of the main-group elements could be explained using a model in which electrons arranged around atoms are conceived as occupying the faces of concentric cubes. This model was based on four assumptions.

1. The number of electrons in the outermost cube of an atom is equal to the number of electrons lost when the atom forms positive ions;
2. each neutral atom has one more electron in its outermost cube than the atom that precedes it in the Periodic Table;
3. it takes eight electrons—an octet—to complete a cube;
4. once an atom has an octet of electrons in its outermost cube, the cube becomes part of the cote of electrons about which the next cube is built.

Lewis determined the formulas of simple ionic compounds (such as NaCI) by theorizing that atoms gain electrons if the outermost cube is more than half full, and lose electrons if the cube is less that half-full (until the cube is either full or empty). Sodium, for example, loses the one electron in its outermost cube at the same time that chlorine gains the electron it needs to fill its outermost cube.

As understanding of the structure of the atom developed, it became apparent why the magic number of electrons for each of the main-group elements was eight. The outermost **atomic orbitals** for these elements are the *s* and *p* orbitals in a given shell, and it takes eight electrons in its outermost shell: [He] $2s^2$ $2p^3$. It therefore has to gain three electrons to fill this shell.

atomic orbital: mathematical description of the probability of finding an electron around an atom

The electrons in an outermost shell are known as **valence** electrons. The number of bonds an element can form is called valence (from the Latin *valens*, "to be strong"). An atom's valence electrons are those electrons that can be gained or lost in a chemical reaction. Because the electrons that occupy filled *d* or *f* subshells are seldom disturbed in a chemical reaction, we can also define an atom's valence electrons as the electrons that are not present in an atom of the preceding rare gas (ignoring filled *d* or *f* subshells). Gallium, for example, has the following electron configuration: [Ar] $4s^2$ $3d^{10}$ $4p^1$. The $4s$ and $4p$ electrons can be lost in a chemical reaction, but the electrons in the filled $3d$ **subshell** cannot. Gallium therefore has three valence electrons.

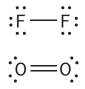
valence: combining capacity

subshell: electron energy sublevel, of which there are four: s, p, d, and f

By 1916 Lewis realized that there was another way that atoms can combine to achieve an octet of valence electrons: They can share electrons and form a **covalent bond**. Two fluorine atoms, for example, by sharing a pair of electrons can form a stable F_2 molecule in which each atom has an octet of valence electrons. A pair of oxygen atoms, by sharing two pairs of electrons, can form an O_2 molecule in which each atom has a total of eight valence electrons.

covalent bond: bond formed between two atoms that mutually share a pair of electrons

Whenever Lewis applied his model to covalent compounds, he noted that the atoms seemed to share pairs of electrons. He also noted that most compounds contained even numbers of electrons, which suggested that electrons exist in pairs. He therefore replaced his cubic model of the atom, in which eight electrons were oriented toward the surfaces of a cube, with a model based on pairs of electrons. In this notation, each atom is surrounded by up to four pairs of dots, corresponding to the eight possible valence electrons. This symbolism is still in use today. The only significant modification is the use of lines to indicate covalent bonds formed by the sharing of a pair of electrons. The Lewis structures for F_2 and O_2 are written as follows:



The prefix "co-" is used to indicate that two or more entities are joined or have equal standing (as in, for example, *coexist*, *cooperate*, and *coordinate*). It is therefore appropriate that the term "covalent bond" is used to describe molecular bonds that result from the sharing of one or more pairs of electrons.

The Lewis structure of a compound can be arrived at by trial and error. We start by notating symbols that contain the correct number of valence electrons for the atoms in the molecule. We then pair electrons to indicate covalent bonds until we come up with a Lewis structure in which each atom (with the exception of hydrogen atoms) has an octet of valence electrons. The trial-and-error method for writing Lewis structures can be time-consuming, however. For all but the simplest molecules, the step-by-step process is faster.

Step 1: Determine the total number of valence electrons.

Step 2: Write the skeleton structure of the molecule.

Step 3: Assign two valence electrons to each covalent bond in the skeleton structure.

Step 4: Try to complete the octets of the atoms by distributing the remaining valence electrons as nonbonding electrons.

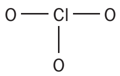
The first step involves calculating the number of valence electrons in the molecule or ion. For a neutral molecule it is the sum of the valence electrons of each atom. If the molecule carries an electric charge, we add one electron for each negative charge or subtract one electron for each positive charge.

Consider the chlorate (ClO_3^-) ion. A chlorine atom (Group VIIa) has seven valence electrons, and each oxygen atom (Group VIa) has six valence electrons. Because the chlorate ion has a charge of −1, it contains one more electron than a neutral ClO_3 molecule. Thus, the ClO_3^- ion has a total of twenty-six valence electrons.

$$ClO_3^-:\ 7 + 3(6) + 1 = 26$$

The second step in this process involves deciding which atoms in the molecule are connected by covalent bonds. This can be the most difficult step in the process. As a rule, the least **electronegative** element is at the center of the molecule. It is also useful to note that the formula of the compound often provides a hint to the skeleton structure. The formula for the chlorate ion, for example, suggests the following skeleton structure.

electronegative: capable of attracting electrons

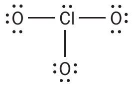


The third step assumes that the skeleton structure of the molecule is based on covalent bonds. The valence electrons are therefore divided into two categories: bonding electrons and nonbonding electrons. Because it takes two electrons to form a covalent bond, we can calculate the number of nonbonding electrons in the molecule by subtracting two electrons for each bond in the skeleton structure from the total number of valence electrons.

There are three covalent bonds in the skeleton structure of the chlorate ion. As a result, six of the twenty-six valence electrons must be used as bonding electrons. This leaves twenty nonbonding electrons in the valence shell.

$$\begin{array}{l} 26 \text{ valence electrons} \\ -6 \text{ bonding electrons} \\ \hline 20 \text{ nonbonding electrons} \end{array}$$

The fourth step in the process by which Lewis structures are generated involves using the nonbonding valence electrons to complete the octets of the atoms in the molecule. Each oxygen atom in the ClO_3^- ion already has two electrons, the electrons in each Cl–O bond. Each oxygen atom therefore needs six nonbonding electrons to complete the octet. Thus, it takes eighteen nonbonding electrons to satisfy the octets of the three oxygen atoms. This leaves one pair of nonbonding electrons, which can be used to fill the octet of the central atom.

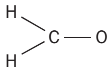


Occasionally, we encounter a molecule that does not seem to have enough valence electrons. When this happens, we have to remember why atoms share electrons in the first place. If we cannot achieve a satisfactory Lewis structure by having two atoms share a single pair of electrons, it may be possible to achieve this goal by having them share two or even three pairs of electrons. Consider **formaldehyde** (H_2CO), for example, which contains twelve valence electrons.

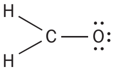
formaldehyde: name given to the simplest aldehyde HC(O)H, incorporating the –C(O)H functional group

$$H_2CO:\ 2(1) + 4 + 6 = 12$$

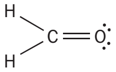
The formula of this molecule suggests the following skeleton structure.



There are three covalent bonds in this skeleton structure, which means that six valence electrons must be used as bonding electrons. This leaves six nonbonding electrons. It is impossible, however, to complete the octets of the atoms in this molecule with only six nonbonding electrons. When the nonbonding electrons are used to complete the octet of the oxygen atom, the carbon atom has a total of only six valence electrons.



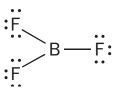
We therefore assume that the carbon and oxygen atoms share two pairs of electrons. There are now four bonds in the skeleton structure, which leaves only four nonbonding electrons. This is enough, however, to satisfy the octets of the carbon and oxygen atoms.



Every once in a while, we encounter a molecule for which it is impossible to write a satisfactory Lewis structure. Consider boron trifluoride (BF_3), for example, which contains twenty-four valence electrons.

$$BF_3:\ 3 + 3(7) = 24$$

There are three covalent bonds in what is the most reasonable skeleton structure for the molecule. Because it takes six electrons to form the skeleton structure, there are eighteen nonbonding valence electrons. Each fluorine atom needs six nonbonding electrons to complete its octet. Thus, all nonbonding electrons are consumed by the three fluorine atoms. As a result, we run out of electrons, and the boron atom still has only six valence electrons.



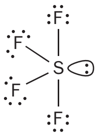
For reasons that are not discussed here, the elements that form strong double or triple bonds are C, N, O, P, and S. Because neither boron nor fluorine falls in this group, we have to stop short with what appears to be an unsatisfactory Lewis structure.

It is also possible to encounter a molecule that seems to have too many valence electrons. When that happens, we expand the valence shell of the central atom. Consider the Lewis structure for sulfur tetrafluoride SF_4, for example, which contains thirty-four valence electrons.

$$SF_4:\ 6 + 4(7) = 34$$

There are four covalent bonds in the skeleton structure for SF_4. Because this structure uses eight valence electrons to form the covalent bonds that hold the molecule together, there are twenty-six nonbonding valence electrons.

Each fluorine atom needs six nonbonding electrons to complete its octet. Because there are four of these atoms, we need twenty-four nonbonding electrons for this purpose. But there are twenty-six nonbonding electrons in this molecule. We have already completed the octets for all five atoms, and we still have one pair of valence electrons. We therefore expand the valence shell of the sulfur atom to hold more than eight electrons.



SEE ALSO Bonding; Lewis, Gilbert N.; Molecules.

George Bodner

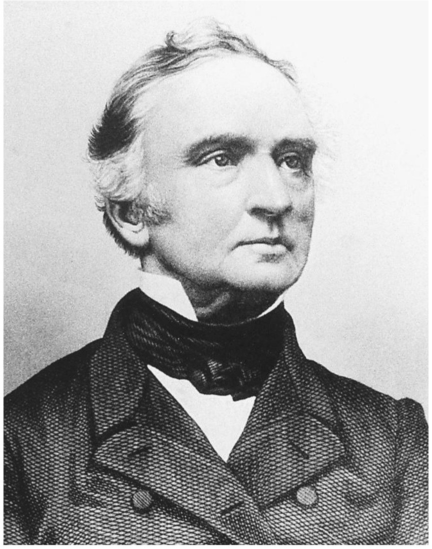
Liebig, Justus von

GERMAN CHEMIST
1803–1873

elemental analysis: determination of the percent of each atom in a specific molecule

Justus von Liebig, one of the founders of modern chemistry, was born on May 12, 1803, in Darmstadt, Hesse, Germany. His father was a manufacturer of drugs and paints. As an adolescent Liebig performed many experiments using materials from his father's business while neglecting other studies. He was apprenticed to an apothecary at age fifteen; however, his real interest was chemistry. He enrolled at the University of Bonn in 1820 to attend the lectures of Wilhelm Kastner. When Kastner left for the University of Erlangen, Liebig followed him there and received his doctoral degree in 1822 after only two years of study.

Liebig soon realized that his knowledge of chemistry was deficient and using the patronage of the grand duke of Hesse was able to study in Paris from 1822 to 1824. Paris was the leading center for the study of chemistry at this time, and here Liebig was able to attend the lectures of such famous chemists as Joseph Gay-Lussac, Louis Thénard, and Pierre Dulong. Parisian chemistry stressed a rigorous and quantitative approach that was lacking in European chemistry. In Paris Liebig had the opportunity to work in the laboratory of Gay-Lussac, where he acquired skills in the **elemental analysis** of inorganic and organic compounds, as well as in the systematic methodology of chemical research.



German chemist Justus von Liebig.

In 1825 Liebig returned to Germany and was offered the professorship of chemistry at the University of Geissen. He stayed in Geissen until 1851, at which time he was called to the chair of chemistry at the University of Munich where he remained until his death on April 18, 1873.

In Geissen Liebig drawing from his studies in Paris established the model for chemical education that was soon copied by other German educators. His students learned by working in the laboratory with their mentor, starting with simple procedures, working their way through more complex exercises, and finally graduating to their own independent research.

One of Liebig's many achievements at Geissen was the development of more efficient **combustion** techniques for the elemental analysis of organic compounds. The impetus for this was his inability to get a good result in his analysis of a compound he had isolated from urine (which he had named hippuric acid) using the conventional methods that were available to him. These methods, which were tedious and time-consuming, included the use of very small amounts of a given sample, which amplified the experimental error. In 1830 Liebig devised a technique that allowed the use of larger samples and he was able to quantify the amounts of carbon and hydrogen in organic compounds. The trapping of the gaseous combustion products water vapor and carbon dioxide on pre-weighed absorbents was part of his technique. This procedure greatly reduced error and was simple enough so that Liebig's students were able to analyze all types of organic compounds almost routinely, which greatly enhanced the existing knowledge of the variety of organic compounds in nature.

combustion: burning, the reaction with oxygen

Liebig pioneered methods for the analysis of nitrogen, sulfur, and **halogens** in organic compounds, in addition to his contributions to the analysis of carbon and hydrogen in these compounds. Liebig was the founding editor of one of the first chemical journals, *Annalen der chemie* in 1832. SEE ALSO GAY-LUSSAC JOSEPH-LOUIS; ORGANIC CHEMISTRY; PROTEINS.

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

Martin D. Saltzman

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Light ***See Radiation.***

Lipid Bilayers

Lipid bilayers form the fundamental structures of cell membranes and thus provide a semipermeable interface between the interior and exterior of a cell and between compartments within the cell. Bilayer-forming lipids are amphipathic molecules (containing both **hydrophilic** and **hydrophobic** components). The hydrophilic fragment, typically termed the lipid headgroup, is charged, or polar, whereas the hydrophobic section consists of a pair of alkyl chains (typically between 14 and 20 carbon atoms in length). A typical class of bilayer-forming lipid is the diacyl phosphatidylcholines, in which phosphate and tetramethyl ammonium moieties comprise the polar head groups and two fatty acids chains constitute the hydrophobic portions.

lipid: a nonpolar organic molecule; fatlike; one of a large variety of nonpolar hydrophobic (water-hating) molecules that are insoluble in water

hydrophilic: a part of a molecule having an affinity for water

hydrophobic: a part of a molecule that repels water

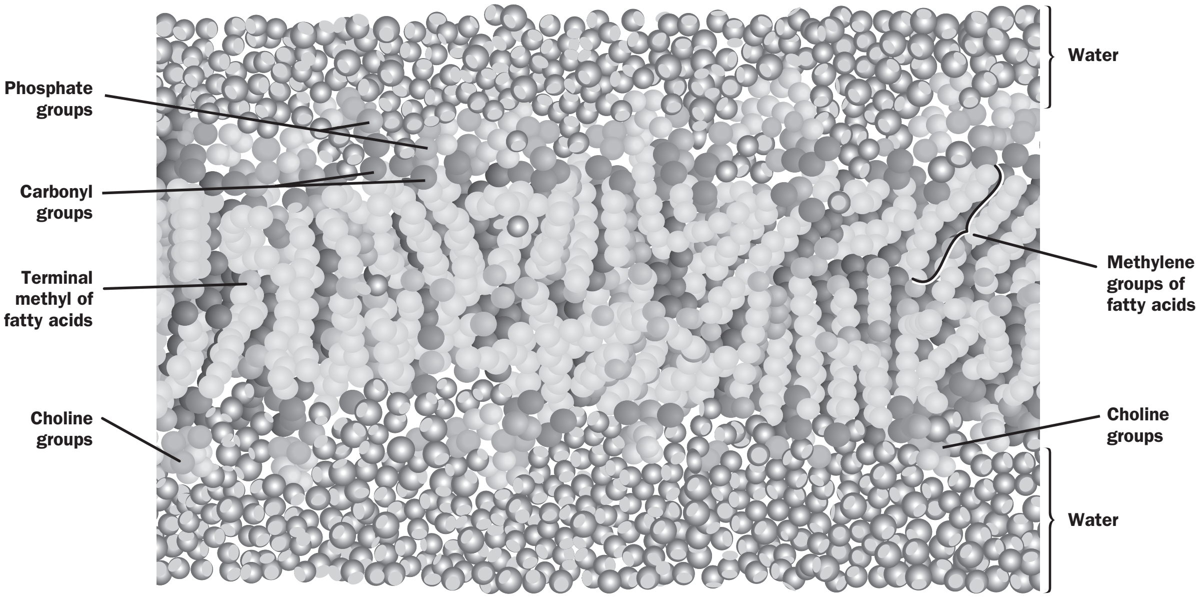

Figure 1. An image of a dipalmitolyphosphatidylcholine lipid bilayer from a molecular dynamics computer simulation.

In an aqueous environment the lipids self-assemble into structures that minimize contact between water molecules and the hydrophobic components of the lipids by forming two leaflets (monolayers); this arrangement brings the hydrophobic tails of each leaflet in direct contact with each other, and leaves the head groups in contact with water (see Figure 1). Lipid bilayers are classified as lyotropic and thermotropic liquid crystals, meaning that their structures are a function of both water content and temperature, respectively. Under conditions of low hydration and/or low temperature, the lipid bilayer is ordered with straight alkyl chains and a regular arrangement of head groups, and is in a gel state. At high water content and/or elevated temperatures the bilayer exists in the (biologically relevant) fluid state, characterized by a high degree of disorder in both chain and head group conformations (Figure 1 represents the fluid bilayer state).

melting point: temperature at which a substance in the solid state undergoes a phase change to the liquid state

phase: homogeneous state of matter

The alkyl chain **melting point**, the gel to fluid transition temperature, is a function of chain length (shorter chains will dissociate at lower temperatures) and the extent of unsaturation within the chains (greater double bond content lowers the melting temperature). The fluid **phase** bilayer has a hydrophobic thickness on the order of 30 angstroms, and (because of the hydrophobic chains) is a significant barrier to the passage of charged or polar solutes. The bilayer is fluid in the sense that lipid molecules and other membrane constituents readily undergo lateral diffusion within the plane of the membrane. SEE ALSO LIPIDS; MEMBRANE.

Scott E. Feller
Ann T. S. Taylor

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Lipids

Lipids are a class of biomolecules that is defined by their solubility in organic solvents, such as chloroform, and their relative insolubility in water. Interactions among lipids and of lipids with other biomolecules arise largely from their **hydrophobic** ("water-hating") nature. Lipids can be divided into two main categories according to their structures: those that are based on fatty acids, and those that are based on **isoprene**, a branched, five-carbon chain.

lipid: a nonpolar organic molecule; fatlike; one of a large variety of nonpolar hydrophobic (water-hating) molecules that are insoluble in water

hydrophobic: a part of a molecule that repels water

isoprene: common name for 2-methyl-1,3 butadiene, the monomer of the natural rubber polymer

Fatty Acid–Based Lipids

Fatty acids are unbranched carboxylic acids, usually containing an even number of carbon atoms (between 12 and 24, inclusive). If there are no double bonds between carbon atoms, the fatty acid is saturated; if there are double bonds between carbon atoms, the fatty acid is unsaturated. Naturally occurring unsaturated fatty acids have one to six double bonds, with the double bonds separated by at least two single bonds; the double bonds have the *cis* configuration. These double bonds inhibit "packing" of the molecules (in solids), which lowers the fatty acid **melting point**. Many physical properties of lipid substances are determined by the extent of unsaturation. Polyunsaturated omega-3 (ω-3) fatty acids, so named because the double bond between the third to last (ω-3) and fourth to last (ω-4) carbons, are commonly found in cold-water fish and are thought to play an important role in many **neurological** functions.

melting point: temperature at which a substance in the solid state undergoes a phase change to the liquid state

neurologic: of or pertaining to the nervous system

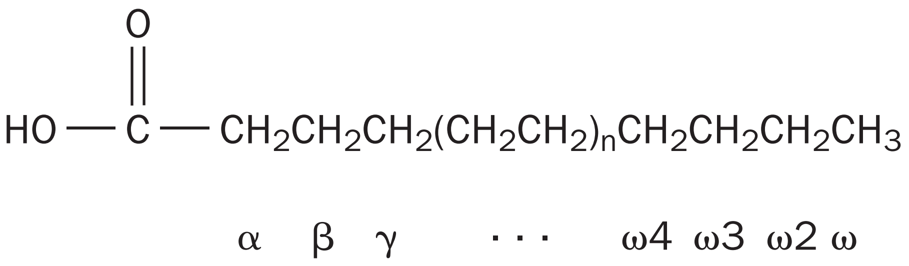
In response to stress conditions, various tissues convert polyunsaturated fatty acids having twenty carbons to a family of compounds called eicosanoids. Eicosanoids include prostaglandins, thromboxanes, prostacyclins, and leukotrienes, and are generally involved in inflammation and pain sensation. Aspirin, acetaminophen, and other **analgesics** work by inhibiting the initial reactions required for the conversion of fatty acids to eicosanoids.

analgesic: compound that relieves pain, e.g., aspirin

The **carboxylic acid** group of a fatty acid molecule provides a convenient place for linking the fatty acid to an alcohol, via an **ester** linkage. If the fatty acid becomes attached to an alcohol with a long carbon chain, the resultant substance is called a wax. Waxes are very hydrophobic, and thus repel water. Glycerol, a three-carbon compound with an alcohol group at each carbon, very commonly forms esters with fatty acids. When glycerol and a fatty acid molecule are combined, the fatty acid portion of the resultant compound is called an "acyl" group, and the glycerol portion is referred to as a "glyceride." Using this nomenclature system, a triacylglyceride has three fatty acids attached to a single glycerol molecule; sometimes this name is shortened to "triglyceride." Triglyceride substances are commonly referred to as

carboxylic acid: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the $-CO_2H$ functional group

ester: organic species containing a carbon atom attached to three moieties: an O via a double bond, an O attached to another carbon atom or chain, and a H atom or C chain; the R(C═O)OR functional group



$$HO-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2CH_2CH_2(CH_2CH_2)_nCH_2CH_2CH_2CH_3$$

Figure 1. Generic fatty acid.

fats or oils, depending on whether they are solid or liquid at room temperature. Triglycerides are an energy reserve in biological systems. Diacylglycerides are commonly found in nature with acyl chains occurring at two adjacent carbons, and are the basis of phospholipid chemistry.

Isoprene-Based Lipids

The other class of lipid molecules, based on a branched five-carbon structure called isoprene, was first identified via steam distillation of plant materials. The extracts are called "essential oils." They are often fragrant, and are used as medicines, spices, and perfumes. A wide variety of structures is obtained by fusing isoprene monomer units, leading to a very diverse set of compounds, including terpenes, such as β-carotene, pinene (turpentine), and carvone (oil of spearmint); and steroids, such as testosterone, cholesterol, and **estrogen**.

estrogen: female sex hormone

Lipid Organization

"Like oil and water" is a saying based on the minimal interaction of lipids with water. Although this saying is apt for isoprene-based lipids and bulky fatty acid–based lipids such as waxes and triglycerides, it is not apt for all lipids (e.g., it does not apply to substances composed of fatty acids or diacylglycerides).

Fatty acids and diacylglycerides are often amphipathic; that is, the carboxylic acid "head" is **hydrophilic** and the hydrocarbon "tail" is hydrophobic. When a fatty acid or triglyceride substance is placed in water, structures that maximize the interactions of the hydrophilic heads with water and minimize the interactions of the hydrophobic tails with water are formed. At low lipid concentrations a monolayer is formed, with hydrophilic heads associating with water molecules and hydrophobic tails "pointing" straight into the air (see Figure 2).

hydrophilic: a portion of a molecule having an affinity for water

As the concentration of lipid is increased, the surface area available for monolayer formation is reduced, leading to the formation of alternative structures (depending on the particular lipid and condition). Compounds that have a relatively large head group and small tail group, such as fatty acids and detergents, form spherical structures known as micelles. The concentration of lipid required for micelle formation is referred to as the critical micelle concentration (CMC). Other hydrophobic molecules, such as molecules within dirt, triacylglycerides, and other large organic molecules, associate with the hydrophobic tail portion of a micelle.

Compounds that have approximately equal-sized heads and tails tend to form bilayers instead of micelles. In these structures, two monolayers of lipid molecules associate tail to tail, thus minimizing the contact of the hydrophobic portions with water and maximizing hydrophilic interactions. Lipid molecules can move laterally (within a single layer of the bilayer, called a leaflet), but movement from one leaflet to the opposing leaflet is much more difficult.

$$H_2CO: 2(l) + 4 + 6 = 12$$

vesicle: small compartment in a cell that contains a minimum of one lipid bilayer

liposome: sac formed from one or more lipid layers that can be used for drug transport to cells in the body

Often these bilayer sheets can wrap around in such a way as to form spherical structures, called **vesicles** or **liposomes** (depending on their size). Several new anticancer treatments are based upon the packaging of chemo-

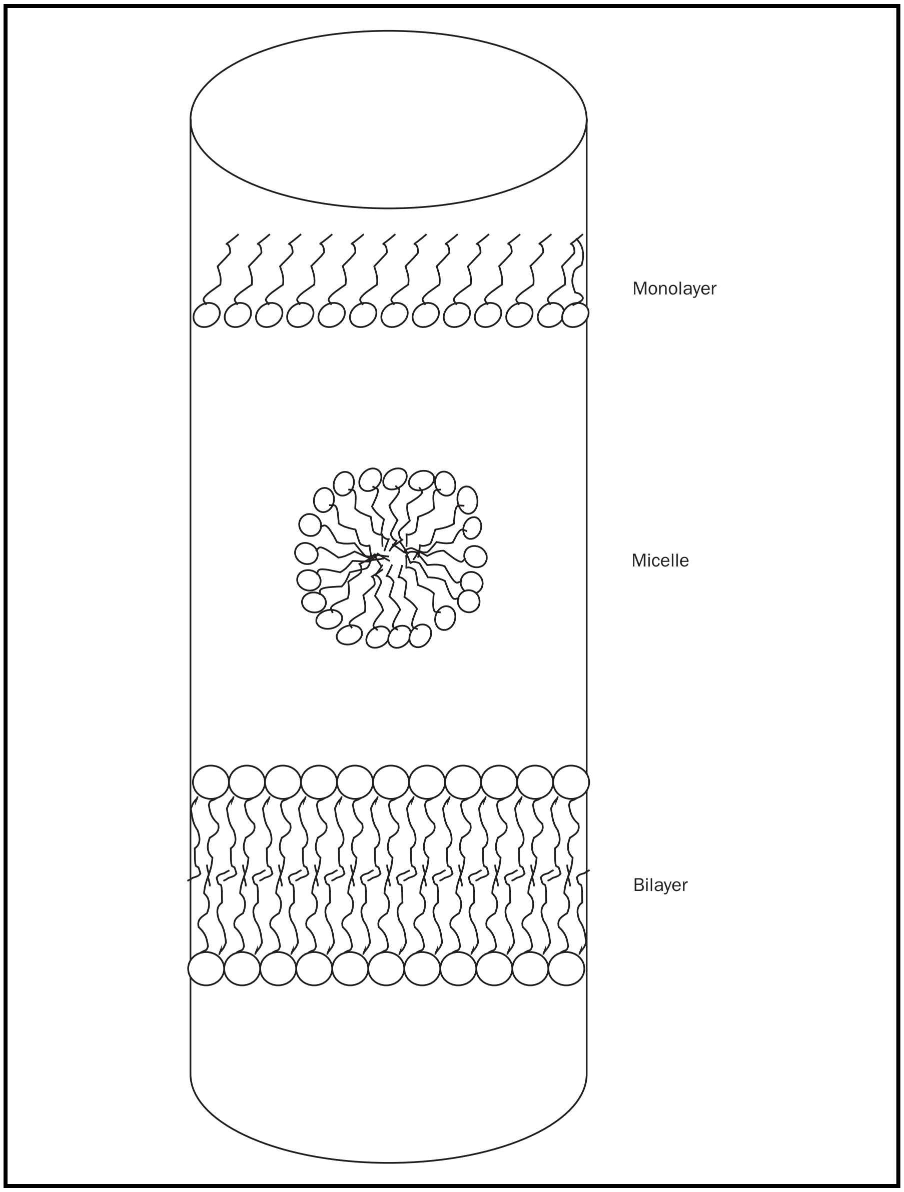


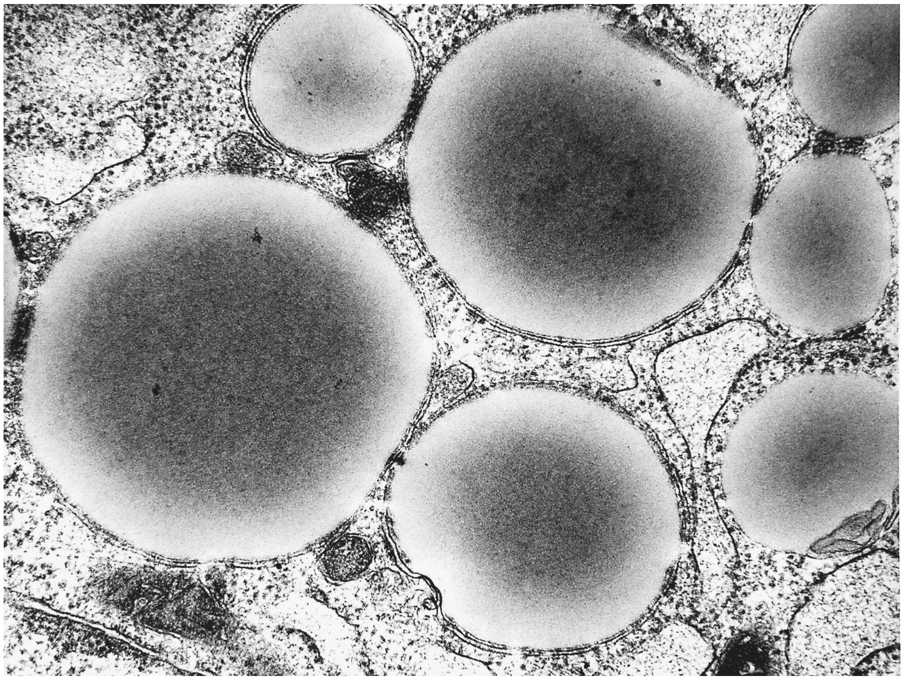
Figure 2. Assembly of lipids into more complex structures. At low concentrations, lipids form monolayers, with the polar head group (represented as a circle) associating with the water, while the hydrophobic tails (represented as lines) associate with the air. As the concentration of lipid increases, either miscelles or bilayers form, depending upon the lipid and conditions.

therapeutic agents inside liposomes and then directing the liposomes to a specific target tissue.

Lipids can also form structures in conjunction with various proteins. A cell membrane consists of a lipid bilayer that holds within it a variety of proteins that either transverse the bilayer or are associated more loosely with the bilayer. Cholesterol can insert into the bilayer, and this helps to regulate the fluidity of the membrane.

A variety of lipid-protein complexes are used in the body to transport relatively water-insoluble lipids, such as triglycerides and cholesterol, in circulating blood. These complexes are commonly called lipoproteins; they contain both proteins and lipids in varying concentrations. The density of these lipoproteins depends on the relative amounts of protein, because lipids are less dense than protein. Low density lipoproteins, or LDLs, have a relatively higher ratio of lipid to protein. LDLs are used to transport cholesterol and triglycerides from the liver to the tissues. In contrast, high density

An electron micrograph of lipid droplets in the fat cell of a rat.



lipoproteins, or HDLs, have a relatively lower ratio of lipid to protein and are used in the removal of cholesterol and fats from tissues.

Functions of Lipids

Lipids perform a variety of tasks in biological systems. Terpenes, steroids, and eicosanoids act as communication molecules, either with other organisms or with other cells within the same organism. The highly reduced carbon atoms in triglycerides help to make fats an ideal energy storage compound.

aqueous solution: homogenous mixture in which water is the solvent (primary component)

Some of the functions of lipids are related to the structures they form. The micelle formation characteristic of fatty acids, detergents, and soaps in **aqueous solution** helps to dissolve dirt and other hydrophobic materials. Lipid bilayers play many vital roles. Liposomes are used to deliver drugs to desired tissues. A cell membrane, because of its hydrophobic core, is a substantial barrier to the passage of ions, allowing the cell interior to have concentrations of ions different from those of the extracellular environment. Bilayers are good electrical insulators, and aid in the transmission of nerve impulses along the conducting portions of nerve fibers. The importance of lipids in neural function is seen in diseases in which these insulators are lost, such as multiple sclerosis, or not properly maintained, such as Tay-Sachs disease.

Although they are a chemically diverse assortment of compounds, lipids share a number of properties. The amphipathic nature of lipid molecules encourages the formation of more complex structures such as micelles, bilayers, and liposomes. These structures, as well as the actual lipid substances themselves, affect all aspects of cell biology. SEE ALSO FATS AND FATTY ACIDS; LIPID BILAYERS; MEMBRANE; PHOSPHOLIPIDS.

Ann T. S. Taylor
Scott E. Feller

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Liquid Crystals

In 1888 the Austrian botanist and chemist Friedrich Reinitzer, interested in the chemical function of cholesterol in plants, noticed that the cholesterol derivative cholesteryl benzoate had two distinct melting points. At 145.5°C (293.9°F) the solid compound melted to form a turbid fluid, and this fluid stayed turbid until 178.5°C (353.3°F), at which temperature the turbidity disappeared and the liquid became clear. On cooling the liquid, he found that this sequence was reversed. He concluded that he had discovered a new state of matter occupying a niche between the crystalline solid and liquid states: the liquid crystalline state. More than a century after Reinitzer's discovery, liquid crystals are an important class of advanced materials, being used for applications ranging from clock and calculator displays to temperature sensors.

Mesophases

In a crystalline solid, the molecules are well ordered in a **crystal lattice**. When a crystal is heated, the thermal motions of the molecules within the **lattice** become more vigorous, and eventually the vibrations become so strong that the crystal lattice breaks down and the molecules assume a disordered liquid state. The temperature at which this process occurs is the **melting point**. Although the transition from a fully ordered structure to a fully disordered one takes place in one step for most compounds, this

crystal lattice: three-dimensional structure of a crystaline solid

lattice: systematic geometrical arrangement of atomic-sized units that constitute the structure of a solid

melting point: temperature at which a substance in the solid state undergoes a phase change to the liquid state

A digital fish finder, the display of which is made with the use of liquid crystal diodes.

transition is not a universal behavior. For some compounds, this process of diminishing order as temperature is increased occurs via one or more intermediate steps. The intermediate phases are called *mesophases* (from the Greek word *mesos*, meaning "between"), or liquid crystalline phases. Liquid crystalline phases have properties intermediate between those of fully ordered crystalline solids and liquids. Liquid crystals are fluid and can flow like liquids, but the magnitudes of some electrical and mechanical properties of individual liquid crystals depend on the direction of the measurement (either along the main crystal axis or in another direction not along the main axis). Typical liquid crystals have rodlike or disklike shapes. Classes of liquid crystalline states or mesophases can be distinguished according to degrees of internal order.

phase: homogeneous state of matter

perpendicular: condition in which two lines (or linear entities like chemical bonds) intersect at a 90-degree angle

helix: form of a spiral or coil such as a corkscrew

The least ordered liquid crystalline **phase** for rodlike molecules is the nematic phase (N), in which the long axes of individual molecules have an approximate direction (which is called the director, n). A nematic phase material has a low viscosity and is therefore very fluid. The term "nematic" is derived from the Greek word for thread (after the threadlike microscopic textures exhibited by nematic phase substances). In the smectic phases, the molecules have more order than molecules existing in the nematic phase. Just as in the nematic phase, the molecules have their long axes more or less parallel to the director. Additionally, the molecules are more or less confined to layers. The term "smectic" is derived from the Greek word for soap (owing to the fact that smectic liquid crystals have mechanical properties similar to those of concentrated aqueous soap solutions). The smectic phases are divided into classes based on degree of molecular order; the smectic A phase (SmA) and the smectic C phase (SmC) are the most studied ones. In the SmA phase, the molecules are **perpendicular** to the smectic layer planes, whereas in the SmC phase they are tilted. Substances assuming these phases have some fluidity, but their viscosities are much higher than that of a nematic phase substance. In Figure 1, the arrangements of molecules in the nematic, smectic A, and smectic C phases are shown schematically. Chiral molecules (molecules lacking a center of symmetry) can assume a *cholesteric* phase, also called a chiral nematic phase. In this mesophase, the molecules have helical arrangements. The pitch is the distance along a longitudinal axis corresponding to a full turn of the **helix**.

Typical mesophases formed by disklike molecules are columnar, wherein the molecules are "stacked" into columns. The columns are in turn packed together to form two-dimensional arrays. In addition to the columnar arrangements, the molecules can become ordered in a way that is comparable to a heap of coins spread on a flat surface—the *discotic nematic* phase.

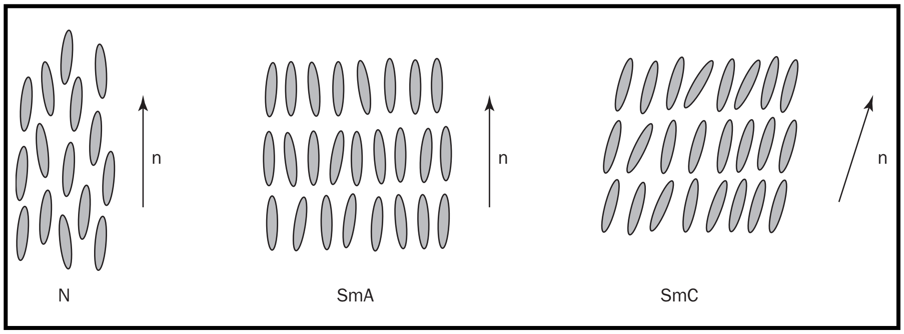

Figure 1. Rodlike molecules in the nematic phase (N), the smectic A phase (SmA) and in the smectic C phase (SmC). The director is denoted as n.

Displays

By far the most important application of liquid crystals is display devices. Liquid crystal displays (LCDs) are used in watches, calculators, and laptop computer screens, and for instrumentation in cars, ships, and airplanes. Several types of LCDs exist. In general their value is due to the fact that the orientation of the molecules in a nematic phase substance can be altered by the application of an external electric field, and that liquid crystals are anisotropic fluids, that is, fluids whose physical properties depend on the direction of measurement. It is not pure liquid crystalline compounds that are used in LCDs, but liquid crystal mixtures having optimized properties.

The simplest LCDs that display letters and numbers have no internal light source. They make use of surrounding light, which is selectively reflected or absorbed. An LCD is analogous to a mirror that is made nonreflective at distinct places on its surface for a certain period. The main advantage of an LCD is low energy consumption. More ad-vanced LCDs need back light, color filters, and advanced electronics to display complex figures. The best-known LCD is the so-called twisted nematic display.

Liquid Crystal Thermometers

The use of liquid crystals as temperature sensors is possible because of the selective reflection of light by chiral nematic (cholesteric) liquid crystals. A chiral nematic liquid crystal reflects light having a characteristic wavelength determined by its pitch and by the viewing angle (the angle between the eye of the observer and the surface of the liquid crystal). Because the pitch of a chiral nematic compound is temperature-dependent, observed color is a function of temperature. Liquid crystals can therefore serve as thermometers. By mixing chiral nematic compounds, thermometers can be customized to be effective in a desired temperature range. The color variation of some liquid crystal thermometers extends across the entire visible light spectrum within changes of a few tenths of a degree centigrade. For use in devices, microcapsules containing chiral nematic mixtures are mixed with binder materials. Liquid crystal thermometers find application in medicine (medical thermography). A liquid crystal thermometer attached to the skin can measure temperature variations of the skin. This can be useful in the detection of skin cancer, as tumors have different temperatures than surrounding tissues. In electronics, liquid crystal temperature sensors can pinpoint bad connections within a circuit board by detecting the characteristic local heating. The color changes of gadgets such as "mood rings" are a manifestation of chiral nematic mixtures. SEE ALSO INORGANIC CHEMISTRY.

Koen Binnemans

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Liquids

A liquid is one state in which matter can exist. A liquid can take the shape of any container it is placed in (unlike a solid), but the volume of the liquid will always remain constant (unlike a gas).

Liquid-Particle Movement

On a molecular level the molecules of a liquid are arranged, or ordered somewhere between the order of a solid and the randomness of a gas. The particles comprising a solid occur in an ordered fashion, producing a characteristic three-dimensional configuration that is present throughout the entire structure. The forces between particles in a solid are strong, holding the particles in a rigid form. A solid is therefore noncompressible and cannot flow to take the shape of its container. Conversely, in a gas the particles have no regularity in their arrangement, have essentially unrestricted movement, and are widely separated. Because the forces between particles are small, the particles may move apart and fill the available space. The shape and volume of a gas may therefore be changed.

intermolecular forces: force that arises between molecules; generally it is at least one order of magnitude weaker than the chemical bonding force

A molecule of a liquid experiences an environment similar to that of a solid—it is in close proximity to its neighbors and has similar packing density. In a liquid, however, particles have no long-range order (i.e., only on a localized basis). The **intermolecular forces** between particles of a liquid are stronger than the kinetic energies of the molecules, which are thus held close together. These forces, however, do not hold the molecules in a rigid structure. Subsequently the molecules can move with respect to each other, allowing a liquid to flow. A liquid is minimally compressible and much denser than a gas, and maintains a constant volume.

hydrogen bonding: intermolecular force between the H of an N–H, O–H, F–H bond and a lone pair on O, N, or F of an adjacent molecule

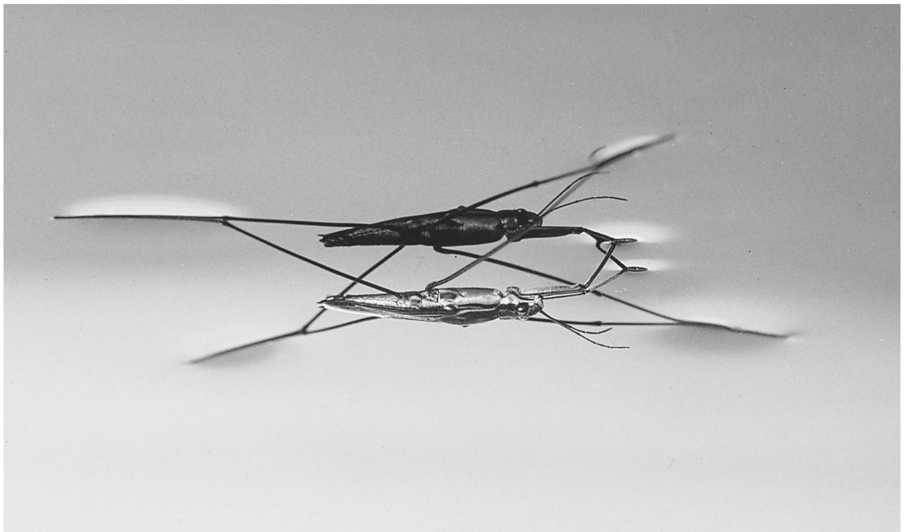
The particles comprising liquids can be molecules or atoms depending on the chemical nature of the substance. The general characteristics of a liquid are the same irrespective of its composition (molecules versus atoms) but **hydrogen bonding** can increase the attractive forces between molecules making a liquid flow less easily.

Decreasing the kinetic energy of particles of a liquid by cooling will eventually result in the change of state from liquid to solid. Similarly, increasing the kinetic energy by heating will result in the state change from liquid to gas. For example, at a pressure of one atmosphere, pure water changes from liquid to solid at 0°C (32°F) and from liquid to gas at 100°C (212°F).

Surface Tension

Surface tension is the appearance of a film over the top of a liquid, making the liquid behave as if it had a skin. It is because of surface tension that a small object like a pin or an insect can be supported on the surface of a liquid. This phenomenon is caused by the attraction between molecules of a liquid. In the bulk of a liquid any individual molecule is attracted equally in all directions by all adjacent molecules. At the surface of the liquid, however, there are no molecules attracting the surface molecules other than those in the liquid itself. This leads to a net attraction for the surface molecules into the liquid, in a direction parallel to the surface.

The most noticeable effect of surface tension is to reduce the surface of the liquid to the smallest possible size. Surface tension on water, for exam-



A waterstrider bug standing on the surface of water, a demonstration of the surface tension of water.

ple, causes water droplets to form the familiar bead shape (particularly noticeable on a wax surface). This surface tension can be destroyed by the addition of a detergent, causing the water droplet to spread out to a thin film covering the surface of the container.

To expand the surface of a liquid, the forces pulling the particles inward must be overcome. Surface tension is a measure of the amount of energy required to increase the surface area of a liquid by a given amount. A liquid displaying hydrogen bonding will have a higher surface tension than one that does not. For example, at 20°C (68°F) water has a surface tension of 7.29×10^{-2} joules per meter squared (the amount of energy that must be applied to water to increase the surface area by 1 meter squared). For mercury the surface tension is even higher (4.6×10^{-1} joules per meter squared at 20°C); this is due to the stronger metallic bonds between the atoms of mercury.

Viscosity

Viscosity is a measure of how thick (viscous) and sticky a liquid is. Viscosity reduces the ability of a liquid to flow. Any liquid that can flow readily (such as water) will have a low viscosity. Liquids with a high viscosity (such as molasses and motor oil) will flow more slowly and with greater difficulty.

Viscosity can be measured by timing how long it takes for the liquid to flow through a capillary tube or how long it takes for a steel ball to fall through the liquid. At a molecular level viscosity is a function of the attractive forces of the molecules of the liquid and, to a lesser extent, the presence of structural components (such as long-chain molecules) that can become entangled (a form of steric hindrance). Temperature also greatly affects viscosity: as temperature increases, viscosity decreases. This is because higher levels of kinetic energy are more able to overcome the intermolecular attractive forces.

Liquid Crystals

The term "liquid crystal" describes an intermediate state between a solid and a liquid. On heating to a specific temperature, some solids become

The liquids in this photograph have different levels of viscosity or fluidity.

cloudy liquids, then become clear when the temperature is raised even further. For such substances, the temperature range at which this intermediate state—called the liquid crystal state—exists is always the same. In 1888 Austrian botanist and chemist Frederich Reinitzer was the first to discover a substance (cholesterol benzoate) that exhibited this behavior. Cholesterol benzoate melts at 145°C (293°F) to form a cloudy, milklike liquid, but at 179°C (354°F) the liquid becomes clear.

Liquid crystals are composed of long, rodlike molecules that can be ordered in a number of ways. There are three groups of liquid crystals: cholesteric, nematic, and smectic. In the cholesteric form all of the molecules in one layer are aligned in the same manner, but adjacent layers have the molecules twisted with respect to each layer (commonly encountered in crystals of cholesterol from which the name originates). In the case of a nematic liquid crystal, the axes of the molecules are aligned but the ends of the molecules are not aligned or adjacent to each other. The smectic liquid crystal is characterized by the axes and the ends of the molecules being aligned. The ordering of the molecules is altered by changes in pressure, temperature, and electric and magnetic fields.

Glasses

Glasses are supercooled liquids that form a noncrystalline solid. The most frequently encountered glass is the supercooled form of liquid silicon dioxide—the glass used in windows, for example. When silicon dioxide is heated to 1,600°C (2,912°F), it forms a viscous liquid. Upon rapid cooling, silicon-oxygen bonds are formed before the atoms are able to arrange themselves in a regular pattern characteristic of a solid.

Glasses share a number of common characteristics regardless of their origins. All glasses are transparent or translucent, hard, brittle, and resistant to chemical attack. Glasses can be made from a range of acidic oxides including lead, boron, and phosphorus. When a glass is heated to its softening point, the material begins to crystallize and becomes more brittle and opaque. Toughening of glass can be brought about by rapid cooling during its production or by chemical treatment of the surface. To produce colored glass, metallic oxides or other compounds are added. For window glass other compounds can be added to make the characteristics more desirable; these include sodium carbonate, calcium oxide (lime), or calcium carbonate. SEE ALSO GLASS; MOLECULAR STRUCTURE; PHYSICAL CHEMISTRY.

Gordon Rutter

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Lister, Joseph

BRITISH SURGEON
1827–1912

Joseph Lister is known as the founder of antiseptic surgery, a significant advance in medicine developed in the nineteenth century. Infection of wounds and surgical incisions was a major cause of hospital deaths before Lister developed a way of preventing these infections with chemical antiseptics. His discovery made surgery much safer and permitted surgeons to perform operations not previously attempted because of the high risk of fatal infections.

Lister attended University College in London, England, for both his undergraduate and medical education, graduating with honors in 1852. His first position following graduation was as a staff surgeon at University College Hospital. In 1854 he accepted an appointment in Edinburgh, Scotland, as an assistant to Dr. James Syme, a prominent surgeon and noted professor of surgery. In 1856 Lister married Dr. Syme's daughter, Agnes, and accepted a position as an assistant surgeon at the Royal Infirmary in Edinburgh. Lister developed a reputation as both a skillful surgeon and excellent teacher. In 1861 he was appointed professor of surgery at the University of Glasgow where he began the experiments that led to the practice of antiseptic surgery.

When Lister became a practicing surgeon in 1852, conditions in surgical wards were truly appalling. Most surgeons operated with unwashed hands and dirty instruments while wearing bloodstained operating coats that were never washed. The patients then rested in beds with dirty linens that were often not even changed between patients. Consequently many patients survived the operation only to die from gangrene or blood poisoning. Nearly all surgical patients experienced infections and the smell of **putrefaction** permeated surgical wards. The cause of infection was generally attributed to "bad air" and was considered an unavoidable aspect of all hospitals.

putrefaction: decomposition of organic matter

In 1864 Lister discussed the possible causes of putrefaction with a chemistry colleague who suggested that Lister read the publications of a French

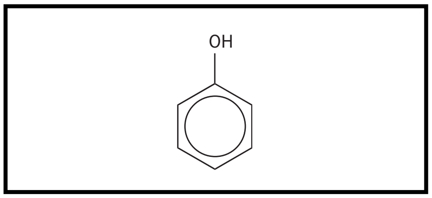
British surgeon Joseph Lister (center), inventor of antiseptic surgery.

chemist named Louis Pasteur. Pasteur had demonstrated that both fermentation of liquids and spoilage of butter were caused by "germs" carried in the air, and if these germs were prevented from entering a flask, fermentation and spoilage could be prevented. Lister saw a connection with hospital infections and concluded that it was not air itself that caused infection, but germs carried in the air. Lister reasoned that if hospital germs could be killed, infections could be prevented.

Pasteur had killed germs by boiling, a technique which could not be used on patients, but chemicals that killed germs could be applied to wounds, instruments, the surgeon's hands, and to bandages. Carbolic acid, now called **phenol**, was already known as a deodorizing agent and preservative, and Lister thought it might kill the germs that were causing infections. In 1865 Lister began using carbolic acid as an antiseptic during surgery and in bandaging afterward, publishing his results in 1867.

phenol: common name for hydroxybenzene (C_6H_5OH)

Initially his procedures were met with scorn and the idea that invisible germs were the cause of hospital infections was widely ridiculed. As his students and visitors witnessed antiseptic surgery's great success in reducing deaths from hospital infections, however, Lister's procedures became accepted. Within a few years Lister was honored in Germany and France, but not yet recognized in London. Following an appointment as professor of clinical surgery at King's College, Lister was able to directly demonstrate the success of his procedures to skeptical London surgeons. In recognition of his contribution to medicine, Lister was made a baronet in 1883 and named Baron Lister in 1897.



Structure of "phenol."

Although use of carbolic acid as a germ-killing antiseptic in surgery was later replaced by more effective techniques, Lister became world-renowned for demonstrating the importance of preventing microbial contamination of wounds and surgical incisions. SEE ALSO IODINE; PASTEUR, LOUIS.

Robert K. Griffith

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Lithium

MELTING POINT: 180.5°C
BOILING POINT: 1,342°C
DENSITY: 0.534 g/cm^3
MOST COMMON IONS: +1

3
Li
LITHIUM
6.941

Lithium is a soft, silvery alkali **metal** and has the lowest density of any metal. The word “lithium” is derived from “lithos” (Greek for “stone”). Johan A. Arfvedson discovered lithium in Stockholm, Sweden, in 1817. Humphry Davy isolated it via electrolysis in 1818. Currently, lithium metal is generated by the electrolysis of a molten mixture of lithium chloride, LiCl, and potassium chloride, KCl. In nature it is never found in its elemental form. Its main sources are the minerals spodumene, petalite, lepidolite, and amblygonite. Lithium’s average crustal abundance is about 18 ppm. It has the highest specific heat of any solid element and is the least reactive alkali metal toward water. Lithium burns crimson in the flame test.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Metallic lithium has a variety of uses. It is used as an anode material in batteries and as a heat transfer agent. Magnesium-lithium **alloys** are used to produce armor plate and aerospace materials, while aluminum-lithium alloys find applications in the aircraft industry. Lithium is also used to produce chemical **reagents** such as $LiAlH_4$ (a **reducing agent**) and *n*-butylithium (a strong base).

alloy: mixture of two or more elements, at least one of which is a metal

reagent: chemical used to cause a specific chemical reaction

reducing agent: substance that causes reduction, a process during which electrons are lost (or hydrogen atoms gained)

Compounds of lithium are also economically important. Air conditioning systems use LiCl and LiBr because they are very hygroscopic and readily absorb water from the air. Thermonuclear weapons incorporate lithium deuteride, LiD. Lithium stearate is obtained by treating tallow with lithium hydroxide, LiOH, and is used as a thickener that imparts high temperature resistance to lubricants. Carbon dioxide removal systems in submarines and spacecraft use LiOH. Lithium carbonate, Li_2CO_3, is used to increase the electrical current flow in the electrolytic production of aluminum from bauxite and to strengthen glasses by substituting for sodium ions. Although lithium carbonate has been used to treat bipolar (manic-depressive) disorder since 1949, its mechanism of operation is still not completely understood. SEE ALSO ALKALI METALS; DAVY, HUMPHRY.

Nathan J. Barrows

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Lonsdale, Kathleen

IRISH CRYSTALLOGRAPHER
1903–1971

English crystallographer Dame Kathleen Lonsdale, who established the molecular structure of benzene.

Kathleen Lonsdale was born Kathleen Yardley in Newbridge, Ireland, on January 28, 1903. She was the youngest of ten children (four of whom died in infancy). In 1908 Lonsdale's mother, Jessie, separated from her husband and emigrated with her children to England. Lonsdale was a bright child, and although the older children had to leave school and go to work, she stayed in school and was allowed to enroll in Bedford College, University of London, at age sixteen, to study mathematics and, later, physics. She graduated in 1922 at the top of her class and her teacher and mentor, the eminent English physicist Sir William Henry Bragg, recruited her to join his research group in London. She began to work in x-ray crystallography (the analysis of crystal structure by means of x rays), then a new field, and became a leading scientist in this field.

In 1927 Lonsdale married Thomas Lonsdale and she and her husband lived in Leeds, England, for three years. There she was given crystals of hexamethylbenzene and hexachlorobenzene for analysis by the English chemist Sir C. K. Ingold. She subsequently confirmed that the benzene ring was flat, with all carbon-carbon angles and bond lengths identical. Hers was the first experimental proof. Ingold said of her published account of benzene structure, "[O]ne paper like this brings more certainty into organic chemistry than generations of activity by us professionals." She was the first scientist to apply Fourier analysis (a type of mathematical analysis) to the analysis of crystal structure.

In 1930 Lonsdale moved back to London. In London she brought up three children while conducting research at home. In 1931 she rejoined Bragg at the Royal Institution of Great Britain and there (using the rooms of the great Michael Faraday) continued her work in the analysis of crystals. She stayed at the Royal Institution until 1946. Her major contribution to chemistry and physics was to establish the theoretical foundation of crystallography. Lonsdale helped to create the structure factor tables that are used by present-day crystallographers, and edited the *International Tables of X-Ray Crystallography* (1935), the "crystallographer's bible."

In 1946 Lonsdale moved to University College, London (UCL), where she became professor of chemistry in 1949 and remained until her retirement in 1968. With great modesty she said she knew very little chemistry, and no organic chemistry. She gathered about herself a large research group and trained many crystallographers. She worked on many crystal structure problems, including the clarification of the structure of diamond and the nature of urinary stones.

Royal Society: The U.K. National Academy of Science, founded in 1660

Lonsdale accrued many "firsts": one of the first two women to be elected Fellow of the **Royal Society** (1945); the first woman professor at UCL (1949); the first woman to become president of the International Union of Crystallography (1966) and of the British Association for Science (1968). It is partly because of her example and influence that women have been so prominent in crystallography.

Lonsdale became a Quaker in 1936 and went to jail in England for her participation in conscientious objection during World War II. After the jail experience she became active in prison reform and later in the international peace movement. Her political activism was as significant to her as her scientific achievements. Among her books were *Is Peace Possible?* (1957) and *The Christian Life Lived Experimentally* (1976) and she saw no conflict between her faith and her science, nor between being a wife and mother and being a scientist.

Lonsdale continued to work in various ways (including scientific, educational, and charitable work) during her official retirement. She died on April 1, 1971. In 1981 the chemistry building at UCL was named the Kathleen Lonsdale Building in her honor. SEE ALSO BRAGG, WILLIAM HENRY; ORGANIC CHEMISTRY; SOLID STATE.

Peter E. Childs

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Low Density Lipoprotein (LDL)

Lipids are **nonpolar** molecules and are relatively insoluble in **aqueous solutions**. At low concentrations, cholesterol and cholesterol **esters**, as well as other lipids, may form microscopic droplets called chylomicrons (lipid-protein complexes) that are somewhat stable in solution. At high concentrations, the lipids would form larger droplets and clog blood vessels, so they must be transported as complexes of lipid and protein called lipoproteins. Lipoproteins are complexes of lipid and precursor protein molecules called apolipoproteins.

Some portions of the apolipoprotein molecules are nonpolar (**hydrophobic**), and these are usually oriented toward the inside (near the lipid portion) of the complex. Polar amino acid side chains in the protein portions are oriented toward the outside of the complex, where they associate with the aqueous environment, rendering the complex soluble in blood plasma. This type of structure resembles that of micelles.

Lipoprotein complexes usually have a lipid core surrounded by one or more apolipoprotein molecules. These complexes can be separated into classes according to density. They range from very low density lipoproteins (VLDL), having densities of less than 1.006 g/mL, to low density lipoproteins (LDL), having densities of between 1.019 and 1.063 g/mL, to high density lipoproteins (HDL), having densities of between 1.063 and 1.210

lipid: a nonpolar organic molecule; fatlike; one of a large variety of nonpolar hydrophobic (water-hating) molecules that are insoluble in water

nonpolar: molecule, or portion of a molecule, that does not have a permanent, electric dipole

aqueous solution: homogenous mixture in which water is the solvent (primary component)

ester: organic species containing a carbon atom attached to three moieties: an O via a double bond, an O attached to another carbon atom or chain, and a H atom or C chain; the R(C═O)OR functional group

hydrophobic: a part of a molecule that repels water

An angiogram of the carotid artery. The darker section indicates blockage. LDL, or "bad cholesterol," which at high concentrations can clog blood vessels, can be detected by the use of an angiogram.

g/mL. In general, the density of the lipoprotein increases as the proportion of apolipoprotein increases.

Small amounts of cholesterol may be transported as part of chylomicrons, but cholesterol is usually carried within lipoproteins, including low density lipoprotein (LDL), which carries cholesterol from the liver to muscle and other tissues, and high density lipoprotein (HDL), which carries cholesterol to the liver for conversion to bile acids. Physicians are especially concerned when patients have high levels of LDL (the so-called bad cholesterol) in blood; moderate exercise and low-cholesterol diets help to increase HDL (the so-called good cholesterol). Either high fat intake or problems with transport of cholesterol can lead to atherosclerosis, which in turn can contribute to heart attack (myocardial infarction) or stroke. SEE ALSO CHOLESTEROL; LIPIDS; PROTEINS.

Dan M. Sullivan

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Lucretius

ROMAN NATURAL PHILOSOPHER
ca. 95 B.C.E.–ca. 55 B.C.E.

Little is known about Titus Lucretius Carus beyond what can be gathered from his poem *De rerum natura*. He was born in about 95 B.C.E., but the exact date is uncertain. The exact date and circumstances of his death are also uncertain, but he probably died in or before the year 55 B.C.E. We do know from his poem that he believed the teachings of the Greek atomists, ranging from those of Democritus of Abdera (ca. 460 B.C.E.–ca. 362 B.C.E.) to those of Epicurus (ca. 341 B.C.E.–270 B.C.E.). Unlike the writings of Democritus or Epicurus, Lucretius's poem was one of the few literary works not lost to European peoples after the collapse of the classical world.

De rerum natura is a poem in the Latin language that gives a summary of the teachings of the Greek atomists. His starting point is a reliance on direct human experience of the natural world. From this starting point he reasons: "Nothing can ever be created by divine power out of nothing" (Lucretius, p. 31). Accordingly, if something could be created out of nothing, things would pop in and out of existence without any pattern at all. From that deduction Lucretius develops a philosophy that does not allow for occult forces, superstition, or magic. Beliefs such as these were pervasive in the Roman world during his lifetime. That philosophy also clearly sets "atomism" against any sort of theistic religion. This religious antagonism would continue to plague atomic theories until the modern era.

According to Lucretius: "All nature as it is in itself consists of two things—bodies and the vacant space in which the bodies are situated and through which they move in different directions" (p. 39). He addresses the question of the immense variety of material things found in nature by recognizing that there must be some way for atoms to combine and at the same time maintain their individual characters: "Material objects are of two kinds, atoms and compounds of atoms. The atoms themselves cannot be swamped by any force, for they are preserved indefinitely by their absolute solidity" (p. 41). Lucretius does not suggest that we directly experience atoms. He makes no claims as to the shapes of atoms or any other of their characteristics. SEE ALSO ATOMS.

David A. Bassett

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Luciferins *Bioluminescence; Chemiluminescence.*

71
Lu
LUTETIUM
174.967

Lutetium

MELTING POINT: **1,675°C**
BOILING POINT: **3,315°C**
DENSITY: **9.84 g/cm^3**
MOST COMMON IONS: **Lu^{3+}**

lanthanides: a family of elements (atomic number 57 through 70) from lanthanum to lutetium having from 1 to 14 4f electrons

aqueous solution: homogenous mixture in which water is the solvent (primary component)

inert: incapable of reacting with another substance

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

diamagnetic: property of a substance that causes it to be repelled by a magnetic field

The mixture of oxides known as ytterbia was obtained from yttria by Jean-Charles-Galissard de Marignac in 1878. From ytterbia the oxides of three elements were isolated: ytterbium (named after the town of Ytterby) by Marignac; scandium (named after Scandinavia) by L. F. Nilson in 1879; and lutetium (named after Lutetia, an ancient name of Paris) by G. Urbain, C. A. von Welsbach, and C. James in 1907. Lutetium is a rare element (comprising 7.5 (10^{-5}% of the igneous rocks of Earth's crust) and is found together with the heavy **lanthanides**. Essentially, there are two methods used to separate lutetium from monazite concentrates: (1) the extraction of **aqueous solutions** of lutetium nitrates with tri-*n*-butyl-phosphate (using kerosene as an **inert** solvent); and (2) using cationic exchange resins and solutions of EDTA, the triammonium salt of ethylenediamino-triacetate, as the eluant. The **metals** are obtained by electrolysis of the fused salts, or by metallothermic reduction of the anhydrous halides (especially the fluoride) with calcium at elevated temperatures. Lutetium is a **diamagnetic** trivalent element.

The lutetium halides (except the fluoride), together with the nitrates, perchlorates, and acetates, are soluble in water. The hydroxide oxide, carbonate, oxalate, and phosphate compounds are insoluble. Lutetium compounds are all colorless in the solid state and in solution. Due to its closed electronic configuration (4f^{14}), lutetium has no absorption bands and does not emit radiation. For these reasons it does not have any magnetic or optical importance. SEE ALSO Cerium; Dysprosium; Erbium; Europium; Gadolinium; Holmium; Lanthanum; Neodymium; Praseodymium; Promethium; Samarium; Terbium; Ytterbium.

Lea B. Zinner

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Magnesium

MELTING POINT: **651°C**
BOILING POINT: **1,107°C**
DENSITY: **1.738 g/cm^3 at 20°C**
MOST COMMON IONS: **Mg^{2+}**

12
Mg
MAGNESIUM
24.31

Magnesium was first recognized as an element by Joseph Black in 1755. In 1808 Sir Humphry Davy isolated the element, and in 1831 H. Bussy devised a method for producing it. Magnesium, in its combined states, is readily abundant and is the eighth most common element in Earth's crust. Magnesium **metal** is silvery white in color.

The most common method for producing elemental magnesium is in fused salt electrolytic cells, wherein magnesium chloride ($MgCl_2$) is decomposed by applying a **voltage** to elemental magnesium and chlorine gas. The magnesium chloride feed is obtained directly from seawater or from magnesium oxide deposits containing magnesite or dolomite. In these cases, the oxide is first chlorinated prior to electrolysis. Another method is to produce magnesium directly from the oxide by reducing the oxide with silicon under vacuum. The resultant Mg vapor is condensed to recover Mg metal. This process is carried out in vacuum retorts and is known as the Pidgeon process.

voltage: potential difference expressed in volts

The principal uses of Mg are for alloying with aluminum, for desulphurizing steel and pig iron, and for nodularizing the graphite in cast irons. Recently, researchers have focused on using Mg **alloys** to produce lightweight components in automobiles. As a result, Mg usage in vehicles is steadily increasing.

alloy: mixture of two or more elements, at least one of which is a metal

Compounds of magnesium, including the hydroxide, the chloride, the citrate, and the sulfate, are used in the medical field. Magnesium is an important element in both animal and plant life. On average, adults require a daily intake of about 300 milligrams (0.011 ounces) of magnesium. SEE ALSO Alkaline Earth Metals; Black, Joseph; Davy, Humphry; Inorganic Chemistry.

Frank Mucciardi

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Magnetic Resonance Imaging ***See Nuclear Magnetic Resonance.***

Magnetism

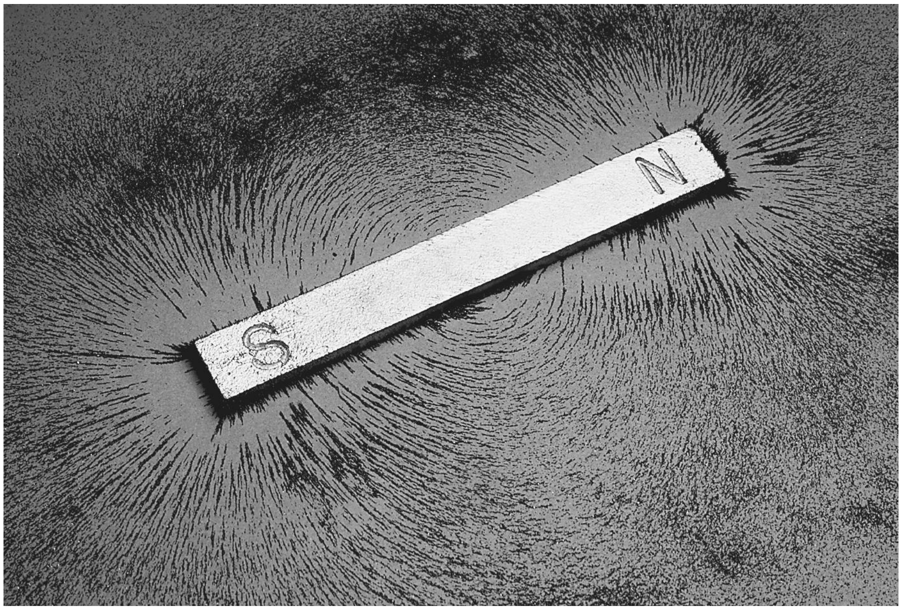
The magnetic properties of materials were recognized by the ancient Greeks, Romans, and Chinese, who were familiar with lodestone, an iron oxide mineral that attracts iron objects. Although the attractive or **repulsive forces** that act between magnetic materials are manifestations of magnetism familiar to everybody, the origin of magnetism lies in the atomic structure of matter. Despite the fact that magnetism can be explained only by the quantum theory developed at the beginning of the twentieth century, qualitative predictions of magnetic properties can be made within the context of classical physics. Magnetic forces originate in the motion of charged particles, such as electrons. The electrons "spin" around their axis and move in orbits around the nucleus of the atom to which they belong. Both motions generate tiny electric currents in closed loops that in turn create magnetic dipole fields, just as the current in a coil does. When placed in a magnetic field, the tiny magnetic dipole fields tend to align with the external field.

repulsive force: force that causes a repulsion between two bodies; charges of the same sign repel each other

According to their behavior in inhomogeneous magnetic fields, materials can be classified into three main categories: **diamagnetic**, paramagnetic, and ferromagnetic. *Paramagnetic materials* are attracted into a magnetic field. The main cause of this effect is the presence in the material of atoms that have a net magnetic moment composed of electron spin and orbital contributions.

diamagnetic: property of a substance that causes it to be repelled by a magnetic field

Iron filings in a circular pattern around a magnet, indicative of the field of force of the magnet.



When placed in a magnetic field, the magnetic moments of the atoms, which are otherwise randomly oriented, tend to align with the field and thus enhance the field. Paramagnetism is temperature dependent because increased thermal motion at higher temperatures impedes the alignment of the magnetic moments with the field. *Diamagnetic materials* are slightly repelled by a magnetic field. This effect occurs for materials that contain atoms in which the spin and orbital contributions to the magnetic moment cancel out. In this case, the interaction between the material and a magnetic field is caused by the occurrence of currents induced by the magnetic field in the atoms. The dipole fields corresponding to these currents are directed opposite to the applied magnetic field and cause expulsion of the material from the field. *Ferromagnetic materials* contain atoms that have magnetic moments that are aligned even in the absence of an applied magnetic field because of mutual interactions, creating a sizable net magnetic moment for domains of the material. The magnetic moments of domains can be randomly oriented unless a magnetic field is applied to the material.

alloy: mixture of two or more elements, at least one of which is a metal

transition metals: elements with valence electrons in d-sublevels; frequently characterized as metals having the ability to form more than one cation

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

octahedral: relating to a geometric arrangement of six ligands equally distributed around a Lewis acid; literally, eight faces

Iron, cobalt, nickel, and their **alloys** are examples of ferromagnetic materials. These three elements are **transition metals**, and their atoms or ions have unpaired electrons in d orbitals. Rare-earth ions also have unpaired electrons situated in f orbitals. A detailed investigation of the properties of molecules that contain such **metal** ions in a magnetic field can provide significant information about how their electrons are distributed in orbitals. Typically, d orbitals of isolated atoms are degenerate (Figure 1a). This situation changes when the metal ions are part of molecules in which they experience a nonspherically symmetric environment. Figures 1b and 1c show the splitting of d orbitals for a transition metal ion that has six unpaired electrons and is situated in an environment of six atoms in an **octahedral** arrangement. Depending on the size of the splitting (the lighter shading in Figure 1) and the interelectron repulsion, the metal ion may have four unpaired electrons (Figure 1b) or no unpaired electrons (Figure 1c). This difference in electron distribution leads to significant differences in the magnetic properties of the molecules that contain such ions, with

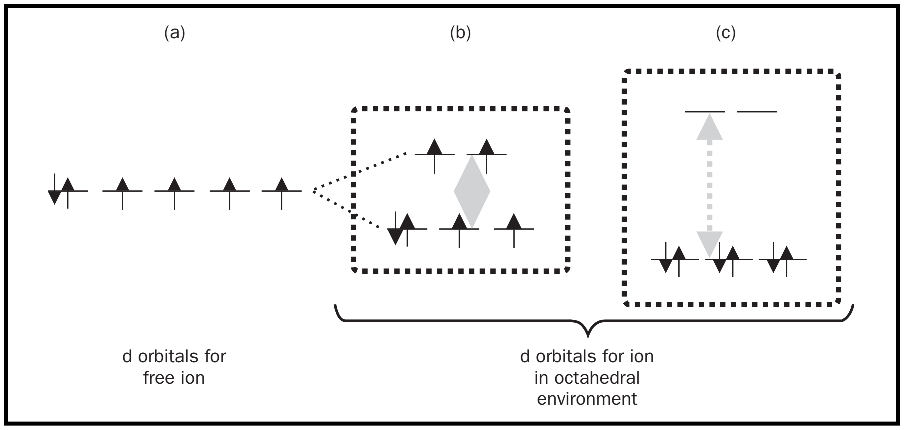


Figure 1. Splitting of d orbitals for a transition metal ion.

the former being paramagnetic and the latter being diamagnetic. When there are multiple metal sites in a molecule, the spins at different metal ions can be either ferro- (parallel) or antiferro-magnetically (antiparallel) aligned to each other. Clever use of the magnetic properties for metal ions and of the interactions between spins manifested in molecular systems enables scientists to design and synthesize molecular systems with interesting properties, such as molecular magnets.

Magnetic materials are widely used for building technological devices and scientific tools. Classical examples are electromagnets that are used in motors, clutches, and breaking systems. The electromagnet makes use of an iron core situated in a solenoid through which electric current is passed. This current creates a magnetic field at the center of the solenoid that orients the magnetic moments in the domains of the iron core, which in turn results in a significant enhancement of the magnetic field at the core of the solenoid. Electromagnets can also be used to record information on magnetic tape, which has a ferromagnetic surface.

Finally, although atomic nuclei have significantly smaller magnetic moments than electrons, the study of their interaction with magnetic fields has many important applications. They enable the scientists in the biological and medical fields to elucidate the structure of biologically relevant molecules such as proteins and to diagnose diseases using magnetic resonance imaging. SEE ALSO Maxwell, James Clerk; Physical Chemistry.

Catalina Achim

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Manganese

MELTING POINT: **1,246 ±3°C**
BOILING POINT: **2,061°C**
DENSITY: **7.21–7.44 g/cm^3, depending upon allotrope**
MOST COMMON IONS: **Mn^{2+}, Mn^{3+}, MnO_4^{3-}, MnO_4^{2-}, MnO_4^{-}**

25
Mn
MANGANESE
54.93805

Manganese is a hard, brittle, gray-white **metal** in group 7B of the Periodic Table. It was recognized as an element in 1774 by Swedish chemist Carl

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Wilhelm Scheele and isolated by his assistant Johan Gottlieb Gahn later that year. The element's name is derived from the Latin word *magnes*, meaning "magnet." This refers to the magnetic property of the common ore pyrolusite.

isotope: form of an atom that differs by the number of neutrons in the nucleus

Manganese is the twelfth most abundant transition element (1,060 parts per million of Earth's crust) with twenty-three known **isotopes**. Large nodules of manganese ore have been discovered on the ocean floor. The pure metal can be obtained by reduction of the oxide with sodium or by electrolysis.

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

aqueous solution: homogenous mixture in which water is the solvent (primary component)

Manganese is more reactive that any of its neighbors on the Periodic Table. It reacts with water to produce hydrogen gas and dissolves in dilute acids to form Mn^{2+}. The most stable **oxidation** state of manganese is +2. The most important oxide formed is MnO_2, which decomposes to Mn_2O_3 if heated above 530°C (932°F). The deep-purple manganate (VII) salts (permanganates) are prepared in **aqueous solution** by oxidation of Mn^{2+}.

alloy: mixture of two or more elements, at least one of which is a metal

trace element: element occurring only in a minute amount

vitamins: organic molecules needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

Manganese metal is used in many **alloys**. In conjunction with aluminum and copper it forms strong ferromagnetic alloys. Ninety-five percent of all manganese ores are used in the production of steel. The element improves the strength and toughness of steel by acting as a scavenger of sulfur, preventing the formation of FeS, which induces brittleness. Biologically, manganese is an important **trace element**; it is essential to the utilization of **vitamin** B^1. Pyrolusite has been used in glassmaking since ancient Egypt, while MnO_2 is used in the manufacture of dry cells. The permanganate ion is a strong oxidizing agent and is used in quantitative analysis and medicine. SEE ALSO COORDINATION COMPOUNDS; INORGANIC CHEMISTRY; SCHEELE, CARL.

Catherine H. Banks

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Manhattan Project

fission: process of splitting an atom into smaller pieces

Nuclear scientists knew in the 1930s that there was a tremendous amount of energy locked in the atomic nucleus. The problem was how to access this energy. With the discovery of nuclear **fission** in Germany by Otto Hahn, Lise Meitner, and Fritz Strassmann in late 1938 and the subsequent explanation of the process by Meitner and Otto Frisch, many scientists who had been forced to flee from Europe became concerned that Germany might somehow take advantage of this discovery and develop weapons based on nuclear energy. Germany had many competent nuclear scientists, access to heavy water in Norway, quantities of uranium oxide, and a strong engineering history. In the fall of 1939, Leo Szilard, a Hungarian-born physicist who had fled Germany for America, drafted a letter with Albert Einstein to send to President Franklin Roosevelt under Einstein's signature to warn

Roosevelt that weapons could be created using a nuclear chain reaction in uranium and that it was very likely that Germany had started working on a uranium bomb. This letter led to the formation of the Advisory Committee on Uranium. The committee did little, however, until Rudolf Peierls and Frisch, working in England, made detailed calculations about the feasibility of nuclear weapons and proposed some possible approaches to making an atomic bomb.

Although government support was relatively weak, important nuclear-science discoveries, unannounced for security reasons, were made in the United States in 1940 and 1941. Potential pathways for enriching ^{235}U, the self-fissioning **isotope** of uranium, were developed, and Glenn Seaborg and Arthur Wahl produced plutonium, an element that had great potential for use in a nuclear weapon. In December 1941, President Roosevelt authorized the formation of the Manhattan Engineer District of the Army Corps of Engineers (**"Manhattan Project"**) as the organization that would oversee the development of the atomic bomb. Groups of scientists, some of whom were already working on nuclear energy research, were organized to work on various aspects of the bomb project. One such project was called the Metallurgical Laboratory at the University of Chicago, where Italian-born physicist Enrico Fermi and other scientists worked on the construction of the first nuclear reactor, powered by uranium enriched in ^{235}U.

isotope: form of an atom that differs by the number of neutrons in the nucleus

Manhattan Project: government project dedicated to creation of an atomic weapon; directed by General Leslie Groves

The Manhattan Project officially began on September 23, 1942, when Colonel Leslie Groves was named director of the project. Groves acquired production sites at Oak Ridge, Tennessee, and Hanford, Washington, and he brought in Robert Oppenheimer, a physicist from the University of California at Berkeley, as the scientific director at Los Alamos, New Mexico. Los Alamos was to be the center of physics research, engineering, and weapons design. Oak Ridge was to be the site to enrich ^{235}U, and Hanford was to produce plutonium in nuclear reactors. Many of the country's leading chemical and engineering firms were called in to design and construct these production facilities

Oak Ridge was to produce uranium enriched in the self-fissioning isotope ^{235}U by gaseous diffusion of the **volatile** compound UF_6 at the K-25 plant, a facility more than a mile long, and by electromagnetic separation at the Y-12 plant. Nuclear reactors were built at Hanford to produce plutonium from natural uranium, ^{238}U. Processes were developed to chemically separate and purify the plutonium isotopes ^{239} Pu and ^{240}Pu. Scientists from Great Britain also played key roles in the efforts at Los Alamos, and they were instrumental in developing the functional design of the atomic bomb. Work went on at a feverish pace during 1943 and 1944, and it was estimated that an atomic weapon would be completed by early 1945.

volatile: low boiling, readily vaporized

In the spring of 1945, preparations began in the Pacific for the use of the atomic bomb. On May 8, 1945, Germany surrendered, and the project was then focused solely on Japan. On July 16, 1945, a test device code-named "Gadget" was detonated at the Alamogordo Bombing Range in New Mexico as part of Project Trinity, the first explosion of a nuclear weapon. The success of the first test of a nuclear weapon was a testament to the ability of the leadership of the Manhattan Project to carry out an unprecedented industrial project, with the world's most talented scientists

From left: J. Robert Oppenheimer, Professor. H. D. Smythe, General Nichols, and Glen Seaborg in 1946 looking at a photograph of the atomic blast at Hiroshima. The atomic bomb was developed in the Manhattan Project.

cooperating and focusing on a single goal. That the people involved in the Manhattan Project were able to achieve such a spectacular success working in a realm of utmost secrecy in isolated locations was a most singular achievement.

On August 6, 1945, after Japan refused to surrender unconditionally, the first atomic bomb, named "Little Boy," a ^{235}U-based bomb, was dropped over Hiroshima, Japan. Three days later, "Fat Man," a plutonium-based weapon, was dropped on Nagasaki.

Whether Germany really attempted to build an atomic weapon is debated even today. German scientists, led by physicist Werner Heisenberg, certainly had the talent to build a device. Germany had access to large uranium mines in Czechoslovakia and produced heavy water, a form of H_2O in which the hydrogen atoms have an extra neutron, in Norway. Most likely there never was a serious effort in Germany to build an atomic weapon, possibly as result of sabotage of the project by Heisenberg or because of a lack of interest by Adolf Hitler. SEE ALSO EINSTEIN, ALBERT; FERMI, ENRICO; HEISENBERG, WERNER; MEITNER, LISE; NUCLEAR FISSION; OPPENHEIMER, ROBERT; RADIATION; SEABORG, GLENN THEODORE.

W. Frank Kinard

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Marsden, Ernest

ENGLISH PHYSICIST
Ca. 1888–1970

Ernest Marsden studied at the University of Manchester under Ernest Rutherford and Hans Geiger. Although a physicist, he would help elucidate something of value to all chemists: the internal structure of the atom. This was accomplished by observing the path of **α-particles** in Rutherford's famous "gold foil experiment," in which it was really the human eye, pressed to a short-focus telescope for hours on end in a thoroughly darkened room, that was the detector.

α-particle: subatomic particle with 2+ charge and mass of 4; a He nucleus

According to Rutherford, Marsden, a twenty-year-old undergraduate, became involved after Rutherford and Geiger decided that Marsden should begin research work. Rutherford thought that Marsden might be able to discover if α-particles could be scattered through a large angle. Geiger and Marsden spent 1909 in the "gloomy cellar" of the physics laboratories at Manchester, watching for the little sparks that announced the unlikely recoil of α-particles. About 1 in 8,000 did, and this result, published in 1909 as "On a Diffuse Reflection of the α-Particle," formed the basis for Rutherford's **nuclear** model of the atom and the discovery of the proton.

nuclear: having to do with the nucleus of an atom

Geiger and Marsden continued to study the deflection of α-particles, and in 1913 (after observing over 100,000 scintillations at a rate of 5 to 90 per minute) correlated nuclear charge with **atomic number**. In 1914 and 1915 Marsden continued to study the impact of α-particles on matter; these experiments led to Rutherford's 1919 fortuitous attainment of the alchemist's dream: the artificial transmutation of the elements.

atomic number: the number assigned to an atom of an element that indicates the number of protons in the nucleus of that atom

Marsden returned to his native New Zealand in 1915 where, on Rutherford's recommendation, he was appointed professor of physics at Victoria University in Wellington. He held various academic and governmental posts until his retirement in 1954. The national fund for the support of science in New Zealand was renamed the Sir Ernest Marsden Fund in his honor. SEE ALSO GEIGER, HANS; RUTHERFORD, ERNEST.

Mark A. Pichaj

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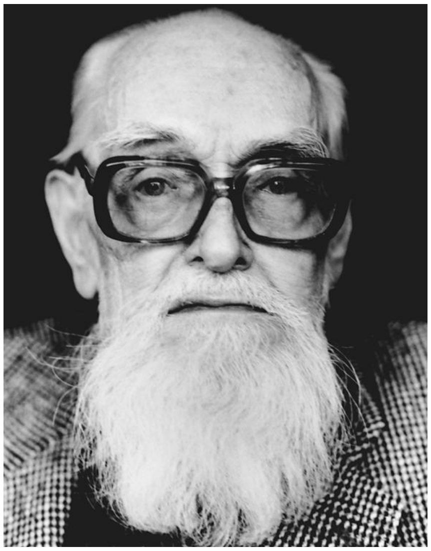
Martin, Archer John Porter

ENGLISH BIOCHEMIST
1910–2002

Very few chemical reactions produce clean, pure products with no trace of starting materials or impurities. Most generate a mixture whose individual components must be purified before the results can be identified. In the nineteenth and early twentieth centuries, purification of a chemical reaction product often required repetitive crystallizations, distillation, or solvent extraction.



British chemist Archer John Porter Martin, co-recipient, with Richard L. M. Synge, of the 1952 Nobel Prize in chemistry, "for their invention of partition chromatography."

Archer John Porter Martin grew up in London, England, and from an early age demonstrated an aptitude for chemistry. As a child, he designed and built an apparatus for distillation from old coffee tins packed with charcoal, some as tall as five feet. He entered Cambridge University with the intention of pursuing a degree in chemical engineering. However, he was influenced by J. B. S. Haldane to specialize in biochemistry. At Cambridge his childhood experience with **fractional distillation** became valuable.

Martin continued with his explorations of multi**phase** separation technology and went to work as a research chemist for the Wool Industries Research Association in Leeds. It was there that he met Richard Lawrence Millington Synge and began to collaborate with Synge on the problem of separating acetylamino acids. Eventually, Martin and Synge came up with the idea that, instead of using a counterflow extraction process with solvents moving against one another, they could partition one phase (hold one phase stationary using an appropriate support). The result was the invention of liquid-liquid partition **chromatography**, first reported in the *Biochemistry Journal* in 1941.

In their landmark paper, Martin and Synge also indicated that partition chromatography that used a carrier gas as the mobile phase was possible. In his Nobel lecture of 1952, Martin casually revealed that he, in collaboration with A. T. James, had devised a mechanism for gas-liquid chromatography. The use of a gas as the mobile phase did place limits on the types of material that could be analyzed, as the compounds had to be **volatile** and better detectors were needed, but these difficulties proved to be surmountable. Today, gas-liquid chromatography is probably the single most widely used analytical tool in chemistry. SEE ALSO ANALYTICAL CHEMISTRY; SYNGE, RICHARD LAURENCE MILLINGTON.

Todd W. Whitcombe

fractional distillation: separation of liquid mixtures by collecting separately the distillates at certain temperatures

phase: homogeneous state of matter

chromatography: the separation of the components of a mixture in one phase (the mobile phase) by passing through another phase (the stationary phase) making use of the extent to which the components are absorbed by the stationary phase

volatile: low boiling, readily vaporized

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Materials Science

After World War II, the application of materials became less empirical and more founded in scientific principles. The term "materials science" emerged in the 1960s to reflect this trend and the realization that solutions to many of the world's most challenging technological problems were increasingly materials-limited. Within the field of engineering, the term "materials science and engineering" has come to describe the subfield concerned with materials applications. This longer term represents a blend of scientific fundamentals and practical engineering. The foundations of materials science are physical chemistry, polymer chemistry, and condensed matter physics. The foundations of materials engineering include the fields of **metallurgy**

metallurgy: the science and technology of metals

A contemporary automobile is comprised of a wide range of materials, from the traditional to the advanced. Science has introduced the manufacturing of parts such as moldable polymers.

and ceramic engineering. Many common themes in the fields of chemical engineering and materials science have led to the creation of academic departments that encompass both areas.

Material possessions have traditionally represented human wealth and defined social relationships. The eras of early human civilization (the Stone Age, the Bronze Age, and the Iron Age) have been named in terms of the materials from which tools and weapons were made. The Bronze Age (approximately 2000 B.C.E. to 1000 B.C.E.), in fact, represents the foundation of metallurgy. Although we do not use the term "pottery age," domestic vessels made from baked clay have been valuable in providing clues to daily life in ancient cultures, and glass articles from ancient Mesopotamia have been traced back to 4000 B.C.E.

Contemporary culture is sometimes described as "plastic," a somewhat critical reference to the pervasive use of polymeric materials in modern life. Others suggest that the current era is rightfully called the "Silicon Age," in honor of the far-ranging impacts of modern electronics based on silicon technology. In any case, modern products, such as automobiles, contain a full spectrum of materials, from the traditional to the advanced.

An underlying principle of materials science is that the properties (or characteristics) of materials are generally understood in terms of the microscopic or atomic structures of the materials. Another underlying principle is that the selection of optimal materials for specific modern technological applications requires consideration of the ways in which those materials are processed.

Types of Materials

Engineers generally build things from a limited "menu" of materials—namely, **metals**, polymers, and ceramics. This menu follows directly from the three types of primary chemical bonding: metallic, covalent, and ionic.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Most of the elements in the Periodic Table (in the pure state) are metallic in nature. Aluminum, copper, and iron are examples. The metallic bond involves a mobile "gas" of electrons. This gas of negatively charged electrons binds together the positively charged atomic cores. The electron gas is also responsible for the electrical conductivities and optical absorption that are characteristic of metals.

Polymers are high molecular weight solids that are an important part of everyday life. An example is polyethylene $(C_2H_4)_n$, where n is the "degree of polymerization," a number of around 1,000 (representing the fact that polyethylene is composed of a large number of ethylene molecules bound together by covalent bonding). All polymers are composed of a relatively small number of elements in the Periodic Table (primarily carbon and hydrogen and a few other "nonmetallic" elements such as nitrogen and fluorine). Each **covalent bond** involves electron sharing between adjacent atoms, with the result that polymers do not have "free" electrons for electrical conduction and are electrical insulators. The use of polymeric insulation for electrical wiring is a practical example of this. The lack of free electrons endows some polymers with optical transparency ("clear plastic" wrap is an excellent example). The alternative name for a polymer substance—"plastic"—comes from the extensive formability of many polymers.

covalent bond: bond formed between two atoms that mutually share a pair of electrons

We can define ceramics by what they are not: They are nonmetallic and inorganic. Ceramics are chemical combinations of at least one metallic element and at least one nonmetallic one. A simple example is aluminum oxide (Al_2O_3). Such chemical combinations represent, in fact, a fundamental tendency in nature. For example, metals tend to combine chemically with nonmetallic elements in their environments. The rusting of iron is a familiar and costly example. It is also interesting to note that the **melting point** of aluminum is 660°C (1,220°F), whereas the melting point of aluminum oxide is 2,020°C (3,668°F). The chemical stability associated with the ionic bonds between aluminum and oxygen (involving electron transfer from aluminum to oxygen to produce Al^{3+} and O^{2-} ions) makes ceramics temperature-resistant and chemically **inert**.

melting point: temperature at which a substance in the solid state undergoes a phase change to the liquid state

inert: incapable of reacting with another substance

The category of ceramics is often broadened to "ceramics and glasses" because of the wide use of silicate glasses, distinctive materials that are chemically similar to ceramics. Silicon dioxide, SiO_2, is a ceramic compound and the basis of a large family of silicate ceramics. Clay minerals and the many clayware ceramics are the most traditional examples. SiO_2 is readily obtained in relatively pure form in common sand deposits. (These deposits, and the presence of SiO_2 in many geological minerals, are the reason that silicon and oxygen together account for roughly 75 percent of the elements in Earth's crust.) Upon heating, many of these silicate materials can be melted and, after cooling, retain the liquidlike structure of the melt. Common window and container glass is made in this way, with a typical composition, by weight, of (roughly): 75 percent SiO_2, 15 percent Na_2O, and 10 percent CaO. Thus, ceramics and glasses are of one category (combinations of ionically bonded positive and negative ions). Their differences are at the atomic scale. Ceramics are crystalline substances, in which the ions are arranged in a regular and repeating order. Glasses are noncrystalline substances, in which the ions are situated in irregular, liquidlike fashion.

In defining the previous three materials (metals, polymers, and ceramics/glasses), we found that each category conveniently related to one of the primary types of chemical bonding: metallic, covalent, and ionic, respectively. To be precise, atomic bonding is seldom "pure." There is generally some covalent nature (electron sharing) to the ionic bonding in ceramics and glasses. The bonding between the adjacent atoms in large polymeric molecules is highly covalent, but the bonding between molecules is often "secondary." For example, there are weak attractions between adjacent polyethylene molecules that involve polarization, not electron transfer or sharing. This weak secondary bonding is the primary reason that commercial "plastics" are characteristically weak and deformable in comparison to metals and ceramics/glasses.

Among the materials available for modern structural applications, a fourth category is generally included—namely, "composites." Composite materials are defined as microscopic-scale combinations of individual materials belonging to the previous three categories (metals, polymers, ceramics/glasses). A good example is fiberglass, a composite of glass fibers (a few micrometers in diameter) embedded in a polymer matrix. Over the past several decades, fiberglass products have become commonplace. The advantage of composites is that they display the best properties of each component, producing products superior to products made of a single component. In the case of fiberglass, the high strength of the small diameter glass fibers is combined with the flexibility of the polymer matrix.

Although most engineered materials can be put into one of the four categories described above, a sorting of the same materials based on electrical conductivity rather than atomic bonding demands an additional, fifth category. We noted above that metals are typically good electrical conductors and that polymers and ceramics/glasses are typically electrical insulators. Composites tend to have properties that are averages of those of their individual components. As an example, fiberglass is an electrical insulator because both glass fibers and the polymer matrix tend to be insulators. Since the middle of the twentieth century, "semiconductors," with intermediate levels of electrical conductivity, have played an increasingly critical role in modern technology. The primary example is elemental silicon, which, as noted above, is a central component of modern, solid-state electronics. Silicon is in column IVA of the Periodic Table. Its neighbor in column IVA, germanium, is also a semiconductor and also widely used in electronic devices. Chemical compounds of the elements near column IVA often display semiconduction—for example, gallium arsenide (GaAs), which is used as a high temperature rectifier and a laser material. The chemical bonding in the various elemental and compound semiconductors is generally strongly covalent. In summary, a full list of the types of engineered materials contains five categories. (See Table 1.)

From Structure to Properties

An underlying principle of materials science is that structure (on the atomic or microscopic scale) leads to properties (on the macroscopic scale of real world, engineering applications). We have already seen that the natures of ceramics and glasses are very different because ceramics have a crystalline atomic arrangement and glasses are noncrystalline. Similarly, transparent glass

TYPES OF MATERIALS

Material Type	Bonding Character	Examples
Metal	Metallic	Iron (Fe); Brass (Cu and Zn)
Polymer	Covalent and secondary	Polyethylene [$(C_2 H_4)_n$]
Ceramic/glass	Ionic/covalent	Silica (SiO_2): crystalline and noncrystalline
Composites	(determined by components)	Fiberglass (glass fibers in polymer matrix)
Semiconductors	Covalent or covalent/ionic	Silicon (Si); Gallium Arsenide (GaAs)

Table 1.

becomes opaque when it has many microscopic air bubbles that scatter light and prevent a clear image from being transmitted through the material. Examples of the structure–property relationship arise throughout the field of materials science.

Processing and Selecting Materials

The use of materials in modern technology depends on our ability to make those materials. Processing is dependent on the nature of the material, and the specific processing technique can, in turn, have an effect on the properties of the material. Given the wide range of materials described in Table 1, and the fact that an individual material's properties are dependent on the way in which it is manufactured, the selection of materials for a given application needs to be done in a systematic way. The selection process and the final decision are dependent on a range of factors, including desired properties, ability to be manufactured, and cost.

Conclusion

Chemical bonding and electrical conductivity provide five major categories of engineered materials: metals, polymers, ceramics/glasses, composites, and semiconductors. The properties of these materials are dependent on atomic- and microscopic-scale structure, as well as on the way in which a given material is processed. Materials science enables the selection of the optimal material for a given application. SEE ALSO Ceramics; Glass; Physical Chemistry; Polymers, Synthetic; Semiconductors.

James F. Shackelford

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Maxwell, James Clerk

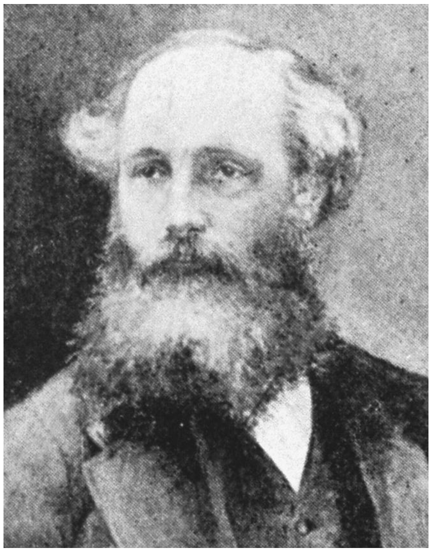
SCOTTISH PHYSICIST
1831–1879

James Clerk Maxwell is generally regarded as one of the outstanding physicists of the nineteenth century. He made important advances in the theory of electricity and magnetism, as well as in thermodynamics and the **kinetic theory** of gases. Many modern ideas about these topics are still based on his work from the mid-1800s.

Maxwell was born in Edinburgh, Scotland, and his father greatly encouraged him in his intellectual pursuits. At the age of fourteen, while a student at the Edinburgh Academy, he wrote a paper on ovals and geometric figures with more than two foci. His paper was read to the **Royal Society** of Edinburgh by an adult member because it was considered inappropriate for a young boy to present it to the society himself. Although some of the ideas in this paper had been discussed earlier by the renowned French mathematician René Descartes, it was still an amazing achievement for a teenage boy.

At sixteen, Maxwell entered Edinburgh University, where he studied physics, mathematics, and logic. Three years later he went to Cambridge University, from which he graduated in 1854 with a degree in mathematics.

In 1856 Maxwell became professor of **natural philosophy** at Marischal College in Aberdeen. There he became interested in the theory of gases and in the study of electricity and magnetism. His position as professor, however, was eliminated in 1860 when Marischal and another college merged.



Scottish physicist James Clerk Maxwell, who identified light as an electromagnetic wave.

kinetic theory: theory of molecular motion

Royal Society: The U.K. National Academy of Science, founded in 1660

natural philosophy: study of nature and the physical universe

Maxwell spent the next five years at King's College in London. He successfully applied statistical methods to describe the movements of the tiny invisible particles of a gas, an approach adopted a century earlier by the Swiss mathematician Daniel Bernoulli, but with less sophisticated mathematics. The Austrian physicist Ludwig Boltzmann also studied the problem of gas behavior at the same time as Maxwell, and the names of both men are usually associated with the kinetic theory of gases.

Because of his overwhelming interest in the science of electricity, Maxwell was drawn to the writings of the English physicist Michael Faraday, who had begun publishing his three-volume *Experimental Researches in Electricity* in 1839. Faraday's approach was almost entirely experimental, and Maxwell saw this as an opportunity to treat the subject in mathematical terms. Beginning in the 1850s, Maxwell published several papers on electricity, including the analogy between electricity and heat from a mathematical point of view. These research efforts culminated in his important writings in the 1860s and 1870s on electromagnetic theory and his identification of light as an electromagnetic wave. Maxwell's theoretical conclusions about electromagnetism are summarized in a set of four equations known as Maxwell's equations, which first appeared in his *Treatise on Electricity and Magnetism* in 1873 and were later cast in their modern form by other physicists.

In 1865 Maxwell resigned his position in London and returned to his family estate Glenair in Scotland, where he continued his scientific work for five years. In 1870, however, a new chair and laboratory of physics were established at Cambridge University, and Maxwell eventually accepted an offer after two other physicists had refused. Maxwell continued his work in electricity and magnetism, organized the new laboratory, and edited the papers of Henry Cavendish for whom the laboratory was named. Early in 1879 Maxwell's health began to decline, and he died several months later during his forty-ninth year. SEE ALSO BOLTZMANN, LUDWIG; CAVENDISH, HENRY; FARADAY, MICHAEL; MAGNETISM; PHYSICAL CHEMISTRY.

Richard E. Rice

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Measurement

British mathematician and physicist William Thomson (1824–1907), otherwise known as Lord Kelvin, indicated the importance of measurement to science:

> When you can measure what you are speaking about and express it in numbers, you know something about it; but when you cannot measure it, when you cannot express it in numbers, your knowledge is of a meager and unsatisfactory kind; it may be the beginning of knowledge, but you have scarcely in your thoughts advanced to the state of science, whatever the matter may be.

combustion: burning, the reaction with oxygen

Possibly the most striking application of Kelvin's words is to the explanation of **combustion** by the French chemist Antoine Lavoisier (1743–1794). Combustion was confusing to scientists of the time because some materials, such as wood, seemed to decrease in mass on burning: Ashes weigh less than wood. In contrast, others, including iron, increased in mass: Rust weighs more than iron. Lavoisier was able to explain that combustion results when oxygen in the air unites with the material being burned, after careful measurement of the masses of the reactants—air and the material to be burned—and those of the products. Because Lavoisier was careful to capture all products of combustion, it was clear that the reason wood seemed to lose mass on burning was because one of its combustion products is a gas, carbon dioxide, which had been allowed to escape.

Lavoisier's experiments and his explanations of them and of the experiments of others are often regarded as the beginning of modern chemistry. It is not an exaggeration to say that modern chemistry is the result of careful measurement.

Most people think of measurement as a simple process. One simply finds a measuring device, uses it on the object to be measured, and records the result. Careful scientific measurement is more involved than this and must be thought of as consisting of four steps, each one of which is discussed here: choosing a measuring device, selecting a sample to be measured, making a measurement, and interpreting the results.

Choosing a Measuring Device

The measuring device one chooses may be determined by the devices available and by the object to be measured. For example, if it were necessary to

A sundial indicates time based on the position of the Sun.

determine the mass of a coin, obviously inappropriate measuring devices would include a truck scale (reading in units of 20 pounds, with a 10-ton capacity), bathroom scale (in units of 1 pound, with a 300-pound capacity), and baby scale (in units of 0.1 ounce, with a 30-pound capacity). None of these is capable of determining the mass of so small an object. Possibly useful devices include a centigram balance (reading in units of 0.01 gram, with a 500-gram capacity), milligram balance (in units of 0.001 gram, with a 300-gram capacity), and analytical balance (in units of 0.00001 gram, with a 100-gram capacity). Even within this limited group of six instruments, those that are suitable differ if the object to be measured is an approximately one-kilogram book instead of a coin. Then only the bathroom scale and baby scale will suffice.

In addition, it is essential that that the measuring device provide reproducible results. A milligram balance that yields successive measurements of 3.012, 1.246, 8.937, and 6.008 grams for the mass of the same coin is clearly faulty. One can check the reliability of a measuring device by measuring a standard object, in part to make sure that measurements are reproducible. A common measuring practice is to intersperse samples of known value within a group of many samples to be measured. When the final results are tallied, incorrect values for the known samples indicate some fault, which may be that of the measuring device, or that of the experimenter. In the example of measuring the masses of different coins, one would include several "standard" coins, the mass of each being very well known.

Selecting a Sample

There may be no choice of sample because the task at hand may be simply that of measuring one object, such as determining the mass of a specific coin. If the goal is to determine the mass of a specific kind of coin, such as a U.S. penny, there are several questions to be addressed, including the following. Are uncirculated or worn coins to be measured? Worn coins may have less mass because copper has worn off, or more mass because copper oxide weighs more than copper and dirt also adds mass. Are the coins of just one year to be measured? Coin mass may differ from year to year. How many coins should be measured to obtain a representative sample? It is likely that there is a slight variation in mass among coins and a large enough number of coins should be measured to encompass that variation. How many sources (banks or stores) should be visited to obtain samples? Different batches of new coins may be sent to different banks; circulated coins may be used mostly in vending machines and show more wear as a result.

The questions asked depend on the type of sample to be measured. If the calorie content of breakfast cereal is to be determined, the sampling questions include how many factories to visit for samples, whether to sample unopened or opened boxes of cereal, and the date when the breakfast sample was manufactured, asked for much the same reason that similar questions were advanced about coins. In addition, other questions come to mind. How many samples should be taken from each box? From where in the box should samples be taken? May samples of small flakes have a different calorie content than samples of large flakes?

These sampling questions are often the most difficult to formulate but they are also the most important to consider in making a measurement. The purpose of asking them is to obtain a sample that is as representative as possible of the object being measured, without repeating the measurement unnecessarily. Obviously, a very exact average mass of the U.S. penny can be obtained by measuring every penny in circulation. This procedure would be so time-consuming that it is impractical, in addition to being expensive.

Making a Measurement

As mentioned above, making a measurement includes verifying that the measuring device yields reproducible results, typically by measuring standard samples. Another reason for measuring standard samples is to calibrate the measuring instrument. For example, a common method to determine the viscosity of a liquid—its resistance to flow—requires knowing the density of that liquid and the time that it takes for a definite volume of liquid to flow through a thin tube, within a device called a viscometer. It is very difficult to construct duplicate viscometers that have exactly the same length and diameter of that tube. To overcome this natural variation, a viscometer is calibrated by timing the flow of a pure liquid whose viscosity is known—such as water—through it. Careful calibration involves timing the flow of a standard volume of more than one pure liquid.

Calibration not only accounts for variations in the dimensions of the viscometer. It also compensates for small variations in the composition of the glass of which the viscometer is made, small differences in temperatures, and even differences in the gravitational acceleration due to different positions on Earth. Finally, calibration can compensate for small variations in technique from one experimenter to another.

These variations between experimenters are of special concern. Different experimenters can obtain very different values when measuring the same sample. The careful experimenter takes care to prevent bias or difference in technique from being reflected in the final result. Methods of prevention include attempting to measure different samples without knowing the identity of each sample. For instance, if the viscosities of two colorless liquids are to be measured, several different aliquots of each liquid will be prepared, the aliquots will be shuffled, and each **aliquot** will be measured in order. As much of the measurement as possible will be made mechanically. Rather than timing flow with a stopwatch, it is timed with an electronic device that starts and stops as liquid passes definite points.

aliquot: specific volume of a liquid used in analysis

Finally, the experimenter makes certain to observe the measurement the same way for each trial. When a length is measured with a meter stick or a volume is measured with a graduated cylinder, the eye of the experimenter is in line with or at the same level as the object being measured to avoid parallax. When using a graduated device, such as a thermometer, meter stick, or graduated cylinder, the measurement is estimated one digit more finely than the finest graduation. For instance, if a thermometer is graduated in degrees, 25.4°C (77.7°F) would be a reasonable measurement made with it, with the ".4" estimated by the experimenter.

Each measurement is recorded as it is made. It is important to not trust one's memory. In addition, it is important to write down the measurements made, not the results from them. For instance, if the mass of a sample of sodium chloride is determined on a balance, one will first obtain the mass of a container, such as 24.789 grams, and then the mass of the container with the sodium chloride present, such as 32.012 grams. It is important to record both of these masses and not just their difference, the mass of sodium chloride, 7.223 grams.

Interpreting Results

Typically, the results of a measurement involve many values, the observations of many trials. It is tempting to discard values that seem quite different from the others. This is an acceptable course of action if there is good reason to believe that the errant value was improperly measured. If the experimenter kept good records while measuring, notations made during one or more trials may indicate that an individual value was poorly obtained—for instance, by not zeroing or leveling a balance, neglecting to read the starting volume in a buret before titration, or failing to cool a dried sample before obtaining its mass.

Simply discarding a value based on its deviation from other values, without sound experimental reasons for doing so, may lead to misleading results besides being unjustified. Consider the masses of several pennies determined with a milligram balance to be: 3.107, 3.078, 3.112, 2.911, 3.012, 3.091, 3.055, and 2.508 grams. Discarding the last mass because of its deviation would obscure the facts that post-1982 pennies have a zinc core with copper **cladding** (representing a total of about 2.4% copper), whereas pre-1982 pennies are composed of an **alloy** that is 95 percent copper. There are statistical tests that help in deciding whether to reject a specific value or not.

cladding: protective material surrounding a second material

alloy: mixture of two or more elements, at least one of which is a metal

It is cumbersome, however, to report all the values that have been measured. Reporting solely the average or mean value gives no indication of how carefully the measurement has been made or how reproducible the repeated measurements are. Care in measurement is implied by the number of significant figures reported; this corresponds to the number of digits to

A scale is a method for determing mass.

which one can read the measuring devices, with one digit beyond the finest graduation, as indicated earlier.

The reproducibility of measurements is a manifestation of their precision. Precision is easily expressed by citing the range of the results; a narrow range indicates high precision. Other methods of expressing precision include relative average deviation and standard deviation. Again, a small value of either deviation indicates high precision; repeated measurements are apt to replicate the values of previous ones.

When several different quantities are combined to obtain a final value—such as combining flow time and liquid density to determine viscosity—standard propagation-of-error techniques are employed to calculate the deviation in the final value from the deviations in the different quantities.

Both errors and deviations combine in the same way when several quantities are combined, even though error and deviation are quite different concepts. As mentioned above, deviation indicates how reproducible successive measurements are. Error is a measure of how close an individual value—or an average—is to an accepted value of a quantity. A measurement with small error is said to be accurate. Often, an experimenter will believe that high precision indicates low error. This frequently is true, but very precise measurements may have a uniform error, known as a systematic error. An example would be a balance that is not zeroed, resulting in masses that are uniformly high or low.

The goal of careful measurement ultimately is to determine an accepted value. Careful measurement technique—including choosing the correct measuring device, selecting a sample to be measured, making a measurement, and interpreting the results—helps to realize that goal. SEE ALSO INTERNATIONAL SYSTEM OF UNITS; LAVOISIER, ANTOINE.

Robert K. Wismer

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Meitner, Lise

AUSTRIAN PHYSICIST
1878–1968

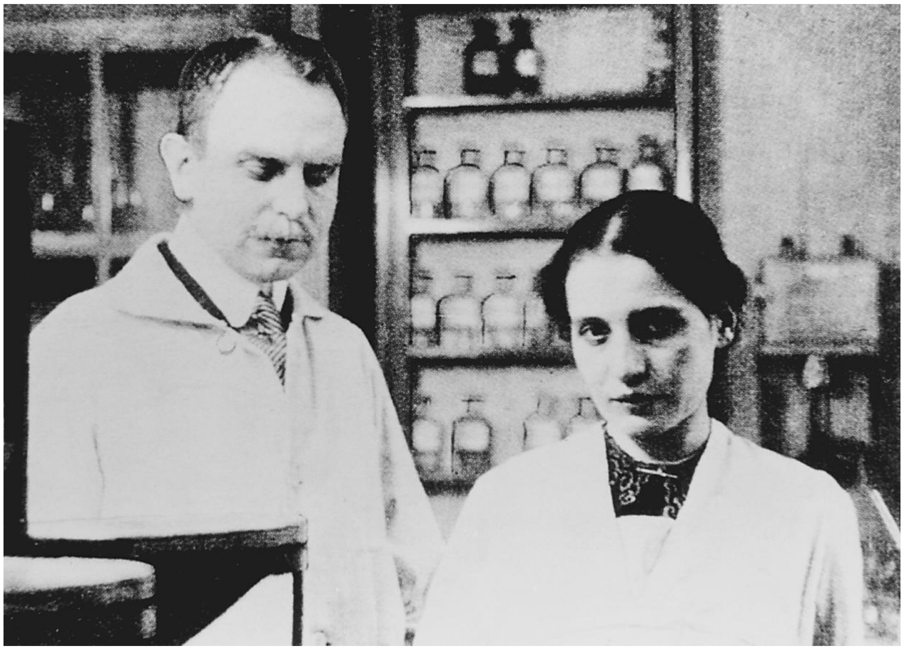
On any list of scientists who should have won a Nobel Prize but did not, Lise Meitner's name would be near the top. She was the physicist who first realized that the atomic nucleus could be split to form pairs of other atomic nuclei—the process of **nuclear fission**. Although she received many honors for her work, the greatest of all was to elude her because of the unprofessional conduct of her colleague Otto Hahn.

nuclear: having to do with the nucleus of an atom

fission: process of splitting an atom into smaller pieces

Born in Vienna, Meitner decided early on that she had a passion for physics. At that time, education for female children in the Austro-Hungarian Empire terminated at fourteen, as it was argued that girls did not need any more education than that to become a proper wife and mother. Willing to support his daughter's aspirations, her father paid for private tutoring so she could cover in two years the eight years of education normally needed for university entrance. In 1901 Meitner was one of only four women admitted to the University of Vienna, and in 1905 she graduated with a Ph.D. in physics.

As a student, Meitner had become fascinated with the new science of radioactivity, but she realized that she would have to travel to a foreign country to pursue her dream of working in this field. She applied for work with Marie Curie, but was rejected. However, she did eventually receive an offer from the University of Berlin, which had just hired a young scientist by



Austrian physicist Lise Meitner standing with Otto Hahn (l.). Meitner discovered nuclear fission, but was never honored as such.

theoretical physics: branch of physics dealing with the theories and concepts of matter, especially at the atomic and subatomic levels

the name of Otto Hahn. Having a chemical background, Hahn was looking for a collaborator with a **theoretical physics** background. Unfortunately, the chemistry institute at the university was run by Emil Fischer who had banned women from the institute's premises. Reluctantly, Fischer agreed to let Meitner work in a small basement room. During this time, she received no salary and relied on her family for enough money to cover her living expenses. Meitner and Hahn's research during this time period resulted in the discovery of the element protactinium.

The post–World War I government in Germany was much more favorable to women, and Meitner became the first woman to serve as a physics professor in that country. By the 1930s scientists were bombarding heavy elements with neutrons and it was claimed that new superheavy elements formed as a result of this process. Using such a procedure, Meitner and Hahn thought they had discovered nine new elements. Meitner was puzzled by all the new elements for which claims were made.

Unfortunately, the Nazi Party's rise to power changed everything for Meitner. Because she was a Jew by birth, although a later convert to Christianity, Meitner's situation became increasingly precarious. With help from a Dutch scientist, Dirk Coster, she escaped across the German border into Holland and then made her way to Stockholm, where the director of the Nobel Institute for Experimental Physics reluctantly offered her a position. Stockholm had one advantage for Meitner, an overnight mail service to Germany so she could keep in regular contact with Hahn.

On December 19, 1938, Hahn sent Meitner a letter describing how one of the new elements had chemical properties strongly resembling those of barium and asking if she could provide an explanation. The physicist Otto Frisch visited Meitner, his aunt, for Christmas to help dispel her loneliness. While there, the two went for the now famous "walk in the snow." During an extended conversation in the woods, they came to realize that if the nucleus was considered a liquid drop, the impact of a subatomic particle could cause the atom to fission. If so, it was possible that the barium-like element was actually barium itself.

Meitner immediately contacted Hahn and his colleague Fritz Strassmann. Through experiment they confirmed that the so-called new element was indeed barium. They reported their discovery of nuclear fission to the world's scientific press, barely mentioning the names of Meitner and Frisch. In fact, Hahn never admitted that it was Meitner who had made the critical conceptual breakthrough. In 1944 Hahn was awarded the Nobel Prize in chemistry for his contribution to the discovery of nuclear fission.

Although nominated several times, Meitner never did receive the Nobel Prize for physics that many scientists considered her due. Only now, with element 109 having been named Meitnerium (symbol Mt) has she finally received some recognition for her crucial work. Meitner retired to England where she died at the age of eighty-nine. SEE ALSO BARIUM; CURIE, MARIE SKLODOWSKA; FISCHER, EMIL HERMANN; NUCLEAR FISSION; PROTACTINIUM; RADIATION.

Marelene Rayner-Canham
Geoffrey W. Rayner-Canham

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Membrane

All living creatures are made of cells. One cellular component, the membrane, plays a crucial role in almost all cellular activities. The primary function of all cell membranes is to act as barriers between the intracellular and extracellular environments, and as sites for diverse biochemical activities. The cell itself is encapsulated by its own membrane, the plasma membrane. Although the composition of membranes varies, in general, **lipid** molecules make up approximately 40 percent of their dry weight; proteins, approximately 60 percent. The lipids and proteins are held together by **noncovalent** interactions.

Among several possible stable arrangements of protein and lipid molecules in membranes, the bilayer model, first described over seventy years ago, characterizes most biological membranes. An important feature of this model is that the **hydrophilic** groups of the lipid molecules are oriented toward the surfaces of the bilayer, and the **hydrophobic** groups toward the interior. In 1972 Jonathan Singer and Garth Nicolson postulated a unified theory of membrane structure called the fluid-mosaic model. They proposed that the matrix, or continuous part, of membrane structure is a fluid bilayer, and that globular amphiphilic proteins are embedded in a single monolayer,

lipid: a nonpolar organic molecule; fatlike; one of a large variety of nonpolar hydrophobic (water-hating) molecules that are insoluble in water

noncovalent: having a structure in which atoms are not held together by sharing pairs of electrons

hydrophilic: having an affinity for water

hydrophobic: repelling water

with some proteins spanning the thickness of both monolayers. Both proteins and lipids are mobile and, thus, the membrane can be viewed as a two-dimensional solution of proteins in lipids.

The major class of lipids in plasma membranes is phospholipids. Phospholipids consist of a glycerol backbone and two fatty acids joined by **ester** linkage to the first two carbons of glycerol, and a phosphate group joined to the third. Different groups can be esterified to the phosphate, and these groups define the different classes of phospholipids. In addition, the fatty acids have varying chain lengths and degrees of unsaturation. The presence of the **nonpolar** acyl chain regions and the polar head groups gives the phospholipid molecules their amphipathic character, which allows them to assume the bilayer arrangements of membranes. In addition to phospholipids, two other kinds of lipids are found in the membranes of animal cells: glycolipids and cholesterol. Glycolipids usually make up only a small fraction of the lipids in the membrane but have been shown to possess many biological functions, one of which is their capacity to function as recognition sites. Cholesterol is an important component of plasma membranes and has been shown to play a key role in the control of membrane fluidity.

RECOGNITION SITES

Glycolipids and glycoproteins can act as recognition sites in a variety of processes involving recognition between cell types or recognition of cellular structures by other molecules. Recognition events are important in normal cell growth, fertilization, transformation of cells, and other processes.

ester: organic species containing a carbon atom attached to three moieties: an O via a double bond, an O attached to another carbon atom or chain, and a H atom or C chain; the R(C-O)OR functional group

nonpolar: molecule, or portion of a molecule, that does not have a permanent, electric dipole

Several membrane functions are believed to be largely mediated by proteins. Membrane proteins have been put into two general categories: peripheral and integral. Peripheral proteins (or extrinsic proteins) are those that do not penetrate the bilayer to any significant degree and are associated with it by virtue of noncovalent interactions (ionic interactions and **hydrogen bonds**) between membrane surfaces and protein surfaces. Integral proteins (or intrinsic proteins), in contrast, possess hydrophobic surfaces that readily penetrate the lipid bilayer, as well as other surfaces that prefer contact with aqueous medium. These proteins can either insert into the membrane or extend all the way across it and expose themselves to the **aqueous solutions** on both sides.

hydrogen bond: interaction between H atoms on one molecule and lone pair electrons on another molecule that constitutes hydrogen bonding

aqueous solution: homogenous mixture in which water is the solvent (primary component)

One of the main functions of the plasma membrane is to separate cytoplasm from extracellular surroundings. In fact, membranes are highly selective permeability barriers, as they contain specific channels and pumps that enable the transport of substances across membranes. These transport systems to a large degree regulate the molecular and ionic composition of intracellular media. Membranes also control the flow of information between cells, and between cells and their extracellular environments, and they contain specific **receptors** that make membranes sensible to external stimuli. In addition, some membranes conduct and pass on signals that can be chemical or electrical, as in the transmission of nerve impulses. Thus, membranes play a central role in signal transduction processes and in biological communication. SEE ALSO CHOLESTEROL; LIPIDS; PHOSPHOLIPIDS; TRANSMEMBRANE PROTEIN.

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

Michèle Auger

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Mendeleev, Dimitri

RUSSIAN CHEMIST
1834–1907

Russian chemist Dimitri Mendeleev, who devised the atomic mass-based Periodic Table.

Dimitri Ivanovich Mendeleev (or Mendeleyev or Mendelejeff) was born in Tobolsk, Siberia, on January 27, 1834. He was the fourteenth and youngest child of the family. His father was the director of the Tobolsk Gymnasium (high school). Tragedy plagued the family in Mendeleev's early years. His father became blind and was forced to retire from his job, and then unexpectedly died. His mother supported the family by managing a glass factory, but in 1848 it burned to the ground. His mother moved the family first to Moscow and then to St. Petersburg. In 1850 Mendeleev began his training as a teacher, following in his father's footsteps at the Pedagogical Institute in St. Petersburg. A few months after this, his mother and older sister died of tuberculosis.

When Mendeleev graduated, he moved to Simferopol on the Crimean Peninsula to assume a post as a science teacher, but the school was soon closed because of the Crimean War. He returned to St. Petersburg and received a master's degree in 1856 after presenting his thesis "Research and Theories on Expansion of Substances Due to Heat."

The years 1859 to 1861, when the Ministry of Public Instruction sent him abroad to study, shaped Mendeleev's career as a scientist. He studied **gas density** with the chemist Henri Victor Regnault in Paris and **spectroscopy** with the physicist Gustav Kirchhoff in Heidelberg. It was while working in Heidelberg that Mendeleev discovered the principle of critical temperature for gases. Once a gas is heated to a temperature above its critical point, no amount of pressure will turn it into a liquid. His work went unnoticed, and the discovery of critical temperatures is usually attributed to the Irish physicist and chemist Thomas Andrews.

gas density: weight in grams of a liter of gas

spectroscopy: use of electromagnetic radiation to analyze the chemical composition of materials

Mendeleev also attended the 1860 Karlsruhe Congress, the first international chemistry conference. Many of the leading chemists of the day were in attendance, and one of the central questions addressed was the appropriate method for calculating **atomic weight**. Different chemists used different systems, leading to widespread confusion over everything from nomenclature to chemical formulas. Mendeleev heard the Italian chemist Stanislao Cannizzaro present Amedeo Avogadro's hypothesis that equal volumes of gas under equal temperature and pressure contained equal numbers of molecules.

atomic weight: weight of a single atom of an element in atomic mass units (AMU)

Mendeleev returned to St. Petersburg determined to make a name for himself and build on the innovations to which he had been exposed. He became a professor of chemistry at the Technological Institute in 1863. His attention to science also extended to practical application, and he often worked as a consultant to the government on farming, mining, and oil production.

In 1866 Mendeleev became professor of general chemistry at the University of St. Petersburg. Finding that no modern organic chemistry textbook existed in Russian, Mendeleev decided to write one (it became a classic work, going through many editions). It was in the course of this project that he made his most important contribution to chemistry. *Principles of*

Table 1. Eka aluminum was predicted by Mendeleev and discovered by the French chemist Paul-Émile Lecoq de Boisbaudran in 1875 and named gallium.

Property	Eka Aluminum	Gallium
Atomic weight	±68	69.9
Density	5.9	5.93
Melting point	Low	30.1˚C

Chemistry was not a mere compilation of facts; it presented chemistry as a unified study. At its heart was the relationship of the elements.

On February 14, 1869, Mendeleev began work on the chapter that would discuss the elements. He already believed that there was some underlying principle connecting the elements. He transcribed his notes onto a set of cards, one for each element containing everything he knew about that element. He arranged and rearranged the cards until he was struck by a similarity between his arrangements and those of the card game patience (solitaire), in which cards are sorted by suit and then in descending numerical order. Exhausted, Mendeleev fell asleep. When he awoke, he devised a grouping of the elements by common property in ascending order of atomic weight. He called his innovation the Periodic Table of the Elements.

Within weeks, Mendeleev's Periodic Table was presented to the Russian Chemical Society and was published in the *Journal of Russian Physical Chemistry*; it was published later the same year in the prestigious German journal *Zeitschrift für Chemie*. Revised and expanded tables appeared in the *Annalen der Chemie* in 1872. Since the German journals were known to every research chemist, Mendeleev's Periodic Table became widely known almost at once. Although details of the tables were subject to argument, and many newly discovered elements were later added, the basic principle of organization behind the table was quickly accepted.

The true insight that informed Mendeleev's work was shown not just in what he had included in the Periodic Table, but also in what he had left out. He did not assume that all elements were known. Where there was a significant gap in atomic weights between the elements in the table, he left a gap in the table. He posited that there were undiscovered elements that existed in the gaps and even predicted the characteristics of three of them. He called these *eka boron*, *eka aluminum*, and *eka silicon* (*eka* being Sanskrit for "first"). See Tables 1 through 3 for the properties of these elements.

When these elements were eventually discovered, and because his system agreed with one developed independently by the German chemist Lothar Meyer in 1864, Mendeleev achieved widespread fame. The Periodic Table of the Elements provided a unifying system for classifying and understanding the elements and their function in the composition of matter.

Mendeleev received the Davy Medal (with Meyer in 1882) and the Copley Medal (in 1905), but Russia's Imperial Academy of Sciences refused to acknowledge his work. He resigned his university position in 1890 and was

Table 2. Eka boron was predicted by Mendeleev and discovered by the Swedish physicist Lars Fredrik Nilson in 1879 and named scandium.

Property	Eka Boron	Scandium
Atomic weight	44	44.1
Density of oxide	3.5	3.8

Property	Eka Silicon	Germanium
Atomic weight	72	72.32
Specific gravity	5.5	5.47
Valence	4	4

Table 3. Eka silicon was predicted by Mendeleev and discovered by the German chemist Clemens Winkler in 1886 and named germanium.

appointed director of the Bureau of Weights and Measures, holding this job until his death on January 20, 1907. SEE ALSO Avogadro, Amedeo; Cannizzaro, Stanislao; Meyer, Lothar; Periodic Table.

Andrew Ede

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Mendelevium

101

Md

MENDELEVIUM

258

MELTING POINT: 827°C
BOILING POINT: Unknown
DENSITY: Unknown
MOST COMMON IONS: Md^{2+}, Md^{3+}

Mendelevium was discovered in 1955 by Albert Ghiorso, Bernard G. Harvey, Gregory R. Choppin, Stanley G. Thompson, and Glenn T. Seaborg via the bombardments of a minute quantity of a rare, radioactive **isotope** of einsteinium (^{253}Es) with **α-particles** in the 60-inch cyclotron of the University of California, Berkeley, which produced ^{256}Md. Only 17 atoms were detected. Md is the first element to be produced and chemically identified on a one-atom-at-a-time basis. Mendelevium-256 decayed by electron capture (with a 1.3-hour half-life) to the known daughter nuclide fermium-256 (^{256}Fm), which decayed primarily by spontaneous **fission** (with a half-life of 2.6 hours). The atoms recoiling from the target were caught in a thin gold catcher foil that was quickly dissolved, and the resulting solution was passed through a cation exchange resin column which sorbed the atoms of Md and its known daughter Fm. Es and Fm were then identified by the order of their elution from the column with alpha-hydroxyisobutyrate solution relative to the known elution positions of Es and Cf tracers.

isotope: form of an atom that differs by the number of neutrons in the nucleus

α-particle: subatomic particle with 2+ charge and mass of 4; a He nucleus

fission: process of splitting a heavy atom into smaller pieces

Mendelevium is the heaviest element whose initial **atomic number** assignment was based on chemical separation. It was named after Dimitri Mendeleev, the great Russian chemist. Mendelevium isotopes of masses 245 through 260 have been reported. All are radioactive, decaying by α-particle emission, electron capture, and/or spontaneous fission, with half-lives ranging from 0.35 second for mass 245 to 31.8 days for mass 260, the heaviest isotope. The ground state electronic configuration of Md is believed to be $[Rn]5f^{13}7s^2$, by analogy to its **lanthanide** homologue thulium (element 69). Its most stable ion in **aqueous solution** is Md^{3+}, although Md^{2+} can be

atomic number: the number assigned to an atom of an element that indicates the number of protons in the nucleus of that atom

lanthanides: a family of elements (atomic number 57 through 70) from lanthanum to lutetium having from 1 to 14 4f electrons

aqueous solution: homogenous mixture in which water is the solvent (primary component)

reducing agent: substance that causes reduction, a process during which electrons are lost (or hydrogen atoms gained)

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

prepared with strong **reducing agents**. The **metal** is believed to be divalent because of its high volatility relative to that of other actinide metals, but this has not been experimentally verified. SEE ALSO ACTINIUM; BERKELIUM; EINSTEINIUM; FERMIUM; LAWRENCIUM; MENDELEEV, DIMITRI; NEPTUNIUM; NOBELIUM; PLUTONIUM; PROTACTINIUM; RADIOACTIVITY; RUTHERFORDIUM; SEABORG, GLENN THEODORE; THORIUM; TRANSMUTATION; URANIUM.

Darleane C. Hoffman

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Menten, Maud

CANADIAN BIOCHEMIST
1879–1960

When biochemists are asked to name a mathematical relationship, it is almost certain that they will choose the Michaelis–Menten equation. This equation enables biochemists to study quantitatively the way in which an enzyme speeds up a biochemical reaction. It was discovered by the German-born American biochemist Leonor Michaelis (1875–1949) and his assistant Maud Leonora Menten.

Though both discoverers deserve recognition, Menten faced the additional challenge of being a woman scientist at a time when professional advancement for women was very difficult. Born in Port Lambton, Ontario, Canada, Menten graduated from the University of Toronto with a B.A. in 1904 and an M.B. in medicine in 1907. For the 1907 to 1908 year, she was appointed a fellow at the Rockefeller Institute for Medical Research, New York, where she studied the effect of radium on tumors. Returning to Canada, Menten continued her medical studies, and in 1911 she became one of the first women in Canada to receive a medical doctorate.

catalysis: the action or effect of a substance in increasing the rate of a reaction without itself being converted

The pivotal year in Menten's life was 1912, when she crossed the Atlantic Ocean to spend a year working with Michaelis at the University of Berlin. While there, they developed the Michaelis–Menten hypothesis that provided a general explanation of the enzyme **catalysis** of biochemical reactions. From the hypothesis, they deduced the mathematical relationship that also bears their name. Their discovery changed scientists' approach to the study of biochemical reactions and helped shape the future of the subject.

Returning to North America, Menten performed doctoral research in biochemistry at the University of Chicago, receiving a Ph.D. in 1916. Despite her strong qualifications and the renown she received for the equation coformulated with Michaelis, she was unable to find any suitable employment in Canada. As a result, in 1918 she joined the medical school at the

University of Pittsburgh as a pathologist. She was appointed assistant professor of pathology in 1923 and promoted to associate professor in 1925. At the same time, she served as a clinical pathologist at the Children's Hospital at Pittsburgh, where she insisted on knowing about every interesting or puzzling case admitted to the hospital. Besides this, Menten maintained an active research program, authoring or coauthoring over seventy research papers. Among her other important discoveries were the use of electric fields to determine differences in human hemoglobin (a process called **electrophoresis**) and the development of a dye reaction to study enzymes in the kidney.

electrophoresis: migration of charged particles under the influence of an electric field, usually in solution; cations, positively charged species, will move toward the negative pole and anions, the negatively charged species, will move toward the positive pole

Menten accomplished much by working long 18-hour days. Medical science, however, was not her whole life. She was fluent in several languages, had her oil paintings exhibited in major exhibitions, and was an avid mountain climber. Although Menten did make tremendous contributions to medical science while in Pittsburgh, it was not until a year before her retirement at the age of seventy that the university promoted her to the highest rank of full professor. Formal retirement nonetheless did not slow down Menten. Returning to Canada in 1950, she conducted cancer research at the British Columbia Research Institute until ill health caused her to resign in 1954. SEE ALSO Enzymes; Radium.

Marelene Rayner-Canham
Geoffrey W. Rayner-Canham

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Mercury

MELTING POINT: −38.87°C
BOILING POINT: 359.6°C
DENSITY: 13.54 g/cm^3
MOST COMMON IONS: Hg_2^{2-}, Hg^{2+}

80
Hg
MERCURY
200.59

Mercury is at room temperature a silver-white, **volatile** liquid **metal**. It is reputed to have been known in ancient Egypt. Dioscorides, a Greek physician who flourished ca. 60 C.E., recounted the condensation of mercury vapor after the heating of cinnabar, the major ore of mercury. In the modern era mercury is produced via a variation on the procedure used by the ancients: The bright red ore (cinnabar) is now heated in oxygen, with lime, or with iron.

volatile: low boiling, readily vaporized

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

$$HgS(s) + O_2(g) \rightarrow SO_2(g) + Hg$$

$$HgS(s) + Fe \rightarrow Hg + FeS$$

$$4HgS(s) + 4CaO(s) \rightarrow 4Hg + 3CaS(s) + CaSO_4(s)$$

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

organometallic compound: compound containing a metal (transition) attached to one or more organic moieties

Mercury has three **oxidation** states: 0, 1+ (mercurous), and 2+ (mercuric). It forms few simple compounds. It does form several simple, water-soluble mercuric compounds: mercuric chloride, $HgCl_2$; mercuric nitrate, $Hg(NO_3)_2$; and mercuric acetate, $Hg(CH_3COO)_2$. The mercurous chloride, Hg_2Cl_2, is insoluble in water. Relatively stable **organometallic compounds** are formed with aliphatic and organic compounds. Methylmercury ($CH_3–Hg^+$) is the major polluting form of mercury. Methylmercury reacts with thiol groups in enzymes.

The mining of mercury has declined in recent decades, as major international concern over the health threat of mercury's extensive pollution of the environment has mounted. Much American freshwater fish is contaminated. The U.S. Environmental Protection Agency estimates 3,000 uses of mercury. Mercury usage is down in the chloroalkali industry, in which mercury is the cathode material used in the electrolysis of sodium chloride solutions, which produce sodium hydroxide and chlorine. An abundance of

500 ppb (0.5 μg/g) in Earth's crust gives rise to a discharge into the atmosphere of mercury on **combustion** of fossil fuels and the manufacture of metals and cement. SEE ALSO Heavy Metal Toxins; Inorganic Chemistry.

Robert A. Bulman

combustion: burning, the reaction with oxygen

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Metal Alloy *See Steel.*

Methylphenidate

Ritalin, the trademarked name of methylphenidate, is commonly prescribed to children ages 7–18 with attention-deficit hyperactivity disorder.

Methylphenidate is a mild stimulant prescribed to individuals (usually for children, and sometimes controversially) who have behavioral problems characterized by hyperactivity and short attention span. The National Institute of Mental Health estimates that approximately 3–5 percent of the general population has attention-deficit disorder (ADD) or attention-deficit hyperactivity disorder (ADHD). The administration of methylphenidate to children diagnosed with hyperactivity and/or attention-deficit disorder can have a calming effect on the children and can enable them to focus on schoolwork. Methylphenidate is also used to treat narcolepsy, a sleep disorder characterized by a permanent and overwhelming feeling of sleepiness and fatigue.

Methylphenidate is similar to **amphetamine** and, like amphetamine, stimulates the central nervous system (CNS), which consists of the brain and spinal cord. Stimulant drugs affect mood and alertness, and depress food appetite by increasing levels of several neurotransmitters in the brain. Although the exact therapeutic mode of action of methylphenidate is not known, the drug has been shown to elevate levels of some of these neurotransmitters, primarily dopamine and norepinephrine (noradrenaline).

amphetamine: class of compounds used to stimulate the central nervous system

Dopamine and norepinephrine are **excitatory** neurotransmitters. When nerve cells in the brain are stimulated, neurotransmitters stored in **vesicles** in nerve cell endings are released to extracellular spaces (synapses). The liberated chemical messengers can then interact with **receptors** on an adjacent nerve cell and can generate a new nerve signal (a nerve impulse). When levels of dopamine or norepinephrine are depressed, regions of the brain that rely on the two substances to regulate nerve impulse conduction are unable to function properly. Research has shown that children with ADD or ADHD have lower levels of dopamine in the CNS. It is believed that drugs acting as CNS stimulants, such as amphetamine, cocaine, and methylphenidate, compensate for lowered levels of excitatory neurotransmitters (i.e., dopamine and norepinephrine) in the brain. Indeed, administration of methylphenidate to healthy adult men has been found to increase dopamine levels.

excitatory: causing cells to become active

vesicle: small compartment in a cell that contains a minimum of one lipid bilayer

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

Different theories have been proposed to explain how methylphenidate increases levels of dopamine in the brain. One such theory propounds that methylphenidate causes dopamine to remain longer in extracellular spaces. Once a neurotransmitter has transmitted its message, it dissociates from the receptor to which it was bound and is taken up by the nerve cell from which it was originally released. Researchers at Brookhaven National Laboratory have demonstrated that methylphenidate inhibits this "reuptake" of dopamine by nerve cells. As a result, extracellular dopamine levels are increased, and the neurotransmitter continues to be available to initiate nerve impulses.

Ritalin is the brand name of a formulation of methylphenidate that is available in tablet form. Ritalin tablets are most often prescribed to children, aged 7 to 18, who have been diagnosed with ADHD. However, individuals who suffer from anxiety or panic disorders are warned not to take the drug, as Ritalin may aggravate symptoms of agitation and/or anxiety. Nervousness and insomnia are the most common side effects associated with Ritalin. There have also been reports of the onset of Tourette's syndrome, a **neurological** disorder characterized by repeated and involuntary body movements (tics), or at least of symptoms resembling those of Tourette's, in patients taking Ritalin, and therefore patients with this disorder are advised not to take Ritalin. In April 2002 the National Institutes of Health reported that a combination of Ritalin and Clonidine, a drug often used to treat **hypertension**, is more effective in the treatment of ADHD than either drug alone. Furthermore, Clonidine is reported to have a tic-suppressing effect, and it is believed that the drug may counteract the apparent tic-accentuating effect of methylphenidate.

neurologic: of or pertaining to the nervous system

hypertension: condition in which blood pressure is abnormally high

During the early 1990s, reports of abuse of methylphenidate began to appear. Nonmedical use of the drug for its stimulant effects impelled the U.S. Drug Enforcement Administration (DEA) to regulate the manufacture, distribution, and prescription of methylphenidate. Because methylphenidate is related to amphetamine, it can be addictive and result in physical and psychological dependence. SEE ALSO NEUROCHEMISTRY; NEUROTRANSMITTERS; PHARMACEUTICAL CHEMISTRY.

Nanette M. Wachter

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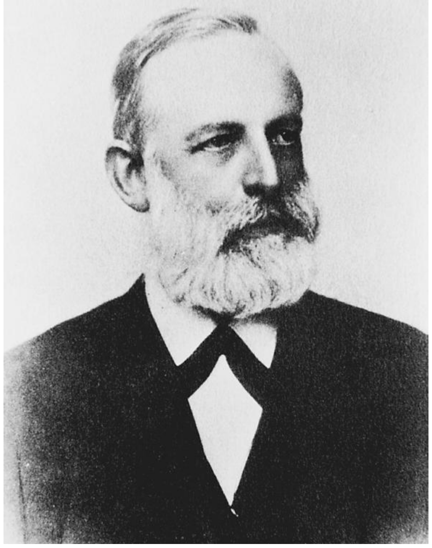
Meyer, Lothar

GERMAN CHEMIST
1830–1895

Lothar Meyer was the son and grandson of physicians, so it was only natural that initially he decided on a career as a physician. At the age of twenty-one, he began his studies in medicine at the University of Zurich and received his M.D. in 1854. By then Meyer had become interested in the chemistry of the body and went on to study under Robert Bunsen at Heidelberg, where he learned how to analyze gases. He used these techniques to study the absorption of oxygen and carbon monoxide by the blood, and was able to establish that they both reacted in a similar fashion with the same constituent present in the blood. Meyer also determined that carbon monoxide was able to displace oxygen from the blood. However, he was unable to identify the particular component in the blood responsible for binding. This substance was identified as hemoglobin eight years later by Felix Hoppe-Seyler, a professor of physiological chemistry at the University of Strasbourg in France. For this work, Meyer received his Ph.D. in 1858 at the University of Breslau, and he became the director of the chemical laboratory in the physiology institute there until 1866.



German chemist Lothar Meyer, known for the discovery of the periodic properties of the elements.

In 1864 Meyer published *Modern Theories of Chemistry*, which went through five editions and was translated into English, French, and Russian. This book contained a prototype of his 1870 Periodic Table, which consisted of only twenty-eight elements arranged in six families that had similar chemical and physical characteristics. Above all he used a number referred to as the combining power of each element, later termed the **valence**, to link together a particular family. For example, carbon, silicon, tin, and lead were assigned to the same family because each exhibited a combining power of four. He also recognized the following from the observation that atomic weights usually increase by a certain amount between family members: A missing element existed between silicon and tin (later this gap was filled by germanium, discovered in 1886 by the German chemist Clemens Winkler). By 1868 he had expanded his table to include fifty-three elements, but this version was not made public until 1895. This was unfortunate because in 1869 the Russian chemist Dimitri Mendeleev published his version of the Periodic Table in a paper entitled, "The Relation of the Properties to the Atomic Weights of the Elements." As well as postulating his table, Mendeleev described how it could be used to predict not only the **atomic weight** of missing elements, but also their actual properties.

valence: combining capacity

atomic weight: weight of a single atom of an element in atomic mass units (AMU)

The most famous of Mendeleev's predictions involved eka-boron (scandium), eka-aluminium (gallium), and eka-silicon (germanium). For example, for eka-silicon he predicted its atomic weight, its density, the compounds it would form, and details about their physical properties. When thirteen years later germanium was discovered and it was determined that Mendeleev's predictions had been correct, scientists began to recognize the importance of the Periodic Table, and its discovery was quite naturally associated with Mendeleev, who encouraged this association.

Even in the twenty-first century, although historians recognize that others, especially Meyer, should be given considerable credit for the discovery of the periodic properties of the elements, most textbooks credit only Mendeleev. SEE ALSO BUNSEN, ROBERT; MENDELEEV, DIMITRI; PERIODIC TABLE.

John E. Bloor

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Millikan, Robert

AMERICAN PHYSICIST
1868–1953

American physicist Robert Millikan, recipient of the 1923 Nobel Prize in physics, "for his work on the elementary charge of electricity and on the photoelectric effect."

Born in Morrison, Illinois, Robert Andrew Millikan was the second son of the Reverend Silas Franklin Millikan and Mary Jane Andrews. When Millikan was seven, his family moved to Maquoketa, Iowa, where he attended high school. In 1886 he entered Oberlin College in Ohio. In 1887 he enrolled in several classics classes there, and because he did quite well in Greek, at the end of his sophomore year, he was asked to teach an introductory-level physics class. He enjoyed teaching physics and accepted a two-year teaching post at Oberlin upon graduation in 1891. It was during this period that he developed an even keener interest in physics.

In 1893 Millikan began his doctoral work at Columbia University, receiving a Ph.D. in 1895. After traveling to Germany, he eventually accepted a faculty position at the University of Chicago. It was as a teacher and textbook author that Millikan first made his mark. He wrote or cowrote a number of elementary physics texts that became the classics in this field. However, while valued activities, they did not lead to his promotion to full professor. Determined to ascend in academic rank, Millikan began his research into the charge on the electron.

At the time, the debate over whether or not atoms were real had almost played out, but the questions surrounding the true nature of the electron were still unanswered. Although the work of the English physicist J. J. Thomson had elucidated the charge-to-mass ratio, determining that the electron had a discrete, fixed charge and mass remained.

voltage: potential difference expressed in volts

Being an experimentalist, Millikan used a tiny, submillimeter drop of oil suspended between capacitor plates to measure the incremental charge on an electron. His reasoned that the oil drop would pick up a charge due to friction as it entered the region between the plates. By ionizing the atmosphere and monitoring the motion of multiple drops, he was able to compare the time that the drop took to fall under the influence of gravity and with the electrical plates off, against the time that it took for the drop to climb under the influence of applied **voltage**. The interaction of the drop with the electric field always occurred in discrete units, indicating that the electron charge was a single value, and that it was the same value for all different forms of electricity.

atomic theory: physical concept that asserts that matter is composed of microscopically tiny particles called atoms and that various elements differ from each other by having different atoms

Millikan's oil-drop experiment settled the argument and determined accurately (within one part in a thousand) both the charge and, by virtue of the charge-to-mass ratio, the mass of the electron. Both numbers allowed the Danish physicist Niels Bohr to finally calculate Rydberg's constant and provided the first and most important proof of the new **atomic theory**.

Millikan went on to demonstrate the photoelectron effect, providing a valuable proof of Albert Einstein's equations. His experiments also aided both Einstein and Bohr in their later research efforts. In 1923 he was awarded a Nobel Prize in physics for both his work in determining the charge on the electron and exploring the photoelectric effect. SEE ALSO BOHR, NIELS; EINSTEIN, ALBERT; THOMSON, JOSEPH JOHN.

Todd W. Whitcombe

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Minerals

Minerals are the building blocks of rocks. A mineral may be defined as any naturally occurring inorganic solid that has a definite chemical composition (that can vary only within specified limits) and possesses a crystalline structure. The study of minerals is known as mineralogy, which dates back to prehistory. The use of minerals in the construction of primitive weapons and as suppliers of color for ancient artists makes mineralogy one of the oldest of the human arts.

Minerals may be characterized by the fundamental patterns of their crystal structures. A crystal structure is commonly identified by its fundamental repeating unit, which upon protraction into three dimensions generates a macroscopic crystal. Crystal structures can be divided into crystal systems, which can be further subdivided into crystal classes—a total of thirty-two crystal classes, which are sometimes referred to as point classes.

More commonly, minerals are described or classified on the basis of their chemical composition. Although some minerals, such as graphite or diamond, consist primarily of a single element (in this instance, carbon), most minerals occur as ionic compounds that consist of orderly arrangements of cations and **anions** and have a specific crystalline structure determined by the sizes and charges of the individual ions. Cations (positively charged ions) are formed by the loss of negatively charged electrons from atoms. Anions consist of a single element, the atoms of which have become negatively charged via the acquisition of electrons, or they consist of several elements, the atoms bound together by **covalent bonds** and bearing an overall negative charge. Pyrite (FeS_2) is a mineral that contains a sulfide ion as its anion. Gypsum [$CaSO_4-2(H_2O)$] contains the polyatomic anion known as sulfate (SO_4^{2-}) as well as two waters of hydration (water molecules that are part of the crystalline structure).

anion: negatively charged chemical unit, like Cl^-, CO_3^{2-}, or NO_3^-

covalent bond: bond formed between two atoms that mutually share a pair of electrons

It has been noted that the chemical composition of minerals could vary within specified limits. This phenomenon is known as solid solution. For example, the chemical composition of the mineral dolomite is commonly designated as $CaMg\ (CO_3)_2$, or as $(Ca, Mg)CO_3$. This does not mean that dolomite has calcium and magnesium existing in a one-to-one ratio. It signifies that dolomite is a carbonate mineral that has significant amounts of

This seacliff in Wales shows strata of banded liassic limestone and shale.

both cations (calcium and magnesium ions) in an infinite variety of proportions. When minerals form, ions of similar size and charge, such as calcium and magnesium ions, can substitute for each other and will be found in the mineral in amounts that depend on the proportions that were present in solution, or in the melt (liquid magma) from which the mineral formed. Thus, many minerals can exist in solid solution. When solid solutions exist, names are often given to the end-members. In the case of the calcium and magnesium carbonates, one end-member, $CaCO_3$ is named calcite or aragonite, depending on the crystalline symmetry, whereas the other end-member, $MgCO_3$, is referred to as magnesite.

Because minerals are naturally occurring substances, the abundance of minerals tends to reflect the abundance of elements as they are found in Earth's crust. Although about 4,000 minerals have been named, there are forty minerals that are commonly found and these are referred to as the rock-forming minerals.

The most abundant element in Earth's crust is oxygen, which makes up about 45 percent of the crust by mass. The second most abundant element is silicon, which accounts for another 27 percent by mass. The next six most abundant elements, in order of abundance, are aluminum, iron, calcium, magnesium, sodium, and potassium, which collectively comprise about 26 percent, leaving only about 2 percent for all other elements. If one classifies minerals according to the commonly accepted system that is based on their anions, it is not surprising that silicates (having anions that are polyatomic combinations of oxygen and silicon) are the most common mineral group.

Silicates

In order to understand the chemical structures and formulas of the silicate minerals, one must begin with the basic building block of all silicates: the silica tetrahedron. A silica tetrahedron is an anionic species, which consists of a silicon atom covalently bound to four oxygen atoms. The silicon atom is in the geometric center of the tetrahedron and at each of the four points of the

The natural matrix of the Kimberlite diamond.

tetrahedron is an oxygen atom. The structure has an overall charge of negative four and is represented as SiO_4^{4-}. The mineral olivine, a green-colored mineral as the name suggests, has the formula $(Mg, Fe)_2SiO_4$. When olivine is a gem-quality crystal it is referred to as peridot. As the formula suggests, olivine is really a group of minerals that vary in composition, from almost pure end-member forsterite (Mg_2SiO_4) to almost pure fayalite (Fe_2SiO_4).

All of the silicate minerals arise from various combinations of silica tetrahedra and a sense of their variety may be gleaned from the understanding that the oxygen atoms at the tetrahedral vertices may be shared by adjacent tetrahedra in such a way as to generate larger structures, such as single chains, double chains, sheets, or three-dimensional networks of tetrahedra. Various **cations** occurring within solid solutions neutralize the negative charges on the silicate backbone. The variation in geometric arrangements generates a dazzling array of silicate minerals, which includes many common gemstones.

cation: positively charged ion

The pyroxene group and the amphibole group, respectively, are representatives of silicate minerals having single-chain and double-chain tetrahedral networks. Pyroxenes are believed to be significant components of Earth's mantle, whereas amphiboles are dark-colored minerals commonly found in continental rocks.

Clays have sheet structures, generated by the repetitious sharing of three of the four oxygen atoms of each silica tetrahedron. The fourth oxygen atom of the silica tetrahedron is important as it has a capacity for cation exchange. Clays are thus commonly used as natural ion-exchange resins in water purification and desalination. Clays can be used to remove sodium ions from seawater, as well as to remove calcium and magnesium ions in the process of water softening. Because the bonds between adjacent sheets of silicon tetrahedra are weak, the layers tend to slip past one another rather easily, which contributes to the slippery texture of clays.

Clays also tend to absorb (or release) water. This absorption or release of water significantly changes clay volume. Consequently, soils that contain significant amounts of water-absorbing clays are not suitable as building construction sites.

Clays are actually secondary minerals—meaning that they are formed chiefly by the weathering of primary minerals. Primary minerals are those that form directly by precipitation from solution or magma, or by deposition from the vapor **phase**. In the case of clays their primary or parent minerals are feldspars, the mineral group with the greatest abundance in Earth's crust. Feldspars and clays are actually aluminosilicates. The formation of an aluminosilicate involves the replacement of a significant portion of the silicon in the tetrahedral backbone by aluminum.

phase: homogeneous state of matter

The feldspar minerals have internal arrangements that correspond to a three-dimensional array of silica tetrahedra that arises from the sharing of all four oxygen atoms at the tetrahedral vertices, and are sometimes referred to as framework silicates. Feldspars, rich in potassium, typically have a pink color and are responsible for the pinkish color of many of the feldspar-rich granites that are used in building construction. The feldspathoid minerals are similar in structure to feldspars but contain a lesser abundance of silica. Lapis lazuli, now used primarily in jewelry, is a mixture of the feldspathoid lazurite and other silicates, and was formerly used in granulate form as the paint pigment ultramarine.

Zeolites are another group of framework silicates similar in structure to the feldspars. Like clays they have the ability to absorb or release water. Zeolites have long been used as molecular sieves, due to their ability to absorb molecules selectively according to molecular size.

One of the most well-known silicate minerals is quartz (SiO_2), which consists of a continuous three-dimensional network of silica and oxygen without any atomic substitutions. It is the second most abundant continental mineral, feldspars being most abundant. The network of covalent bonds (between silicon and oxygen) is responsible for the well-known hardness of quartz and its resistance to weathering. Although pure quartz is clear and without color, the presence of small amounts of impurities may result in the formation of gemstones such as amethyst.

Nonsilicate Minerals

Although minerals of other classes are relatively scarce in comparison to the silicate minerals, many have interesting uses and are important economically. Because of the great abundance of oxygen in Earth's crust, the oxides are the most common minerals after the silicates. Litharge, for example, is a yellow-colored oxide of lead (PbO) and is used by artists as a pigment. Hematite (Fe_2O_3), a reddish-brown ore, is an iron oxide and is also used as a pigment. Other important classes of nonsilicate minerals include sulfides, sulfates, carbonates, halides, phosphates, and hydroxides. Some minerals in these groups are listed in Table 1.

Although minerals are often identified by the use of sophisticated optical instruments such as the polarizing microscope or the x-ray diffractometer, most can be identified using much simpler and less expensive methods. Color can be very helpful in identifying minerals (although it can also be misleading). A very pure sample of the mineral carborundum (Al_2O_3) is colorless but the presence of small amounts of impurities in carborundum may yield the deep red gemstone ruby or the blue gemstone sapphire. The streak

EXAMPLES OF COMMON NONSILICATE MINERALS AND THEIR USES

Mineral	Formula	Economic Use
Pyrite	FeS_2	sulfuric acid production
Anhydrite	$CaSO_4$	plaster
Calcite	$CaCO_3$	lime
Halite	NaCl	table salt
Turquoise	$CuAl_6(PO_4)_4(OH)_8$	gemstone
Bauxite	$Al(OH)_3.nH_2O$	aluminum ore
Rutile	TiO_2	jewelry, semiconductor

SOURCE: Tarbuck, Edward J., and Lutgens, Frederick K. (1999). *Earth: An Introduction to Physical Geology*, 6th edition. Upper Saddle River, NJ: Prentice Hall.

Table 1. Examples of common nonsilicate minerals and their uses.

of a mineral (the color of the powdered form) is actually much more useful in identifying a mineral than is the color of the entire specimen, as it is less affected by impurities. The streak of a mineral is obtained by simply rubbing the sample across a streak plate (a piece of unglazed porcelain), and the color of the powder is then observed. Virtually all mineral indexes used to identify minerals, such as those found in *Dana's Manual of Mineralogy*, list streaks of individual minerals.

Streak is used along with other rather easily determined mineral properties, such as hardness, specific gravity, cleavage, double refraction, the ability to react with common chemicals, and the overall appearance, to pinpoint the identity of an unknown mineral. Mineral hardness is determined by the ability of the sample to scratch or be scratched by readily available objects (a knife blade, a fingernail, a glass plate) or minerals of known hardness. Hardness is graded on the Moh's scale of hardness, which ranges from a value of one (softest) to ten (hardest). The mineral talc (used in talcum powder) has a hardness of one, whereas diamond has a hardness of ten. A fingernail has a hardness of 2.5; therefore quartz, which has a hardness of seven, would be able to scratch talc or a fingernail, but quartz could not scratch diamond or topaz, which has a hardness of eight. Conversely, topaz or diamond would be able to scratch quartz. Specific gravity is the ratio of the weight of a mineral to the weight of an equal volume of water and is thus in concept similar to density. The cleavage of a mineral is its tendency to break along smooth parallel planes of weakness and is dependent on the internal structure of the mineral. A mineral may exhibit double refraction. That is, the double image of an object will be seen if one attempts to view that object through a transparent block of the mineral in question. Calcite is a mineral that exhibits double refraction. Some minerals react spontaneously with common chemicals. If a few drops of hydrochloric acid are placed on a freshly broken surface of calcite, the calcite will react vigorously. **Effervescence**, caused by reaction of the calcite with hydrochloric acid to form the gas carbon dioxide, is observed. In contrast, dolomite will effervesce in hydrochloric acid only upon the first scratching the surface of the dolomite.

effervescence: bubbling or foaming

Minerals are a part of our daily lives. They comprise the major part of most soils and provide essential nutrients for plant growth. They are the basic building blocks of the rocks that compose the surface layer of our planet. They are used in many types of commercial operations, and the mining of minerals is a huge worldwide commercial operation. They are also used in water purification and for water softening. Finally, minerals are perhaps most valued for their great beauty. SEE ALSO GEMSTONES; INORGANIC CHEMISTRY; MATERIALS SCIENCE; ZEOLITES.

Mary L. Sohn

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Mole Concept

In chemistry the mole is a fundamental unit in the Système International d'Unités, the SI system, and it is used to measure the amount of substance. This quantity is sometimes referred to as the *chemical amount.* In Latin *mole* means a "massive heap" of material. It is convenient to think of a chemical mole as such.

Visualizing a mole as a pile of particles, however, is just one way to understand this concept. A sample of a substance has a mass, volume (generally used with gases), and number of particles that is proportional to the chemical amount (measured in moles) of the sample. For example, one mole of oxygen gas (O_2) occupies a volume of 22.4 L at standard temperature and pressure (STP; 0°C and 1 atm), has a mass of 31.998 grams, and contains about 6.022×10^{23} molecules of oxygen. Measuring one of these quantities allows the calculation of the others and this is frequently done in stoichiometry.

The *mole* is to the *amount of substance* (or chemical amount) as the *gram* is to *mass.* Like other units of the SI system, prefixes can be used with the mole, so it is permissible to refer to 0.001 mol as 1 mmol just as 0.001 g is equivalent to 1 mg.

Formal Definition

According to the National Institute of Standards and Technology (NIST), the Fourteenth Conférence Générale des Poids et Mesures established the definition of the mole in 1971.

> The mole is the amount of a substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon-12; its symbol is "mol." When the mole is used, the elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles.

One Interpretation: A Specific Number of Particles

When a quantity of particles is to be described, mole is a grouping unit analogous to groupings such as pair, dozen, or gross, in that all of these words represent specific numbers of objects. The main differences between the mole and the other grouping units are the magnitude of the number represented and how that number is obtained. One mole is an amount of substance containing Avogadro's number of particles. Avogadro's number is equal to 602,214,199,000,000,000,000,000 or more simply, $6.02214199 \times 10^{23}$.

Unlike pair, dozen, and gross, the exact number of particles in a mole cannot be counted. There are several reasons for this. First, the particles are too small and cannot be seen even with a microscope. Second, as naturally occurring carbon contains approximately 98.90% carbon-12, the sample would need to be purified to remove every atom of carbon-13 and carbon-14. Third, as the number of particles in a mole is tied to the mass of exactly 12 grams of carbon-12, a balance would need to be constructed that could determine if the sample was one atom over or under exactly 12 grams. If the first two requirements were met, it would take one million machines counting one million atoms each second more than 19,000 years to complete the task.

Obviously, if the number of particles in a mole cannot be counted, the value must be measured indirectly and with every measurement there is some degree of uncertainty. Therefore, the number of particles in a mole, Avogadro's constant (N_A), can only be approximated through experimentation, and thus its reported values will vary slightly (at the tenth decimal place) based on the measurement method used. Most methods agree to four significant figures, so N_A is generally said to equal 6.022×10^{23} particles per mole, and this value is usually sufficient for solving textbook problems. Another key point is that the formal definition of a mole does not include a value for Avogadro's constant and this is probably due to the inherent uncertainty in its measurement. As for the difference between Avogadro's constant and Avogadro's number, they are numerically equivalent, but the former has the unit of mol^{-1} whereas the latter is a pure number with no unit.

A Second Interpretation: A Specific Mass

Atoms and molecules are incredibly small and even a tiny chemical sample contains an unimaginable number of them. Therefore, counting the number of atoms or molecules in a sample is impossible. The multiple interpretations of the mole allow us to bridge the gap between the submicroscopic world of atoms and molecules and the macroscopic world that we can observe.

To determine the chemical amount of a sample, we use the substance's *molar mass*, the mass per mole of particles. We will use carbon-12 as an example because it is the standard for the formal definition of the mole. According to the definition, one mole of carbon-12 has a mass of exactly 12 grams. Consequently, the molar mass of carbon-12 is 12 g/mol. However, the molar mass for the element carbon is 12.011 g/mol. Why are they different? To answer that question, a few terms need to be clarified.

On the Periodic Table, you will notice that most of the atomic weights listed are not round numbers. The atomic weight is a weighted average of the atomic masses of an element's natural isotopes. For example, bromine has two natural isotopes with atomic masses of 79 u and 81 u. The unit *u* represents the atomic mass unit and is used in place of grams because the value would be inconveniently small. These two isotopes of bromine are present in nature in almost equal amounts, so the atomic weight of the element bromine is 79.904. (i.e., nearly 80, the arithmetic mean of 79 and 81). A similar situation exists for chlorine, but chlorine-35 is almost three times as abundant as chlorine-37, so the atomic weight of chlorine is 35.4527. Technically, atomic weights are ratios of the average atomic mass to the unit *u* and that is why they do not have units. Sometimes atomic weights are given the unit *u*, but this is not quite correct according to the International Union of Pure and Applied Chemistry (IUPAC).

To find the molar mass of an element or compound, determine the atomic, molecular, or formula weight and express that value as g/mol. For bromine and chlorine, the molar masses are 79.904 g/mol and 35.4527 g/mol, respectively. Sodium chloride (NaCl) has a formula weight of 58.443 (atomic weight of Na + atomic weight of Cl) and a molar mass of 58.443 g/mol. Formaldehyde (CH_2O) has a molecular weight of 30.03 (atomic weight of C + 2 [atomic weight of H]) + atomic weight of O] and a molar mass of 30.03 g/mol.

The concept of molar mass enables chemists to measure the number of submicroscopic particles in a sample without counting them directly simply by determining the chemical amount of a sample. To find the chemical amount of a sample, chemists measure its mass and divide by its molar mass. Multiplying the chemical amount (in moles) by Avogadro's constant (N_A) yields the number of particles present in the sample.

Occasionally, one encounters gram-atomic mass *(GAM)*, gram-formula mass *(GFM)*, and gram-molecular mass *(GMM)*. These terms are functionally the same as molar mass. For example, the GAM of an element is the mass in grams of a sample containing N_A atoms and is equal to the element's atomic weight expressed in grams. GFM and GMM are defined similarly. Other terms you may encounter are formula mass and molecular mass. Interpret these as formula weight and molecular weight, respectively, but with the units of *u*.

Avogadro's Hypothesis

Some people think that Amedeo Avogadro (1776–1856) determined the number of particles in a mole and that is why the quantity is known as Avogadro's number. In reality Avogadro built a theoretical foundation for determining accurate atomic and molecular masses. The concept of a mole did not even exist in Avogadro's time.

Much of Avogadro's work was based on that of Joseph-Louis Gay-Lussac (1778–1850). Gay-Lussac developed the law of combining volumes that states: "In any chemical reaction involving gaseous substances the volumes of the various gases reacting or produced are in the ratios of small whole numbers." (Masterton and Slowinski, 1977, p. 105) Avogadro reinterpreted Gay-Lussac's findings and proposed in 1811 that (1) some molecules were diatomic and (2) "equal volumes of all gases at the same temperature and pressure contain the same number of molecules" (p. 40). The second proposal is what we refer to as Avogadro's hypothesis.

The hypothesis provided a simple method of determining relative molecular weights because equal volumes of two different gases at the same temperature and pressure contained the same number of particles, so the ratio of the masses of the gas samples must also be that of their particle masses. Unfortunately, Avogadro's hypothesis was largely ignored until Stanislao Cannizzaro (1826–1910) advocated using it to calculate relative atomic masses or atomic weights. Soon after the 1st International Chemical Congress at Karlsrule in 1860, Cannizzaro's proposal was accepted and a scale of atomic weights was established.

To understand how Avogadro's hypothesis can be used to determine relative atomic and molecular masses, visualize two identical boxes with oranges in one and grapes in the other. The exact number of fruit in each box is not known, but you believe that there are equal numbers of fruit in each box (Avogadro's hypothesis). After subtracting the masses of the boxes, you have the masses of each fruit sample and can determine the mass ratio between the oranges and the grapes. By assuming that there are equal numbers of fruit in each box, you then know the average mass ratio between a grape and an orange, so in effect you have calculated their relative masses (atomic masses). If you chose either the grape or the orange as a standard, you could eventually determine a scale of relative masses for all fruit.

A Third Interpretation: A Specific Volume

By extending Avogadro's hypothesis, there is a specific volume of gas that contains N_A gas particles for a given temperature and pressure and that volume should be the same for all gases. For an ideal gas, the volume of one mole at STP (0°C and 1.000 atm) is 22.41 L, and several real gases (hydrogen, oxygen, and nitrogen) come very close to this value.

The Size of Avogadro's Number

To provide some idea of the enormity of Avogadro's number, consider some examples. Avogadro's number of water drops (twenty drops per mL) would fill a rectangular column of water 9.2 km (5.7 miles) by 9.2 km (5.7 miles) at the base and reaching to the moon at perigee (closest distance to Earth). Avogadro's number of water drops would cover the all of the land in the United States to a depth of roughly 3.3 km (about 2 miles). Avogadro's number of pennies placed in a rectangular stack roughly 6 meters by 6 meters at the base would stretch for about 9.4×10^{12} km and extend outside our solar system. It would take light nearly a year to travel from one end of the stack to the other.

History

Long before the mole concept was developed, there existed the idea of chemical equivalency in that specific amounts of various substances could react in a similar manner and to the same extent with another substance. Note that the historical equivalent is not the same as its modern counterpart, which involves electric charge. Also, the historical equivalent is not the same as a mole, but the two concepts are related in that they both indicate that different masses of two substances can react with the same amount of another substance.

The idea of chemical equivalents was stated by Henry Cavendish in 1767, clarified by Jeremias Richter in 1795, and popularized by William Wollaston in 1814. Wollaston applied the concept to elements and defined it in such a way that one equivalent of an element corresponded to its atomic mass. Thus, when Wollaston's equivalent is expressed in grams, it is identical to a mole. It is not surprising then that the word "mole" is derived from "molekulargewicht" (German, meaning "molecular weight") and was coined in 1901 or 1902. SEE ALSO AVOGADRO, AMEDEO; CANNIZZARO, STANISLAO; CAVENDISH, HENRY; GAY-LUSSAC, JOSEPH-LOUIS.

Nathan J. Barrows

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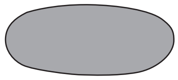
Molecular Geometry

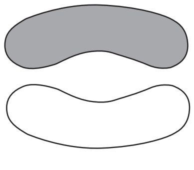
Molecules, from simple diatomic ones to macromolecules consisting of hundreds of atoms or more, come in many shapes and sizes. The term "molecular geometry" is used to describe the shape of a molecule or polyatomic ion as it would appear to the eye (if we could actually see one). For this discussion, the terms "molecule" and "molecular geometry" pertain to polyatomic ions as well as molecules.

Molecular Orbitals

When two or more atoms approach each other closely enough, pairs of valence shell electrons frequently fall under the influence of two, and sometimes more, nuclei. Electrons move to occupy new regions of space (new orbitals—molecular orbitals) that allow them to "see" the nuclear charge of multiple nuclei. When this activity results in a lower overall energy for all involved atoms, the atoms remain attached and a molecule has been formed. In such cases, we refer to the interatomic attractions holding the atoms together as covalent bonds. These molecular orbitals may be classified according to strict mathematical (probabilistic) determinations of atomic behaviors. For this discussion, the two most important classifications of this kind are *sigma* (σ) and *pi* (π). Though we may be oversimplifying a highly complex mathematics, it may help one to visualize sigma molecular orbitals as those that build up electron density along the (internuclear) axis connecting bonded nuclei, and pi molecular orbitals as those that build up electron density above and below the internuclear axis.



sigma molecular orbital



pi molecular orbital

Bonding Theories

This discussion will examine two approaches chemists have used to explain bonding and the formation of molecules, the molecular orbital (MO) theory and the valence bond (VB) theory. At their simplest levels, both approaches ignore nonvalence shell electrons, treating them as occupants of molecular orbitals so similar to the original (premolecular formation) atomic orbitals that they are localized around the original nuclei and do not participate in bonding. The two approaches diverge mainly with respect to how they treat the electrons that are extensively influenced by two or more nuclei. Though the approaches differ, they must ultimately converge because they describe the same physical reality: the same nuclei, the same electrons.

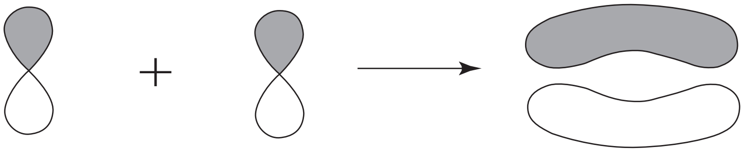
Molecular orbital theory. In MO theory, there are three types of molecular orbitals that electrons may occupy.

1. Nonbonding molecular orbitals. Nonbonding molecular orbitals closely resemble atomic orbitals localized around a single nucleus. They are called nonbonding because their occupation by electrons confers no net advantage toward keeping the atoms together.

2. Bonding molecular orbitals. Bonding molecular orbitals correspond to regions where electron density builds up between two, sometimes more, nuclei. When these orbitals are occupied by electrons, the electrons "see" more positive nuclear charge than they would if the atoms had not come together. In addition, with increased electron density in the spaces between the nuclei, nucleus-nucleus repulsions are minimized. Bonding orbitals allow for increased electron-nucleus attraction and decreased nucleus-nucleus repulsion, therefore electrons in such orbitals tend to draw atoms together and bond them to each other.

two *s* orbitals overlap

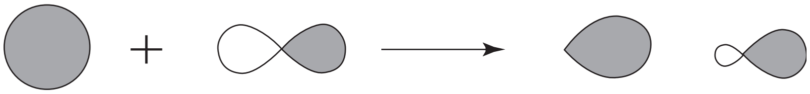
s and *p* orbitals overlap



two *p* orbitals overlap

3. Antibonding molecular orbitals. One antibonding molecular orbital is formed for each bonding molecular orbital that is formed. Antibonding orbitals tend to localize electrons outside the regions *between* nuclei, resulting in significant nucleus-nucleus repulsion—with little, if any, improvement in electron-nucleus attraction. Electrons in antibonding orbitals work against the formation of bonds, which is why they are called antibonding.

s orbitals overlap forming antibonding molecular orbital



s and *p* orbitals overlap forming antibonding molecular orbital

p orbitals overlap forming antibonding molecular orbital

According to MO theory, atoms remain close to one another (forming molecules) when there are more electrons occupying lower energy sigma and/or pi *bonding* orbitals than occupying higher energy antibonding orbitals; such atoms have a lower overall energy than if they had not come together. However, when the number of bonding electrons is matched by the number of antibonding electrons, there is actually a *dis*advantage to having the atoms stay together, therefore no molecule forms.

Valence bond theory. Valence bond (VB) theory assumes that atoms form covalent bonds as they share pairs of electrons via overlapping valence shell orbitals. A single covalent bond forms when two atoms share a pair of electrons via the sigma overlap of two atomic orbitals—a valence orbital from each atom. A double bond forms when two atoms share two pairs of electrons, one pair via a sigma overlap of two atomic orbitals and one via a pi overlap. A triple bond forms by three sets of orbital overlap, one of the sigma type and two of the pi type, accompanied by the sharing of three pairs of electrons via those overlaps. (When a pair of valence shell electrons is localized at only one atom, that is, when the pair is not shared between atoms, it is called a lone or nonbonding pair.)

Let us apply this greatly simplified picture of VB theory to three diatomic molecules: H_2, F_2, and HF. VB theory says that an H_2 molecule forms when a 1*s* orbital containing an electron that belongs to one atom overlaps a 1*s* orbital with an electron of opposite spin belonging to the other, creating a sigma molecular orbital containing two electrons. The two nuclei share the pair of electrons and draw together, giving both electrons access to the positive charge of both nuclei. Diatomic fluorine, F_2, forms similarly, via the sigma overlap of singly occupied 2*p* orbitals. The HF molecule results from the sharing of a pair of electrons whereby an electron in a hydrogen 1*s* orbital experiences sigma overlap with an electron in a fluorine 2*p* orbital.

Molecular Geometries

This VB approach allows us to return to the focus of our discussion. The geometry of a molecule or polyatomic ion is determined by the positions of individual atoms and their positions relative to one another. It can get very complicated. However, let us start with some simple examples and your imagination will help you to extend this discussion to more complicated ones. What happens when two atoms are bonded together in a diatomic molecule? The only possible geometry is a straight line. Hence, such a molecular geometry (or shape) is called "linear." When we have three bonded atoms (in a triatomic molecule), the three atoms may form either a straight line, creating a linear molecule, or a bent line (similar to the letter V), creating a "bent," "angular," "nonlinear," or "V-shaped" molecule. When four atoms bond together, they may form a straight or a zigzag line, a square or other two-dimensional shape in which all four atoms occupy the same flat plane, or they may take on one of several three-dimensional geometries (such as a pyramid, with one atom sitting atop a base formed by the other three atoms). With so many possibilities, it may come as a surprise that we can "predict" the shape of a molecule (or polyatomic ion) using some basic assumptions about electron-electron repulsions.

We start by recognizing that, ultimately, the shape of a molecule is the equilibrium geometry that gives us the lowest possible energy for the system. Such a geometry comes about as the electrons and nuclei settle into positions that minimize nucleus-nucleus and electron-electron repulsions, and maximize electron-nucleus attractions.

Modern computer programs allow us to perform complex mathematical calculations for multiatomic systems with high predictive accuracy. However, without doing all the mathematics, we may "predict" molecular geometries quite well using VB theory.

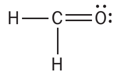
Valence shell electron pair repulsion approach. In the valence shell electron pair repulsion (VSEPR) approach to molecular geometry, we begin by seeing the valence shell of a bonded atom as a spherical surface. Repulsions among pairs of valence electrons force the pairs to locate on this surface *as far from each other as possible.* Based on such considerations, somewhat simplified herein, we determine where all the electron pairs on the spherical surface of the atom "settle down," and identify which of those pairs correspond to bonds. Once we know which pairs of electrons bond (or glue) atoms together, we can more easily picture the shape of the corresponding (simple) molecule.

However, in using VSEPR, we must realize that in a double or triple bond, the sigma and pi orbital overlaps, and the electrons contained therein, are located in the same basic region between the two atoms. Thus, the four electrons of a double bond or the six electrons of a triple bond are not independent of one another, but form coordinated "sets" of four or six electrons that try to get as far away from other sets of electrons as possible. In an atom's valence shell, a lone pair of electrons or, collectively, the two, four, or six electrons of a single, double, or triple bond each form a set of electrons. It is repulsions among *sets* of valence shell electrons that determine the geometry around an atom.

Consider the two molecules carbon dioxide (CO_2) and formaldehyde (H_2CO). Their Lewis structures are

$$:\ddot{O}=C=\ddot{O}:$$

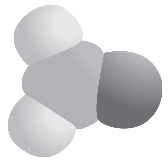
and

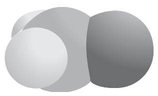


$$H-\underset{\displaystyle H}{\underset{|}{C}}=\ddot{O}:$$

In CO_2, the double bonds group the carbon atom's eight valence electrons into two sets. The two sets get as far as possible from each other by residing on opposite sides of the carbon atom, creating a straight line extending from one set of electrons through the carbon nucleus to the other. With oxygen atoms bonded to these sets of electrons, the oxygen–carbon–oxygen axis is a straight line, making the molecular geometry a straight line. Carbon dioxide is a linear molecule.

In H_2CO, the carbon atom's eight valence electrons are grouped into three sets, corresponding to the two single bonds and the one double bond. These sets minimize the repulsions among themselves by becoming as distant from one another as possible—each set pointing at a vertex of a triangle surrounding the carbon atom in the center. Attaching the oxygen and hydrogen atoms to their bonding electrons has them forming the triangle with the carbon remaining in the center; all four atoms are in the same plane. Formaldehyde has the geometry of a trigonal (or triangular) planar molecule, "planar" emphasizing that the carbon occupies the same plane as the three peripheral atoms.





COMMONLY ENCOUNTERED ELECTRON GEOMETRIES

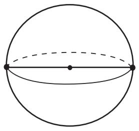
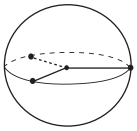
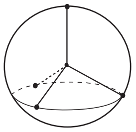
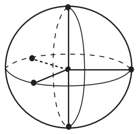
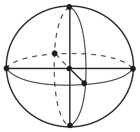
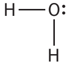
Number of Sets	Most Common "Set" Geometry	Appearance
2	Linear	
3	Trigonal (Triangular) Planar	
4	Tetrahedral	
5	Trigonal Pyramidal	
6	Octahedral	

Table 1.

We may extend this approach to central atoms with four, five, six, or even more sets of valence shell electrons. The most common geometries found in small molecules appear in Table 1.

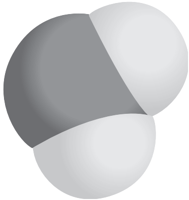
Until now, this article has focused on all the electrons in a central atom's valence shell, including sets not engaged in bonding. Though all such sets must be included in the conceptualization of the electron-electron repulsions, a molecule's geometry is determined solely by where its atoms are: A molecule's geometry is identified by what people would see if they could see atoms. In the carbon dioxide and formaldehyde examples, the molecules have the same overall geometries as the electron sets, because in both cases all sets are attached to peripheral atoms: Carbon dioxide is a linear molecule and formaldehyde is a trigonal (or triangular) planar one.

On the other hand, a water molecule (H_2O)

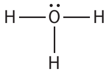


$$\begin{array}{rl} \mathrm{H}-\!\!\! & \ddot{\mathrm{O}}\!: \\ & | \\ & \mathrm{H} \end{array}$$

has four sets of electrons around the O atom (two lone pairs and those making up two sigma bonds) that assume a tetrahedral arrangement, but the molecular geometry as determined by the positions of the three atoms is a bent, or V-shaped, molecule, with a H–O–H angle approaching the tetrahedral angle of 109.5°.

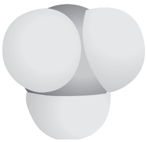


Similarly, a hydronium ion (H_3O^+)



$$\mathrm{H}-\underset{\underset{\mathrm{H}}{|}}{\ddot{\mathrm{O}}}-\mathrm{H}$$

has four sets of electrons around the central O atom (one lone pair and those making up three sigma bonds) in a tetrahedral arrangement, but the molecular geometry as determined by the four atoms is a trigonal (three-pointed base) pyramidal ion with the O atom “sitting” atop the three H atoms. The hydronium ion also has a H–O–H angle approaching the tetrahedral angle of 109.5°.



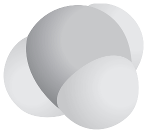
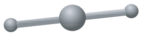
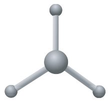
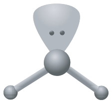
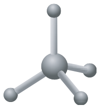
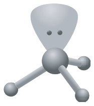
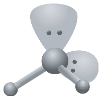


Table 2 outlines the most common molecular geometries for different combinations of lone pairs and up to four total sets of electrons that have assumed positions around a central atom, and the hybridizations (see below) required on the central atom.

Hybridization. Finally, what does valence bond theory say about the atomic orbitals demanded by VSEPR? For example, though the regions occupied by sets of electrons having a tetrahedral arrangement around a central atom make angles of 109.5° to one another, valence *p*-orbitals are at 90° angles.

To reduce the complex task of finding orbitals that “fit” VSEPR, we base their descriptions on mathematical combinations of “standard” atomic orbitals, a process called *hybridization;* the orbitals thus “formed” are *hybrid orbitals.* The number of hybrid orbitals is equal to the number of “standard” valence atomic orbitals used in the mathematics. For example, combining two *p*-orbitals with one *s*-orbital creates three unique and equivalent sp^2 (*s*-*p*-two) hybrid orbitals pointing toward the vertices of a triangle surrounding the atom.

ELECTRON SETS, HYBRIDIZATION AND MOLECULAR GEOMETRIES

Number of Electrons Sets	Electron "Set" Geometry	Number of Lone Pairs	Molecular Geometry	Hybridization	Appearance
2	Linear	–	Linear	sp	
3	Trigonal (Triangular) Planner	0	Trigonal Planar	sp^2	
		1	Bent or V-shaped		
		2	Linear		
4	Tetrahedral	0	Tetrahedral	sp^3	
		1	Trigonal Pyramid		
		2	Bent or V-shaped		
		3	Linear		

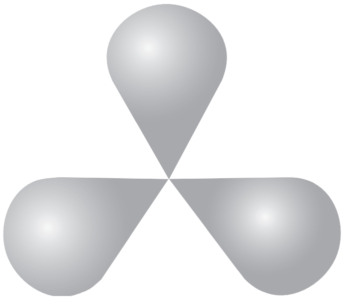


Table 2.

Valence electron sets (lone pairs and electrons in sigma bonds) are "housed," at least in part, in hybrid orbitals. This means that an atom surrounded by three electron sets uses three hybrid orbitals, as in formaldehyde. There, the central carbon atom uses hybrid orbitals in forming the C–H single bonds and the sigma portion of the C=O double bond. The carbon's remaining unhybridized *p*-orbital overlaps a *p*-orbital on the oxygen, creating the pi bond that completes the carbon-oxygen double bond. The H–C–O and H–C–H angles are 120°, as is found among sp^2 hybridized orbitals in general. The hybridizations required for two, three, and four electron sets are given in Table 2, along with their corresponding electron geometries. SEE ALSO ISOMERISM; LEWIS STRUCTURES; MOLECULES; NUCLEAR MAGNETIC RESONANCE.

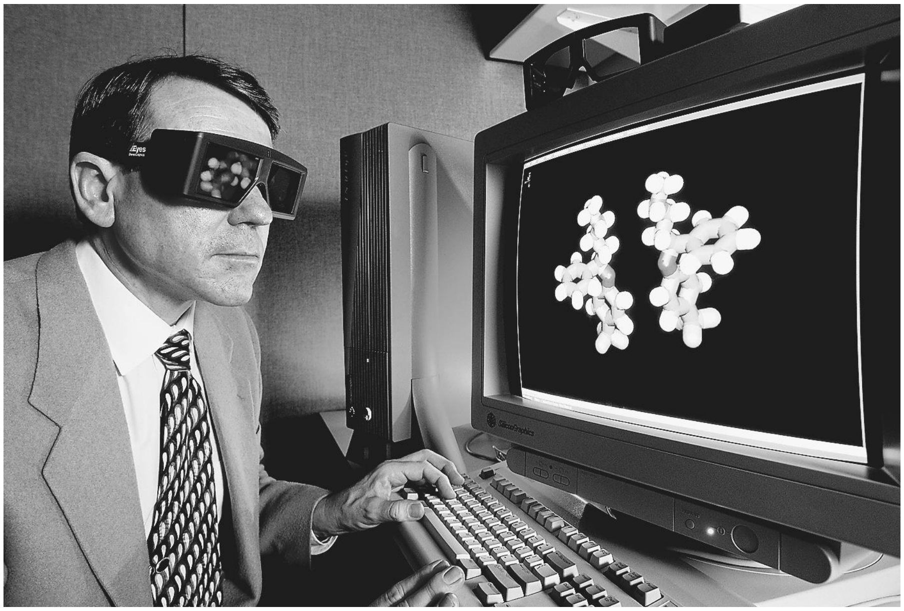
Mark Freilich

Molecular Modeling

A model is a semblance or a representation of reality. Early chemical models were often mechanical, allowing scientists to visualize structural features of molecules and to deduce the stereochemical outcomes of reactions. The disadvantage of these simple models is that they only partly represent (model) most molecules. More sophisticated physics-based models are needed; these other models are almost exclusively computer models.

Two major categories of physics-based, computational molecular models exist: macroscopic and microscopic. Macroscopic models describe the coarse-grained features of a system or a process but do not describe the atomic or molecular features. Microscopic or atomistic models take full account of all atoms in the system.

Atomistic modeling can be done in two ways: by applying theory or by using fitting procedures. The fitting procedures are attempts to rationalize connections between molecular structure and physicochemical properties (quantitative structure property relationships, QSPR), or between molecular structure and biological response (quantitative structure activity relationships, QSAR). Usually, a molecule's biological response is regressed onto a set of molecular descriptors.



Michael Chaney of Lilly Research Labs wearing 3-D glasses to view a computer model of Fluoxetine, or Prozac. The glasses dim and brighten in response to the flashing of the computer monitor.

$$\log(1/C) = b_0 + \sum_i b_i D_i$$

Here C is the minimum concentration of a compound that elicits a response to an assay of some sort (e.g., an LD$_{50}$, or something else), b$_0$ is a constant, b$_i$ is the least-squares multiple regression coefficient, and D$_i$ is the molecular descriptor. For example, the best model for determining the retention index (RI) of drug molecules on a gas-liquid **chromatography** column was found to be RI = 9.92 MW − 3.11 (number of ring atoms) + 139 (number of ring nitrogens) + 296 (total σ charge) + 921 Σ atomic IDs on nitrogen − 335 ^{6}XCH − 211 ^{3}XC − 49$^2\kappa_\alpha$ − 1958 (X and κ are topological and topographical descriptors). One can then predict an unknown drug's RI very accurately by substituting the values of the descriptors for that drug into the above equation. There are no rules about what kind of descriptors may or may not be used, but descriptors often include information about molecular size, shape, electronic effects, and lipophilicity. Microscopic modeling based on fitting methodologies requires the use of existing data to create a model. The model is then used to predict the properties or activities of as yet unknown molecules.

chromatography: the separation of the components of a mixture in one phase (the mobile phase) by passing it through another phase (the stationary phase) making use of the extent to which the components are absorbed by the stationary phase

The other approach to microscopic molecular modeling implements theory, and uses various sampling strategies to explore a molecule's potential energy surface (PES). Knowing a molecule's PES is convenient, because one can interpret directly from it the molecule's shape and reactivity. Popular modeling tools used for determining PES are shown in Figure 1.

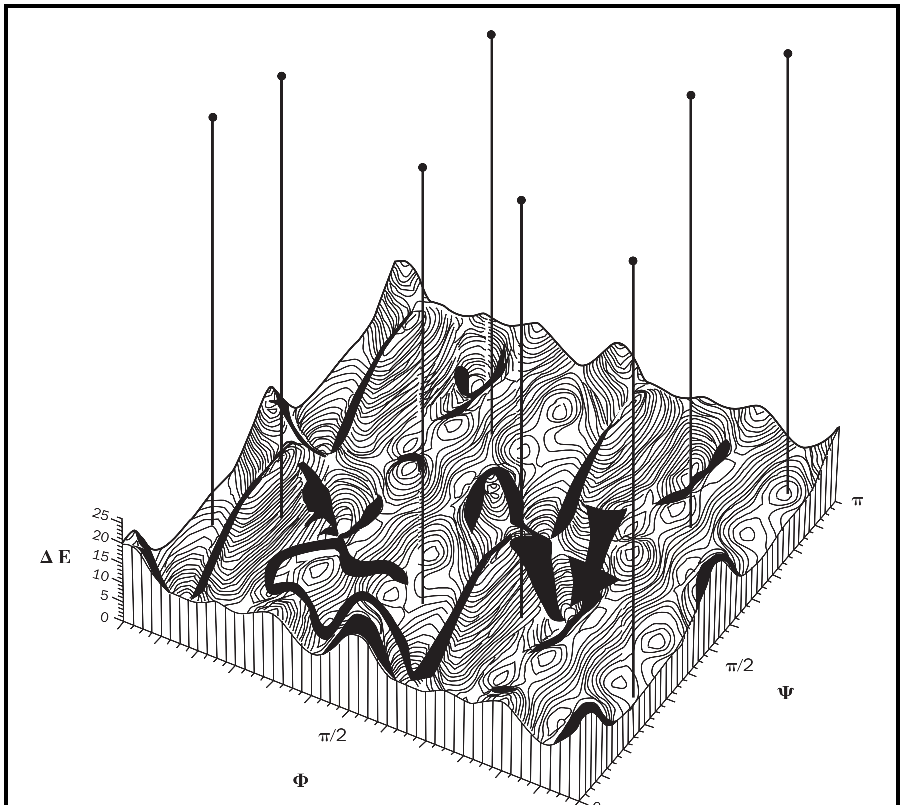


Figure 1. A PES illustrating the differences between modeling methods. Energy minimization is portrayed by the large black arrow. Only minima near the initially guessed structure are located. Monte Carlo methods randomly select many points on the PES (dropped lines), whereas Molecular Dynamics moves over the surface (winding line)

Quantum Mechanics (QM). The objective of QM is to describe the spatial positions of electrons and nuclei. The most commonly implemented QM method is the molecular orbital (MO) theory, in which electrons are allowed to flow around fixed nuclei (the Born-Oppenheimer approximation) until the electrons reach a self-consistent field (SCF). The nuclei are then moved, iteratively, until the energy of the system can go no lower. This energy minimization process is called geometry optimization.

Molecular Mechanics (MM). Molecular mechanics is a non-QM way of computing molecular structures, energies, and some other properties of molecules. MM relies on an empirical force field (EFF), which is a numerical recipe for reproducing a molecule's PES. Because MM treats electrons in an implicit way, it is a much faster method than QM, which treats electrons explicitly. A limitation of MM is that bond-making and bond-breaking processes cannot be modeled (as they can with QM).

Newtonian: based on the physics of Isaac Newton

Molecular Dynamics (MD). Energy-minimized structures are motionless and, accordingly, incomplete models of reality. In molecular dynamics, atomic motion is described with **Newtonian** laws: $F_i(t)=m_i a_i$, where the force F_i exerted on each atom a_i is obtained from an EFF. Dynamical properties of molecules can be thus modeled. Because simulation periods are typically in the nanosecond range, only inordinately fast processes can be explored.

Monte Carlo (MC). The same EFFs used in the MM and MD methods are used in the Monte Carlo method. Beginning with a collection of particles, the system's initial energy configuration is computed. One or more particles are randomly moved to generate a second configuration, whose energy is "accepted" for further consideration, or "rejected," based on energy criteria. Millions of structures on the PES are sampled randomly. Averaged energies and averaged properties are thus obtained.

Most atomistic modeling involves the exploration of a complex and otherwise unknown PES. Simple energy minimization with QM or MM locates a single, stable structure (the local minimum) on the PES, which may or may not be the most stable structure possible (the global minimum). MD and MC sampling methods involve a more complete searching of the PES for low energy states and, accordingly, are more time-consuming. SEE ALSO Quantum Chemistry; Theoretical Chemistry.

Kenneth B. Lipkowitz
Jonathan N. Stack

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Molecular Orbital Theory

The molecular orbital (MO) theory is a way of looking at the structure of a molecule by using *molecular* orbitals that belong to the molecule as a whole

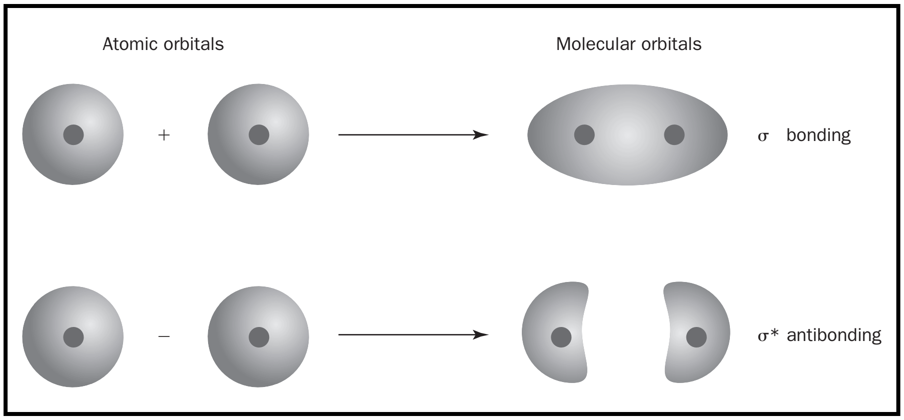


Figure 1. Combination of two 1*s* atomic orbitals to form a sigma bonding orbital or a sigma-starred antibonding orbital.

rather than to the individual atoms. When simple bonding occurs between two atoms, the pair of electrons forming the bond occupies an MO that is a mathematical combination of the wave functions of the atomic orbitals of the two atoms involved. The MO method originated in the work of Friedrich Hund and Robert S. Mulliken.

When atoms combine to form a molecule, the number of orbitals in the molecule equals the number of orbitals in the combining atoms. When two very simple atoms, each with one atomic orbital, are combined, two molecular orbitals are formed. One is a *bonding* orbital, lower in energy than the atomic orbitals, and derived from their sum. It is called *sigma.* The other is an *antibonding* orbital, higher in energy than the atomic orbitals, and resulting from their difference. It is called *sigma-starred* (σ^*). (See the diagram in Figure 1.)

The basic idea might best be illustrated by considering diatomic molecules of hydrogen and helium. The energy diagrams are shown in Figure 2. Each hydrogen atom has one 1*s* electron. In the H_2 molecule the two hydrogen electrons go into the lowest energy MO available, the sigma orbital. In the case of helium, each helium atom has two electrons, so the He_2 molecule would have four. Two would go into the lower energy bonding orbital, but the other two would have to go into the higher energy sigma-starred orbital.

Figure 2. Molecular orbital energy diagrams for (a) H_2 showing both electrons in the bonding sigma MO; and (b) He_2 in which two of the electrons are in the antibonding sigma-starred MO

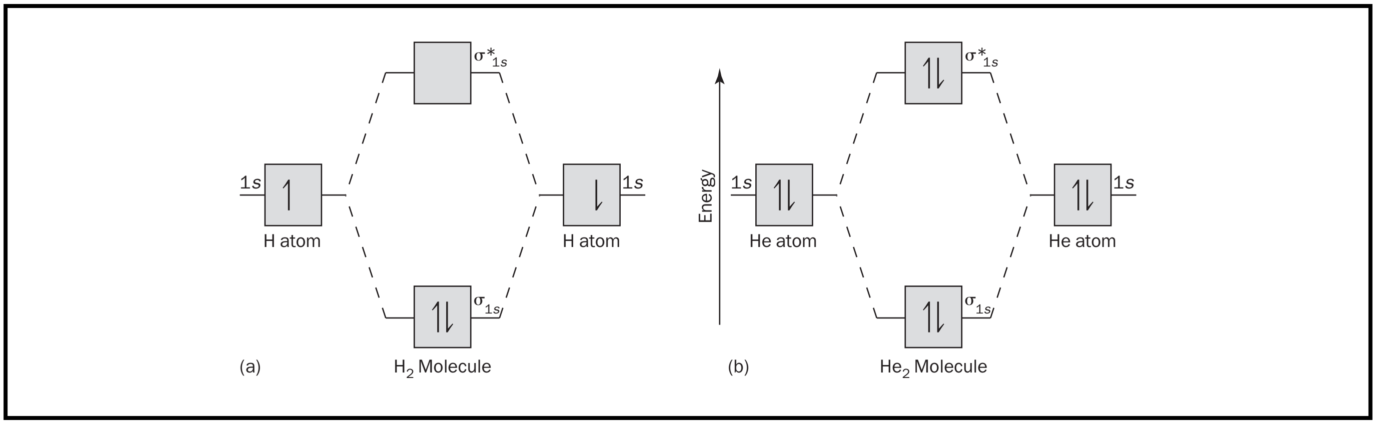
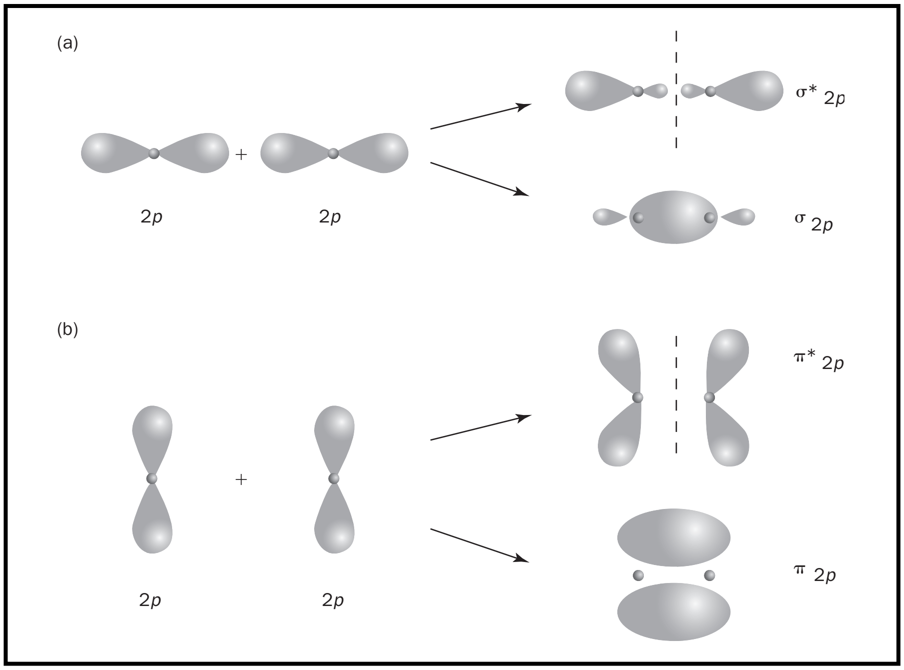


Figure 3. Combination of *p* atomic orbitals to form (a) sigma MOs by end-to-end interactions or (b) pi MOs by sideways interaction.



Bond Order

The bond order for a molecule can be determined as follows: bond order = $\frac{1}{2}$ (bonding electrons − antibonding electrons).Therefore, the H_2 molecule has a bond order of $\frac{1}{2}$ (2 − 0) = 1. In other words, there is a single bond connecting the two H atoms in the H_2 molecule. In the case of He_2, on the other hand, the bond order is $\frac{1}{2}$ (2 − 2) = 0. This means that He_2 is not a stable molecule.

Multiple Bonds

Double or triple bonds involve two or three pairs of bonding electrons. Single bonds are always sigma bonds, but in multiple bonds the first bond is sigma, while any second or third bonds are pi bonds. The overlap of *p* orbitals can yield either pi or sigma MOs, as shown in Figure 3. When they overlap end to end, they form sigma orbitals, but when they overlap side to side, they form pi orbitals.

Consider now the oxygen molecule. The Lewis structure for oxygen is :Ö::Ö: The double bond is necessary in order to satisfy the octet rule for both oxygen atoms. The measured bond length for oxygen supports the presence of a double bond. Yet we know that this Lewis formula cannot be the correct structure for oxygen because oxygen is paramagnetic, which means that the oxygen molecule must have unpaired electrons.

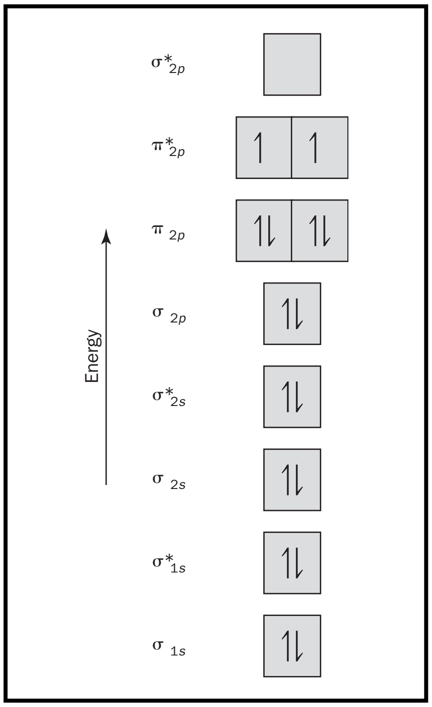


Figure 4. MO energy diagram for O_2. Eight electrons from each oxygen atom add up to 16 electrons in the O_2 molecule. They combine to form the molecular orbitals indicated above.

Look now at the MO diagram for oxygen, which is shown in Figure 4. It still indicates a bond order of 2 [$\frac{1}{2}$(10 − 6) = 2], but it also shows two unpaired electrons.

The MO theory also works well for larger molecules such as N_2O, CO_2, and BF_3 and for ions such as NO_3^- and CO_3^{2-}, in which the bonding MOs are delocalized, involving three or more atoms. It is especially useful for aromatic molecules such as benzene. In this case all six C atoms in the ring are equally involved in a delocalized pi electron cloud that envelops the entire molecule. The MO theory can even be extended to complex ions and to solids, including materials such as superconductors and semiconductors. SEE ALSO BONDING; LEWIS STRUCTURES; VALENCE BOND THEORY.

Doris K. Kolb

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Molecular Structure

The Rise and Reemergence of Atomism

Throughout history, humans have created models to help them explain the observed character of substances and phenomena in the material world. The ancient philosophers Democritus and **Lucretius** were among the first to speculate that matter was discontinuous, and that small, indivisible particles not only made up substances but also gave them their observed properties. The Greeks called these particles "atoms" (the English equivalent), a word that meant indivisible. Lucretius imagined that the particles that made up vapor had smooth surfaces and could not interconnect, giving vapors (gases) their extreme mobility. Liquids, on the other hand, were thought to be made up of particles, each particle having a few hooks. These few hooks would get entwined but would not immobilize the particles, thereby causing the particles to cling, yet still be fluid. The particles that made up solids, by contrast, were thought to have many hooks, resulting in the extremely sturdy nature of solid materials. The hypothesis of finite particles implied empty space between them. Yet, the majority of Greek philosophers did not believe that nothingness (the vacuums between particles) could exist, so the idea of atoms did not last long in the ancient times. Ironically, the objection was not to the existence of particles, but to the vacancies that must exist between them.

Lucretius: Roman poet of first century B.C.E., also known as Titus Carus; author of *De rerum natura*

Most cultures have linked properties of matter with religious and/or superstitious ideas. The term "gold" derives from an Old English word meaning "something shiny and yellow like the Sun"; it served not only as the name of the **metal** but also identified its properties. Polished gold nearly captures the sunlight it reflects, and the astronomical, astrological, medical, and religious attributes of the Sun were thought to be present in gold metal. For thousands of years, substances were said to contain essences or essential parts that gave them their characters. In a sense modern ideas about molecular structure do something similar. Chemists construct explanations for observed, **macroscopic phenomena** (e.g., reactivity) by describing the assemblages, shapes, and motions of submicroscopic particles.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

macroscopic phenomena: events observed with human vision unassisted by instrumentation

The theory of atoms did not reemerge until the seventeenth century. The discovery of elements rapidly led to the idea that nonelementary substances were made up of molecules that were, in turn, collections of elemental atoms. During the first years of chemical analyses, different substances were observed to have different compositions; the deduction was made that substances were different because their compositions were different. One type of mineral might be 34 percent iron and 66 percent oxygen. Each sample of that mineral would give the same results (34% iron and 66% oxygen). A different mineral, that is, one with different properties, might be 56 percent iron and 44 percent oxygen. Although there was still no concept of bonding between atoms or of molecular geometry at the beginning of the nineteenth century, chemists had developed the idea that different molecules were different collections of atoms.

Isomerism and the Development of Molecular Structural Models

elemental analysis: determination of the percent of each atom in a specific molecule

constitutional isomer: form of a substance that differs by the arrangement of atoms along a molecular backbone

Scientific theories are sometimes discarded. When information that contradicts a theory is reliable, the theory must be changed to fit the new data. As the **elemental analysis** of compounds expanded greatly during the early 1800s, observations that different substances were of the same elemental composition were inevitable. In his *History of Chemistry* (1830), Thomas Thomson drew illustrations of varying hypothetical particle arrangements, using symbols that were used at that time (those of John Dalton), as a way to explain why two acids of the same elemental composition could have different physical and chemical properties (see Figure 1). These are believed to be the earliest recorded representations of molecular structure that showed varying arrangements of the same atoms; the phenomenon would soon be called isomerism (from the Greek *iso*, meaning same, and *meros*, meaning part). In 1828 Friedrich Wöhler (1800–1882) synthesized urea, $(NH_2)_2C{=}O$ or CH_4N_2O, that was indistinguishable from that that had been isolated from urine. He prepared this organic substance from the clearly inorganic (mineralogical) starting material ammonium cyanate, $NH_4(+)\ NCO(-)$, also CH_4N_2O, the result of the combination of ammonium chloride and silver cyanate. Urea and ammonium cyanate are **constitutional isomers**, and together illustrate the fact that fixed arrangements of atoms, molecular structures, must be invoked to explain observed phenomena.

The constitution of a molecule (number of, kind of, and connectivities of atoms) may be represented by a two-dimensional "map" in which the interatomic linkages (bonds) are drawn as lines. There are two constitutional isomers that are represented by the molecular formula C_2H_6O: ethanol and dimethyl ether. The differences in connectivities, which are not evident in the common constitutional inventory C_2H_6O, can be conveyed by typographical line formulas (CH_3CH_2OH for ethanol and CH_3OCH_3 for dimethyl ether), or by structural representations (see Figure 2). As the number and kinds of atoms in substances increase, the number of constitutional isomers increases.

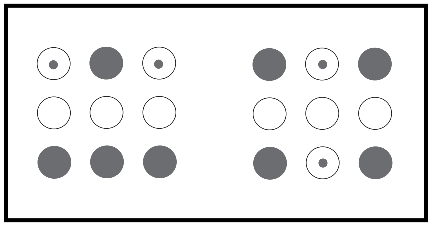
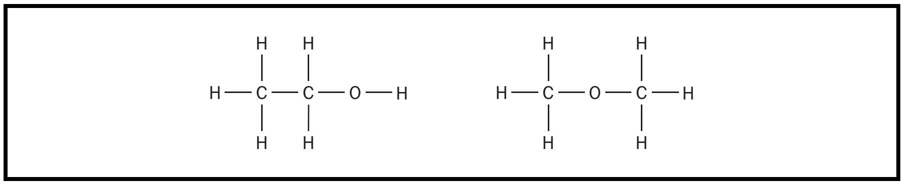


Figure 1. Early representations for isomers using Daltonian symbols.

By the mid-1850s, a new theory of molecular structure had emerged. Given a unique collection of atoms, it was not the identities of the atoms that distinguished one molecule from another, but rather the connectivity,



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & O - H \\ & & | & & | & & \\ & & H & & H & & \end{array} \qquad \begin{array}{ccccccc} & & H & & & & H \\ & & | & & & & | \\ H & - & C & - & O & - & C - H \\ & & | & & & & | \\ & & H & & & & H \end{array}$$

Figure 2. Structural representations for ethanol (CH_3CH_2OH) and dimethyl ether (CH_3OCH_3)

or bonding, of those atoms. The nature of the chemical bond was unknown, and the phenomenon of chemical bonding was described as "chemical affinity." Because it was observed that the passing of electricity through some substances, such as water, could "break" the molecules apart into their elements (electrolysis), the electrostatic attractions of charged particles (ions) were used to contribute to an explanation of chemical affinity. Just as the hypothesis of the varying connectivities of atoms emerged as a response to observations that could not be explained, variation in the three-dimensional arrangements of atoms in space was proposed to reconcile other observed phenomena. Jacobus van't Hoff (1852–1911) and Joseph-Achille Le Bel (1847–1930) proposed (independently of one another, in 1874) that molecules of the same connectivity yet different physical properties (e.g., optical activity) might be explained if, in the case of four different particles, the arrangement (configuration) of the particles was tetrahedral. Macroscopically or microscopically, a tetrahedral array of four different things gives rise to two and only two different arrangements that are nonsuperimposable mirror images (enantiomers; see Figure 3). Distinct molecular structural units that have the same connectivities but varying three-dimensional arrangements are also isomers. The term "stereoisomer" was introduced by Viktor Meyer in 1888 to describe molecules that differ only in their three-dimensional arrangements.

Connectivity and stereoisomerism give chemists a way to uniquely differentiate one molecular structure from another. The molecular formula C_4H_9Br, for instance, represents five different substances (see Figure 4). Predictably, although there is only one compound for each of the connectivities designated 1-bromobutane, 2-bromo-2-methylpropane, and 1-bromo-2-methylpropane, there are two compounds represented by the connectivity designated 2-bromobutane (carbon 2 has four different groups attached, and thus two three-dimensional arrangements of the molecule, whose geometries are labeled *R* and *S*, exist). There are no other isomers of C_4H_9Br that are predicted, and none that are observed.

Although the arrangement of molecular atoms around a given point is fixed, molecules are not static objects. The sequence of links in a chain, for instance, is constant, but the chain can be twisted and knotted into countless shapes. In the case of a molecule, twists do not affect the identity of a substance, but the overall molecular shape is part of molecular structure and can have an impact on the observed properties. According to Ernest Eliel and Samuel Wilen (1994, p. 102), *configurational stereoisomers* result from "arrangements of atoms in space of a molecule with a defined constitution, without regard to arrangements that differ only by rotation about one or more single bonds, providing that such a rotation is so fast as not to allow isolation of the species so differing." Conformational stereoisomers are

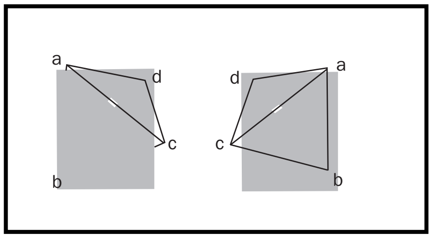
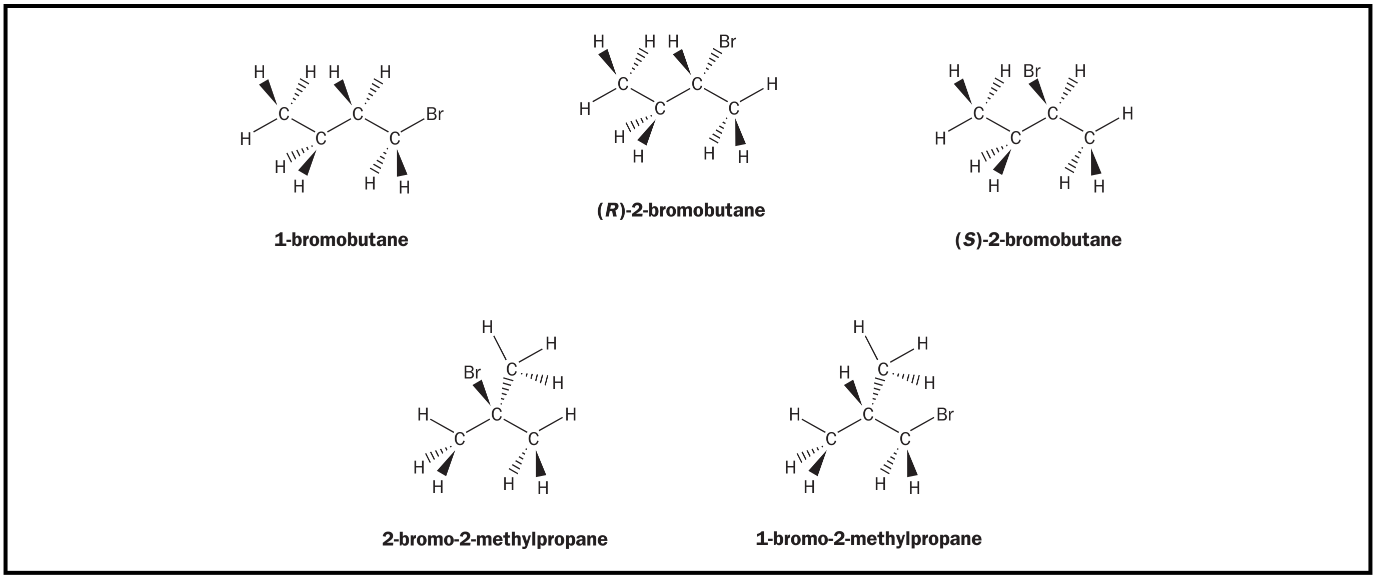


Figure 3. Tetrahedral arrays of four different objects create enantiomorphic shapes.



1-bromobutane

(*R*)-2-bromobutane

(*S*)-2-bromobutane

2-bromo-2-methylpropane

1-bromo-2-methylpropane

Figure 4. Structural representations for the five different C_4H_9Br molecules.

molecular shapes resulting from bond rotations that do not affect **molecular identity**. The drawings shown in Figure 5 represent some of the different conformational shapes that the single molecule (*S*)-2-bromobutane can assume.

molecular identity: "fingerprint" of a molecule describing the structure

The overall geometry of a molecule was recognized as contributing to its chemical reactivity in the 1950s, and methods used to determine molecular structure have grown dramatically since that time. Throughout the early 1900s, direct experimental evidence of the three-dimensional arrangements of atoms was becoming available as a result of x-ray diffraction crystallography. **Nuclear** magnetic resonance **spectroscopy** (first used in the 1960s) and atomic force microscopy (in the 1980s) are two techniques of many that are now used to gather experiment-based information about molecular structure. What might have taken years to determine in 1950, and what was impossible to know about extremely large biopolymers (e.g., **DNA**, enzymes, and polysaccharides at a cell surface) as late as 1990 can now sometimes be determined in a matter of seconds.

nuclear: having to do with the nucleus of an atom

spectroscopy: use of electromagnetic radiation to analyze the chemical composition of materials

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

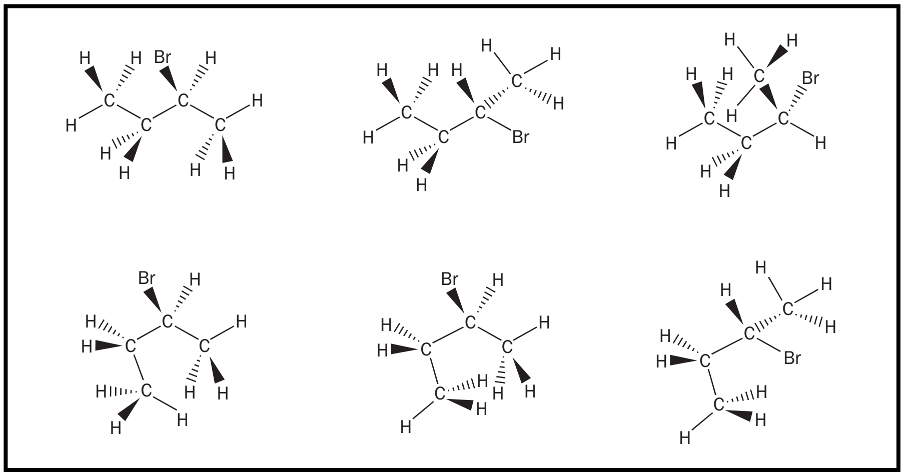


Figure 5. Conformational isomers of (*S*)-2-bromobutane.

Molecular environment influences molecular structure. The shape that a molecule assumes within a **crystal lattice** is necessarily different from its shape in water and will vary according to solvent and other environmental factors (e.g., temperature and pH). Beginning in the late 1980s the significance of the **noncovalent aggregation** of large numbers of molecular entities began to be understood. A protein, for instance, folds into its three-dimensional shape because water is present; without water, the shape is quite different. Thus, molecular structure is determined by a combination of extrinsic as well as intrinsic factors. The field of molecular structure and reactivity that deals with large aggregations of molecules and how they influence each other is called supramolecular chemistry.

crystal lattice: three-dimensional structure of a regular solid

noncovalent aggregation: nonspecific interaction leading to the association of molecules

Molecular Structural Theory

The electron was discovered in 1900, and it took about twenty years for the electronic nature of the chemical bond to come into wide acceptance. Particle-based models for atomic and molecular structure soon gave way to the **quantum mechanical** view, in which electrons are not treated as localized, discrete particles (electrons orbiting around a nucleus), but as **delocalized** areas of wavelike charge, each possessing a given probability of being found in a given location near an atomic nucleus (an orbital). The chemical bonding in molecules, which began the twentieth century as shared electron pairs between atoms, evolved to become a matter of molecular orbitals. Molecular orbitals describe three-dimensional arrangements of the atomic nuclei in a molecule and the probability that any given electron of a given energy will occupy a given location with respect to those nuclei. Single bonds are explained by the overlap of **atomic orbitals** along the **internuclear** axis of two atoms. Multiple bonds are the combination of sigma plus pi bonding, the latter corresponding to the overlap of atomic orbitals that is not along the internuclear axis. A rough guide to the bonding molecular orbitals in methane is depicted in Figure 6. The eight **valence** shell electrons (four from carbon, four from the four hydrogens) are

quantum mechanical: theoretical model to describe atoms and molecules by wave functions

delocalized: of a type of electron that can be shared by more than one orbital or atom

atomic orbital: mathematical description of the probability of finding an electron around an atom

internuclear: distance between two nuclei

valence: combining capacity

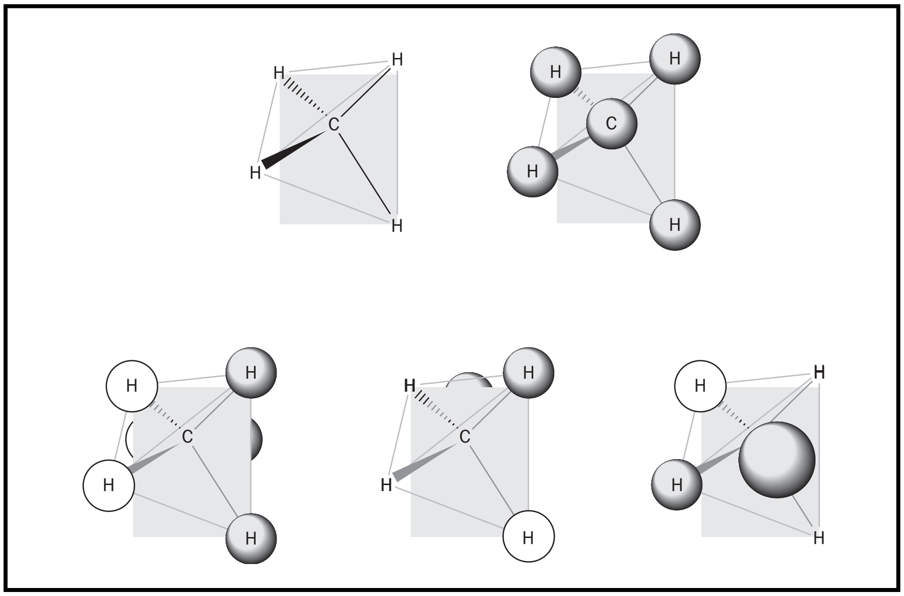


Figure 6. Representations for the bonding molecular orbitals in methane.

distributed among four molecular orbitals. One of the four orbitals is composed of favorable bonding interactions between the 2*s*-orbital of carbon and the four 1*s*-orbitals of the hydrogen atoms, whereas the other three are the equally likely combinations of one of the three 2*p*-orbitals of carbon and the 1*s* orbitals of hydrogen atoms. Computer-based models for chemical bonding are as important to modern molecular structural theory as experimental measurements. SEE ALSO Isomerism; Le Bel, Joseph-Achille; Molecules; Nuclear Magnetic Resonance; van't Hoff, Jacobus; Wöhler, Friedrich.

Brian P. Coppola

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Molecules

A molecule is the smallest entity of a pure compound that retains its characteristic chemical properties, and consequently has constant mass and atomic composition. It is an assembly of nonmetallic atoms held together into specific shapes by **covalent bonds**. As much as a car is a single unit made up of many parts, a molecule is a unit made up of atoms bonded around each other in certain fixed geometries. Shapes influence the physical and chemical properties and consequently much of the chemistry of a molecule.

covalent bond: bond formed between two atoms that mutually share a pair of electrons

While molecules may be monoatomic (such as the **inert** gases helium, neon, or krypton), most molecules are diatomic, triatomic, or polyatomic, consisting of two or more atoms (some molecules may be a collection of thousands of atoms). A diatomic molecule may be **homonuclear** (e.g., O_2 or N_2) or **heteronuclear** (e.g., CO or NO). Similarly, a triatomic molecule may be homonuclear (e.g., O_3) or heteronuclear (e.g., HCN).

inert: incapable of reacting with another substance

homonuclear: having identical nuclei

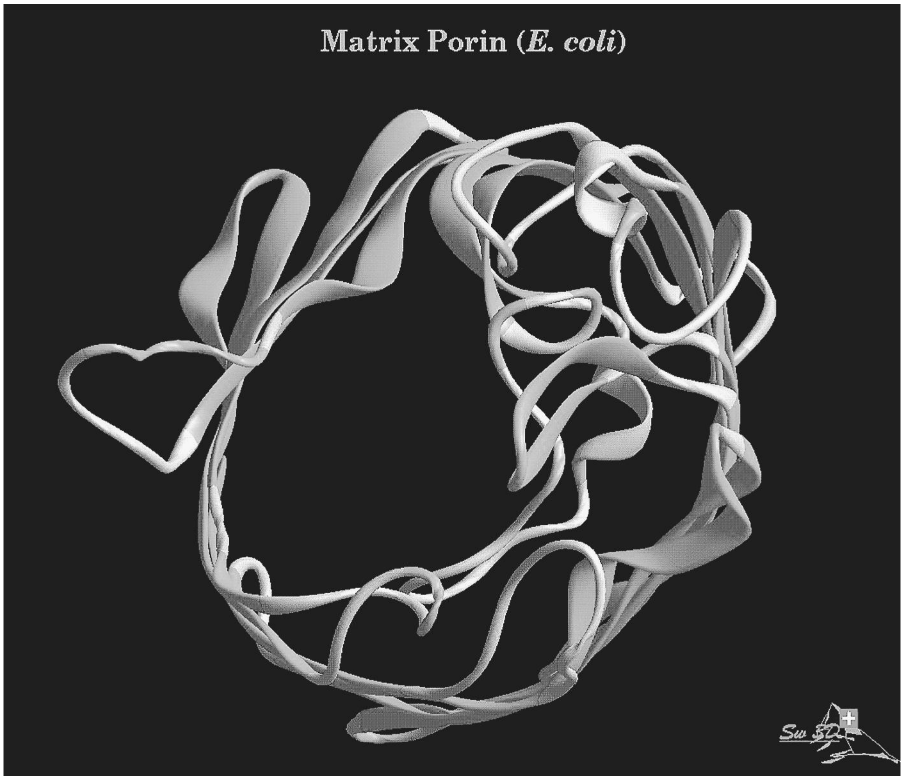
heteronuclear: having different nuclei

The modern concept of the covalent bond has resulted in the ability to predict the geometry and hence the properties of matter such as reactivity, toxicity, and solubility. A fundamental challenge in chemistry is to determine the arrangement of atoms in a molecule in order to elucidate its bonding, geometry, and properties.

Historical Development

Since Roman times matter had been viewed by some as discrete particles somehow linked together. Early in the eighteenth century the behavior of gases was viewed as a function of **kinetic theory**. Kinetic theory is a group of assumptions to explain the behavior of gases. Among these assumptions are that gases are individual molecules moving in straight lines, that they do not react chemically and occupy essentially no volume compared to the volume between molecules. In 1805 English chemist and physicist John Dalton (1766–1844) proposed that atoms form compounds by joining together in simple, whole numbers. In 1811 Italian chemist Amedeo Avogadro (1776–1856) solidified the distinction between molecules and atoms by proposing that, at constant temperature and pressure, equal volumes of all

kinetic theory: theory of molecular motion



A three-dimensional computer model of a protein molecule of matrix porin found in the *E. coli* bacteria.

gases contain equal numbers of molecules. While Avogadro's theory was published, it was ignored by the scientific community until 1858, when it was revived by Italian chemist Stanislao Cannizzaro (1826–1910), thereby reconciling many inconsistencies chemists were observing. During this same time, valency (the combining capacity of an atom) was defined as the number of hydrogens an atom can combine with.

Initially the structure of molecules was studied using chemical methods, thereby identifying composition, chemical reactions, and the existence of **isomers**. It was understood that bonds had direction, rigidity, and a certain degree of independence from molecule to molecule. The discovery of the electron in 1897 by English physicist Joseph John Thomson (1856–1940) immediately linked electrons with covalent bonding. Though attacked vigorously for his views, Dutch physical chemist Jacobus Hendricus van't Hoff (1852–1911) discarded the flat-molecule model in favor of geometric relations within each molecule. His brilliant postulate of the tetrahedral arrangement of carbon (proposed simultaneously, but independently, by French chemist Joseph-Achille Le Bel [1847–1930]) was a major breakthrough for chemistry. Later in the nineteenth century the advent of physical methods of investigation led to a great deal of additional information regarding atomic configuration.

isomer: molecules with identical compositions but different structural formulas

Danish physicist Niels Bohr (1885–1962) proposed a quantum theory of the hydrogen atom by suggesting that the electron moves about its nucleus in discrete **quanta** (the energies of electrons are restricted to having only certain values, quanta, much as stairs do as opposed to a ramp), establishing a balance between the electron's centrifugal force and its **attraction** for the nucleus. It was not until 1927 that covalent bonding was properly

quantum: smallest amount of a physical quantity that can exist independently, especially a discrete amount of electromagnetic energy

attraction: force that brings two bodies together, such as two oppositely charged bodies

understood, thanks to the contributions of American physical chemist Gilbert N. Lewis (1875–1946), American physicist Edward Uhler Condon (1902–1974), German physicist Walter Heitler (1904–1981), and German physicist Fritz London (1900–1954).

In his 1916 paper *The Atom and the Molecule*, Lewis proposed that a chemical (covalent) bond between two atoms involves the sharing of electrons between the nuclei. Thus a single bond (for hydrogen, H-H) results when an electron from each atom forms an electron pair that is shared between the two nuclei (H:H); a double bond involves two electrons from each atom (e.g., the carbon-carbon bond in $(H:)_2C::C(:H)_2$); and a triple bond involves three electrons from each atom (e.g., the carbon-carbon bond in H:C:::C:H). Such representations are referred to as Lewis dot structures. Lewis further postulated that an electron octet (and in a few cases an electron pair) forms a complete shell of electrons with spatial rigidity and chemical inertness—hence a stable arrangement.

American chemist Irving Langmuir (1881–1957) proposed that many chemical facts could be coordinated by applying these new ideas. Others followed by suggesting that a bond is a balance between nucleus-nucleus and electron-electron repulsions and electron-nuclei attractions. American chemist Linus Pauling (1901–1994) assembled these ideas in his seminal book, *The Nature of the Chemical Bond.*

Valence Shell Electron Pair Repulsion Theory

Molecular geometries are determined by the number and locations of valence electrons around the atoms. Both bonded and lone pair electrons repel each other, staying as far apart as possible, thereby causing the molecule to occupy specific shapes (much as balloons assume fixed arrangements when tied together). These geometries are important in determining chemical properties. One method for determining the structure of covalent molecules is the valence shell electron pair repulsion (VSEPR) method, proposed in 1957 by Canadian chemist Ronald Gillespie and Australian chemist Ronald Nyholm in a classic paper titled "Inorganic Stereochemistry." The theory states that the geometry around a given atom is a function primarily of minimizing the electron pair repulsions. The key postulates of the VSEPR theory are:

- All electrons are negatively charged.
- Bonds are electron groups.
- Lone pair and bonded electrons (and therefore bonds) repel each other.

Geometries of most covalent molecules may be determined by following these steps:

- Determine the central atom. This may be the atom present singly (e.g., B in BF_3), the larger atom (e.g., P in $POCl_3$), the atom written in the center (e.g., C in HCN), or the atom with the largest number of bonds (e.g., C in Cl_2CO).
- Determine the number of bonds needed for each atom to be bonded to the central atom and write the corresponding Lewis dot structure. Thus, for Cl_2CO, each chlorine needs a single bond and oxygen needs

GEOMETRIES OF MOLECULES WITH VARIOUS BONDED ELECTRON GROUPS

Electron Groups About the Central Atom	Example	Shape
2	$BeCl_2$	linear
3	BCl_3	trigonal planar
4	CH_4	tetrahedral
5	PF_5	trigonal bipyramidal
6	SF_6	octahedral

Table 1. Geometries of molecules with various bonded electron groups

two bonds; the Lewis dot structure would be $(Cl:)_2C::O$. Note that a single bond needs a pair of electrons (one group), a double bond needs two pairs (also one group), and a triple bond needs three pairs (still just one group, since it points in one direction only).

- Count the total number of bonded and lone pair electron groups about the central atom. For Cl_2CO it would be three (all bonded) groups. In the case of $:NH_3$ it would be one lone pair group and three bonded groups for a total of four groups.
- Establish the best electronic (counting all electron groups) and molecular (counting only bonded groups) geometries. Table 1 summarizes this information for bonded groups.

The **trigonal bipyramidal** shape merits a special note. Contrary to the other shapes, it possesses two types of bonds: the two **axial bonds** located at 180° from each other, and the three **equatorial bonds** located perpendicularly to the axis and at 120° from each other.

trigonal bipyramidal: geometric arrangement of five ligands around a central Lewis acid, with ligands occupying the vertices of two trigonal pyramids that share a common face; three ligands share an equatorial plane with the central atom, two ligands occupy an axial position

axial bond: covalent bond pointing along a molecular axis

equatorial bond: covalent bond perpendicular to a molecular axis

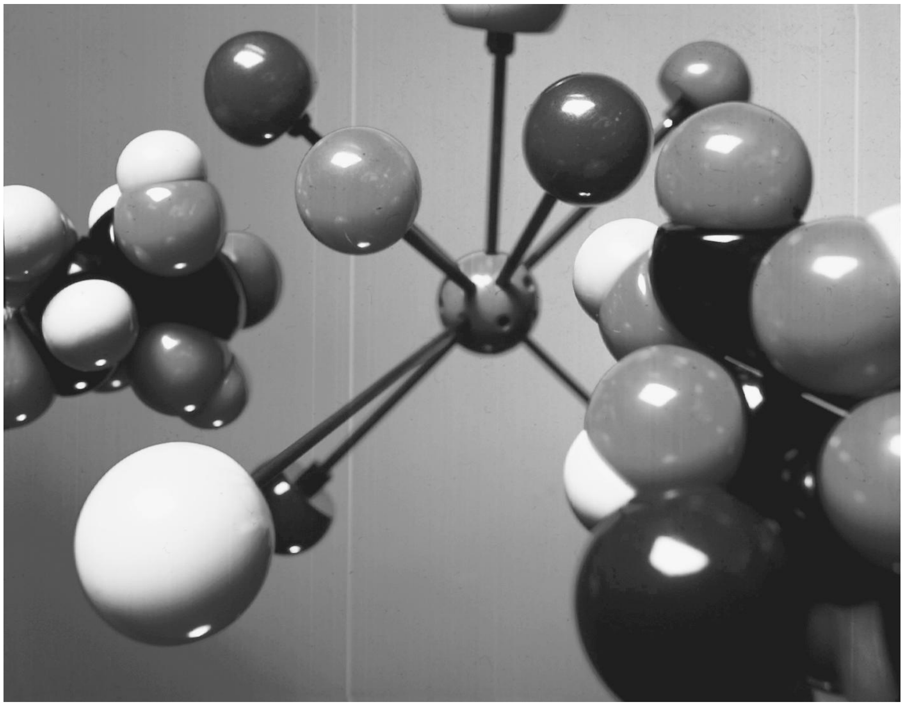
Each of the examples given in Table 1 has only bonded electrons around its central atom. The existence of lone pair electrons has an effect on the geometry, as seen in Table 2.

For example, water (H_2O) has two bonded and two lone pair valence electrons about the central atom, oxygen. Its electronic geometry, determined by four total groups, is tetrahedral, and its molecular geometry (meaning the H-O-H shape) is bent. Similarly, the $:NH_3$ molecule has three

Table 2. Electronic and molecular geometries of covalent molecules with bonded and lone pair electrons about the central atom

ELECTRONIC AND MOLECULAR GEOMETRIES OF COVALENT MOLECULES WITH BONDED AND LONE PAIR ELECTRONS ABOUT THE CENTRAL ATOM

Electron Groups About the Central Atom			Shape	
Bonded	Lone Pair	Example	Electronic	Molecular
1	1	TlCl	linear	linear
1	2	BiCl	trigonal	linear
1	3	HCl	tetrahedral	linear
2	1	$SnCl_2$	trigonal	bent
2	2	H_2O	tetrahedral	bent
2	3	XeF_2	trigonal bipyramidal	linear
3	1	PCl_3	tetrahedral	pyramidal
3	2	BrF_3	trigonal bipyramidal	T-shaped
4	1	SF_4	trigonal bipyramidal	distorted tetrahedral
4	2	XeF_4	octahedral	square planar
5	1	$XeOF_4$	octahedral	pyramidal



Models representing the arrangement of atoms in a chemical molecule.

bonded and one lone pair electron groups about nitrogen, giving an electronic geometry that is nearly tetrahedral, and a molecular geometry that is **pyramidal**. Because two bonded pairs repulse less than a bonded pair and a lone pair, which in turn repulse less than two lone pairs, the H-O-H bond angle in water is not 109.5° as expected for a tetrahedron, but 104.5°, with the H-O bonds having been pushed by the lone pairs toward each other. For the trigonal bipyramidal shape, lone pairs always occupy equatorial planar positions. Thus, the molecular geometry of BrF_3 is T-shaped, rather than trigonal planar.

pyramidal: relating to a geometric arrangement of four electron-donating groups at the four vertices of a pyramid

Properties

Both physical and chemical properties are affected by the geometry of a molecule. For instance, the polarity of a molecule is determined by the electronegativity differences of its atoms (electronegativity is the ability of an atom in a molecule to draw electrons toward itself), and the relative geometries of the atoms within the molecule. The molecule BCl_3, for example, displays a flat triangle (120°) with each Cl atom pulling electrons symmetrically, making the molecule **nonpolar**. In the pyramidal molecule PCl_3, however, all chlorines are pulling electrons more or less to one side, making the molecule polar. Since polarity goes hand in hand with solubility, CF_4 is a nonpolar tetrahedral molecule not soluble in water, whereas SF_4, a distorted tetrahedron, is instantly hydrolyzed by water.

nonpolar: molecule, or portion of a molecule, that does not have a permanent, electric dipole

Chemical properties are also very dependent on geometries. For example, in the square planar molecule $Pt(NH_3)_2Cl_2$, the chloro (and hence the ammonia) **ligands** may be placed adjacent to each other (cis isomer), or they may be opposite each other (trans isomer). In addition to having different physical properties, their chemical reactivities are also quite remarkable. The cis isomer is an effective treatment of testicular, ovarian,

ligand: molecule or ion capable of donating one or more electron pairs to a Lewis acid and certain other cancers, whereas the trans isomer is ineffective. Similarly, the linear, nonpolar CO_2 molecule is inert, whereas the polar CO molecule is a poison.

Other Theories

The VSEPR theory allows chemists to successfully predict the approximate shapes of molecules; it does not, however, say why bonds exist. The **quantum mechanical** valence bond theory, with its overlap of **atomic orbitals**, overcomes this difficulty. The resulting hybrid orbitals predict the geometries of molecules. A quantum mechanical graph of radial electron density (the fraction of electron distribution found in each successive thin spherical shell from the nucleus out) versus the distance from the nucleus shows maxima at certain distances from the nucleus—distances at which there are higher probabilities of finding electrons. These maxima correspond to Lewis's idea of shells of electrons.

quantum mechanical: theoretical model to describe atoms and molecules by wave functions

atomic orbital: mathematical description of the probability of finding an electron around an atom

This theory, however, treats electrons as localized, does not account for unpaired electrons, and does not give information on bond energies. The molecular orbital theory attempts to solve these shortcomings by considering nuclei arranged as in a molecule and determining the resulting molecular orbitals when electrons are fed in one by one.

The electronic and molecular geometries of covalent molecules, and hence their resulting polarities, can thus be predicted fairly accurately. Armed with these tools, one can predict whether or not a molecule should be soluble, reactive, or even toxic. SEE ALSO Bonding; Avogadro, Amedeo; Bohr, Niels; Cannizzaro, Stanislao; Dalton, John; Le Bel, Joseph-Achille; Lewis, Gilbert N.; Lewis Structures; Pauling, Linus; Thomson, Joseph John; van't Hoff, Jacobus.

Erwin Boschmann

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Molybdenum

42
Mo
MOLYBDENUM
95.94

MELTING POINT: **2,623°C**
BOILING POINT: **4,639°C**
DENSITY: **10.22 g/cm^3**
MOST COMMON IONS: **Mo^{3+}, $Mo_2(OH)_2^{4+}$, $M_2O_4^{2+}$**

Molybdenum is a hard, silver-white **metal** discovered by Swedish chemist Carl Wilhelm Scheele in 1778. Scheele had been researching a mineral called molybdenite, which many suspected of containing lead (the Greek word *molybdos* means "lead"). He instead found that it contained a new element

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

which he named "molybdenum" after the mineral. Molybdenum was first isolated by Swedish mineralogist Peter Jacob Hjelm in 1782.

Molybdenum has an abundance in Earth's crust of approximately 1.1 parts per million (ppm) or 1.2 milligrams per kilogram. Its chief source is the mineral molybdenite (MoS_2), but it is also found in the ores wulfenite ($PbMoO_4$) and powellite ($CaMoO_4$) or obtained as a by-product of copper mining. The leading producers of molybdenum are the United States, Canada, Chile, Mexico, Peru, China, Russia, and Mongolia.

isotope: form of an atom that differs by the number of neutrons in the nucleus

There are seven known **isotopes** of molybdenum that occur naturally: ^{92}Mo, ^{94}Mo, ^{95}Mo, ^{96}Mo, ^{97}Mo, ^{98}Mo, and ^{100}Mo. Their natural abundances range from 9.25 percent (^{94}Mo) to 24.13 percent (^{98}Mo). Common compounds of molybdenum include molybdenum disulfide (MoS_2), molybdenum trioxide (MoO_3), molybdic acid (H_2MoO_4), molybdenum hexafluoride (MoF_6), and molybdenum phosphide (MoP_2).

alloy: mixture of two or more elements, at least one of which is a metal

Molybdenum's melting point (2,623°C, or 4,753.4°F) exceeds that of steel by 1,000°C (1,832°F) and that of most rocks by 500°C (932°F). For this reason, the element is used in various **alloys** to improve strength, particularly at high temperatures. Approximately 75 percent of molybdenum produced is used by the iron and steel industries. The element is also utilized to make parts for furnaces, light bulbs, missiles, aircraft, and guns. Molybdenum disulfide is used as a high temperature lubricant. SEE ALSO Coordination Compounds; Inorganic Chemistry; Scheele, Carl.

Stephanie Dionne Sherk

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Monosaccharides ***See Carbohydrates.***

Morgan, Agnes Fay

AMERICAN CHEMIST AND NUTRITIONIST
1884–1968

Born in Peoria, Illinois, on May 4, 1884, Agnes Fay Morgan excelled in high school and studied chemistry at the University of Chicago. After receiving a master of science in chemistry in 1905, she spent the next several years teaching at various colleges across the United States. She returned to the University of Chicago in 1914 to obtain a Ph.D. in chemistry.

In 1915 Morgan was appointed assistant professor of nutrition in the Department of Home Economics at the University of California at Berkeley. Her shift in focus from chemistry to nutrition was a result of the limited professional opportunities available to female chemists at the time. In 1919 Morgan became associate professor of household science, and in 1923 she was promoted to full professor.

As chairperson of the department, Morgan worked vehemently to change the prestige of home economics. She strove to establish a scientific basis for the field, which was generally perceived as the course of study in which young women learned how to become proficient wives and mothers. Under her leadership, the home economics curriculum at Berkeley became largely science-based, with strict requirements. It was not until 1960, however, that her efforts to change the name of the department to better define its work were successful. At that time, six years after her retirement, the department was renamed the Department of Nutritional Sciences.

Throughout the course of her career, Morgan published more than 250 papers on topics with far-reaching effects. Her research would become the foundation for understanding the nutritional effects of many **vitamins**. It also established that certain vitamin deficiencies can lead to health problems. She was the first to determine that a deficiency in pantothenic acid, a B vitamin, can lead to damage to the adrenal glands and abnormal skin and hair pigmentation. Morgan also showed that high doses of vitamin D can have a toxic effect on the body. Her studies on vitamins A and C led to their discovery in a wide variety of foods. She demonstrated that proteins become denatured (i.e., their physical structure becomes changed) when heated, reducing their nutritional value. Other areas of Morgan's research included the analysis of processed foods, the association between vitamins and hormones, the effects of food preservation on vitamin content, and the basis for low weight gain in children.

vitamins: organic molecules needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

Despite the importance of Morgan's research, much of her efforts remained unrecognized until late in her career. In 1949 she was awarded the prestigious Garvan Medal by the American Chemical Society for her groundbreaking research in nutrition. In 1950 she became the first woman to receive the status of faculty research lecturer at the University of California. Other honors imparted on Morgan included the 1954 Borden Award from the American Institute of Nutrition and the Phoebe Apperson Hearst Gold Medal, which recognized her as one of ten outstanding women in San Francisco in 1963. In 1961 the home economics building at Berkeley was renamed Agnes Fay Morgan Hall.

Morgan maintained her research efforts well after her official retirement in 1954. She continued to frequent her office until her death in 1968, two weeks after a heart attack. As a former staff member was quoted as saying in a 1969 memorial, "We can only feel that her going marked the end of an era in the education of women." SEE ALSO DENATURATION; FOOD PRESERVATIVES.

Stephanie Dionne Sherk

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English physicist Henry Moseley, who arranged the Periodic Table in order of the atomic numbers of the elements.

Moseley, Henry

ENGLISH PHYSICIST
1887–1915

Henry Moseley's research career lasted only forty months before tragically ending with his death on a Gallipoli battlefield in World War I. But in his classic study of the x-ray spectra of elements, he established the truly scientific basis of the Periodic Table by arranging chemical elements in the order of their atomic numbers.

Henry Gwyn Jeffreys Moseley, who was always called "Harry" by his family, was born in Weymouth, England, on November 23, 1887. His family was wealthy, aristocratic, and scientifically accomplished, and young Henry showed an early interest in **zoology**. He attended Eton on a King's scholarship, where he excelled in mathematics, and was introduced to the study of x rays by his physics teacher. He entered Trinity College, Oxford, in 1906. At that time, Oxford did not have a particularly notable science curriculum, but Moseley chose the school in order to be near his widowed mother. He graduated in 1910 with high honors in mathematics and science, and secured a position in the laboratory of Ernest Rutherford at the University of Manchester.

zoology: branch of biology concerned with the animal kingdom

It was a time of great excitement and ferment in science, and Rutherford's laboratory was one of the epicenters of discovery in atomic physics. The first coherent theory of the structure of the atom was just then being developed by Rutherford and his research group, which, besides Moseley, included Niels Bohr, Hans Geiger, Kasimir Fajans, and others.

The nature of x rays was also receiving new interest because of the discovery by the German physicist Max von Laue in 1912 that they were diffracted by their passage through crystals and therefore possessed a wave nature. Succeeding experiments by William L. Bragg the same year showed that similar results could be obtained by the reflection of x rays from the face of a crystal. Moseley persuaded Rutherford to allow him and a colleague, C. S. Darwin, to further study the nature of x rays. Their work demonstrated that the **spectral line** of platinum, which they were using as the anticathode in their x-ray tube, was characteristic of that element alone. Moseley returned to Oxford, and despite the experimental deficiencies of his laboratories, measured the x-ray spectral lines of nearly all the elements from aluminum to gold. The results of his study showed a clear and simple progression of the elements that was based on the number of protons in the atomic nucleus, rather than the order based on atomic weights that was then the basis of the Periodic Table.

spectral line: line in a spectrum representing radiation of a single wavelength

His work, called a "classical example of the scientific method," was the second and last of his independent publications. Despite the pleadings of his colleagues, he enlisted in the British Army at the outbreak of World War I, and was killed in battle on August 10, 1915. SEE ALSO BOHR, NIELS; BRAGG, WILLIAM LAWRENCE; LANTHANIDES; RADIATION; RUTHERFORD, ERNEST.

Bartow Culp

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Mutagen

Mutagens are chemical agents that cause changes in the genetic **code** which are then passed on to future generations of an organism. Mutations are usually chemical in nature and often carcinogenic, but may also be caused by physical damage produced by x rays or other causes. A mutation changes the activity of a gene. Mutations are frequent in lower forms of life and may help these organisms adapt to changes in their environments.

Proteins are composed of chains of amino acids. In the genetic code of deoxyribonucleic acid (**DNA**), a codon or three-base sequence codes for the placement of each amino acid; for example, the codon UUU places phenylalanine at that location in the protein and replacement of the third base with **adenine** results in the placement of leucine instead of phenylalanine. If a portion of the original code read . . . UUUACG . . . , deleting one of the uridine bases would cause that portion of the code to read . . . UUACG . . . ; the sequence UUA would then specify leucine. A point mutation changing one base might result in the formation of a different protein.

Mutations can occur by several mechanisms, such as replacing one nucleotide base with another or by adding or removing a base; they can also develop when a carcinogenic agent such as an aromatic hydrocarbon molecule is inserted between the strands of DNA, causing the code to be misread. Some chemical mutagens such as nitrites change one base into another, resulting in a new sequence of amino acids and the **synthesis** of a new protein. The modified protein might function normally or might not be useful at all, but it could be dangerous.

Many mutagenic agents are also carcinogenic, and the Ames test provides a quick method for screening foods and other substances for potential cancer-causing agents. SEE ALSO Carcinogen; Codon.

Dan M. Sullivan

HOW DOES THE AMES TEST WORK?

The Ames test is a method for screening potential mutagens. The test uses auxotrophs (strains that have lost the ability to synthesize a needed substance) of *Salmonella typhimurium* that carry mutant genes, making them unable to synthesize histidine. They can live on media containing histidine, but die when the amino acid is depleted. The bacteria are especially sensitive to back mutations that reactivate the gene for the synthesis of histidine; exposure to mutagenic substances allows the bacteria to grow rapidly, developing large and numerous colonies.

code: mechanism to convey information on genes and genetic sequence

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

adenine: one of the purine bases found in nucleic acids, $C_5H_5N_5$

synthesis: combination of starting materials to form a desired product

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Mutation

Any heritable change in the genetic information or **DNA** is called a mutation. A change in the base sequence of DNA that is then replicated and transmitted to future generations of cells becomes a permanent change in the **genome**. Mutations, all of which appear to occur as random events, can range from a single replacement of a base (substitution) to larger changes that result from the deletion or addition of more than one base (often large stretches of a DNA molecule).

genome: total genetic material in a cell or organism

Most mutations are thought to be harmful to the life of the cell. These harmful mutations occur during the development of a cancer cell, for example. In these cases (cancerous transformation), numerous point mutations or deletion mutations are well-established as causative agents. A point mutation

A six-legged frog, a result of a genetic disorder.

occurs when a single base is changed in a DNA sequence. This can be either: (1) a transition, in which a **purine base** is replaced by another purine base, or pyrimidine by pyrimidine (e.g., base pair AT becomes base pair GC); or (2) a transversion, in which a purine is replaced by a pyrimidine, or vice versa (e.g., base pair AT becomes base pair CG). A point mutation that changes a codon with the result that it codes for a different amino acid is called a missense mutation. Such a mutation can change the nature of the protein being formed. It can change the amino acid composition and the protein sequence and, therefore, the structure of that protein. This process may have a deleterious effect on protein activity in essential metabolic functions in the cell. In contrast, there are cases in which a mutation can change the protein sequence but have little or no consequence on the protein function. These are silent mutations. In these cases, the change is a conservative one (a single amino acid is substituted for another of similar type, such as lysine for an arginine, or the **amino acid residue** may reside on the outside surface of the protein where it will have little effect on protein structure). Such silent mutations exhibit no phenotypic (observable) changes. Alternatively, a mutation can occur in intergenic or noncoding regions and thus have no direct effect on the protein product. There can also be rare changes in DNA sequence that may provide a selective advantage to an organism.

purine base: one of two types of nitrogen bases found in nucleic acids

amino acid residue: in a protein, which is a polymer composed of many amino acids, that portion of the amino acid that remains to become part of the protein

Mutations may occur spontaneously, or as a result of external physical agents (radiation) or chemical agents (mutagens). The most common spontaneous mutations result from errors in DNA replication that are not corrected. Virtually all forms of life are exposed to ultraviolet light from the Sun, which can react with adjacent **thymine** bases in DNA in such a way as to link them together to produce an intrastrand thymine dimer. A number of chemicals, including dimethylsulfate, nitrous acid, and nitrogen mustards, react with bases in DNA so as to modify them. As a result, the subsequent replication cycle changes the complementary base or bases and leads to a permanent change in the form of a transition or transversion. In the case of the thymine dimers or the loss of a base, repair enzymes exist that scan the DNA in an attempt to correct the problem. There are a number of inher-

thymine: one of the four bases that make up a DNA molecule ited disease conditions, such as xeroderma pigmentosum and Cockayne syndrome, that result from defects in genes associated with DNA repair.

In a number of cancers, a deletion of much or all of a gene that completely inactivates the gene has occurred. It is claimed that about 80 percent of human cancers may be caused by carcinogens that damage DNA or interfere with its replication and/or repair. Bruce Ames, a microbiologist at the University of California at Berkeley, developed a simple experimental procedure using bacterial cells that can detect mutagenic chemicals. It has been shown that about 80 percent of carcinogenic compounds are also mutagenic using the Ames test. SEE ALSO DNA; MUTAGEN; TERATOGEN.

William M. Scovell

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NAD/NADH ***See Nicotinamide Adenine Dinucleotide.***

Nanochemistry

In recent years nanoscale science and technology have grown rapidly. Nanochemistry, in particular, presents a unique approach to building devices with a molecular-scale precision. One can envision the advantages of nanodevices in medicine, computing, scientific exploration, and electronics, where nanochemistry offers the promise of building objects atom by atom. The main challenges to full utilization of nanochemistry center on understanding new rules of behavior, because nanoscale systems lie at the threshold between classical and quantum behavior and exhibit behaviors that do not exist in larger devices.

Although nanochemical control was proposed decades ago, it was only recently that many of the tools necessary for studying the nanoworld were developed. These include the scanning tunneling microscope (STM), atomic force microscope (AFM), high resolution scanning and transmission electron microscopies, x rays, ion and electron beam probes, and new methods for nanofabrication and lithography.

Studies of nanochemical systems span many areas, from the study of the interactions of individual atoms and how to manipulate them, how to control chemical reactions at an atomic level, to the study of larger molecular assemblies, such as dendrimers, clusters, and polymers. From studies of assemblies, significant new structures—such as nanotubes, nanowires, three-dimensional molecular assemblies, and lab-on-a-chip devices for separations and biological research—have been developed.

Single Atoms

The ultimate frontier of nanochemistry is the chemical manipulation of individual atoms. Using the STM, single atoms have been assembled into larger structures, and researchers have observed chemical reactions between two atoms on a surface. The use of atoms as building blocks opens new routes to novel materials and offers the ability to create the smallest features possible in integrated circuits (IC) and to explore areas like quantum computing. Until now the ever-decreasing size of IC circuitry has been well described by Moore's law, but further shrinkage of circuit size will halt by 2012 because of **quantum mechanical** effects. Quantum computing provides a way to circumvent this apparent roadblock and use these quantum effects to advantage. Atomic-scale devices, although promising, present major challenges in how to achieve spatial control and stability.

quantum mechanical: theoretical model to describe atoms and molecules by wave functions

Dendrimers

Dendrimers are highly branched three-dimensional nanoscale molecular objects of the same size and weight as traditional polymers. However, dendrimers are synthesized in a stepwise fashion, allowing for extremely precise control of their size and geometry (see Figure 1, a molecular model of a dendrimer). In addition, the chemical reactivity and properties of their periphery and core can be controlled easily and independently. Dendrimers are already being used in molecular recognition, nanosensing, light harvesting, and optoelectrochemical devices. Because they are built up layer by layer and the properties of any individual layer can be controlled through selection of the monomer, they are ideal building blocks in nanochemistry for the creation of more complex three-dimensional structures.

Nanocrystals and Clusters

Nanocrystals are crystals of nanometer dimensions, usually consisting of aggregates of a few hundred to tens of thousands of atoms combined into a cluster. Nanocrystals have typical dimensions of 1 to 50 nanometers (nm),

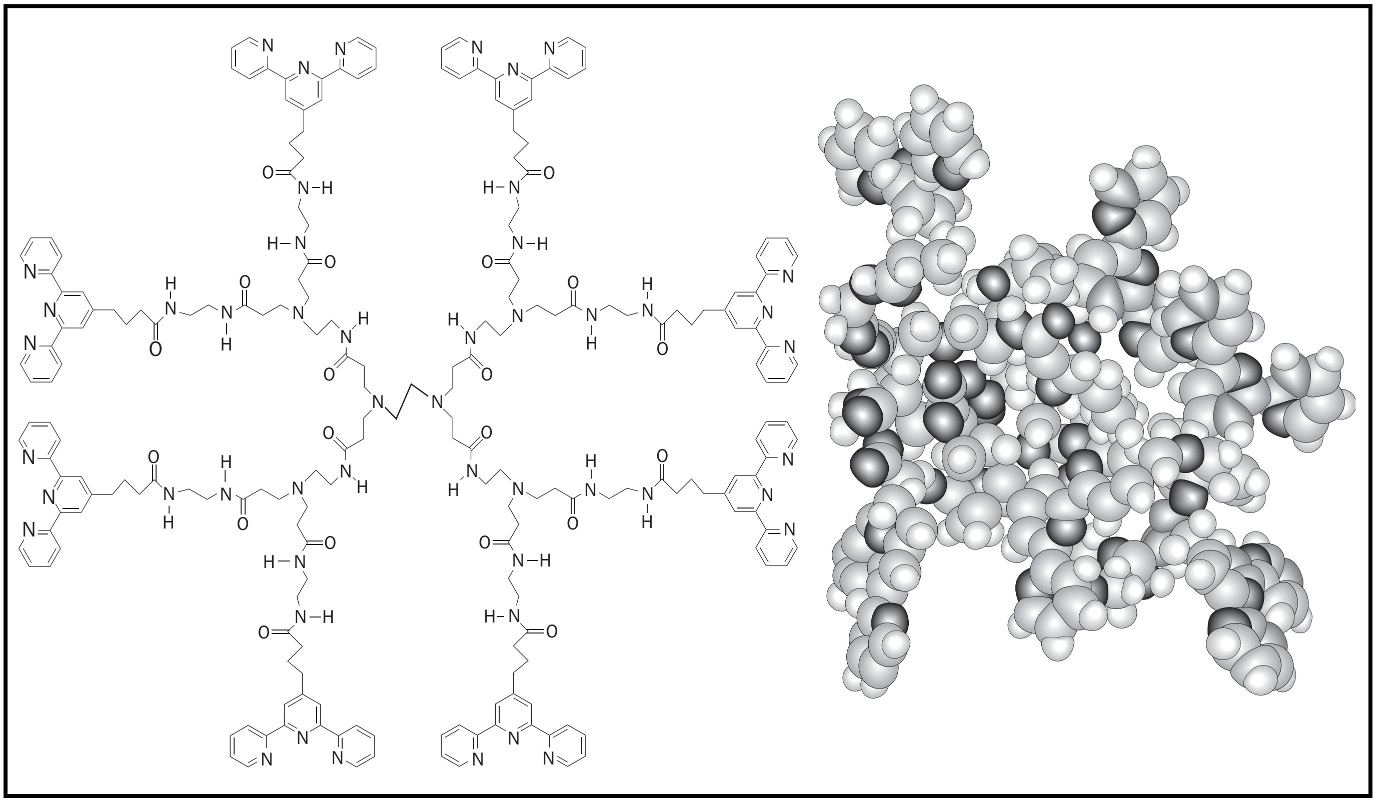

Figure 1. Molecular representation of a dendrimer (left) and a 3-D molecular model of the same dendrimer (right).

and thus they are intermediate in size between molecules and bulk materials and exhibit properties that are also **intermediate**. For example, the small size of semiconductor quantum "dots" leads to a shifted light emission spectrum through quantum confinement effects—with the magnitude of the shift being determined by the size of the nanocrystal. Nanocrystals are of great interest because of their promise in high density data storage and in optoelectronic applications, as they can be efficient light emitters. Nanocrystals have also found applications as biochemical tags, as laser and optical components, for the preparation of display devices, and for chemical **catalysis**.

intermediate: molecule, often short-lived, that occurs while a chemical reaction progresses but is not present when the reaction is complete

catalysis: the action or effect of a substance in increasing the rate of a reaction without itself being converted

Nanotubes

Recently, hollow carbon tubes of nanometer dimensions have been prepared and studied. These nanotubes constitute a new form of carbon, configurationally equivalent to a graphite sheet rolled into a hollow tube (see Figure 2, a molecular model of a carbon nanotube). Carbon nanotubes may be synthesized, with sizes ranging from a few microns to a few nanometers and with thicknesses of many carbon layers down to single-walled structures. The unique structure of these nanotubes gives them advantageous behavior relative to properties such as electrical and thermal conductivity, strength, stiffness, and toughness. Carbon nanotubes can also be functionalized with molecular recognition agents so that they may bind specifically to discrete molecular targets, allowing them to be used as high resolution AFM probes, as channels for materials separation, and as selective gates for molecular sensing.

Nanowires

Like nanotubes, nanowires are very small rods of atoms, but nanowires are solid, dense structures, much like a conventional wire. Controlling the atom (material) used for building the wire, as well as its impurity **doping**, allows for control of its electrical conduction properties. Ultimately, chemists wish to fabricate and control nanowires that are a single atom or molecule in diameter, thus creating an unprecedented laboratory for studying how small structures affect electron transfer within the wire and between the wire and external agents. Clearly, nanowires offer the potential for creating very small IC components.

dope: to add a controlled amount of an impurity to a very pure sample of a substance, which can radically change the properties of a substance

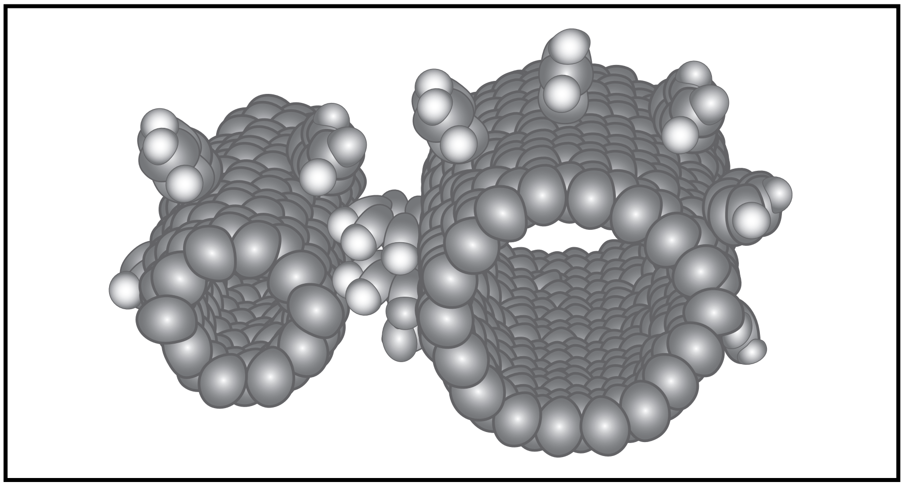

Figure 2. Molecular diagram of a carbon nanotube.

THE SCANNING TUNNELING MICROSCOPE AND ATOMIC FORCE MICROSCOPE

The scanning tunneling microscope (STM) and the atomic force microscope (AFM) are very high resolution microscopes that allow scientists to obtain high resolution images of surfaces with atomic or molecular resolution. Both microscopes work by scanning a very sharp tip on a surface and measuring current (STM) or intermolecular forces (AFM) between the tip and the surface.

synthesis: combination of starting materials to form a desired product

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

Nanocomposites

Nanocomposites encompass a large variety of systems composed of dissimilar components that are mixed at the nanometer scale. These systems can be one-, two-, or three-dimensional; organic or inorganic; crystalline or amorphous. A critical issue in nanocomposite research centers on the ability to control their nanoscale structure via their **synthesis**. The behavior of nanocomposites is dependent on not only the properties of the components, but also morphology and interactions between the individual components, which can give rise to novel properties not exhibited by the parent materials. Most important, the size reduction from microcomposites to nanocomposites yields an increase in surface area that is important in applications such as mechanically reinforced components, nonlinear optics, batteries, sensors, and catalysts.

Lab on a Chip

Lab-on-a-chip devices are designed to carry out complex chemical processes at an ultrasmall scale, for example, synthesizing chemicals efficiently; carrying out biological, chemical, and clinical analyses; performing combinatorial chemistry; and conducting separations and analysis on a single, miniaturized device. When the amount of material in a sample is small or when it is highly toxic or dangerous, lab-on-a-chip devices offer an ideal way to complete complex chemical manipulations with extremely small sample sizes. Further, because the volumes used to carry solutions are extremely small, even very small sample amounts can be present in reasonable concentrations. Lab-on-a-chip technology has been aggressively pursued in biotechnology, where better ways to separate and analyze **DNA** and proteins are of great interest. It has also sparked great interest in the analysis of dangerous materials where it can be used, for example, by law enforcement or the military to analyze explosives and biological or chemical agents, while maintaining low risks.

Nano-Electro-Mechanical Systems

Nano-electro-mechanical systems have also generated significant interest in the creation of tiny devices that can use electrochemical energy to carry out mechanical tasks, for example, nanomotors. One can envision that the coupling of chemical energy to mechanical transducers will enable the construction of devices that may be applied in medicine to treat illnesses, explore dangerous areas, or just reach places that larger-scale devices cannot. Research in this area focuses on understanding the preparation of nanoscale components to build such devices as well as the interactions between the components, especially the coupling between the electrochemical and mechanical components. In addition, a new understanding of effects such as friction and wear is required as the nanoscale components obey a different set of rules than their macroscopic counterparts. SEE ALSO COMPUTATIONAL CHEMISTRY; FULLERENES; MATERIALS SCIENCE.

Diego J. Díaz
Paul W. Bohn

MOORE'S LAW

In 1965 Gordon Moore, cofounder of Intel, predicted the trend that the number of transistors on integrated circuits (IC) was going to follow. The number of transistors in IC has grown exponentially, with the implication that the size of such transistors has decreased in a similar fashion. His law stills hold, but it is predicted that the law will not be applicable by the year 2012 as further shrinking of transistors will not be possible after that time.

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Natural Gas ***See Fossil Fuels.***

Neodymium

MELTING POINT: 1,021°C
BOILING POINT: 3,127°C
DENSITY: 7.0 g/cm^3
MOST COMMON IONS: Nd^{2+}, Nd^{3+}, Nd^{4+}

60
Nd
NEODYMIUM
144.24

Neodymium oxide was first isolated from a mixture of oxides called didymia. The element neodymium is the second most abundant **lanthanide** element in the igneous rocks of Earth's crust. Hydrated neodymium(III) salts are reddish and anhydrous neodymium compounds are blue. The compounds neodymium(III) chloride, bromide, iodide, nitrate, perchlorate, and acetate are very soluble; neodymium sulfate is somewhat soluble; the fluoride, hydroxide, oxide, carbonate, oxalate, and phosphate compounds are insoluble.

lanthanides: a family of elements (atomic number 57 through 70) from lanthanum to lutetium having from 1 to 14 4f electrons

Neodymium is used to color special glasses, giving these glasses a blue-violet shade. It is also used to color television faceplates, to reduce the reflectivity of television screens. $Nd_2Fe_{14}B$ magnets are among the most powerful. Neodymium compounds are used as laser materials, specifically as optically pulsed solid-state laser materials. One of the most important of these is Nd–YAG garnet (YAG = $Y_3A_{l5}O_{12}$), which generates light having wavelengths of 1.06 micrometers (4.17×10^{-5} inches). This garnet laser has potential use in dental caries prevention. Finally, neodymium is used in the making of photographic filters (Nd_2O_3), magnets used in headphones, and ceramic capacitors. SEE ALSO Cerium; Dysprosium; Erbium; Europium; Gadolinium; Holmium; Lanthanum; Lutetium; Praseodymium; Promethium; Samarium; Terbium; Ytterbium.

Lea B. Zinner
Geraldo Vicentini

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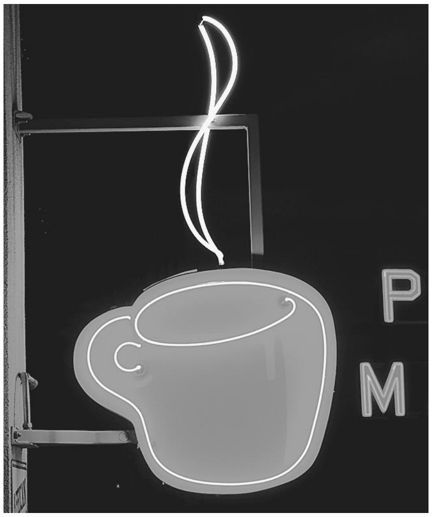
10
Ne
NEON
20.179

Neon

MELTING POINT: −248.59°C
BOILING POINT: −246.08°C
DENSITY: 0.8999 kg/m^3
MOST COMMON IONS: None

Neon (from the Greek word *neos*, meaning "new") is the second lightest of the **noble gases**. It forms no stable compounds with other elements. Discovered in 1898 by Sir William Ramsay and Morris Travers during their experiments with liquid air, neon accounts for 18 millionths (18 ppm) of the volume of Earth's atmosphere. Trace amounts are also found in the oceans. It is present in the Sun and in the atmosphere of Mars.



Neon in a vacuum discharge tube is commonly used in electric signage.

At room temperature neon is a colorless, odorless gas. Upon freezing it forms a crystal with a face-centered cubic structure. In a vacuum discharge tube, neon emits its famous red-orange light, which has long been used in advertising signs and discharge display tubes. More recently neon (mixed with helium) has been used in common lasers and laser pointers, which produce a characteristic red neon **spectral line** corresponding to light of wavelength 632.8 nanometers (2.49 × 10^{-5} inches).

Neon is produced within stars during **nucleosynthesis**. It has three stable **isotopes**, of which neon-20 is the most abundant (90.5%). SEE ALSO GASES; NOBLE GASES; RAMSAY, WILLIAM; TRAVERS, MORRIS.

Richard Mowat

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93
Np
NEPTUNIUM
237.048

Neptunium

MELTING POINT: 640°C
BOILING POINT: 3,930°C
DENSITY: 20.45 g/cm^3
MOST COMMON IONS: Np^{3+}, Np^{4+}, or NpO_2^{+}, NpO_2^{2+}, NpO_3^{+}

Neptunium was discovered by the U.S. physicists Edwin M. McMillan and Philip Abelson, in 1940, via the bombardment of ^{238}U with neutrons. The name of the element is related to the planet Neptune. Neptunium-237 occurs as a product of ^{238}U **fission**, and appears in uranium fuel elements.

$$^{238}_{92}U + ^{1}_{0}n \rightarrow ^{239}_{92}U \xrightarrow{-\beta^-} ^{239}_{93}Np(t_{1/2} = 2.35 \text{ days})$$

Neptunium is used to produce plutonium (^{238}Pu), via the irradiation of NpO_2 with neutrons. The **isotope** $^{238}{}_{94}$Pu is used as a power source for satellites.

$$^{237}_{93}Np + ^{1}_{0}n \rightarrow ^{238}_{93}Np \xrightarrow{-\beta^-} ^{238}_{94}Pu$$

noble gas: element characterized by inert nature; located in the rightmost column in the Periodic Table

spectral line: line in a spectrum representing radiation of a single wavelength

nucleosynthesis: creation of heavier elements from lighter elements via fusion reactions in stars

Neptunium has several **valence** states: Np^{3+} (purplish in solution), stable in water, is easily oxidized in air to Np^{4+} (yellow-green), and then slowly oxidized in air to the stable ion, NpO_2^{2+} (pink); NpO_2^{+} (green) is obtained by the **oxidation** of Np^{4+} with hot nitric acid. NpO_2^{2+} can also be obtained by the oxidation of lower state ions with Ce^{4+}, MnO^{4-}, O_3, and BrO_3^{-}. The production of ^{237}Np (as NpO_2^{+}) involves the oxidation of Np^{3+} by nitric acid, followed by the extraction of the NpO_2^{+} compound with tributylphosphate in kerosene.

isotope: form of an atom that differs by the number of neutrons in the nucleus

fission: process of splitting an atom into smaller pieces

valence: combining capacity

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

The oxide NpO_2, **isostructural** with UO_2, is obtained by heating neptunium nitrates or hydroxides in air. The oxide Np_3O_8, isomorphous with U_3O_8, is also obtained by heating such compounds in air at specific temperatures. The oxidation of Np^{4+} hydroxide compounds with ozone gives the hydrated trioxides $NpO_3 \cdot 2H_2O$ (brown) and $NpO_3 \cdot H_2O$ (red-gold). The fluorides NpF_3 and NpF_4 are precipitated from **aqueous solutions**.

isostructural: relating to an arrangement of atomic constituents that is geometrically the same although different atoms are present

aqueous solution: homogenous mixture in which water is the solvent (primary component)

$$NpO_2 + 1/2H_2 + 3HF(g) \xrightarrow{500°C} NpF_3 + 2H_2O$$

Other neptunium halides are: NpF_3 (purple-black); $NpCl_3$ (white); $NpBr_3$ (green); NpI_3 (brown); NpF_4 (green); $NpCl_4$ (red-brown); $NpBr_4$ (red-brown); and NpF_6 (orange). The removal of highly radioactive neptunium solids or solutions must be performed via remote control. Neptunium is one of the actinides that is found in **nuclear** waste (in oxidate states +3, +4, +5, +6, and maybe +7) and must be kept out of the environment. SEE ALSO Actinium; Berkelium; Einsteinium; Fermium; Lawrencium; Mendelevium; Nobelium; Plutonium; Protactinium; Rutherfordium; Thorium; Uranium.

nuclear: having to do with the nucleus of an atom

Lea B. Zinner
Geraldo Vicentini

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Nernst, Walther Hermann

GERMAN CHEMIST
1864–1941

Walther Hermann Nernst, born in Briesen, Prussia (now Wabrzezno, Poland), was a pioneer in the field of chemical thermodynamics in a wide range of areas. His most outstanding contributions were his laws for electrochemical cells and his heat theorem, also known as the third law of thermodynamics, for which he was awarded the Nobel Prize in chemistry in 1920.

Nernst first studied physics before he became an assistant in 1887 to German physical chemist Friedrich Wilhelm Ostwald at the University of Leipzig, then the only institute for physical chemistry in Germany. In 1891

German chemist and physicist Walther Hermann Nernst (front holding vial), recipient of the 1920 Nobel Prize in chemistry, "in recognition of his work in thermochemistry."

he was appointed associate professor at the university in Göttingen and, three years later, convinced officials there to create an institute for physical chemistry modeled on the Leipzig center. He served as its director until his move in 1905 to Berlin, where he once again established an institute renowned worldwide.

galvanic: relating to direct current electricity especially when produced chemically

During his Leipzig period, Nernst performed a series of electrochemical studies from which, at the age of twenty-five, he arrived at his well-known equations. These equations described the concentration dependence of the potential difference of **galvanic** cells, such as batteries, and were of both great theoretical and practical importance. Nernst started with the investigation of the diffusion of electrolytes in one solution. Then he turned to the diffusion at the boundary between two solutions with different electrolyte concentrations; he determined that the osmotic pressure difference would result in an electric potential difference or electromotive force (emf). Next he divided both solutions into two concentration half-cells, connected to each other by a liquid junction, and measured the emf via electrodes dipped into both solutions. The data supported his first equation where the emf was proportional to the logarithm of the concentration ratio. Finally, he investigated galvanic cells where a redox reaction (e.g., $Zn + 2Hg^+ \rightarrow Zn^{2+} + 2Hg$) was divided such that **oxidation** ($Zn \rightarrow Zn^{2+} + 2e^-$) and reduction ($2Hg^+ + 2e^- \rightarrow 2Hg$) occurred at the electrodes in two half-cells. By combining this with Helmholtz's law, which related thermodynamics to the emf of electrochemical cells, and van't Hoff's equation, which related chemical equilibria to thermodynamics, Nernst derived his second equation for galvanic cells. Supported by many measurements, the equation described the emf of galvanic cells as a function of the concentration of all substances involved in the reaction.

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

$$E = E^0 - \frac{RT}{NF}\left(\frac{[\text{Products}]}{[\text{Reactants}]}\right)$$

Nernst's formulation of the third law of thermodynamics was originally an ingenious solution to a crucial practical problem in chemical thermodynamics, namely, the calculation of chemical equilibria and the course of chemical reactions from thermal data alone, such as reaction heats and heat capacities. Based on the first two laws of thermodynamics and van't Hoff's equation, chemical equilibria depended on the free reaction enthalpy ΔG, which was a function of both the reaction enthalpy ΔH and the reaction entropy ΔS according to the Gibbs-Helmholtz equation:

$$E = \frac{E^\circ - RT}{NF}$$

The problem was that, although enthalpy values could be calculated from thermal measurements, entropy values required data at the absolute zero of temperature, which was practically inaccessible. Guided by theoretical reasoning and then supported by a huge measurement program at very low temperatures, Nernst in 1906 suggested his heat theorem. According to a later formulation, it stated that all entropy changes approach zero at the absolute zero.

The theorem not only allowed the calculation of chemical equilibria, it was also soon recognized as an independent third law of general thermodynamics with many important consequences. One such consequence was that it is impossible to reach the absolute zero. Another consequence was that one could *define* a reference point for entropy functions, such that the entropies of all elements and all perfect crystalline compounds were taken as zero at the absolute zero.

Nernst made numerous other important contributions to physical chemistry. For example, his distribution law described the concentration distribution of a solute in two immiscible liquids and allowed the calculation of extraction processes. He also formulated several significant theories, such as those on the electrostriction of ions, the diffusion layer at electrodes, and the solubility product. In addition, he established new methods to measure dielectric constants and to synthesize ammonia, on which the German chemist Fritz Haber later successfully followed up. SEE ALSO Electrochemistry; Haber, Fritz; Ostwald, Friedrich Wilhelm; Physical Chemistry.

Joachim Schummer

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Neurochemistry

Neurochemistry refers to the chemical processes that occur in the brain and nervous system. The fact that one can read this text, remember what has been read, and even breathe during the entire time that these events take place relies on the amazing chemistry that occurs in the human brain and the nerve cells with which it communicates.

There are two broad categories of chemistry in nerve systems that are important. The first is the chemistry that generates electrical signals which propagate along nerve cells. The key chemicals involved in these signals are sodium and potassium ions. To see how they give rise to a signal, one must first look at a nerve cell that is at rest.

Like any other cell, a nerve cell has a membrane as its outer "wall." On the outside of the membrane, the concentration of sodium ions will be relatively high and that of potassium ions will be relatively low. The membrane maintains this concentration gradient by using channels and enzymes.

The channels are pores that may be opened or closed by enzymes which are associated with them. Some ion channels allow the movement of sodium ions and others allow potassium ions to cross the membrane. They are also called "gated" channels because they can open and close much like a gate in a fence. The **voltage** they experience dictates whether the gate is open or closed. Thus, for example, a gated sodium ion channel in a membrane opens at certain voltages to allow sodium ions to pass from regions of high concentration to regions of low concentration.

voltage: potential difference expressed in volts

Active transport mechanisms are also present. Enzymes that span the membrane can actively pump sodium and potassium ions from one side of the membrane to another. When the nerve cell is at rest, these mechanisms maintain a high potassium and low sodium environment inside the cell.

Even when it is at rest, a nerve cell is in contact with many other nerve cells. When a neighboring cell passes on a signal to the resting cell (by a mechanism to be discussed shortly), a dramatic change occurs in the ion concentrations. Once the nerve cell at rest has received a sufficient signal from a neighbor to surpass a threshold level, some of the sodium ion channels near the connection point open and sodium ions flow into the cell. This flow of charge results in an electrical potential that is called the action potential. The action potential does not stay localized, however. Farther down the nerve cell, more sodium ion channels surpass their threshold and open so that the sodium ions flow into them as well. Thus, the action potential moves down the nerve. After the sodium ion gates open, the potassium ion gates also open and potassium ions flow out of the cell. This flow of ions offsets the charge from sodium ions flowing into the cell and the signal has receded in that region (and has moved on).

Once the cell propagates a signal, how does that cell send its signal to a neighbor? This question leads to the second broad category of neurochemistry: the chemistry at the synapse. Nerve cells do not actually touch their neighbors, but rather form a small gap called the synapse. The signal is transferred across this gap by chemicals called neurotransmitters.

The communication that occurs across the synapse may either excite or inhibit the action of the neighboring nerve cell. Thus, synapses are further categorized as either **excitatory** synapses or **inhibitory** synapses. The cell that is **propagating** the signal is called the presynaptic cell, and the cell that receives the signal is the postsynaptic cell.

excitatory: causing cells to become active

inhibitory: relating to the prevention of an action that would normally occur

propagating: reproducing; disseminating; increasing; extending

The end of the presynaptic cell contains small **vesicles**, spherical collections of the same **lipid** molecules that make up the cell membrane. Inside these vesicles, neurotransmitters exist in high concentrations. When the action potential reaches the end of the presynaptic cell, some of the vesicles merge with the cell membrane and release their contents (a process called exocytosis). The released neurotransmitters experience an immediate concentration gradient. They diffuse away from the release point to counteract the gradient, and in doing this, they cross the synapse and arrive at the neighboring cell.

vesicle: small compartment in a cell that contains a minimum of one lipid bilayer

lipid: a nonpolar organic molecule; fatlike; one of a large variety of nonpolar hydrophobic (water-hating) molecules that are insoluble in water

On the postsynaptic cell, there are **receptors** that are capable of interacting with the neurotransmitters. Once these messenger molecules cross the synapse, they connect with the receptors and the two cells have successfully communicated. The proteins of the receptors are capable of opening sodium gated ion channels, and a new action potential is engaged in the postsynaptic cell.

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

The remaining step in the process is also a critical one. Somehow the action of the neurotransmitters must cease. If they continue to cross the synapse, or are not removed from the receptors of the postsynaptic cell, they will continue to activate that cell. An overexcited or inhibited nerve cell is not capable of proper function. For example, schizophrenia is a mental disease that is caused by the brain's inability to eliminate excitatory neurotransmitters. The nerve cells continue firing, even when they need not, and the incorrect brain chemistry results in debilitating symptoms such as auditory hallucinations—hearing voices that are not actually there. SEE ALSO Enzymes; Neurotoxins; Neurotransmitters; Stimulants.

Thomas A. Holme

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Neurotoxins

Many chemical compounds, some natural and some made by humans, show toxic effects in humans or other animals. Every **toxin** is harmful, but toxins that target the nervous system have been developed into chemical warfare agents, so the public concern about them is enhanced.

toxin: poisonous substance produced during bacterial growth

Despite the connection with weapons of mass destruction, the most common neurotoxin in society is ethanol, found in alcoholic beverages. Neurons convey signals by manipulating ion concentrations, and neurotoxins reduce their ability to do so. Alcohol does this by essentially overloading the entire cell and hindering its ability to function. Many of the characteristics of alcohol intoxication, such as slurred speech and erratic motion, are the result of improper function of neurons in the brain. As the body metabolizes the alcohol and removes it from the blood, the neurotoxic effects wear off. With large overdoses of alcohol, however, the effects do not wear off, and death due to alcohol poisoning is a dramatic and unfortunately too common manifestation of neurotoxins.

The neurotoxins that are associated with chemical warfare typically operate in a different fashion. A neuron carries a signal as a miniature electric current. Ions carry charges, and when they move across the cell membrane in a specific region of a neuron at a rapid rate they change the electrical potential in that region. The rapid movement of ions migrates along the neuron and propagates an electrical signal (called an *action potential*). When this signal reaches the end of the neuron, it must somehow trigger a response in the next neuron. In a few cases, neurons are packed closely enough so that the charge associated with the moving action potential directly excites the next neuron. In most cases, the first neuron releases small molecules called *neurotransmitters* that diffuse across a small gap (the **synaptic cleft**) and interact with the next neuron, triggering its response. Many neurotoxins, including both human-made agents of chemical warfare and natural agents found in venoms and other natural toxins, work by disrupting this communication process.

synaptic cleft: tiny space between the terminal button of one neuron and the dendrite or soma of another

There are two common mechanisms by which nerve signaling is disrupted. The cell that receives the signal does so when **receptors** within its membrane interact with the neurotransmitters. Some neurotoxins act by blocking these receptors, making it impossible for them to receive signals. When signaling stops, nerve function is impaired or eliminated and, the neurotoxin has caused its damage.

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

The other key component of interneuron communication is that the neurotransmitters, once they have carried a signal across a synaptic cleft, must be removed. If a "receiving" neuron is continually stimulated because neurotransmitters continue to activate it, the neuron's function will be impaired, and the neuron may even be killed. There are special enzymes in the synaptic cleft that break down certain neurotransmitters, such as **acetylcholine**, to end the signaling. Some neurotoxins block the actions of these hydrolytic enzymes, thereby preventing the removal of acetylcholine (or other neurotransmitters), leading to continuous stimulation of the neurons and, ultimately, cell death. SEE ALSO ACETYLCHOLINE; INHIBITORS; NEUROTRANSMITTERS.

acetylcholine: neurotransmitter with the chemical forumula $C_7H_{17}NO_3$; it assists in communication between nerve cells in the brain and central nervous system

Thomas A. Holme

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Neurotransmitters

Neurotransmitters are chemical messengers produced by the nervous systems of higher organisms in order to relay a nerve impulse from one cell to another cell. The two cells may be nerve cells, also called neurons, or one of the cells may be a different type, such as a muscle or gland cell. A chemical messenger is necessary for rapid communication between cells if there are small gaps of 20 to 50 nanometers (7.874×10^{-7}–19.69×10^{-7} inches), called synapses or synaptic clefts, between the two cells. The two cells are referred to as either presynaptic or postsynaptic. The term "presynaptic" refers to the neuron that produces and releases the neurotransmitter, whereas "postsynaptic" refers to the cell that receives this chemical message.

Neurotransmitters include small molecules with amine **functional groups** such as **acetylcholine**, certain amino acids, amino acid derivatives, and peptides. Through a series of chemical reactions, the amino acid **tyrosine** is converted into the catecholamine neurotransmitters dopamine and norepinephrine or into the hormone epinephrine. Other neurotransmitters that are amino acid derivatives include γ-aminobutyric acid, made from glutamate, and serotonin, made from the amino acid tryptophan.

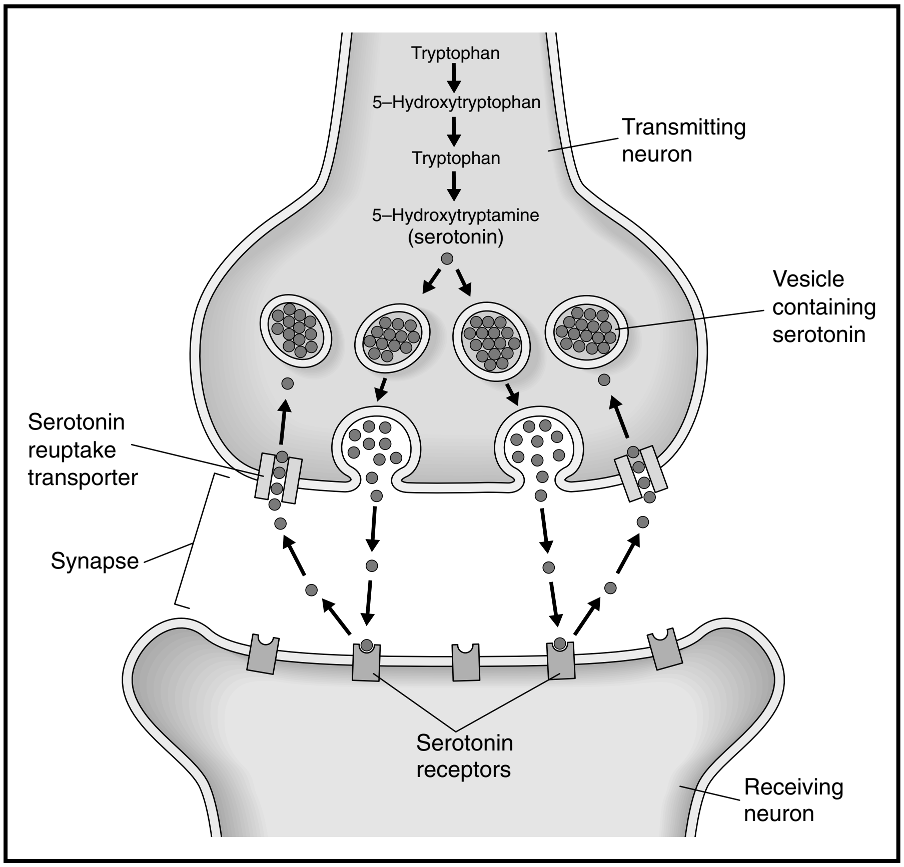
Peptide neurotransmitters include the enkephalins, the endorphins, oxytocin, substance P, vasoactive intestinal peptide, and many others. The gaseous free radical **nitric oxide** is one of the more recent molecules to be added to the list of possible neurotransmitters. It is commonly believed that there may be fifty or more neurotransmitters. Although there are many

functional group: portion of a compound with characteristic atoms acting as a group

acetylcholine: neurotransmitter with the chemical forumula $C_7H_{17}NO_3$; it assists in communication between nerve cells in the brain and central nervous system

tyrosine: one of the common amino acids

nitric oxide: compound, NO, which is involved in many biological processes; the drug Viagra enhances NO-stimulation of pathways to counteract impotence; may be involved in killing tumors



This diagram shows the transmission and reception of neurons and the role of serotonin in communication between neurons.

different neurotransmitters, there is a common theme by which they are released and exert their actions. In addition, there is always a mechanism for termination of the chemical message.

General Mechanism of Action

vesicle: small compartment in a cell that contains a minimum of one lipid bilayer

Neurotransmitters are formed in a presynaptic neuron and stored in small membrane-bound sacks, called **vesicles**, inside this neuron. When this neuron is activated, these intracellular vesicles fuse with the cell membrane and release their contents into the synapse, a process called exocytosis.

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

Once the neurotransmitter is in the synapse, several events may occur. It may (1) diffuse across the synapse and bind to a **receptor** on the postsynaptic membrane, (2) diffuse back to the presynaptic neuron and bind to a presynaptic receptor causing modulation of neurotransmitter release, (3) be chemically altered by an enzyme in the synapse, or (4) be transported into a nearby cell. For the chemical message to be passed to another cell, however, the neurotransmitter must bind to its protein receptor on the postsynaptic side. The binding of a neurotransmitter to its receptor is a key event in the action of all neurotransmitters.

Mechanism of Fast-Acting Neurotransmitters

ligand: molecule or ion capable of donating one or more electron pairs to a Lewis acid

depolarization: process of decreasing the separation of charge in nerve cells; the opposite of hyperpolarization

hyperpolarization: process of causing an increase in charge separation in nerve cells; opposite of depolarization

Some neurotransmitters are referred to as fast-acting since their cellular effects occur milliseconds after the neurotransmitter binds to its receptor. These neurotransmitters exert direct control of ion channels by inducing a conformational change in the receptor, creating a passage through which ions can flow. These receptors are often called **ligand**-gated ion channels since the channel opens only when the ligand is bound correctly. When the channel opens, it allows for ions to pass through from their side of highest concentration to their side of lowest concentration. The net result is **depolarization** if there is a net influx of positively charged ions or **hyperpolarization** if there is a net inward movement of negatively charged ions. Depolarization results in a continuation of the nerve impulse, whereas hyperpolarization makes it less likely that the nerve impulse will continue to be transmitted.

excitatory: causing cells to become active

amino acid sequence: twenty of the more than five hundred amino acids that are known to occur in nature are incorporated into a variety of proteins that are required for life processes; the sequence or order of the amino acids present determines the nature of the protein

inhibitory: relating to the prevention of an action that would normally occur

The first ligand-gated ion channel whose structure and mechanism were studied in detail was the nicotinic acetylcholine receptor of the neuromuscular junction. This receptor contains five protein subunits, each of which spans the membrane four times. When two acetylcholine molecules bind to this receptor, a channel opens, resulting in sodium and potassium ions being transported at a rate of 10^7 per second. Acetylcholine's action at these receptors is said to be **excitatory** due to the resulting depolarization. Other receptors for fast transmitters have a similar **amino acid sequence** and are believed to have a similar protein structure. Glycine and γ-aminobutyric acid (GABA) also act on ligand-gated ion channels and are fast-acting. However, they cause a net influx of chloride ions, resulting in hyperpolarization; thus, their action is **inhibitory**.

Mechanism of Slow-Acting Neurotransmitters

Slower-acting neurotransmitters act by binding to proteins that are sometimes called G-protein-coupled receptors (GPCRs). These receptors do not form ion channels upon activation and have a very different architecture than the ion channels. However, the timescale for activation is often relatively fast, on the order of seconds. The slightly longer time frame than that for fast-acting neurotransmitters is necessary due to additional molecular interactions that must occur for the postsynaptic cell to become depolarized or hyperpolarized. The protein structure of a GPCR is one protein subunit folded so that it transverses the membrane seven times. These receptors are referred to as G-coupled protein receptors because they function through an interaction with a **GTP**-binding protein, called G-protein for short.

GTP: guanosine triphosphate, a nucleotide consisting of ribose, guanine, and three linked phosphate groups

The conformational change produced when a neurotransmitter binds to a GPCR causes the G-protein to become activated. Once it becomes activated, the protein subunits dissociate and diffuse along the intracellular membrane surface to open or close an ion channel or to activate or inhibit an enzyme that will, in turn, produce a molecule called a second messenger. Second messengers include cyclic **AMP**, cyclic **GMP**, and calcium ions and phosphatidyl inositol. They serve to activate enzymes known as protein kinases. Protein kinases in turn act to phosphorylate a variety of proteins within a cell, possibly including ion channels. Protein **phosphorylation** is a common mechanism used within a cell to activate or inhibit the function of various proteins.

AMP: adenosine monophosphate, a form of ATP after removal of two phosphate groups

GMP: guanosine monophosphate, a nucleotide consisting of ribose, guanine, and one phosphate group

phosphorylation: the process of addition of phosphates into biological molecules

Termination of Transmission

For proper control of neuronal signaling, there must be a means of terminating the nerve impulse. In all cases, once the neurotransmitter dissociates from the receptor, the signal ends. For a few neurotransmitters, there are enzymes in the synapse that serve to chemically alter the neurotransmitter, making it nonfunctional. For instance, the enzyme acetylcholinesterase hydrolyzes acetylcholine. Other neurotransmitters, such as catecholamines and glutamate, undergo a process called reuptake. In this process, the neurotransmitter is removed from the synapse via a transporter protein. These proteins are located in presynaptic neurons or other nearby cells.

Drugs of Abuse

The actions of neurotransmitters are important for many different physiological effects. Many drugs of abuse either mimic neurotransmitters or otherwise alter the function of the nervous system. Barbiturates act as depressants with effects similar to those of anesthetics. They seem to act mainly by enhancing the activity of the neurotransmitter GABA, an inhibitory neurotransmitter. In other words, when barbiturates bind to a GABA receptor, the inhibitory effect of GABA is greater than before. Opiates such as heroin bind to a particular type of opiate receptor, resulting in effects similar to those of naturally occurring endorphins. **Amphetamines** can displace catecholamines from synaptic vesicles and block reuptake of catecholamines in the synapse, prolonging the action of catecholamine neurotransmitters. SEE ALSO ACETYLCHOLINE; DOPAMINE; HYDROLYSIS; ION CHANNELS; NOREPINEPHRINE.

amphetamine: class of compounds used to stimulate the central nervous system

Jennifer L. Powers

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Neutrons ***See Atomic Nucleus; Atomic Structure.***

New Battery Technology

The need for better batteries is a recurring theme in the effort to reduce energy consumption and in the effort to make electricity increasingly portable. As the world depends more and more on portable devices and turns to electric vehicles to reduce pollution, it becomes important that lightweight, long-lived batteries be developed. Additional desirable features of batteries include safety, dependability, environmental friendliness, and cost. This article considers battery technology currently used in transportation, including in electric vehicles and spacecraft.

Battery Basics

A battery is a collection of one or more electrochemical cells that convert chemical energy into electrical energy via electrochemical reactions (**oxidation-reduction reactions**). These reactions take place at the battery’s anode and cathode. The electrochemical cells are connected in series or in parallel depending on the desired **voltage** and capacity. Series connections provide a higher voltage, whereas parallel connections provide a higher capacity, compared with one cell.

oxidation-reduction reaction: reaction, sometimes called redox, that involves the movement of electrons between reactants to form products

voltage: potential difference expressed in volts

A cell typically consists of a negative electrode, a positive electrode, and an electrolyte. A cell discharges when a load such as a motor is connected between the negative and positive electrodes. The negative electrode, the anode, produces electrons that flow in an external circuit. The positive electrode, the cathode, consumes the electrons from the external circuit. The uniform flow of electrons around the circuit results in an electric current. Within the cell, the electrons received at the positive electrode react with the active material of this electrode, in reduction reactions that continue the flow of charge by sending ions through the electrolyte to the negative electrode. At the negative electrode, oxidation reactions between the active material of this electrode and the ions flowing through the electrolyte results in a surplus of electrons that are donated to the external circuit. For every electron generated in an oxidation reaction at the negative electrode, there is an electron consumed in a reduction reaction at the positive electrode. As the electrode reactions continue spontaneously, the active materials become depleted and the reactions slow down until the battery is no longer capable of supplying electrons; the battery is said to be fully discharged.

A battery is either a primary or a secondary battery. Primary batteries, such as those used in a flashlight, are used once and replaced. The chemical reactions producing the current in such batteries are too difficult to make it worth trying to reverse them. Secondary batteries, such as car batteries, can be recharged and reused because the chemical reactions are easily reversed. By reversing the flow of electricity (i.e., putting current in rather than taking it out), the chemical reactions are reversed to restore active material that had been depleted. Secondary batteries are also known as rechargeable or storage batteries and are used in transportation applications.

Battery performance is measured in terms of voltage and capacity. The voltage is determined by the chemistry of the **metals** and electrolytes used in the battery. The capacity is the number of electrons that can be obtained from a battery. Since current is the number of electrons released per unit time, cell capacity is the current supplied by a cell over time and is normally measure in ampere-hours. Battery specialists experiment with many different redox combinations and try to balance the energy output with the costs of manufacturing the battery. Other factors, such as battery weight, shelf life, and environmental impact also factor into the battery's design.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Present-Day Battery Technology

Lead-acid batteries are used in gasoline-driven automobiles and in electric and hybrid vehicles. They have the best discharge rate of secondary battery technology, they are the cheapest to produce, and they are rechargeable. The chemical reactions are:

Cathode (+):

$$PbO_2 + H_2SO_4 \xrightarrow{discharge} PbSO_4 + 2H_2O$$

Anode (–):

$$Pb + H_2SO_4 \xrightarrow{discharge} PbSO_4 + 2H^+ + 2e$$

The positive electrode is made of lead dioxide (PbO_2) and is reduced to lead sulfate ($PbSO_4$), while sponge metallic lead (Pb) is oxidized to lead sulfate at the negative electrode. The electrolyte is sulfuric acid (H_2SO_4), which provides the sulfate ion (SO_4^{2-}) for the discharge reactions.

The nickel-cadmium battery (Ni-Cd) is the most common battery used in communication satellites, in Earth orbiters, and in space probes. The chemical reactions are:

Cathode (+):

$$2NiO(OH) + 2H_2O + 2e \xrightarrow{discharge} 2Ni(OH)_2 + 2OH^-$$

Anode (–):

$$Cd + 2OH^- \xrightarrow{discharge} Cd(OH)_2 + 2e$$

Nickel hydroxide, NiO(OH), is the active cathode material, cadmium, Cd, is the active anode material, and aqueous potassium hydroxide, KOH, is the electrolyte.

There is considerable interest in the development of nickel-metal hybrid (Ni/MH) batteries for electric and hybrid vehicles. These batteries operate in concentrated KOH electrolyte. The electrode reactions are:

Cathode (+):

$$\mathrm{NiO(OH)} + \mathrm{H_2O} + e \xrightarrow{\text{discharge}} \mathrm{Ni(OH)_2} + \mathrm{OH^-}$$

Anode (–):

$$\mathrm{MH} + \mathrm{OH^-} \xrightarrow{\text{discharge}} \mathrm{M} + \mathrm{H_2O} + e$$

Ni/MH batteries use nickel hydoxide, NiO(OH), as the active material for the cathode, a metal hydride, MH, as the anode, and a potassium hydroxide, KOH, solution as the electrolyte. The metal hydride is a type of **alloy** (hydrogen absorption alloy) that is capable of undergoing a reversible hydrogen absorbing-desorbing process while the battery is discharged and charged. Current research is directed at improving the performance of the metal hydride anode and making the battery rechargeable.

alloy: mixture of two or more elements, at least one of which is a metal

Lithium ion (Li-ion) batteries are environmentally friendly batteries that offer more energy in smaller, lighter packages and thus are promising candidates for electric and hybrid vehicle applications. The electrode reactions are:

Cathode (+):

$$\mathrm{xLi^+} + \mathrm{xe} + \mathrm{Li_{1-x}AB} \xrightarrow{\text{discharge}} \mathrm{LiAB}$$

Anode (–):

$$\mathrm{Li_xC_6} \xrightarrow{\text{discharge}} \mathrm{xLi^+} + \mathrm{C_6} + \mathrm{xe}$$

Li-ion batteries use various forms of carbon (C) as anode material because carbon can reversibly accept and donate significant amounts of lithium (as Li_xC_6. Li-intercalation compounds (such as $LiCoO_2$, $LiMn_2O_4$, and $LiNiO_2$) are used as cathode materials. Electrolyte mixtures include a lithiated salt ($LiPF_6$ or $LiClO_4$) dissolved into a nonaqueous solvent (ethylene carbonate, propylene carbonate, or dimethyl carbonate). Because Li is a highly reactive metal in **aqueous solution**, Li-ion batteries are constructed to keep Li in its ionic state, and nonaqueous solvents are used. The next step in lithium-ion battery technology is believed to be the lithium polymer battery, in which a gelled or solid electrolyte will replace the liquid electrolyte.

aqueous solution: homogenous mixture in which water is the solvent (primary component)

Fuel Cells

Unlike the batteries described in the previous section, a fuel cell does not run down or require recharging; it will produce energy in the form of electricity and heat as long as fuel is supplied. Additionally, the electrode materials (usually platinum) serve only as a site for the reactions to occur (i.e., as a **catalyst**) and are not involved in the chemical reactions. As hydrogen flows over the anode, it is oxidized to hydrogen ions and electrons in a proton-exchange membrane or PEM fuel cell. The hydrogen ions pass through the membrane to the cathode, where they combine with oxygen from the air and with the electrons flowing in the external circuit from the anode to form water, which is expelled from the cell. A fuel cell system that includes a “fuel reformer” utilizes hydrogen from any hydrocarbon fuel, such as natural gas or methanol. This also makes a fuel cell quiet, dependable, and very fuel-efficient. Fuel cell reactions include:

catalyst: substance that aids in a reaction while retaining its own chemical identity

Cathode (+):

$$\mathrm{O_2} + 4\mathrm{H^+} + 4\mathrm{e} \rightarrow 2\mathrm{H_2O}$$

Anode (–):

$$2\mathrm{H_2} \rightarrow 4\mathrm{H^+} + 4\mathrm{e}$$

Fuel cells are lighter and more compact, compared with batteries that make available the same amount of energy.

Solar Cells

Solar cells (photovoltaic cells) convert sunlight to electricity. Photovoltaic cells are made of semiconductor materials such as silicon and gallium arsenide. When light strikes the cell, photons are absorbed within the semiconductor and create electron-hole pairs that move within the cell. This generates the energy that is used to power space vehicles.

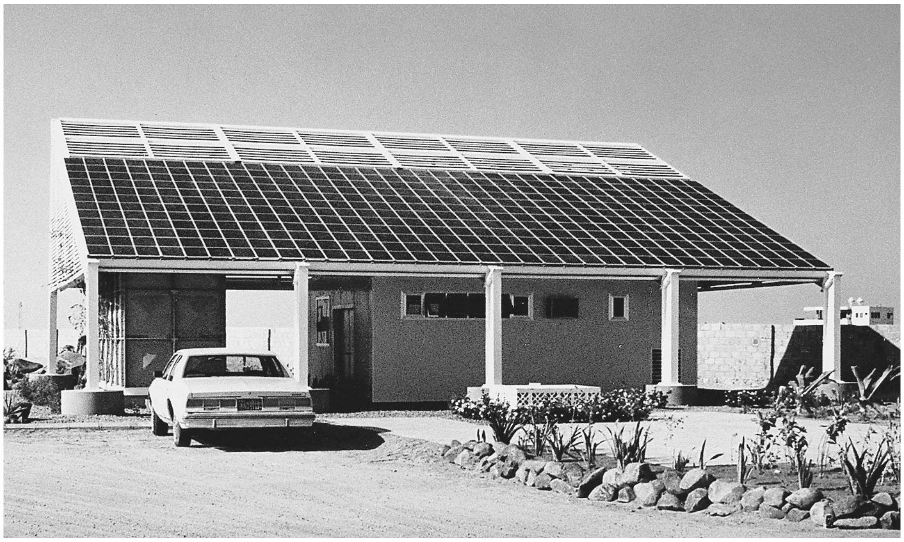
Electric and Hybrid Vehicles

Electric vehicles have an electric motor rather than a gasoline engine. The electric motor is usually powered by two banks of twenty-five 12-volt lead-acid rechargeable batteries, providing a total of 300 volts for each battery bank. Problems with lead-acid battery technology include battery weight (a typical lead-acid battery pack weighs 1,000 pounds or more), limited capacity (a typical battery pack holds about 15 kilowatt-hours of electricity, giving the car a range of approximately 80 kilometers [50 miles]), long recharging times (typically between four and ten hours for full charge), short life (three to four years) and cost (about $2,000 for each battery pack). The hybrid vehicle, in which a small gas engine is combined with an electric motor, is a compromise between gas-powered and electric vehicles.

The car of the future will likely be an electric or hybrid vehicle that gets its electricity from a fuel cell. It is unlikely that these vehicles will ever be solar powered, because solar cells produce too little power to make using them to run a full-size car practical.

Space Power

Spacecraft and space stations are powered by solar cells or collections of solar cells called solar panels. To get the most power, solar panels must be pointed directly at the Sun. Spacecraft are built so that the solar panels can be pivoted as the spacecraft moves, so that they can always stay in the direct path of the rays of light.



A desalination system on this roof in Jeddah, Saudi Arabia, is using 210 photovoltaic modules to supply operating power.

Solar cells generate electricity in the sunshine but not in the dark. Thus space stations and spacecraft run on power from batteries during dark periods. As of June 2003, solar power has been practical for spacecraft operating no farther from the Sun than the orbit of Mars. For example, Magellan, Mars Global Surveyor, Mars Observer, and the Earth-orbiting Hubble Space Telescope operate on solar power.

A Look to the Future

Exciting research is underway to improve the performance and longevity of batteries, fuel cells, and solar cells. Much of this research is directed at enhancing the chemistry in these systems through the use of polymer electrolytes, nanoparticle catalysts, and various membrane supports. Additionally, considerable effort is being put into the construction of three-dimensional microbatteries. SEE ALSO Electrochemistry; Materials Science; Solar Cells.

Cynthia G. Zoski

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Newton, Isaac

ENGLISH PHYSICIST AND MATHEMATICIAN
1642–1727

Royal Society: The U.K. National Academy of Science, founded in 1660

alchemy: medieval chemical philosophy having among its asserted aims the transmutation of base metals into gold

Sir Isaac Newton was born on December 25, 1642, in Woolsthorpe, Lincolnshire, England. His father died shortly before he was born. Newton attended Trinity College, starting in 1661, and remained there for the early part of his career. During the year of the plague (1665 to 1666), Trinity College was closed and Newton returned to his family home in the country. It was during this one incredibly productive year that much of Newton's most important work began. In 1703 Newton was knighted and elected president of the **Royal Society**, a post he held until his death in 1727.

English physicist Sir Isaac Newton, author of *Philosophiae Naturalis Principia Mathematica.*

Newton's best-known contributions to science were his three laws of motion and law of universal gravitation. These were first published in his *Principia* of 1687. Newton's other seminal work was *Opticks*, initially published in 1704. Newton also developed differential and integral calculus (although with different terminology and notation than used today), fluid mechanics, equations describing heat transfer, and an experimental scientific method. His other major intellectual interests were **alchemy**, theology, history, and biblical chronology. While working at the Royal Mint, Newton successfully oversaw the recoinage of the nation's currency to control coin clipping (the illicit trimming of gold or silver from the edges of coins) and its related inflation.

It is historically known that Newton owned one of Europe's largest book collections on alchemy. Unfortunately, this part of his library was dispersed at the time of his death without an adequate inventory. Although Newton did not publish any large work on alchemy, the subject did continue to preoccupy him during the course of his life. Alchemy had obvious relevance to his work at the mint and its associated work on **metallurgy**. It also interested him because of its relevance to questions about the ultimate structure of matter. Much of Newton's published work on chemistry or alchemy appears in the form of "Queries" placed at the end of *Opticks.* These are rhetorical questions with postulated answers, some of which are quite extensive. Together, the Queries cover some sixty-seven pages. Query 31 alone is thirty text pages long.

metallurgy: the science and technology of metals

Newton's postulated answers concerning the ultimate structure of matter by advancing the idea of atoms with some level of internal structure, a notion anticipating the modern concept of molecules. Newton also postulated on the existence of a nonmaterial substance, an imponderable (unweighable) fluid called ether, which might work at very small distances to repel atoms from one another. Heat, light, electricity, or the reactions of chemistry might be used, Newton suggested, to probe this subtle, imponderable fluid. SEE ALSO ALCHEMY; ATOMS.

David A. Bassett

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Niacin ***See Nicotinamide.***

Nickel

MELTING POINT: 1,455°C
BOILING POINT: 2,913°C
DENSITY: 8.9 g/cm^3
MOST COMMON IONS: Ni^{2+}, Ni^{3+}, Ni^{4+}

28
Ni
NICKEL
58.6934

Nickel is a silver-white, lustrous **metal**. It was first isolated by Swedish chemist Axel Fredrik Cronstedt in 1751. Cronstedt had been attempting to **isolate** copper from a mineral called niccolite (the German word *kupfernickel* means "Devil's copper" or "Old Nick's copper"). He instead found nickel, which he named after the mineral.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

isolate: part of a reaction mixture that is separated and contains the material of interest

The abundance of nickel in Earth's crust is 90 parts per million (ppm); in ocean water, its abundance is 2 parts per billion (ppb). In meteorites, however, its abundance approaches 13,000 ppm. Much of the world's supply of nickel is found in Ontario, Canada, where it is isolated from the ores pentlandite and pyrrhotite. Other large deposits are found in Australia, New Caledonia, Cuba, Indonesia, and Greenland.

isotope: form of an atom that differs by the number of neutrons in the nucleus

The most common **isotope** of nickel is ^{58}Ni, which has a natural abundance of 68.1 percent. Other stable isotopes include ^{60}Ni (26.2%), ^{61}Ni (1.1%), ^{62}Ni (3.6%), and ^{64}Ni (0.9%). Important nickel compounds include nickel oxides (NiO and Ni_2O_3), nickel sulfides (NiS, NiS_2, Ni_3S_2), and nickel chloride ($NiCl_2$).

ductile: property of a substance that permits it to be drawn into wires

alloy: mixture of two or more elements, at least one of which is a metal

Nickel metal is malleable, **ductile**, and a fairly good conductor of electricity and heat. Its most common use is in stainless steels, where it may be combined with various other metals (such as iron, chromium, chromium, copper, etc.) to form **alloys** that are highly resistant to corrosion. Nickel is also used to make coins (U.S. five-cent pieces contain 25 percent nickel), batteries, magnets, and jewelry; to protectively coat other metals; and to color glass and ceramics green. SEE ALSO COORDINATION COMPOUNDS; INORGANIC CHEMISTRY.

Stephanie Dionne Sherk

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Nicotinamide

Nicotinamide is the most common form of the vitamin niacin. Nicotinamide is found in the body as part of nicotinamide adenine dinucleotide (NAD), an important cofactor of many enzymes involved in metabolism and the production of energy from sugars and fats. The structure of nicotinamide, shown in Figure 1, incorporates a six-atom ring, with one nitrogen atom in the ring and another in the amide group side chain. Nicotinic acid is the other common form of niacin. It has the same ring structure but, as shown in Figure 2, oxygen atoms replace the nitrogen atom in the side chain. The nicotinic acid form of the vitamin produces severe side effects when taken in large doses; however, it is sometimes used as a medication to reduce high cholesterol levels in blood. Nicotinic acid was first produced from nicotine long before it was known to be a nutrient. Despite the similarities between nicotine and nicotinic acid, their functions are very different.

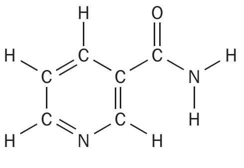

Figure 1. Structure of nicotinamide.

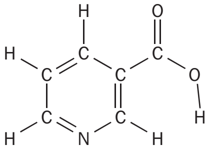

Figure 2. Structure of nicotinic acid.

Niacin and Pellagra

Pellagra is a disease characterized by skin rashes, diarrhea, mental deterioration, and death. Early in the last century it was a serious health problem. Alan Kraut in "Dr. Joseph Goldberger & the War on Pellagra" describes the situation as follows. In 1912 South Carolina alone reported 30,000 cases of pellagra and a mortality rate of 40 percent. In 1914 Dr. Joseph Goldberger (1874–1929) was assigned to study the disease. Goldberger had extensive prior experience treating yellow fever, dengue fever, and typhus. He noted that unlike these other diseases, pellagra was never transmitted from patients to doctors or hospital staff. He also determined that those patients likely to exhibit symptoms of pellagra shared a diet of refined corn flour, molasses, and pork fat. Such observations led Goldberger to deduce that poor nutrition might be the cause of the disease. In 1915 he tested his hypothesis with volunteers from a Mississippi prison. They were fed only the suspect diet and half developed the signs of pellagra within a few months. The symptoms disappeared when meat and vegetables were added to the volunteers' diet. Despite the fact that his study clearly indicated poor nutrition was the cause of pellagra, Goldberger spent the rest of his career attempting to convince political and medical authorities that germs were not the root cause of this dreaded disease. He was perhaps hampered in his efforts by the inability to determine exactly what was missing in the diet. Not until 1937 did Conrad Elvehjem identify the chemical nicotinamide as the cure for pellagra in dogs, followed almost immediately by the work of Thomas Spies, who demonstrated that niacin also cures human pellagra.

Sources of Niacin

The Federal Enrichment Act of 1942 required the millers of flour to restore iron, niacin, thiamin and riboflavin lost in the milling process. Enriched flours and baked goods made from them are now excellent sources of niacin. Niacin may also be found in meat, poultry, fish, whole grains, and peanut butter. Besides direct niacin intake, humans can convert the amino acid tryptophan to niacin. Many people take daily vitamin supplements to ensure they get enough niacin and other essential nutrients. SEE ALSO COENZYME; NICOTINAMIDE ADENINE DINUCLEOTIDE.

David Speckhard

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Nicotinamide Adenine Dinucleotide

Nicotinamide **adenine** dinucleotide (NAD) is the coenzyme form of the **vitamin** niacin. Most biochemical reactions require protein catalysts (enzymes). Some enzymes, lysozyme or trypsin, for example, catalyze reactions by themselves, but many require helper substances such as coenzymes, **metal** ions, and **ribonucleic acid** (RNA). Niacin is a component of two coenzymes: NAD, and nicotinamide adenine dinucleotide phosphate (NADP). NAD^+ (the oxidized form of the NAD coenzyme) is important in **catabolism** and in the production of metabolic energy. $NADP^+$ (the oxidized form of NADP) is important in the **biosynthesis** of fats and sugars.

Hans von Euler is generally recognized as the first to establish the chemical structure of NAD (Metzler, p. 468). Von Euler and Arthur Harden shared the 1929 Nobel Prize in physiology or medicine for the discovery of coenzymes (including NAD). Later von Euler showed that NAD contains two units of the sugar ribose, two phosphate groups, one adenine unit, and

adenine: one of the purine bases found in nucleic acids, $C_5H_5N_5$

vitamins: organic molecules needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

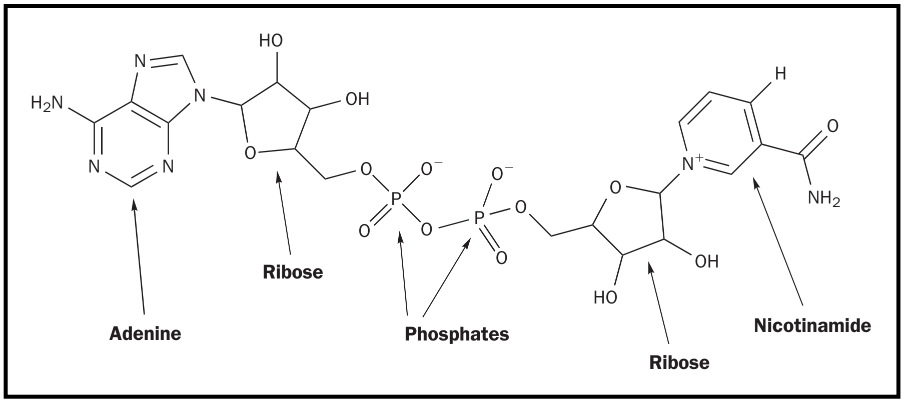
metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

ribonucleic acid: a natural polymer used to translate genetic information in the nucleus into a template for the construction of proteins

catabolism: metabolic process involving breakdown of a molecule into smaller ones resulting in a release of energy

biosynthesis: formation of a chemical substance by a living organism

Figure 1a. Structure of NAD+



one nicotinamide unit (derived from niacin). (See Figure 1a.) The adenine, ribose, and phosphate compounds are linked exactly as in the nucleotide molecule adenosine diphosphate (ADP). In the case of NAD$^+$, the nicotinamide ring has a positive charge on its nitrogen atom: This is the + indicated in the designation NAD$^+$. This is often confusing, because the molecule as a whole is negatively charged due to the presence of the phosphate groups, as shown in the figure. In 1934 Otto Warburg and William Christian discovered a variant of NAD$^+$ in human red blood cell extracts (Metzler, p. 466). This form, called NADP$^+$, contains a third phosphate group attached to one of the ribose rings (see Figure 1b).

NAD$^+$ and NADP$^+$ play an essential role in many biochemical reactions, especially redox reactions in which oxidoreductase enzymes transfer hydrogen. (See Table 1 for a partial list of enzymes that require NAD$^+$ and NADP$^+$.) The redox reaction shown in Figure 2 is catalyzed by the oxidoreductase enzyme alcohol dehydrogenase. In this reaction, two hydrogen atoms and two electrons (the two electrons of the C-H bond) are removed from the ethanol molecule. One hydrogen atom and both electrons, shown in red, are transferred to NAD$^+$, generating NADH. (A molecule's acquisition of electrons is called reduction, thus NADH is the reduced form of NAD$^+$. Conversely, NAD$^+$ is the oxidized form, the form with fewer electrons.) NADP$^+$ can be reduced to NADPH, just as NAD$^+$ can be reduced to NADH, although different enzymes will be involved. Enzymes that use NAD$^+$ rarely use NADP$^+$ and vice versa, making it possible to separate the

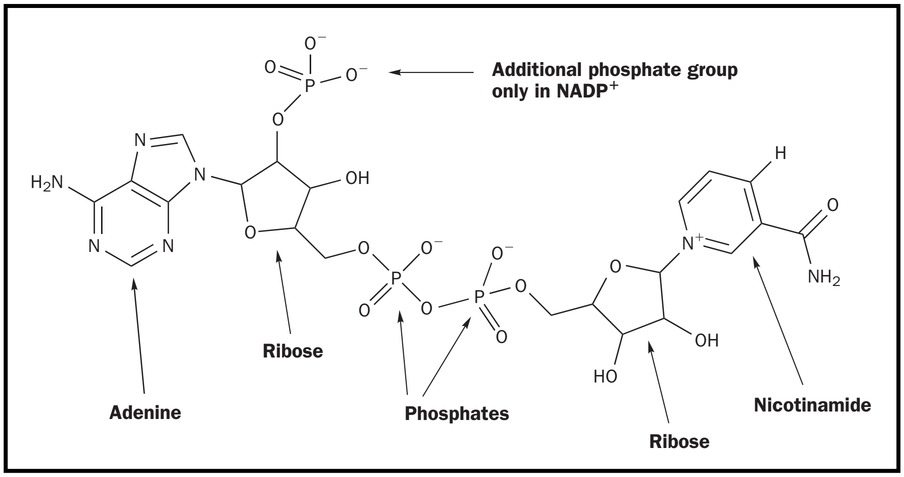


Figure 1b. Structure of NADP+

ENZYMES THAT REQUIRE NAD AND NADP

	Enzyme	Function
Enzymes that use NAD^+/NADH	Alcohol dehydrogenase	Metabolizes alcohol
	Glyceraldehyde phosphate dehydrogenase	Catalyzes important step in glycolysis
	Lactate dehydrogenase	Catalyzes reactions in muscle and liver cells
	Pyruvate dehydrogenase	Catalyzes reactions connecting glycolysis to the Krebs cycle
	α-keto-glutarate dehydrogenase, isocitrate dehydrogenase, malate dehydrogenase	Catalyzes reactions in the Krebs cycle, aerobic metabolism
	NADH dehydrogenase	Catalyzes oxidative phosphorylation reactions
	Hydroxy-acyl-SCoA dehydrogenase	Important in fat catabolism
Enzymes that use $NADP^+$/NADPH	Glucose 6-phosphate dehydrogenase	Catalyzes reactions in the pentose phosphate pathway
	β-ketoacyl-ACP reductase β-enoyl-ACP reductase	Catalyzes reactions in fatty acid synthesis
	Chloroplast glyceraldehyde Phosphate dehydrogenase	Catalyzes reactions in the Calvin cycle, glucose synthesis

Table 1. Enzymes that use NAD^+/NADH and enzymes that use $NADP^+$/NADPH

biosynthetic and energy-producing functions of $NADP^+$ and NAD^+. NAD^+ and $NADP^+$ act as electron acceptors in oxidoreductase catalyzed reactions; NADH and NADPH act as electron donors.

The transfer of hydrogen to NAD^+ is **stereospecific**, and dehydrogenases are now classified as H_A side or H_B side enzymes, according to the "side" of the NAD molecule they act on. Alcohol dehydrogenase, which catalyzes the reaction shown in Figure 2, is an H_A side enzyme, as it promotes the transfer of hydrogen from ethanol to the "A position" of NADH. This specificity was somewhat unexpected, as the flat nicotinamide group can be approached (by a dehydrogenase enzyme) equally well from either side in solution, when NAD^+ is bound to the enzyme; however, one side or the other of NAD is more approachable and therefore preferred.

stereospecific: yielding one product when reacted with a given compound but the opposite product with its stereoisomer

Both NADH and NADPH have a distinctive signal in ultraviolet **spectroscopy**. This signal is lost when NADH or NADPH is oxidized (to NAD^+ or $NADP^+$). This phenomenon has been employed by thousands of scientists to monitor a wide variety of enzyme-catalyzed reactions. SEE ALSO COENZYME; ENZYMES; NICOTINAMIDE.

David Speckhard

spectroscopy: use of electromagnetic radiation to analyze the chemical composition of materials

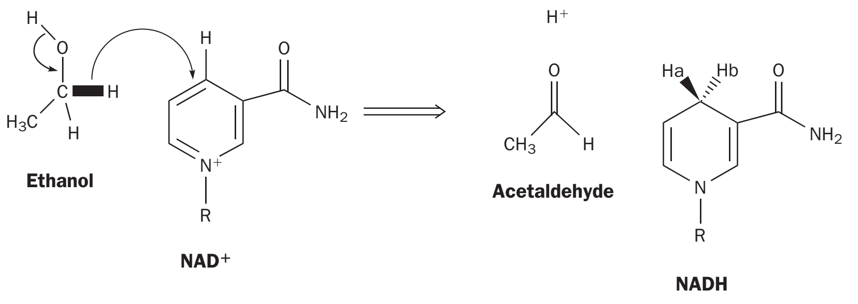


Figure 2. Reduction of NAD to NADH by alcohol dehydrogenase. Note R stands for the remainder of the NAD+ and NADH molecules not shown in the figure or changed in the reaction.

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Nicotine

alkaloid: alkaline nitrogen-based compound extracted from plants

Nicotine, $C_{10}H_{14}N_2$, is a highly toxic, pale yellow **alkaloid** produced in tobacco plants in response to leaf damage. Nicotine is synthesized in the roots of tobacco plants in response to hormones released by damaged tissue, and it is then carried to the leaves, where it is stored in concentrations of between 2 percent and 8 percent by weight. Nicotine is used commercially as an insecticide (it is one of the few poisons to which insects have not become resistant). Tobacco smoke contains nicotine, believed to be the active (and addictive) ingredient.

Mayan peoples of South America used tobacco for recreational and ceremonial, as well as medicinal, purposes. Mayan sculptures depict high-ranking persons smoking cigars and priests blowing tobacco smoke over human sacrifices. By the time of the arrival of Christopher Columbus in the New World, tobacco use had spread throughout both North America and South America. Early accounts by European explorers describe Native Americans carrying glowing sticks from which they inhaled, and many pipes are found among Native American artifacts. Tobacco was often chewed by Native Americans; the juice was dropped into eyes to improve night vision and applied to skin as an agent having antiseptic properties.

The men who accompanied Columbus encountered many users of tobacco, but early European explorers showed little interest in the plant until they acquired an awareness that it might be used to treat diseases. Europeans at first forbade tobacco use, but tobacco gradually gained a reputation among court physicians as a medicine. For many Europeans, tobacco was suddenly a valuable New World commodity.

nonpolar: molecule, or portion of a molecule, that does not have a permanent, electric dipole

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

Nicotine is the active ingredient of tobacco. Nicotine is soluble in water and in **nonpolar** solvents. It can be absorbed by the body from smoke that has been taken into the lungs, or through the skin. It rapidly crosses the blood-brain barrier, appearing in brain tissue minutes after its absorption into capillaries lining the alveoli of the lungs. The presence of nicotine in the body stimulates nicotinic-cholinergic **receptors** of the nervous system, resulting in increased attention span, increased heart rate and blood pressure, and increases in the concentrations of some hormones. Habitual users have a feeling of well-being after intake of nicotine, ascribed to the increased concentrations of dopamine in the brain. The increased metabolic rate that is associated with nicotine use may be what is in back of the common belief that it is easier to lose weight when using nicotine.

Nicotinic-cholinergic receptors that are part of the autonomic nervous system may be stimulated at low concentrations of nicotine, but blocked at higher concentrations. The repeated use of nicotine-containing products (which includes chewing tobacco, chewing nicotine-containing gum, or the use of therapeutic patches that release nicotine for skin absorption) promotes the formation of (new) nicotinic-cholinergic receptors. The tolerance and eventual addiction that go along with repeated use may result in increased craving for nicotine.

Many environmentally hazardous substances, such as asbestos and radon, are much more hazardous when they become mixed with cigarette smoke, probably because the particulate matter in smoke in the atmosphere may adsorb these dangerous substances and carry them into the alveoli of lungs. Many cancers may be caused by substances or materials associated with nicotine use, such as tobacco smoke or the tobacco plant itself (as in chewing tobacco). Nicotine itself, although not known to cause cancer directly, causes proliferation of both healthy and neoplastic cells, and may further the development of cancer by stimulating angiogenesis (the growth of new blood vessels) and thus providing cancerous tissues with increased blood supplies. The effect of nicotine on cell growth is especially strong in tissue environments having low concentrations of carbon dioxide, for example, in damaged lungs; thus, the effect would be greater in persons whose breathing was already impaired. Nicotine's stimulation of cell growth may account for the observation that atherosclerotic plaques (which are intracellular accumulations of **lipids**) grow more rapidly in the presence of this alkaloid substance. This effect may actually become the basis of medical treatments intended to improve blood flow to tissues damaged by atherosclerosis.

lipid: a nonpolar organic molecule; fatlike; one of a large variety of nonpolar hydrophobic (water-hating) molecules that are insoluble in water

Single exposure to nicotine in quantities as small as 50 mg (0.0018 oz) may result in vomiting and seizures; the average cigarette yields about 3 mg (0.00011 oz). As nicotine can be absorbed through skin, accidental exposures in persons working with nicotine-containing pesticide preparations may be fatal. Extracts of chewing tobacco are effective insecticides; commercial insecticide products contain much higher amounts of nicotine than products intended for human consumption. SEE ALSO Dopamine; Radon; Toxicity.

Dan M. Sullivan

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Niobium

MELTING POINT: **2,475°C ±10°C**
BOILING POINT: **~4,740°C**
DENSITY: **8.57g/cm^3 at room temperature**
MOST COMMON IONS: **Nb^{3+}**

41
Nb
NIOBIUM
92.906

Niobium **metal** is typically gray or dull silver in color. It is one of the refractory metals along with tantalum, tungsten, molybdenum, and rhenium, due to its very high melting point. It is estimated that niobium has a natural occurrence in Earth's crust of approximately 20 parts per million (ppm). The largest niobium-containing mineral reserves are located in Brazil and Canada.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

English chemist Charles Hatchett originally discovered niobium in 1801 while examining an ore sample obtained in Connecticut. Since the ore sample came from the United States, he named the unknown material columbium (at the time, Columbia was another name for America). In the 1840s German chemist Heinrich Rose rediscovered the element and named it niobium. Chemically, niobium and the element tantalum are very similar, so niobium was named for Niobe, a daughter of Tantulus (root name for the element tantalum) in ancient mythology. It was not until 1950, at a meeting of the International Union of Pure and Applied Chemistry, that it was finally settled that the element would be called niobium. Many metallurgists and engineers, especially in the United States, still refer to the element as columbium.

alloy: mixture of two or more elements, at least one of which is a metal

nuclear: having to do with the nucleus of an atom

Pure niobium has relatively poor mechanical properties and readily oxidizes in air to niobium pentoxide (Nb_2O_5) at elevated temperatures. Various niobium-containing **alloys** such as Nb-1Zr and C-103 have been successfully used in specific liquid-metal based **nuclear** applications and in the fabrication of various rocket components. SEE ALSO Inorganic Chemistry.

Daniel P. Kramer

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7
N
NITROGEN
14.0067

Nitrogen

MELTING POINT: −210°C
BOILING POINT: −196°C
DENSITY: 0.0012506 g/cm^3
MOST COMMON IONS: NH_4^+, N^{3-}, NO_2^-, NO_3^-

Nitrogen is a gaseous element that is abundant in the atmosphere as the molecule dinitrogen (N_2). Scottish chemist Daniel Rutherford, Swedish chemist Carl Wilhelm Scheele, and English chemist Henry Cavendish independently discovered the element in 1772. Nitrogen received its name in 1790 from French chemist Jean-Antoine Chaptal, who realized that it was present in nitrate (NO_3^-) and nitric acid (HNO_3).

isotope: form of an atom that differs by the number of neutrons in the nucleus

spectroscopy: use of electromagnetic radiation to analyze the chemical composition of materials

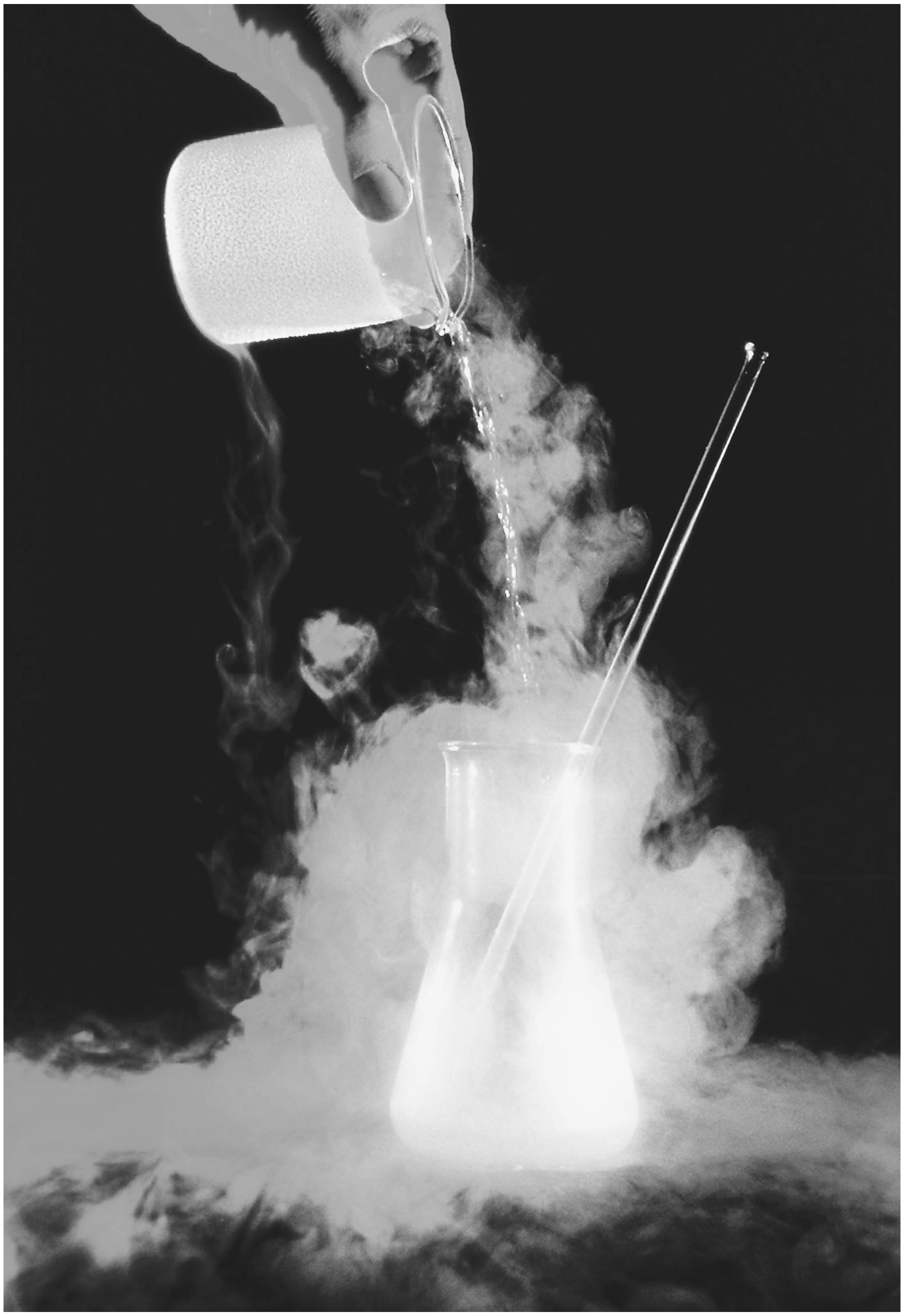
Nitrogen is the most abundant terrestrial element in an uncombined state, as it makes up 78 percent of Earth's atmosphere as N_2, but it is a minor component (19 parts per million) of Earth's crust. Nitrogen exists as two **isotopes**: ^{14}N (99.63% relative abundance) and ^{15}N (0.4% abundance). Both isotopes are nuclear magnetic resonance (NMR) active, with the rarer ^{15}N isotope being utilized more commonly in NMR **spectroscopy** because of its nuclear spin of one-half.

RNA: natural polymer used to translate genetic information in the nucleus into a template for the construction of proteins

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

saltpeter: potassium nitrate; chile saltpeter is sodium nitrate

In its reduced state nitrogen is essential for life because it is a constituent of the nucleotides of deoxyribonucleic acid (**DNA**) and ribonucleic acid (**RNA**) molecules that encode genetic information) and of the amino acids of proteins. The nitrogen-containing minerals **saltpeter** (KNO_3) and sodium nitrate ($NaNO_3$) are found in Chile, India, Bolivia, the former Soviet Union, Spain, and Italy; they were significant as fertilizers and explo-



Liquid nitrogen is being poured into a beaker.

sives precursors prior to modern industrial nitrogen fixation. The global nitrogen cycle between the atmosphere and the biosphere is based on continuous exchanges whereby dinitrogen is fixed by the enzyme nitrogenase in symbiotic bacteria associated with some plant roots, by the Haber-Bosch industrial process for the reduction of N_2 with H_2 to ammonia, and by atmospheric **oxidation** during electrical discharges such as lightning.

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

Dinitrogen possesses the strongest known chemical bond, with a high bond dissociation energy of 945 kJ mol^{-1} and a short N-N triple bond length of 109.8 picometers. This colorless, tasteless, odorless gas is relatively unreactive because of its strong N-N triple bond, a stable electronic configuration, and the lack of a dipole moment. Dinitrogen is reduced by lithium **metal** at room temperature to give the saline (saltlike) lithium nitride (Li_3N).

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Dinitrogen is obtained from the atmosphere by either membrane separations or repetitive cycles of compression and cooling (termed **liquefaction**), followed by **fractional distillation** to separate it from other gases. The major uses of dinitrogen are as blanketing atmospheres for chemical processing and metallurgical production, in glove boxes for handling of dioxygen- and water-sensitive compounds, in electronic materials manufacturing, and in food packaging. Liquid dinitrogen is used as a refrigerant in the laboratory and food industry and in the preservation of biological samples.

liquefaction: process of changing to a liquid form

fractional distillation: separation of liquid mixtures by collecting separately the distillates at certain temperatures

The major industrial applications of nitrogen-containing compounds are in fertilizers and explosives. The most important nitrogenous compounds are ammonia (NH_3), which is used as a fertilizer, refrigerant, nonaqueous solvent, and precursor for many nitrogen compounds including nylon and plastics; nitric acid (HNO_3); ammonium nitrate (NH_4NO_3), a fertilizer and explosive; fertilizers ammonium phosphate and urea ($H_2NC[O]NH_2$). Other important oxides include nitrous oxide (N_2O), used as a dental anesthetic and aerosol propellant, and **nitric oxide** (NO), the simplest stable odd-electron molecule and a short-lived, biologically active neurotransmitter, cytotoxic agent in immunology, vasoconstrictor for blood pressure control, and major component along with NO_2 in **acid rain** and smog. The strong **reducing agent** hydrazine (N_2H_4) is used in controlling the attitude of spacecraft and in rocket fuels.

nitric oxide: compound, NO, which is involved in many biological processes; the drug Viagra enhances NO-stimulation of pathways to counteract impotence; may be involved in killing tumors

acid rain: precipitation that has a pH lower than 5.6; term coined by R. A. Smith during the 1870s

reducing agent: substance that causes reduction, a process during which electrons are lost (or hydrogen atoms gained)

Covalent, intermetallic metal nitrides are among the most stable compounds and are hard, refractory materials that can possess useful properties. For example, titanium nitride (TiN) is used as a gold-colored coating on costume jewelry and as a wear-resistant coating on tool bits; silicon nitride (Si_3N_4) is a strong, thermally stable ceramic material; and gallium nitride (GaN) is a compound semiconductor with optoelectronic applications (e.g., lasers, LEDs). SEE ALSO CAVENDISH, HENRY; GASES; INORGANIC CHEMISTRY; SCHEELE, CARL.

Louis Messerle

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Nitrogen Fixation ***See Haber, Fritz.***

Nobel, Alfred Bernhard

SWEDISH MANUFACTURER, INVENTOR, AND PHILANTHROPIST
1833–1896

Alfred Bernhard Nobel was born in Stockholm, Sweden, on October 21, 1833, as the third of four sons to Immanuel and Andriette (Ahlsell) Nobel. That same year, his father, an engineer and builder, went bankrupt when barges full of building materials were lost at sea. In 1837 Immanuel left Stockholm and moved to St. Petersburg, Russia, where he started manufacturing equipment for the Russian army. His factory flourished, especially with the manufacture and sale of naval mines of his own construction.

Immanuel was eventually able to bring his family to Russia, where his sons were given a private education. Alfred Nobel's interests ranged from literature and poetry to physics and chemistry. Nobel's command of foreign languages was excellent; by the age of seventeen he was fluent in Swedish, Russian, French, English, and German, which aided him in his future business transactions.

In 1863 Nobel began trying to master the process of the **synthesis** of nitroglycerine. His first partial success was a mixture of nitroglycerine with black gunpowder, called "blasting oil." The danger of working with such an unstable material was a problem. After an explosion in Nobel's Stockholm factory that claimed five lives, including that of his brother Emil (1843–1864), the municipal authorities forbade him to carry out further experiments in the town. He then continued his work on a ship anchored on Lake Mälaren.

Swedish manufacturer Alfred Nobel, the inventor of dynamite.

synthesis: combination of starting materials to form a desired product

Nobel began to realize that, for handling purposes, nitroglycerine would have to be absorbed in some kind of stabilizing carrier. After many unsuccessful trials using sawdust, charcoal, paper, and brick-dust, he finally succeeded with Kieselguhr, a diatomaceous earth found in Germany. Even when saturated with nitroglycerine, this earth was quite safe to handle, a blasting cap and detonator being required to force it to explode. Originally called "Kieselguhr-dynamite," its name was later abridged to "dynamite" (the Greek *dynamis* meaning "power"). Nobel was granted a patent for dynamite in England on May 7, 1867, and on September 13 of the same year in Sweden.

In 1868 Nobel and his father were awarded the Letterstedt Prize by the Royal Swedish Academy of Sciences. Nobel highly valued this award, which was the only prize he ever received, and which was perhaps the source of his idea for a similar prize he later established.

Nobel, one of the wealthiest men of his time, constantly moved between his factories and his houses equipped with laboratories. He was both an industrialist and an administrator, handling his business without a secretary. As he wrote in a letter: "My home is where I work, and I work everywhere." His prodigious activities had a negative effect on his health, which had been poor since his youth. After 1890 he preferred to stay at his home in San Remo, Italy. By that time he had 350 patents and ninety-three factories in several countries.

On November 27, 1895, Nobel wrote his last will, in which he generously bequeathed his wealth to his relatives and friends. The second part of his will, however, is more famous, for it is here that he established the Nobel Prizes. Nobel's property that was designated for the fund was worth seventy million Swedish crowns, and has continued to grow since then. Nobel Prizes are awarded in physics, chemistry, medicine, literature, and peace. Since 1969 a Nobel Prize, funded by the Swedish Bank, has also been awarded for outstanding achievements in economy.

Nobel died on December 10, 1896, in San Remo. Shortly before his death he wrote: "It sounds like the irony of fate that I should be ordered to take nitroglycerin internally," which had been prescribed to him as a treatment for angina pectoris. The Nobel Foundation, established in accordance with his will, awarded the first Nobel Prizes in 1901. SEE ALSO EXPLOSIONS.

Vladimir Karpenko

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102
No
NOBELIUM
259

Nobelium

MELTING POINT: **Unknown**
BOILING POINT: **Unknown**
DENSITY: **Unknown**
MOST COMMON IONS: **No^{2+}, No^{3+}**

The first claim for the discovery of the element nobelium was made in Sweden in 1957. However, neither American nor Soviet researchers could duplicate the original results, which are now known to have been interpreted incorrectly. The actual discovery of nobelium is credited to researchers in Berkeley, California, who in 1958 bombarded a curium target (95% ^{244}Cm and 4.5% ^{246}Cm) plated on a nickel foil with 60 to 100 MeV ^{12}C ions, and detected both the 8.4 MeV α-particles created by the **radioactive decay** of ^{252}No and the ^{250}Fm created from the α-decay of ^{254}No. Known **isotopes** of nobelium possess 148 to 160 neutrons and 102 protons; all are radioactive, with half-lives ranging between 2.5 milliseconds and 58 minutes, and decay by spontaneous **fission**, α-particle emission, or electron capture. ^{259}No has the longest half-life: 58 minutes.

radioactive decay: process involving emission of subatomic particles from the nucleus, typically accompanied by emission of very short wavelength electromagnetic radiation

isotope: form of an atom that differs by the number of neutrons in the nucleus

fission: process of splitting an atom into smaller pieces

Nobelium is a member of the actinide series of elements. The ground state electron configuration is assumed to be (Rn)5f147s2, by analogy with the equivalent **lanthanide** element ytterbium ([Kr]4f146s2); there has never been enough nobelium made to experimentally verify the electronic configuration. Unlike the other actinide elements and the lanthanide elements, nobelium is most stable in solution as the dipositive cation No^{2+}. Consequently its chemistry resembles that of the much less chemically stable dipositive lanthanide cations or the common chemistry of the alkaline earth elements. When oxidized to No^{3+}, nobelium follows the well-established chemistry of the stable, tripositive **rare earth elements** and of the other tripositive actinide elements (e.g., americium and curium). SEE ALSO Actinium; Berkelium; Einsteinium; Fermium; Lawrencium; Mendelevium; Neptunium; Plutonium; Protactinium; Rutherfordium; Thorium; Uranium.

lanthanides: a family of elements (atomic number 57 through 70) from lanthanum to lutetium having from 1 to 14 4f electrons

rare earth elements: older name for the lanthanide series of elements, from lanthanum to lutetium

Mark Jensen

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Nobel Metals ***See Gold; Palladium; Platinum; Silver.***

Noble Gases

The noble gases, also known as rare or **inert** gases, form Group 18 of the Periodic Table, embedded between the alkali **metals** and the **halogens**. The elements helium, neon, argon, krypton, xenon, and radon are the members of this group.

inert: incapable of reacting with another substance

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

Discovery

In 1785 English physicist and chemist Henry Cavendish performed an experiment in which he passed electric sparks through an air bubble enclosed by a soap solution (NaOH). While nitrogen and oxygen were absorbed by the solution, about 1/120th of the volume of the original bubble remained—it is now known that the residual gas was mainly argon. However, it was a century later before argon was finally recognized as a new element. In 1894 English physicist John William Strutt noticed that nitrogen produced from air had a slightly higher density than that from nitrogen compounds. Sir William Ramsay, together with Strutt, repeated the Cavendish experiment and identified argon as the unreactive species. The **liquefaction** of air in 1895 by Carl von Linde allowed Ramsay the further discovery of neon, krypton, and xenon. Extraterrestrial helium had been discovered earlier (in 1868), based on its **spectral lines** in the Sun. Ramsay realized that the new elements did not fit into the contemporary periodic system of the elements and suggested that they form a new group, bridging the alkali metals and the halogens. The last member of the family, radon, was discovered in 1900 by Ernest Rutherford and Frederick Soddy as a decay product of radium.

liquefaction: process of changing to a liquid form

spectral line: line in a spectrum representing radiation of a single wavelength

Physical and Chemical Properties

The chemical inertness of the noble gases is based on their electronic structure. Each element has a completely filled **valence** shell. In fact their inertness helped to develop the key idea of a stable octet.

valence: combining capacity

The atomic sizes of the noble gas elements increase from top to bottom in the Periodic Table, and the amount of energy needed to remove an electron from their outermost shell, the **ionization** energy, decreases in the same order. Within each period, however, the noble gases have the largest ionization energies, reflecting their chemical inertness. Based on increasing atomic size, the electron clouds of the spherical, **nonpolar**, atoms become increasingly polarizable, leading to stronger interactions among the atoms (van der Waals forces). Thus, the formation of solids and liquids is more easily attained for the heavier elements, as reflected in their higher melting points and boiling points. As their name implies, all members of the family are gases at room temperature and can, with the exception of helium, be liquefied at atmospheric pressure.

ionization: dissociation of a molecule into ions carrying + or − charges

nonpolar: molecule, or portion of a molecule, that does not have a permanent, electric dipole

Compounds

Until 1962 only physical inclusion compounds were known. Argon, krypton, and xenon form cage or clathrate compounds with water (clathrate hydrates) and with some organics such as quinol. The host molecules are arranged in such a way that they form cavities that can physically trap the noble gas atoms, referred to as "guests." The noble gas will be released upon dissolution or melting of the host **lattice**.

lattice: systematic geometrical arrangement of atomic-sized units that constitute the structure of a solid

A scientist studying helium being released from a hot spring in Yellowstone National Park.

In 1962 the first chemical noble gas compound, formulated as $XePtF_6$, was synthesized by Neil Bartlett. This result spurred intense research activity and led to the discovery of numerous xenon and krypton compounds. In 2000 the formation of the first argon compound, argon fluorohydride (HArF), was reported by Leonid Khriachtchev and colleagues. SEE ALSO ARGON; CAVENDISH, HENRY; HELIUM; KRYPTON; NEON; RAMSAY, WILLIAM; RUTHERFORD, ERNEST; SODDY, FREDERICK; STRUTT, JOHN; XENON.

Tanja Pietraß

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Nomenclature of Inorganic Chemistry

The purpose of nomenclature in chemistry is to convey information about the material being described. The designation chosen should be unequivocal, at least within the limitations of the type of nomenclature adopted. The type adopted will depend in part on the total amount of information to be conveyed, the kind of compound to be described, and the whim of the person describing the compound.

Nomenclaturists use the terms “trivial” and “systematic” to describe two major divisions of nomenclature. Systematic nomenclature is based on established principles so that it can be extended in a logical way to describe known, new, and hypothetical compounds. A trivial nomenclature is one established by rule of thumb and includes many of the older names (spirit of salt, aqua regia, etc.) and lab nomenclatures (the green chelate, etc.).

Actual usage is often a mixture of the two types, and the fundamental bases of all chemical names, those of the elements, are essentially trivial. Note that the name methane is trivial, but that the name pentane is not. For this discussion, a formula representing a compound can be regarded simply as a kind of name. The principal general (but by no means the only) types of nomenclature used in inorganic chemistry are substitutive and additive (coordination).

Substitutive Nomenclature

Substitutive nomenclature is essentially an organic invention and follows the historical development of organic chemistry. It starts with the designation of an appropriate parent compound from which the compound under discussion can be developed formally by substitution or replacement processes. In organic chemistry these parents can be the paraffins, and in inorganic chemistry they are generally (and arbitrarily) taken to be the hydrides of the elements of Periodic Groups 14, 15, and 16, plus boron, which also has an additional rather specific nomenclature of its own. Thus the formula SiH_3Cl can be named chlorosilane, as a substituted derivative of the saturated parent SiH_4, silane (compare chloromethane). The generation of a radical by the loss of a hydrogen atom from the parent is indicated by modification of the termination, silane becoming silyl, $SiH_3^{\cdot}$ (the superscript dot indicates an unpaired electron). The name silyl can be used to represent a substituent group in another parent hydride (compare methyl) or for the unbound radical, and the procedure is quite general for all parent hydrides to which the methodology is applied. Silane can also be modified formally by the removal of a proton, yielding the **anion** SiH_3^-. The name then takes the characteristic anion ending -ide: silanide. The formal addition of a proton is indicated by another termination (-ium), giving SiH_5^+, silanium. These terminations are used generally in inorganic nomenclature, as in chloride for Cl^- and ammonium for NH_4^+. Other formal operations recognized in substitutive nomenclature include addition or removal of a hydride from the parent. This can be indicated by the termination -ylium, giving the name silylium for SiH_3^+.

anion: negatively charged chemical unit, like Cl^-, CO_3^{2-}, or NO^{3-}

Other Modifications of Names

The terminations cited above can be used generally in inorganic nomenclature. However, they are sometimes not applicable, especially where parent hydrides are not reasonably definable. Inorganic chemists have tended to assign electropositive and **electronegative** character to elements, though numerical values are not necessarily easy to define. **Metals** are generally assigned electropositive character and nonmetals electronegative character. The names developed on this basis may imply formally a saltlike nature even in compounds that are not really salts at all. Thus common salt is called sodium chloride, which is ionic, but phosphorus trichloride is certainly not saltlike.

electronegative: tending to attract electrons

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

It is not wise to infer the detailed physical nature of a compound from the name alone. In this system the name of the (electropositive) metal is not modified from that of the element, but the name of the electronegative element is, and in the way described in the Substitutive Nomenclature section, above. Similarly we derive oxide and sulfide, for example, from oxygen and sulfur. The same division between electronegative and electropositive parts is evident in the covalent nonionic compound $SiCl_4$, which can be named silicon **tetrachloride**, though an equally valid substitutive name is tetrachlorosilane.

tetrachloride: term that implies a molecule has four chlorine atoms present

Inorganic chemists also use a further termination to indicate the name of a cation. This is the ending -ate, and it is used as a modification of the name of an oxoacid. Thus sulfuric acid, H_2SO_4, gives rise to sulfate, SO_4^{2-}, phosphoric acid to phosphate, PO_4^{3-}, and nitric acid to nitrate, NO_3^-. The partially deprotonated anions such as HSO_4^- and $H_2PO_4^{2-}$ are rather more complicated to deal with, and are discussed in *Nomenclature of Inorganic Chemistry*, often referred to as the Red Book.

In an older procedure that is no longer recommended, the name of an electropositive element displaying more than one **oxidation** state in its compounds was sometimes modified to indicate the particular oxidation state involved. Thus iron chlorides were often named ferrous chloride and ferric chloride to convey the two oxidation states of II and III (note that, like normal arabic numbers, these Roman numerals are positive unless otherwise shown by a negative sign). However, the use was not consistent. Cuprous and cupric chlorides indicated oxidation states I and II, and phosphorous and phosphoric chlorides indicated oxidation states III and V. Modern nomenclature specifies the oxidation state of the electropositive partner in these compounds directly: iron(II) chloride, iron(III) chloride, copper(I) chloride, copper(II) chloride, phosphorus(III) chloride, and phosphorus(V) chloride. These designations are unequivocal. The number of counter anions, 1, 2, 3, or 5, should immediately be evident. Examples of negative oxidation states include oxide(-II) or oxide(2-), and dioxide(-I) or dioxide(2-). Note that in a multi-atom group, of which PO_4^{3-} may be taken as an example, the charge on any given atom may not be evident, even if the overall charge is known. In contrast, the oxidation states phosphorus(V) and oxide(–II) are much more readily defined. The use of such charges in names and formulae in these circumstances is not recommended.

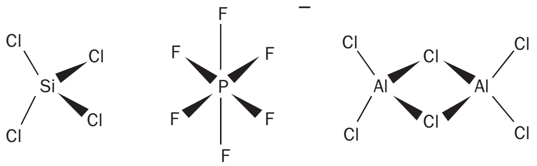
oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

Formulae

The rules for formulae for the compounds discussed above are rather elastic. At its simplest, a formula is a list of element symbols accompanied by multiplying subscripts indicating the atomic proportions of each kind of atom. These formulae may be empirical, simply corresponding to the atom ratios, or stoichiometric, representing the totality of the atoms within a molecule. The latter can be used to calculate a molecular weight. Strictly speaking, for a compound that exists as discrete molecules, this latter can also be termed a molecular formula, but this is a misnomer for ionic compounds and for compounds of which the structure changes with temperature. The ordering of these symbols can be adjusted to suit the requirements of the user. At the simplest, an alphabetical order is used, since this is the same in most European languages. Many chemists emphasize the importance of carbon and hydrogen and adopt a sequence C, H, N, and then the remaining element symbols in alphabetical order. Such devices are often employed in indexes. Inorganic chemists often group the atomic symbols in a formula in electropositive and electronegative groups, designated as discussed above. This can be a somewhat arbitrary procedure, and the relative positions of atoms in an electronegativity sequence may be established using the Periodic Table. For simple cases, formulae such as NaCl or $SiCl_4$ are used. Anionic groups are assumed to be electronegative, hence $Ca_3(PO_4)_2$. The parentheses are used to define the associated groups of atoms within the formula.

Formulae can also be used to indicate two- or three-dimensional structures. This is particularly useful for coordination compounds, which are discussed next. However, this use is not restricted to classical coordination compounds, as the following examples show. Special devices are often adopted to indicate bonds or lines that are not in the plane of the paper. Their use is not consistent throughout chemistry, but the meaning in any given case is generally obvious.

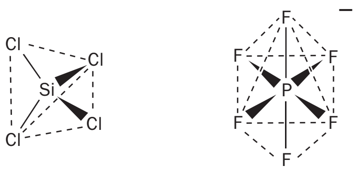
Figure 1.



The first example represents a tetrahedral arrangement, because the solid defined by the four chlorine atoms at its apices is a tetrahedron. The second is **octahedral**, and the third represents two edge-fused tetrahedra. The wedge bonds are pointing in front of or behind the plane of the paper; the thin lines designate bonds in the plane of the paper.

octahedral: relating to a geometric arrangement of six ligands equally distributed around a Lewis acid; literally, eight faces

Figure 2.



Inorganic chemists often represent tetrahedra, octahedra, and other shapes in their formulae, to help the reader identify molecular shapes. The broken lines designating these shapes are not intended to represent bonds between atoms.

Oxidation states may also be indicated in formulae where this is helpful, though the need to do so is not common in the simplest cases. The following examples show the formalism employed: $Fe^{II}Cl_2$, $Fe^{III}Cl_3$, $Cu^{I}Cl$, $Cu^{II}Cl_2$, $P^{III}Cl_3$, $P^{V}Cl_5$.

Coordination Nomenclature

This is an additive nomenclature, and just as organic chemists have developed substitutive nomenclature in parallel with the methodology of substitutive chemistry, inorganic chemists have developed a nomenclature for coordination compounds that arises from the formal assembly of a

ligand: molecule or ion capable of donating one or more electron pairs to a Lewis acid

organometallic compound: compound containing both a metal (transition) and one or more organic moieties

coordination entity from its components, a central metal ion (in the simplest cases) and its **ligands**. Such a coordination entity may be neutral or it may carry a charge, positive or negative. Any such charge may be shown in the usual way, using formalisms such as 2- and 3-. Clearly **organometallic compounds**, depending upon their type, may be named either from substituted parent hydrides or as coordination entities.

Formulae in Coordination Nomenclature

The general rule is that the formula of a coordination entity should always appear within square brackets, even when the entity itself is an infinite polymer. The use of enclosing marks (square brackets, curly brackets, and parentheses) is slightly different for the usage that is common in organic chemistry. The usual priority sequence is [( )], [{( )}], [{[( )]}], [{{[( )]}}], and so on. Brackets should always be used if they make the formula clearer. The order of symbol citation within the formula of a coordination entity should begin with the metal ion followed by the ligands, ideally with charged ligands cited in alphabetical order using the first symbol of the ligand formula, and these are then followed as a class by the neutral ligand formulae, similarly ordered. The division into neutral and charged ligands can be somewhat arbitrary. Since a ligand is generally assumed to present a lone pair of electrons to the central metal, groups such as CH_3 are formally regarded as anions rather than as radicals with unpaired electrons, even though they usually carry the names of radicals. Compounds that really do possess unpaired electrons in the free state can cause problems, especially when calculating oxidation states. For coordination nomenclature purposes, NO, nitrogen(II) oxide, is considered to be a neutral ligand. Complicated ligands may be represented by abbreviations rather than formulae, and lists of recommended abbreviations have been published in sources such as *Nomenclature of Inorganic Chemistry*. Some examples of these usages are shown in Table 1. The use of square brackets to indicate the coordination entity is fundamental and is a particularly useful device.

Note the negative oxidation state and the η (hapto) connectivity symbol in the last two examples. Where appropriate, stereochemical descriptors, such as *cis*-, *trans*-, *mer*-, and *fac*-, polyhedral descriptors, and chirality descriptors may be added to give structural information, but these are more often used in names, except for the simplest formulae. Polynuclear species may be described using the appropriate multiplicative suffixes, and bridging ligands can also be shown. The bridging symbol μ_n is useful for this pur-

Compound formulae	Complex ion formulae	Showing oxidation state
$[Co(NH_3)_6]Cl_3$	$[Co(NH_3)_6]^{3+}$	$[Co^{III}(NH_3)_6]^{3+}$
$[CoCl(NH_3)_5]Cl_2$	$[CoCl(NH_3)_5]^{2+}$	$[Co^{III}Cl(NH_3)_5]^{2+}$
$[CoCl(NO_2)(NH_3)_4]Cl$	$[CoCl(NO_2)(NH_3)_4]^{+}$	$[Co^{III}Cl(NO_2)(NH_3)_4]^{+}$
$[PtCl(NH_2CH_3)(NH_3)_2]Cl$	$[PtCl(NH_2CH_3)(NH_3)_2]^{+}$	$[Pt^{II}Cl(NH_2CH_3)(NH_3)_2]^{+}$
$[CuCl_2\{O{=}C(NH_2)_2\}_2]$		$[Cu^{II}Cl_2\{O{=}C(NH_2)_2\}_2]$
$K_2[PdCl_4]$	$[PdCl_4]^{2-}$	$[Pd^{II}Cl_4]^{2-}$
$K_2[OsCl_5N]$	$[OsCl_5N]^{2-}$	$[Os^{VI}Cl_5N]^{2-}$
$Na[PtBrCl(NO_2)(NH_3)]$	$[PtBrCl(NO_2)(NH_3)]^{-}$	$[Pt^{II}BrCl(NO_2)(NH_3)]-$
$[Co(en)_3]Cl_3$	$[Co(en)_3]^{3+}$	$[CoI^{III}(en)_3]^{3+}$
$Na_2[Fe(CO)_4]$	$[Fe(CO)_4]^{2-}$	$[Fe^{-II}(CO)_4]^{2-}$
$[Co(\eta^5-C_5H_5)_2]Cl$	$[Co(\eta^5-C_5H_5)2]^{+}$	$[Co^{II}(\eta^5-C_5H_5)_2]^{+}$

Table 1.

pose. The subscript may be omitted if a ligand bridges only two groups. Polymeric materials can be indicated in an empirical formula using the indeterminate subscript *n*. When there are different central metal ions present in a polynuclear compound, the established priority sequence for metal ions should be used to determine the order of citation.

$$[\{Cr(NH_3)_5\}(OH)\{Cr(NH_3)_5\}]^{5+} \text{ or } [\{Cr(NH_3)_5\}_2(\mu\text{-}OH)]^{5+}$$

$$[Re_2Br_8]^{4-} \text{ or } [(ReBr_4)_2]^{4-}$$

$$[[IrCl_2(CO)\{P(C_6H_5)_3\}_2](HgCl)]$$

$$[\{PdCl_2\}_n] \text{ or } [\{Pd(\mu\text{-}Cl)_2\}_n]$$

Names in Coordination Nomenclature

The names of coordination entities are assembled using principles similar, but not identical, to those used for formulae. The central atom is always cited last. Its name may be modified by an oxidation state symbol. The ligands are presented in the alphabetical order of their initial letters, neglecting for this purpose any multiplicative prefixes. It is not necessary to divide the ligands into neutral and charged groups. However, the names of negatively charged ligands are generally modified by adding the postfix suffix -o in place of the final -e where it occurs, to indicate that they are indeed bound and not free. As an exception, this is not the case with hydrocarbon ligands such as methyl and ethyl, which retain the names of radicals. The names of neutral ligands are not modified. If the coordination entity itself is negatively charged (but not when it is neutral or positively charged), then the name of the central atom is modified by the ending -ate. These practices are illustrated below.

$[Co(NH_3)_6]Cl_3$	hexaamminecobalt(III) trichloride
$[Co(NH_3)_6]^{3+}$	hexaamminecobalt(3+)
$[CoCl(NH_3)_5]Cl_2$	pentaamminechlorocobalt(III) trichloride
$[CoCl(NH_3)_5]^{2+}$	pentaamminechlorocobalt(2+)
$[CoCl(NO_2)(NH_3)_4]Cl$	tetraamminechloronitritocobalt(III) chloride
$[CoCl(NO_2)(NH_3)_4]^{+}$	tetraamminechloronitritocobalt(1+)
$[PtCl(NH_2CH_3)(NH_3)_2]Cl$	bisamminechloromethylamineplatinum(II) chloride
$[PtCl(NH_2CH_3)(NH_3)_2]^{+}$	diamminechloromethylamineplatinum(+)
$[CuCl_2\{O{=}C(NH_2)_2\}_2]$	dichlorobis(urea)copper(II)
$K_2[PdCl_4]$	potassium tetrachloropalladate(II)
$K_2[OsCl_5N]$	potassium pentachloronitrodoosmate(VI)
$[Co(H_2O)_2(NH_3)_4]Cl$	tetraamminediaquacobalt(III) chloride

Note that in some cases it may be useful to introduce additional enclosing marks to ensure clarity: for example, to avoid possible confusion between chloromethylamine, $ClCH_2NH_2$, and (chloro)methylamine, which implies two separate ligands, Cl and CH_3NH_2. It is for the writer to decide whether such a strategy is useful, depending on the particular case under review. Ammonia as a ligand has the name ammine. Similarly, water has the coordination name aqua.

$Na[PtBrCl(NO_2)(NH_3)]$	sodium amminebromochloronitrito-platinate(II)
$[Co(en)_3]Cl_3$	tris(ethane-1,2-diamine)cobalt(II) trichloride
$Na_2[Fe(CO)_4]$	sodium tetracarbonylferrate(-II)
$[Co(\eta^5\text{-}C_5H_5)_2]Cl$	bis(cyclopentadienyl)cobalt(III) chloride or bis(η^5-cyclopentadienyl)cobalt(III) chloride.

coordination chemistry: chemistry involving complexes of metal ions surrounded by covalently bonded ligands

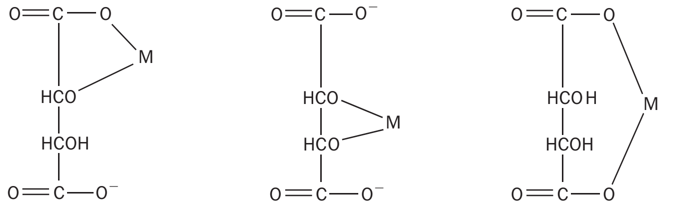
The symbol η is used above and also quite generally throughout organometallic **coordination chemistry** to indicate the number of carbon atoms in a ligand that are coordinated to the metal. Other devices to indicate connectivity are the italicized atomic symbols of the donor atoms (useful for indicating structure in complexes containing chelating and polydentate ligands), and for some complicated cases, the κ symbolism may be useful. Examples follow in Figure 3.

Further devices are used in coordination names to show polymeric structures, which may contain bridging groups and metal-metal bonds.

$[\{Pd(\mu\text{-}Cl)_2\}_n]$	poly(di-μ-chloropalladium)
$[\{Cr(NH_3)_5\}(OH)\{Cr(NH_3)_5\}]^{5+}$	μ-hydroxo-bis[pentaamminechromium(III)](5+)
$[(ReBr_4)_2]^{4-}$	bis(tetrabromorhenate)(*Re-Re*)(2-)
$[[IrCl_2(CO)\{P(C_6H_5)_3\}_2](HgCl)]$	carbonyl-1κC-trichloro-1κ^2,2κCl-bis(triphenylphosphine-1κP)iridium mercury(*Hg-Ir*)

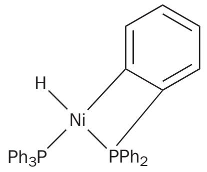
Where different metals are present, priority rules must be applied to assign metal locants.

For more information on this and other topics cited above, as well as for descriptions of the use of geometrical and stereo descriptors, polyhedral



tartrato(3-)-O^1,O^2 **tartrato(4-)-O^2,O^3** **tartrato(2-)-O^1,O^4**

Possible modes of binding of tartrate to a metal M



[2-(diphenylphosphino-κP)phenyl-κC^1]hydrido(triphenylphosphine-κP)nickel(II)

Figure 3.

symbols, and configuration indices in names, the reader is referred to the books cited in the bibliography. The international authority with the task of formalizing nomenclature rules, assigning the names of new elements, etc., is the International Union of Pure and Applied Chemistry (IUPAC). All the publications cited in the bibliography carry the authority of IUPAC. Some more specialized inorganic nomenclatures are described in *Nomenclature of Inorganic Chemistry II. Principles of Chemical Nomenclature* and *A Guide to IUPAC Nomenclature of Organic Compounds* offer more general treatments suitable for those not requiring the most detailed information. SEE ALSO BONDING.

G. J. Leigh

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Norepinephrine

Norepinephrine (noradrenaline) belongs to a family of biological compounds called catecholamines. These compounds are synthesized in sympathetic neurons and in the adrenal glands. Norepinephrine is produced from the catecholamine dopamine by the action of the enzyme dopamine β-hydroxylase. This enzyme is responsible for the addition of a hydroxyl (–OH) group at the β carbon. (See Figure 1.) In certain cells of the adrenal glands, norepinephrine is chemically transformed into epinephrine (adrenaline), the hormone responsible for the fight-or-flight response. Epinephrine differs from norepinephrine by the presence of a methyl ($-CH_3$) group on the nitrogen atom.

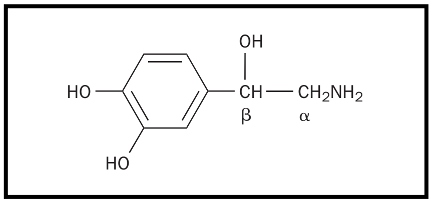

Figure 1. The structure of norepinephrine. Carbon atoms of the side chain are labeled.

Norepinephrine functions biologically as a neurotransmitter, transmitting a signal from one neuron to another neuron or muscle cell. After release from a neuron, norepinephrine diffuses through the tiny space between the cells (the synapse), where it can bind to a **receptor** protein on the surface of a nearby cell. Nerve impulses are typically short-lasting because the neurotransmitter dissociates from its receptor. Once this happens, the neurotransmitter can quickly be chemically altered or transported into another cell, either of these terminating the nerve impulse.

The family of receptors that responds to norepinephrine and related compounds are called adrenergic receptors. Adrenergic receptors in the peripheral nervous system are important in the activity of smooth muscle and cardiac muscle and in **metabolism**. The effect on most smooth muscle is relaxation, whereas the effect on cardiac muscle is to increase the force and rate of **contraction**. Drugs that mimic the action of norepinephrine are

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

metabolism: the complete range of biochemical processes that take place within living organisms; comprises processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those that break down complex food molecules, thus liberating energy (catabolism)

contraction: the shortening of a normal trend of a quantity

often used to treat asthma because they relax bronchial smooth muscle, helping the asthma patient to breathe more easily. Drugs called β-blockers bind to adrenergic receptors but block activation. Because this results in a decrease in blood pressure, β-blockers are commonly prescribed to treat high blood pressure. Adrenergic receptor activity is also important within the central nervous system. Some drugs used to treat depression prolong the adrenergic nerve impulse by allowing norepinephrine to remain in synapses for longer periods. SEE ALSO EPINEPHRINE; INHIBITORS; NEUROTRANSMITTERS.

Jennifer L. Powers

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Northrop, John

AMERICAN BIOCHEMIST
1891–1987

John Northrop shared the Nobel Prize in chemistry in 1946 with Wendell Stanley, awarded to them "for their preparation of enzymes and virus proteins in a pure form," and with James Sumner, "for his discovery that enzymes can be crystallized." Although Sumner had been the first, in 1926, to crystallize an enzyme (urease) and to aver that enzymes were proteins, Northrop did more than any other scientist to establish that pure enzymes are indeed proteins.

crystallization: process of producing crystals of a substance when a saturated solution in an appropriate solvent is either cooled or some solvent removed by evaporation

About 1920 Northrop repeated the earlier claim of Cornelis Pekelharing that he had isolated a protein from gastric juice (the enzyme pepsin). Neither Pekelharing nor Northrop was able to crystallize the protein. However, Sumner's **crystallization** of urease encouraged Northrop to take up the problem again. In 1930 Northrop isolated a crystalline substance from a commercial pepsin preparation, and the crystallized substance appeared to be the enzyme pepsin. Subsequently Northrop, together with Moses Kunitz, isolated and crystallized trypsin, trypsinogen, chymotrypsin, and chymotrypsinogen.

electrophoresis: migration of charged particles under the influence of an electric field, usually in solution; cations, positively charged species, will move toward the negative pole and anions, the negatively charged species, will move toward the positive pole

Northrop carefully tested his enzyme preparations by means of solubility measurements, ultracentrifuge analysis, and **electrophoresis**, and concluded that they were essentially pure proteins. From measurements of diffusion, denaturation, hydrolysis, and the formation of active enzyme from inactive precursor, he concluded that enzymatic activity was a property of the protein molecule itself and was not due to a nonprotein impurity.

Northrop had long had an interest in viruses and bacteriophage—things that occupied his attention increasingly in his later years. Though he was more concerned with the protein component of bacteriophage than their nucleic acid component, in 1951 he made the prophetic suggestion: "The nucleic acid may be the essential autocatalytic self-reproducing part of the molecule, and the protein portion may be necessary only to allow the entrance to the host cell."

John Howard Northrop was born into an academic family in Yonkers, New York, in 1891. He entered Columbia University in 1908, from which institution he received his Ph.D. in chemistry in 1915. In 1916 he was appointed to the Rockefeller Institute, and he remained there for the rest of his working life. In 1924 he transferred to the Princeton branch of the institute, where most of his significant work on proteins was performed. In 1949, when the institute closed its Princeton branch, Northrop moved to the University of California at Berkeley as professor of bacteriology and biophysics, while remaining a member of the institute and continuing to receive its support for his work. He retired in 1959. He died in 1987, aged ninety-five. SEE ALSO Hydrolysis; Proteins.

Keith L. Manchester

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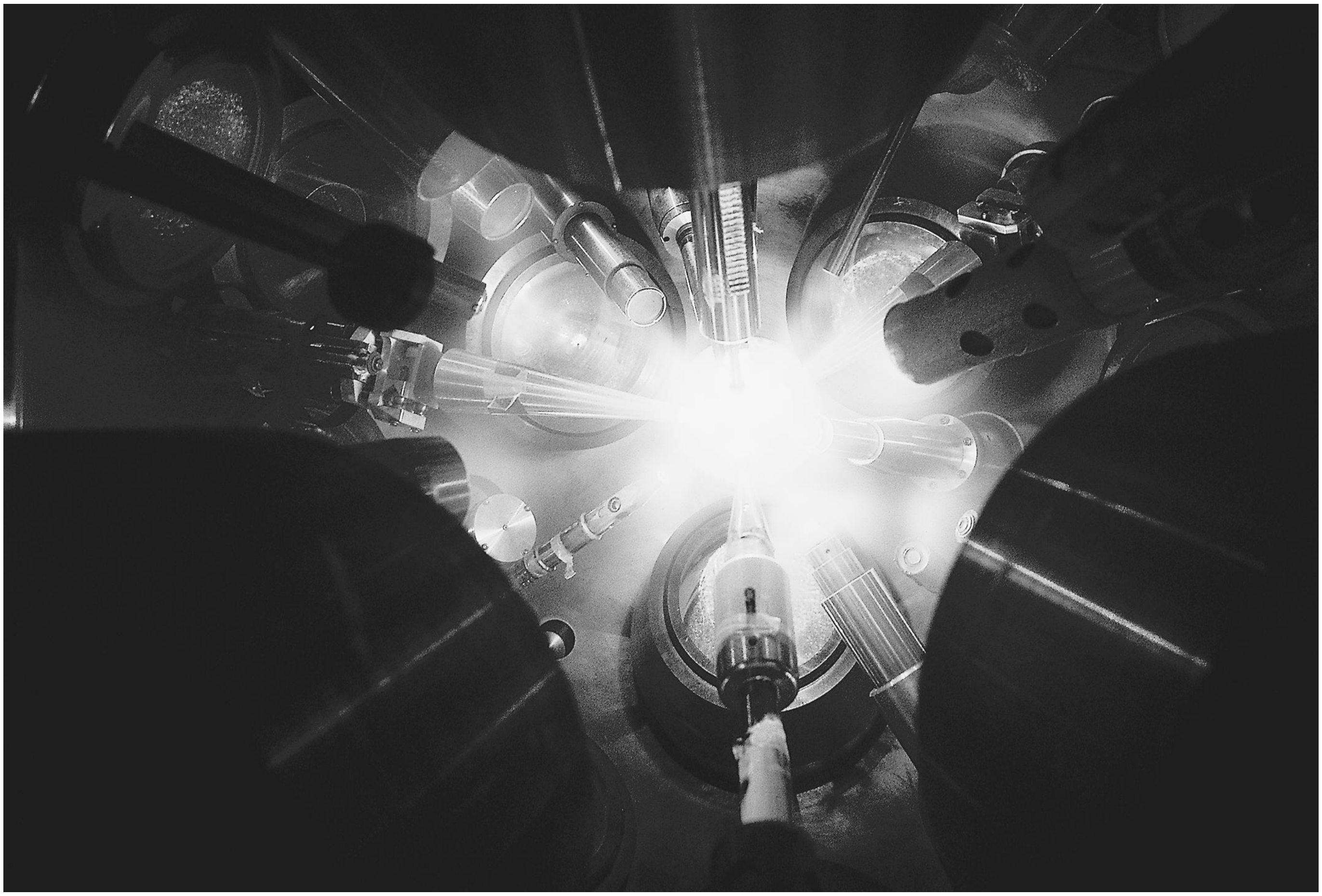
Nuclear Chemistry

Nuclear chemistry is the study of the chemical and physical properties of elements as influenced by changes in the structure of the atomic nucleus. Modern nuclear chemistry, sometimes referred to as radiochemistry, has become very interdisciplinary in its applications, ranging from the study of the formation of the elements in the universe to the design of radioactive drugs for diagnostic medicine. In fact, the chemical techniques pioneered by nuclear chemists have become so important that biologists, geologists, and physicists use nuclear chemistry as ordinary tools of their disciplines. While the common perception is that nuclear chemistry involves only the study of radioactive nuclei, advances in modern mass spectrometry instrumentation has made chemical studies using stable, nonradioactive **isotopes** increasingly important.

isotope: form of an atom that differs by the number of neutrons in the nucleus

There are essentially three sources of radioactive elements. Primordial nuclides are radioactive elements whose half-lives are comparable to the age of our solar system and were present at the formation of Earth. These nuclides are generally referred to as naturally occurring radioactivity and are derived from the radioactive decay of thorium and uranium. Cosmogenic nuclides are atoms that are constantly being synthesized from the bombardment of planetary surfaces by cosmic particles (primarily protons ejected from the Sun), and are also considered natural in their origin. The third source of radioactive nuclides is termed anthropogenic and results from human activity in the production of nuclear power, nuclear weapons, or through the use of particle accelerators.



Lasers focus on a small pellet of fuel in attempt to create a nuclear fusion reaction (the combination of two nuclei to produce another nucleus) for the purpose of producing energy.

Marie Curie was the founder of the field of nuclear chemistry. She was fascinated by Antoine-Henri Becquerel's discovery that uranium minerals can emit rays that are able to expose photographic film, even if the mineral is wrapped in black paper. Using an electrometer invented by her husband Pierre and his brother Jacques that measured the electrical conductivity of air (a precursor to the Geiger counter), she was able to show that thorium also produced these rays—a process that she called radioactivity. Through tedious chemical separation procedures involving **precipitation** of different chemical fractions, Marie was able to show that a separated fraction that had the chemical properties of bismuth and another fraction that had the chemical properties of barium were much more radioactive per unit mass than the original uranium ore. She had separated and discovered the elements polonium and radium, respectively. Further purification of radium from barium produced approximately 100 milligrams of radium from an initial sample of nearly 2,000 kilograms of uranium ore.

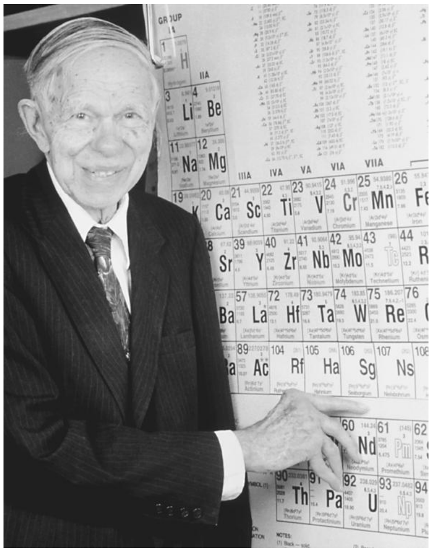
precipitation: process involving the separation of a solid substance from a solution

In 1911 Ernest Rutherford asked a student, George de Hevesy, to separate a lead impurity from a decay product of uranium, radium-D. De Hevesy did not succeed in this task (we now know that radium-D is the radioactive isotope ^{210}Pb), but this failure gave rise to the idea of using radioactive isotopes as tracers of chemical processes. With Friedrich Paneth in Vienna in 1913, de Hevesy used ^{210}Pb to measure the solubility of lead salts—the first application of an isotopic tracer technique. De Hevesy went on to pioneer the application of isotopic tracers to study biological processes and is generally considered to be the founder of a very important area in which nuclear chemists work today, the field of nuclear medicine. De Hevesy also is credited with discovering the technique of neutron activation analysis, in which samples are bombarded by neutrons in a nuclear reactor or from a neutron generator, and the resulting radioactive isotopes are measured, allowing the analysis of the elemental composition of the sample.

In Germany in 1938, Otto Hahn and Fritz Strassmann, skeptical of claims by Enrico Fermi and Irène Joliot-Curie that bombardment of uranium by neutrons produced new so-called transuranic elements (elements beyond uranium), repeated these experiments and chemically isolated a radioactive isotope of barium. Unable to interpret these findings, Hahn asked Lise Meitner, a physicist and former colleague, to propose an explanation for his observations. Meitner and her nephew, Otto Frisch, showed that it was possible for the uranium nucleus to be split into two smaller nuclei by the neutrons, a process that they termed "**fission**." The discovery of nuclear fission eventually led to the development of nuclear weapons and, after World War II, the advent of nuclear power to generate electricity. Nuclear chemists were involved in the chemical purification of plutonium obtained from uranium targets that had been irradiated in reactors. They also developed chemical separation techniques to isolate radioactive isotopes for industrial and medical uses from the fission products wastes associated with plutonium production for weapons. Today, many of these same chemical separation techniques are being used by nuclear chemists to clean up radioactive wastes resulting from the fifty-year production of nuclear weapons and to treat wastes derived from the production of nuclear power.

fission: process of splitting an atom into smaller pieces

In 1940, at the University of California in Berkeley, Edwin McMillan and Philip Abelson produced the first manmade element, neptunium (Np), by the bombardment of uranium with low energy neutrons from a nuclear accelerator. Shortly thereafter, Glenn Seaborg, Joseph Kennedy, Arthur Wahl, and McMillan made the element plutonium by bombarding uranium targets with deuterons, particles derived from the heavy isotope of hydrogen, deuterium (^2H). Both McMillan and Seaborg recognized that the chemical properties of neptunium and plutonium did not resemble those of rhenium and osmium, as many had predicted, but more closely resembled the chemistry of uranium, a fact that led Seaborg in 1944 to propose that the transuranic elements were part of a new group of elements called the actinide series that should be placed below the lanthanide series on the periodic chart. Seaborg and coworkers went on to discover many more new elements and radioactive isotopes and to study their chemical and physical properties. At the present, nuclear chemists are involved in trying to discover new elements beyond the 112 that are presently confirmed and to study the chemical properties of these new elements, even though they may exist for only a few thousandths of a second.



Nobel laureate Glenn T. Seaborg was among those who discovered many radioactive elements and isotopes.

As early as 1907 Bertram Boltwood had used the discovery of radioactive decay laws by Ernest Rutherford and Frederick Soddy to ascribe an age of over two billion years to a uranium mineral. In 1947 Willard Libby at the University of Chicago used the decay of ^{14}C to measure the age of dead organic matter. The cosmogenic radionuclide, ^{14}C, becomes part of all living matter through photosynthesis and the consumption of plant matter.

Once the living organism dies, the ^{14}C decays at a known rate, enabling a date for the carbon-containing relic to be calculated. Today, scientists ranging from astrophysicists to marine biologists use the principles of radiometric dating to study problems as diverse as determining the age of the universe to defining food chains in the oceans. In addition, newly developed analytical techniques such as accelerator mass spectrometry (AMS) have allowed nuclear chemists to extend the principles of radiometric dating to nonradioactive isotopes in order to study modern and ancient processes that are affected by isotopic fractionation. This isotopic fractionation results from temperature differences in the environment in which the material was formed (at a given temperature, the lighter isotope will be very slightly more reactive than the heavier isotope), or from different chemical reaction sequences.

The newest area in which nuclear chemists play an important role is the field of nuclear medicine. Nuclear medicine is a rapidly expanding branch of health care that uses short-lived radioactive isotopes to diagnose illnesses and to treat specific diseases. Nuclear chemists synthesize drugs from radionuclides produced in nuclear reactors or accelerators that are injected into the patient and will then seek out specific organs or cancerous tumors. Diagnosis involves use of the radiopharmaceutical to generate an image of the tumor or organ to identify problems that may be missed by x rays or physical examinations. Treatment involves using radioactive compounds at carefully controlled doses to destroy tumors. These nuclear medicine techniques hold much promise for the future because they use biological chemistry to specify target cells much more precisely than traditional radiation therapy, which uses radiation from external sources to kill tumor cells, killing nontarget cells

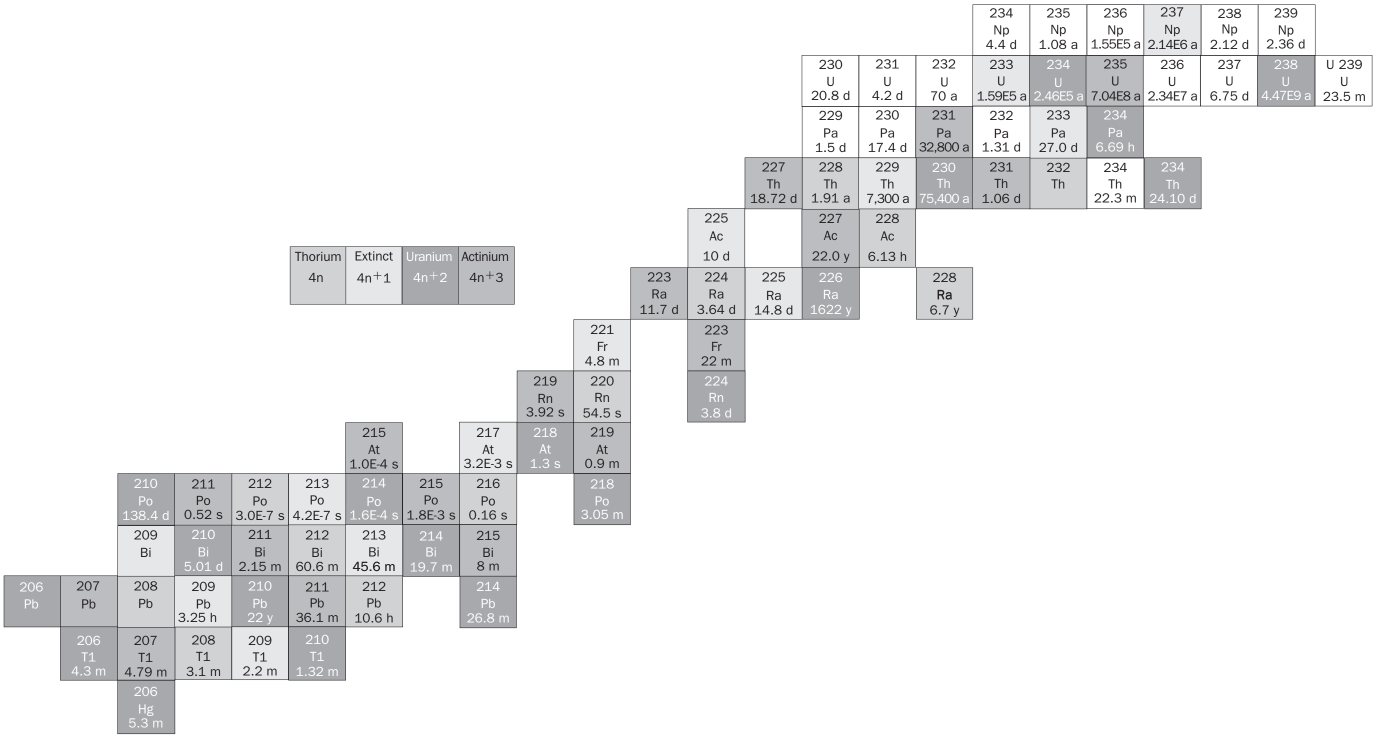


Table of naturally occurring radionuclides.

as well. Additionally, the use of nuclear pharmaceuticals containing the short-lived isotope ^{11}C has allowed nuclear chemists and physicians to probe brain activity to better understand the biochemical basis of illnesses ranging from Parkinson's disease to drug abuse. SEE ALSO BECQUEREL, ANTOINE-HENRI; CURIE, MARIE SKLODOWSKA; FERMI, ENRICO; MEITNER, LISE; NEPTUNIUM; PLUTONIUM; POLONIUM; RADIATION; RADIOACTIVITY; RADIUM; RUTHERFORD, ERNEST; SEABORG, GLENN THEODORE; SODDY, FREDERCK; URANIUM.

W. Frank Kinard

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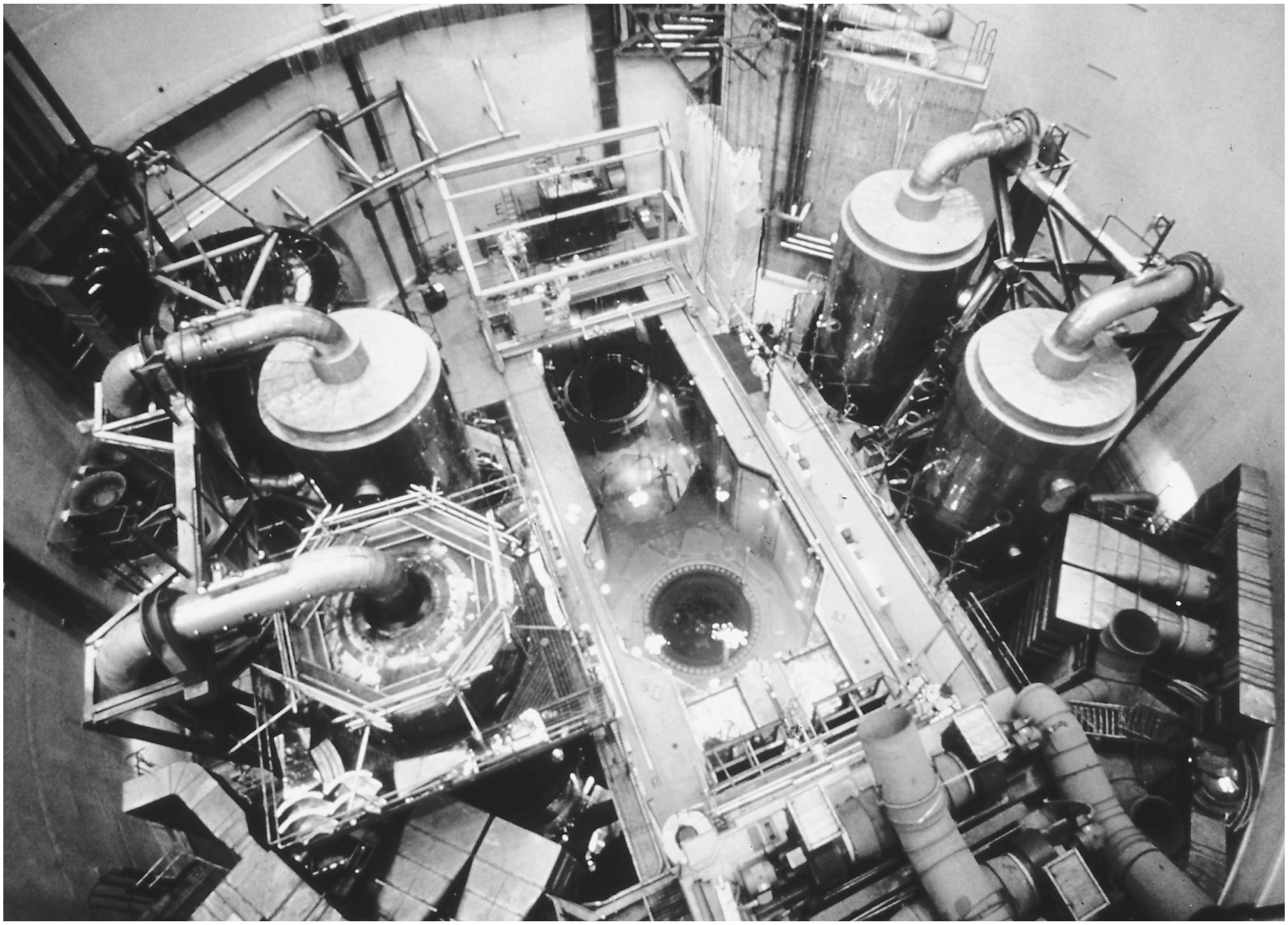
American Institute of Physics History Center. Available from <http://www.aip.org/history/>.

Division of Nuclear Chemistry and Technology of the American Chemical Society. Available from <http://www.cofc.edu/~nuclear/>.

Society of Nuclear Medicine. Available from <http://www.snm.org/>.

Nuclear Fission

Following the discovery of the neutron in the early 1930s, nuclear physicists began bombarding a variety of elements with neutrons. Enrico Fermi in Italy included uranium (atomic number 92) among the elements he bombarded which resulted in formation of nuclei that decayed by emission of negative β-rays. Such decay produces nuclei of higher atomic number, so Fermi assumed that the bombardment of uranium led to a new element with atomic number 93. By 1938 similar research had resulted in reports of the discovery of four new elements with atomic numbers 93, 94, 95, and 96. In 1938 Otto Hahn and Fritz Strassmann in Berlin bombarded uranium with neutrons to study the possibility of production of nuclides with atomic numbers less then 92 due to emission of protons and α-particles. To their surprise, they found that they had made barium ($z = 56$). Hahn informed a former colleague, Lise Meitner, who, with Otto Frisch, reviewed the data and reached the conclusion that the uranium atom was splitting (fissioning) into two new, smaller nuclei with the accompanying release of a large amount of energy. Many laboratories quickly confirmed the occurrence of this process of nuclear fission. Niels Bohr and John Wheeler, within a few months, published a paper explaining many features of fission using a model of nuclear behavior based on an analogy to a droplet of liquid, which, when given extra energy, can elongate from a spherical shape and split into two smaller droplets. Nuclei have two opposing energies: a disruptive energy resulting from the mutual electrostatic repulsion of the positive protons in the nucleus, and an attractive energy due to nuclear forces present between the nuclear particles (both neutrons and protons). The repulsive electrostatic energy of the protons increases as the number of protons increases and decreases as the average distance between them increases. The attractive nu-



The interior of the containment building at the Trojan Nuclear Plant near Rainier, Oregon. The splitting, or fission, of atoms is a source of energy.

clear force energy increases with the total number of nucleons (protons and neutrons) in the nucleus. The nuclear attractive force is at a maximum when the nucleus has a spherical shape and at a minimum when the nucleus is distorted into two roughly equal fragments.

Nuclei formed in fission, known as fission products, range in atomic number (number of protons) from approximately 30 to 64. The original fissioning nuclide has a neutron to proton ration of about 1.6, whereas stable nuclei having the same range of atomic numbers as the fission products have neutron to proton ratios of 1.3 to 1.4. This means that nuclei formed in fission have too great a number of neutrons for stability and undergo beta (β^-) decay to convert neutrons to protons. In general, fission is restricted to nuclei with atomic numbers above 82 (Pb), and the probability of fission increases as the atomic number increases. Fission produces nuclei of atomic masses from above 60 to about 150.

With very-low-energy neutrons, uranium of mass number 235 emits an average of two to three neutrons per fission event. Because more neutrons are released than absorbed, fission can result in a multiplication of successive fission events. This multiplication can reach very high numbers in about 10^{-14} to 10^{-17} seconds, resulting in the release of a great amount of energy in that time. This was the basis of the development of nuclear weapons. Soon after the discovery of fission it had been calculated that if a sufficient quantity of the fissionable material was assembled under proper conditions, a self-sustaining nuclear explosion could result. The *critical mass* of the fissionable material necessary for explosion is obtained with a spherical shape (minimum surface area per mass). The uranium isotope of mass 235 and the plutonium isotope of mass 239 are incited to fission and release energy in the use of nuclear weapons and in nuclear reactors. Nuclear reactors control the rate of fission and maintain it at a constant level, allowing the released energy to be used for power. Nuclear reactors are used in many nations as a major component of their natural energy. In the United States, approximately 20 percent of the electricity is provided by nuclear reactors, whereas France uses reactors to produce almost 80 percent of its electricity. Reactors used for power have four basic components: (1) fuel, either natural uranium or uranium enriched in ^{235}U or ^{239}Pu; (2) a moderator to reduce neutron energies, which increases the probability of fission; (3) control rods of cadmium and boron to control the rate of fission; and (4) coolants to keep the temperature of the reactor at a reasonable level and to transfer the energy for production of electricity. In power reactors the coolant is commonly H_2O or D_2O, but air, graphite, or a molten mixture of sodium and potassium can be used. Reactors are surrounded by a thick outer shield of concrete to prevent release of radiation.

LEO SZILARD (1898–1964)

Leo Szilard determined that the formation of neutrons occurs during the fission of uranium. This is crucial to sustaining a chain reaction necessary to build an atomic bomb, the first of which he helped to construct in 1942. Shortly thereafter, realizing the destructive power of the atom bomb, Szilard argued for an end to nuclear weapons research.

—Valerie Borek

There have been two major accidents (Three Mile Island in the United States and Chernobyl in the former Soviet Union) in which control was lost in nuclear power plants, with subsequent rapid increases in fission rates that resulted in steam explosions and releases of radioactivity. The protective shield of reinforced concrete, which surrounded the Three Mile Island Reactor, prevented release of any radioactivity into the environment. In the Russian accident there had been no containment shield, and, when the steam explosion occurred, fission products plus uranium were released to the environment—in the immediate vicinity and then carried over the Northern Hemisphere, in particular over large areas of Eastern Europe. Much was learned from these accidents and the new generations of reactors are being built to be "passive" safe. In such "passive" reactors, when the power level increases toward an unsafe level, the reactor turns off automatically to prevent the high-energy release that would cause the explosive release of radioactivity. Such a design is assumed to remove a major factor of safety concern in reactor operation. SEE ALSO BOHR, NIELS; FERMI, ENRICO; MANHATTAN PROJECT; PLUTONIUM; RADIOACTIVITY; URANIUM.

Gregory R. Choppin

Nuclear Fusion

Nuclear fusion is a reaction whereby two smaller nuclei are combined to form a larger nucleus. It results in the release of energy for reactions that form nuclei of mass number below 60, with the largest energy release occurring with the lightest nuclides. This stands in contrast to the process of nuclear **fission** in which a heavy nucleus is split into two smaller nuclei with the release of energy. Since light nuclei have smaller repulsion energies (the energy required to bring two like charges together), fusion is much more likely to occur among these nuclei. Two deuterons, ^{2}H, must have a total kinetic energy of 0.02 million electron volts (MeV) to be able to collide and

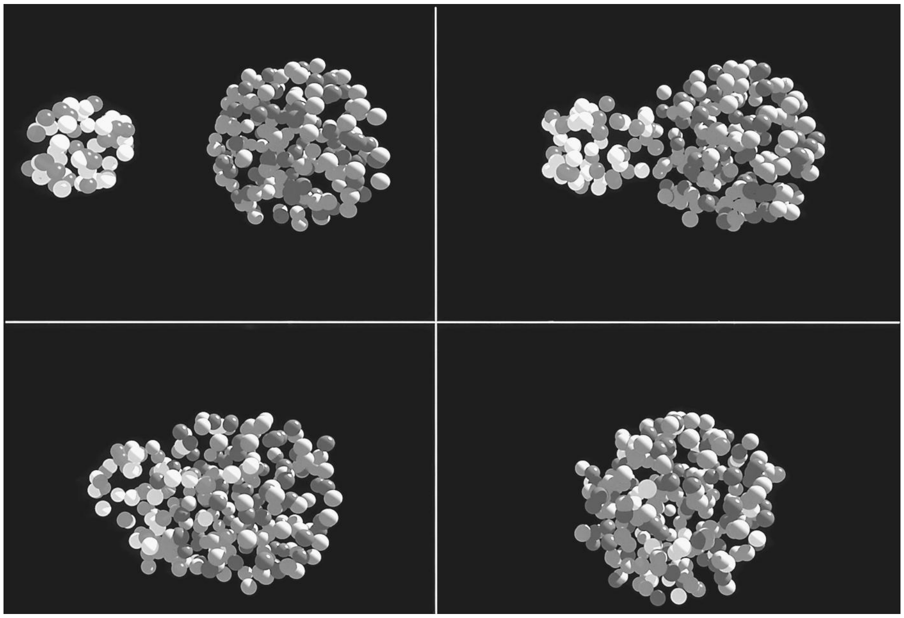
fission: process of splitting an atom into smaller pieces react. Temperatures of greater than 200 million°C (360 million°F) are required for such kinetic energies. Atoms with kinetic energies of 0.02 MeV exist only as gases in which the atoms have lost their electrons. Such gases of ions and electrons are known as plasmas.

Temperatures required for fusion reactions exist in stars where fusion reactions are the principle components of energy release. In the Sun, approximately 90 percent of solar energy is a result of proton–proton interactions in several steps to form helium of mass number 4. These steps all involve binuclear collisions since multinuclei collisions are very improbable events. Initially, two protons interact to form a deuterium nucleus (deuterium is an **isotope** of hydrogen with one proton and one neutron; the nucleus is a **deuteron**) that collides with another proton to form a ^{3}He (tritium) nucleus. This nucleus collides with a neutron or another ^{3}He nucleus (with the emission of two protons) to form ^{4}He. The net reaction can be represented as four protons fusing to form a ^{4}He nucleus releasing 26.7 MeV. When a sufficient number of the ^{3}He and ^{4}He nuclei are formed in the star, they begin fusion reactions to form heavier nuclei such as ^{7}Li and ^{7}Be. The number of proton–proton fusion reactions in the Sun amounts to 1.8×10^{38} s^{-1}. At present the Sun is 73 percent hydrogen, 25 percent helium, 2 percent carbon, nitrogen, oxygen, and all the other elements in the Periodic Table. Approximately 6 percent of the hydrogen originally in the Sun's stellar core has now been burnt.

isotope: form of an atom that differs by the number of neutrons in the nucleus

deuteron: nucleus containing one proton and one neutron, as is found in the isotope deuterium

Since the average mass of elements increases in stars, there is a transition from a proton cycle to a carbon cycle, as was proposed by American physicist Hans Bethe and German physicist Carl F. von Weizsacker in the 1930s. In such stars, the temperature and pressure reach higher values and the consumption of hydrogen accelerates. Since helium has a greater mass then hydrogen, it accumulates in the stellar core, while most of the hydrogen burning fusion of its nuclei moves to a layer outside that core. With an increased average mass in stars, reactions such as ^{8}Be + ^{4}He forming ^{12}C begin to occur. The formation of ^{12}C in sufficient quantities leads to reac-



A computer simulation of gold (Au) and nickel (Ni) nuclei fusing.

tions with ^{4}He to form oxygen, neon, and higher elements. Eventually, there is sufficient carbon present in some stars for the fusion of a pair of ^{12}C nuclei to begin.

In stars with very heavy average masses, helium burning may last for only a few million years before it is replaced by carbon fusion. In time this leads to the production of elements such as calcium, titanium, chromium, iron, and nickel fusion partly by helium capture, partly by the direct fusion of heavy nuclides. For example, two ^{28}Si can combine to form ^{56}Ni that can decay to ^{56}Co which then decays to stable ^{56}Fe. These last steps of production may occur rather rapidly in a few thousand years. When the nuclear fuel for fusion is exhausted, the star collapses and a supernova results.

Nuclear fusion became important on Earth with the development of hydrogen bombs. A core of uranium or plutonium is used to initiate a fission reaction that raises the core's temperature to approximately 10^{8} K, sufficient to cause fusion reactions between deuterium and tritium. In fusion bombs, LiD is used as ^{6}Li reacts with fission neutrons to form tritium that then undergoes fusion with deuterium. It is estimated that approximately half the energy of a 50 megaton thermonuclear weapon comes from fusion and the other half from fission. Fusion reactions in these weapons also produce secondary fission since the high energy neutrons released in the fusion reactions make them very efficient in causing the fission of ^{238}U.

The deuterium plus tritium and deuterium plus deuterium reactions are of interest in the development of controlled fusion devices for producing energy. A number of designs have been proposed for these fusion reactors, with most attention given to inertial confinement and magnetic confinement systems.

Inertial confinement is a pulsed system in which small pellets of D_2 and T_2 are irradiated by intense beams of photons or electrons. The surface of the pellet rapidly vaporizes, causing a temperature-pressure wave to move through the pellet, increasing its central temperature to greater than 10^{8} K and causing fusion. If a fusion rate of approximately 100 pellets per second can be achieved, the result is a power output between 1 and 10 gigawatts.

At temperatures equal or greater than 10^{7} K, hydrogen atoms are completely dissociated into protons and free electrons (the plasma state). Since construction material cannot withstand a plasma of this energy, the plasma is kept away from the walls by magnetic fields. The plasma density is limited by heat transfer and other considerations to approximately 10^{20} to 10^{21} particles m^{-3}. For a particle density of 3×10^{20} particles m^{-3}, confined for 0.1 to 1 second, the power density is estimated to be tens of megawatts per cubic meter. Several large machines based on magnetic confinement have been built, and confinement times of 2 seconds with particle densities of 5×10^{19} achieved. However, it seems unlikely that controlled thermonuclear reactors will be in operation for the purpose of power production before the year 2050 as significant technical problems remain to be solved. The availability of hydrogen and deuterium in the sea is so vast that nuclear fusion would outlast other nonrenewable energy sources. For example, a liter of seawater contains deuterium with an energy content equivalent to 300 liters (79.25 gallons) of gasoline. SEE ALSO EXPLOSIONS; NUCLEAR CHEMISTRY; NUCLEAR FISSION.

Gregory R. Choppin

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FusEdWeb: Fusion Energy Educational Web Site. Available from <http://fusedweb.pppl.gov>.

General Atomics' Educational Web Site. Available from <http://fusioned.gat.com>.

Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) is one of the most useful analytical methods in modern chemistry. It is used to determine the structure of new natural and synthetic compounds, the purity of compounds, and the course of a chemical reaction as well as the association of compounds in solution that might lead to chemical reactions. Although many different kinds of nuclei will produce a spectrum, hydrogen (H) nuclei historically have been the ones most studied. NMR spectroscopy is particularly useful in the study of organic molecules because these usually incorporate a large number of hydrogen atoms.

NMR Spectrometers

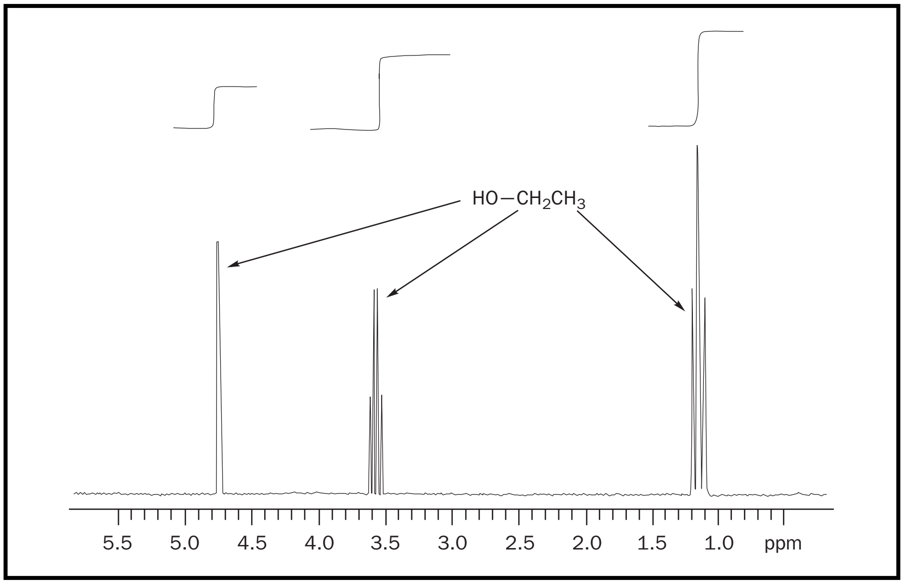
While the original NMR spectrometers were built to scan either the frequency or the magnetic field, the usual procedure is to use Fourier transform spectroscopy (FT NMR). The protocol for obtaining a FT NMR spectrum is to place a solution of the compound to be studied in a homogenous magnetic field and irradiate it with a short pulse of the appropriate radio-frequency. The shortness of the radio-frequency pulse results in a band of frequencies that simultaneously radiate all of the nuclei of a particular type to be studied. Each magnetic nucleus that absorbs this radio-frequency energy will then radiate radio-frequency energy at a very specific frequency. The frequencies generated by the various nuclei are then detected, Fourier transformed, and displayed as a plot of frequency versus intensity. This plot is called an NMR spectrum. The frequency at which magnetic resonance occurs depends on the strength of the magnetic field used and on the nucleus to be studied. The stronger the magnetic field used the higher the resonance frequency, the greater the dispersion (separation) of the bands, and the greater the sensitivity of the experiment. Thus, the higher the magnetic field the better the NMR spectrometer. Over the years this has led to the development of spectrometers of ever increasing magnetic fields. Superconducting magnets can be built with much higher fields than the usual electromagnets. Thus most NMR spectrometers used incorporate superconducting magnets. Although most of the elements in the Periodic Table have an isotope that is magnetic, the most common nucleus to be observed by NMR is that of hydrogen. This has led to the common use of the hydrogen resonant frequency for a given NMR spectrometer as a measure of the magnetic field strength of that spectrometer. NMR spectrometers that use permanent or electromagnets range from 60 MHz up to 100 MHz, while spectrometers with superconducting magnets range from 200 MHz to many hundred megacycles.

Data Analysis

In a hydrogen NMR spectrum, the presence of any resonance explains first that the molecule of study contains hydrogen. Second, the number of bands in the spectrum shows how many different positions there are on the molecule to which hydrogen is attached. The frequency of a particular resonance in the NMR spectrum is referred to as the chemical shift. This is the most important measurable part of the NMR spectrum and contains information about the environment of each hydrogen atom and the structure of the compound under study. The third bit of information that an NMR spectrum provides is the ratio of the areas of the different bands, thus explaining the relative number of hydrogen atoms that exist at each position on a given molecule. This ratio is direct evidence of the structure of molecular structure and must correspond absolutely to any proposed structure before that structure may be considered correct.

Finally, the complex structure of the bands may contain information about the distance that separate the various hydrogen atoms through covalent bonds and the spatial arrangement of the hydrogen atoms attached to the molecule, including secondary structure. Secondary structure refers to folding or self-assembly of a molecule due to long-range bonding, such as in the spiral structure of DNA. The complex structure of the NMR bands is due primarily to spin coupling between the various hydrogen atoms. This coupling is, in turn, a function of the distance through the bonds and the geometry of the molecule. In the case of small molecules, the band complexity may be simulated exactly with quantum mechanical calculations or approximated using quantum mechanically derived rules.

Fundamental to the use of NMR is the ready correlation of measurable spectrum quantities with the structure of a molecule under study. Consider the simple molecule ethanol. Ethanol has three bands in its hydrogen NMR spectrum that correlate with the three distinct types of hydrogen atoms present in the molecule. The area ratio of the three bands is 1:2:3 and this reflects the number ratio of the hydrogen atoms seen in the structure of



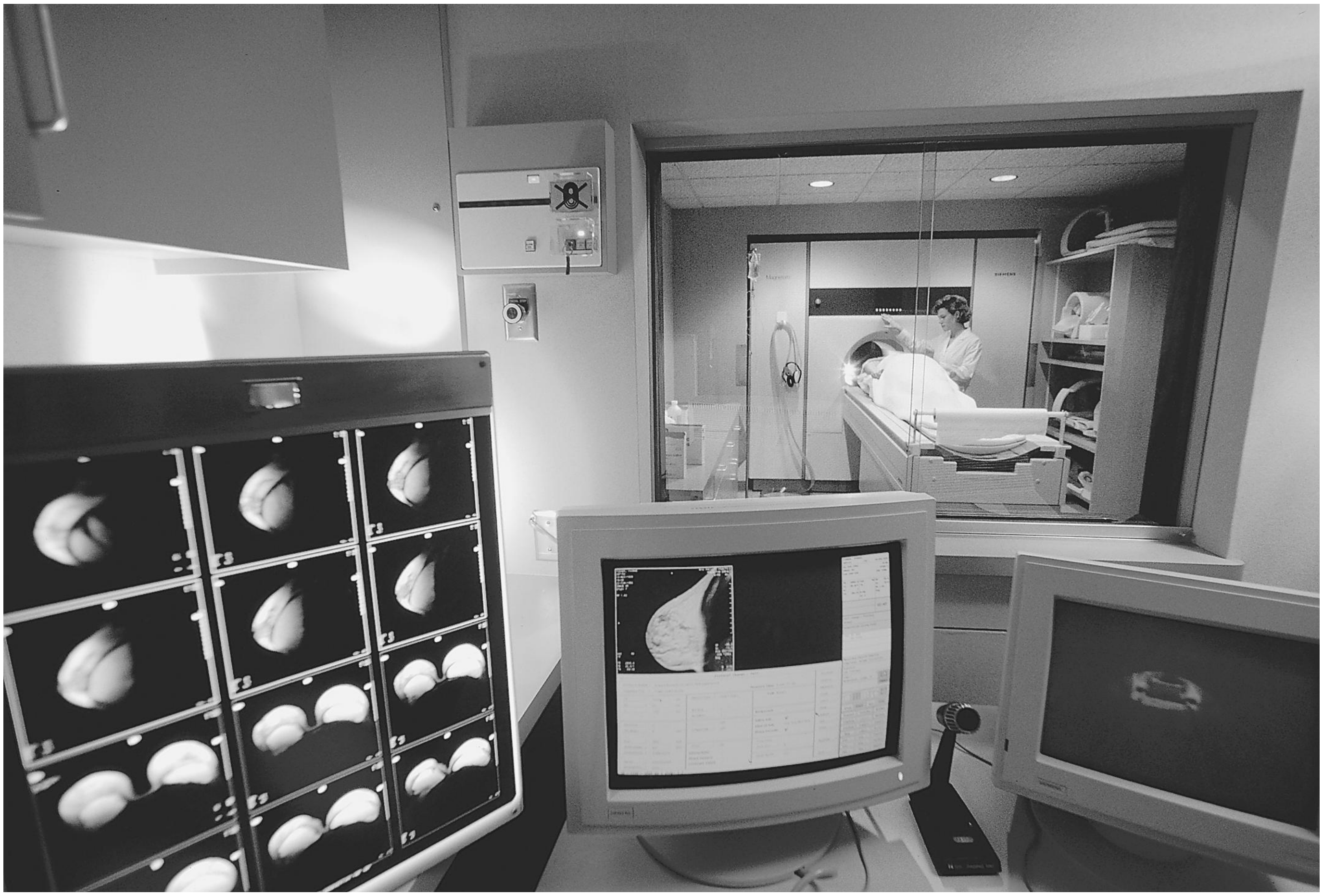
The 300 MHz NMR spectrum of ethanol. This simple alcohol has three types of hydrogen atoms and thus there are three bands. The relative area of the bands is indicated by the vertical displacement of the integral at the top of the spectrum. The relative band area of 1:2:3 is sufficient data to assign all three bands.

ethanol. The fine structure of the bands in this spectrum may also be correlated with the structure of ethanol using simple rules. As more complex molecules are considered, more complex rules must be used until finally two-dimensional NMR (2D NMR) and even more complex spectroscopic procedures must be used for complete analysis.

Discovery

Although NMR was thought to be possible for many years, it was first demonstrated in 1946 simultaneously and independently by two physicists working on the East Coast and the West Coast of the United States: Felix Bloch at Stanford University and Edward Mills Purcell at Harvard University. For their work they shared the Nobel Prize in physics in 1952. The first commercial spectrometers appeared later in the 1950s and quickly became an indispensable tool for research chemists. The first commercial spectrometers were based on conventional electromagnets and permanent magnets, but during the 1960s the superconducting magnetic had already been largely adopted. In 1966 the chemist Richard Ernst demonstrated Fourier transform nuclear magnetic resonance (FT NMR). This procedure quickly replaced the older scanning techniques and earned Ernst the Nobel Prize in chemistry in 1991. He continued to make contributions to many areas of NMR but most notable are his contributions to 2D NMR and magnetic resonance imaging (MRI).

A magnetic resonance imaging (MRI) system is used to diagnose maladies in the soft tissues of the body.



Magnetic Resonance Imaging

Magnetic resonance imaging (MRI) is a spin-off of NMR. The two techniques differ in two important respects. First, in NMR spectrums the individual resonance bands of different frequency are displayed in a spectrum to reveal structural and purity information while in MRI all of the resonance bands are grouped together as a single quantity. Second, in NMR the magnetic field is very homogeneous so that the different frequency bands may be clearly separated; however, with MRI a linear magnetic gradient is superimposed on the main magnetic field so that the frequency of the NMR signal is a function of space instead of structure. The gradient is alternated along different axes so that an image may be constructed. The resulting image is a two-dimensional slice through the sample. Several slices may be accumulated so that a three-dimensional image may then be constructed if needed. Since the 1980s, MRI has grown to be an indispensable tool in the medical diagnosis of many maladies—especially of soft tissue, such as the brain and the spine. In an MRI body scan, the image is constructed primarily from the detected radiation of the hydrogen atoms in water and **lipids** of the various tissues. While the varying concentration of water and lipids in various tissues contribute to the formation of an MRI image, the dominant factor is the variation in the length of time that the hydrogen atoms found in different tissues will radiate. This difference in radiation time is referred to as relaxation time. Contrast, and thus good images, may be achieved by delaying the onset of radio-frequency detection until some tissues have almost quit radiating while other tissues are still radiating strongly. Particularly noteworthy is the difference in relaxation time of normal tissue compared to malignant tissue. MRI may be optimized best for imaging specific tissues using a combination of radio-frequency pulse parameters, delay times, and magnetic gradients. These same parameters may be used to measure the flow of fluids through tissues, such as the flow of blood through muscle tissue. The contrast and thus the quality of the MRI for some specific tissues may be significantly increased by the use of specially engineered compounds called MRI contrast **reagents**. These compounds have two required properties: They must associate specifically with a tissue under investigation and they must be magnetic. The presence of a contrast reagent in a tissue changes the relaxation time of the water in this tissue in such a way that the MRI image is enhanced. SEE ALSO Molecular Structure; Organic Chemistry; Spectroscopy.

lipids: a nonpolar organic molecule; fatlike; one of a large variety of nonpolar hydrophobic (water-hating) molecules that are insoluable in water

reagent: chemical used to cause a specific chemical reaction

Ben Shoulders

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Nuclear Medicine

Nuclear medicine involves the injection of a radiopharmaceutical (radioactive drug) into a patient for either the diagnosis or treatment of disease. The history of nuclear medicine began with the discovery of radioactivity from uranium by the French physicist Antoine-Henri Becquerel in 1896, followed shortly thereafter by the discovery of radium and polonium by the renowned French chemists Marie and Pierre Curie. During the 1920s and 1930s radioactive phosphorus was administered to animals, and for the first time it was determined that a metabolic process could be studied in a living animal. The presence of phosphorus in the bones had been proven using radioactive material. Soon ^{32}P was employed for the first time to treat a patient with leukemia. Using radioactive iodine, thyroid physiology was studied in the late 1930s. Strontium-89, another compound that localizes in the bones and is currently used to treat pain in patients whose cancer has spread to their bones, was first evaluated in 1939.

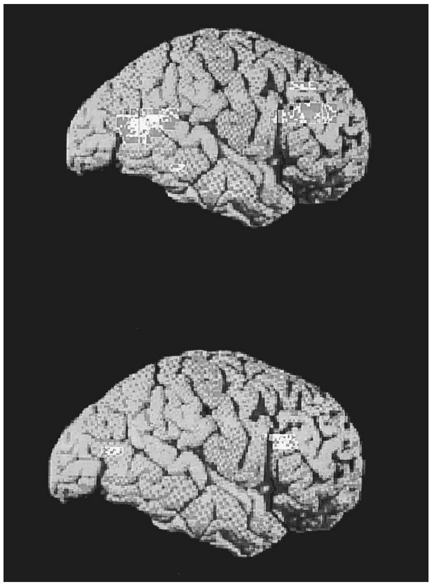
radioactive decay: process involving emission of subatomic particles from the nucleus, typically accompanied by emission of very short wavelength electromagnetic radiation

A nuclide consists of any configuration of protons and neutrons. There are approximately 1,500 nuclides, most of which are unstable and spontaneously release energy or subatomic particles in an attempt to reach a more stable state. This nuclear instability is the basis for the process of **radioactive decay**, and unstable nuclides are termed *radionuclides.* During the 1940s and 1950s nuclear reactors, accelerators, and cyclotrons began to be widely used for medical radionuclide production. Reactor-produced radionuclides are generally electron-rich and therefore decay by β^--emission. The main application of β^--emitters is for cancer therapy, although some reactor-produced radionuclides are used for nuclear medicine imaging. Cyclotron-produced radionuclides are generally prepared by bombarding a stable target (either a solid, liquid, or gas) with protons and are therefore proton-rich, decaying by β^+-emission. These radionuclides have applications for diagnostic imaging by positron-emission tomography (PET). One of the most convenient methods for producing a radionuclide is by a *generator.* Certain parent–daughter systems involve a long-lived parent radionuclide that decays to a short-lived daughter. Since the parent and daughter nuclides are not **isotopes** of the same element, chemical separation is possible. The long-lived parent produces a continuous supply of the relatively short-lived daughter radionuclide and is therefore called a generator.

isotope: form of an atom that differs by the number of neutrons in the nucleus

Currently, the majority of radiopharmaceuticals are used for diagnostic purposes. These involve the determination of a particular tissue's function, shape, or position from an image of the radioactivity distribution within that tissue or at a specific location within the body. The radiopharmaceutical localizes within certain tissues due to its biological or physiological characteristics. The diagnosis of disease states involves two imaging modalities: Gamma (γ) scintigraphy and PET. In the 1950s γ scintigraphy was developed by Hal O. Anger, an electrical engineer at Lawrence Berkeley Laboratory. It requires a radiopharmaceutical containing a radionuclide that emits γ radiation and a γ camera or single **photon** emission computed tomography (SPECT) camera capable of imaging the patient injected with the γ-emitting radiopharmaceutical. The energy of the γ-photons is of great importance, since most cameras are designed for particular windows of energy, generally in the range of 100 to 250 kilo-electron volts (keV). The most widely used radionuclide for imaging by γ scintigraphy is ^{99m}Tc ($T_{\frac{1}{2}}$ = 6 hours), which is produced from the decay of ^{99}Mo ($T_{\frac{1}{2}}$ = 66 hours). In 1959 the Brookhaven National Laboratory (BNL) developed the ^{99}Mo/^{99m}Tc generator, and in 1964 the first ^{99m}Tc radiotracers were developed at the University of Chicago. The low cost and convenience of the ^{99}Mo/^{99m}Tc generator, as well as the ideal photon energy of ^{99m}Tc (140

photon: a quatum of electromagnetic energy keV), are the key reasons for its widespread use. A wide variety of ^{99m}Tc radiopharmaceuticals have been developed during the last forty years, most of them coordination complexes. Many of these are currently used every day in hospitals throughout the United States to aid in the diagnosis of heart disease, cancer, and an assortment of other medical conditions.



Two positron-emission tomography (PET) scans showing the brain of a depressed person (top) and a healthy person (bottom).

PET was developed during the early 1970s by Michel Ter-Pogossian and his team of researchers at Washington University. It requires a radiopharmaceutical labeled with a positron-emitting radionuclide (β^+) and a PET camera for imaging the patient. Positron-decay results in the emission of two 511 keV photons 180° apart. PET scanners contain a circular array of detectors with coincidence circuits designed to specifically detect the 511 keV photons emitted in opposite directions. The positron-emitting radionuclides most frequently used for PET imaging are ^{15}O ($T_{\frac{1}{2}}$ = 2 minutes), ^{13}N ($T_{\frac{1}{2}}$ = 10 minutes), ^{11}C ($T_{\frac{1}{2}}$ = 20 minutes), and ^{18}F ($T_{\frac{1}{2}}$ = 110 minutes). Of these, ^{18}F is most widely used for producing PET radiopharmaceuticals. The most frequently used ^{18}F-labeled radiopharmaceutical is 2-deoxy-2- [^{18}F]fluoro-D-**glucose** (FDG). This agent was approved by the Food and Drug Administration (FDA) in the United States in 1999 and is now routinely used to image various types of cancer as well as heart disease.

glucose: common hexose monosaccharide; monomer of starch and cellulose; also called grape sugar, blood sugar, or dextrose

The use of radiopharmaceuticals for therapeutic applications (α- or β^--emitters) is increasing. The first FDA-approved radiopharmaceutical in the United States was, in fact, for therapeutic use. Sodium [^{131}I] iodide was approved in 1951 for treating thyroid patients. There are currently FDA-approved radiopharmaceuticals for alleviating pain in patients whose cancer has metastasized to their bones. These include sodium ^{32}P-phosphate, ^{89}Sr-chloride, and ^{153}Sm-EDTMP (where EDTMP stands for ethylenediaminetetramethylphosphate). In February 2002 the first radiolabeled monoclonal **antibody** was approved by the FDA for the radioimmunotherapy treatment of cancer. Yttrium-90-labeled anti-CD20 monoclonal antibody is used to treat patients with non-Hodgkin's lymphoma.

antibody: protein molecule that recognizes external agents in the body and binds to them as part of the immune response of the body

Many branches of chemistry are involved in nuclear medicine. Nuclear chemistry has developed accelerators and reactors for radionuclide production. Inorganic chemistry has provided the expertise for the development of **metal**-based radiopharmaceuticals, in particular, ^{99m}Tc radiopharmaceuticals, whereas organic chemistry has provided the knowledge base for the development of PET radiopharmaceuticals labeled with ^{18}F, ^{13}N, ^{11}C, and ^{15}O. Biochemistry is involved in understanding the biological behavior of radiopharmaceuticals, while medical doctors and pharmacists are involved in clinical studies. Nuclear medicine, which benefits the lives of millions of people every day, is truly a multidisciplinary effort, one in which chemistry plays a significant role. SEE ALSO BECQUEREL, ANTOINE-HENRI; CURIE, MARIE SKLODOWSKA; NUCLEAR CHEMISTRY; NUCLEAR FISSION; RADIATION EXPOSURE; RADIOACTIVITY.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Carolyn J. Anderson

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Nucleic Acids

Nucleic acids are a family of macromolecules that includes deoxyribonucleic acid (**DNA**) and multiple forms of ribonucleic acid (**RNA**). DNA, in humans and most organisms, is the genetic material and represents a collection of instructions (genes) for making the organism. This collection of instructions is called the genome of the organism. The primary classes of RNA molecules either provide information that is used to convert the genetic information in DNA into functional proteins, or are important players in the **translational process**, in which the actual process of protein **synthesis** (on **ribosomes**) occurs.

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

RNA: ribonucleic acid—a natural polymer used to translate genetic information in the nucleus into a template for the construction of proteins

translational process: transfer of information from codon on m-RNA to anticodon on t-RNA; used in protein synthesis

synthesis: combination of starting materials to form a desired product

ribosome: large complex of proteins used to convert amino acids into proteins

Discovery of and Evidence for DNA as the Genetic Material

DNA was first discovered in 1869 by a Swiss biochemist, Johann Friedrich Miescher. He extracted a gelatinous material that contained organic phosphorus from cells in human pus that was obtained from the bandages of wounded soldiers. He named this material *nuclein.* Ten years later Albrecht Kossel explored the chemistry of nuclein (for which he received the Nobel Prize) and discovered that it contained the organic bases **adenine**, **thymine**, **guanine**, and **cytosine**. In 1889 Richard Altman removed the proteins from the nuclein in yeast cells and named the deproteinized material *nucleic acid.* It was not until about 1910 that it was realized that there were two types of nucleic acid, DNA and RNA. A great deal of chemistry during the early part of the twentieth century focused on characterizing the composition of and the linkages in both DNA and RNA. A chemical test for deoxyribose, developed by Robert Feulgen during the 1920s, was the first test capable of distinguishing DNA from RNA. Because of the simplicity of the composition of DNA, which has only four bases (and early reports indicated erroneously that there were equimolar quantities of each), it was originally thought that DNA molecules functioned in chromosomal stability and maintenance. It was only after Erwin Chargaff, in 1950, showed that the molar amounts of the bases varied widely in different organisms that the notion that DNA might be the genetic material became an attractive idea.

adenine: one of the purine bases found in nucleic acids, $C_5H_5N_5$

thymine: one of the four bases that make up a DNA molecule

guanine: heterocyclic, purine, amine base found in DNA

cytosine: heterocyclic, pyrimidine, amine base found in DNA

The general consensus prior to the mid-1940s was that proteins (which contain twenty different amino acids) were the most logical candidate for the genetic material. Three later, however, findings pointed toward the conclusion that DNA was the genetic material. During the 1920s Frederick Griffith examined the activity of cell extracts in an attempt to identify a "transforming principle" (and a specific molecule related to this principle) in experiments with the bacterium *Streptococcus pneumoniae*. Unfortunately, his experiments failed to identify a specific molecule. In 1944 Oswald Avery, Colin MacLeod, and Maclyn McCarty partially purified cell extracts and presented evidence that the genetic component of these cells was DNA. In 1952 Alfred Hershey and Martha Chase investigated the infection of *Escherichia coli* cells with phage T2 (a virus) and their results were further corroboration that DNA was the genetic material. Since that time, a large body of evidence has confirmed the (nearly) universal truth that DNA is the genetic, heritable material in organisms. (The only exception to this is the case of RNA viruses, such as the AIDS virus, in which RNA is the only nucleic acid present in the virus and the genetic material.)

Modern research took a giant step forward when James Watson and Francis Crick, analyzing the collected findings of a number of laboratories, proposed the double **helix** structure of DNA in 1953. Their announcements motivated scientists to find corroboration for this proposal. During the 1980s detailed x-ray crystallographic analyses of DNA became acknowledged as proof of the structural arrangement that had been described by Watson and Crick, including the Watson–Crick complementary base-pairing arrangements. The elucidation of the structure of DNA led to an enormous and rapid expansion of our understanding of DNA's function in the living cell.

helix: form of a spiral or coil such as a corkscrew

Types of Nucleic Acids: Composition and Structure

All nucleic acids are linear, nonbranching polymers of nucleotides, and are therefore polynucleotides. DNA is double-stranded in virtually all organisms. (It is single-stranded in some viruses.) DNA occurs in many, but not all, small organisms as double-stranded and circular (without any ends). Higher organisms (eukaryotes) have approximately ten million base pairs or more, with the genetic material parceled out into multiple genetic pieces called chromosomes. For example, humans have twenty-three pairs of chromosomes in the nucleus of each **somatic cell**. Within the nucleus, the DNA molecules are found in "looped arrangements" that mimic the circular DNA observed in many prokaryotes.

somatic cell: cells of the body with the exception of germ cells

All RNA molecules are single-stranded molecules. RNA molecules are synthesized from DNA templates in a process known as **transcription**; these molecules have a number of vital roles within cells. It is convenient to divide RNA molecules into the three functional classes, all of which function in the cytoplasm.

transcription: enzyme-catalyzed assembly of an RNA molecule complementary to a strand of DNA

Messenger RNA (mRNA) contains the information (formerly residing in DNA) that is decoded in a way that enables the manufacture of a protein, and migrates from the nucleus to ribosomes in the cytoplasm (where proteins are assembled). A triplet of nucleotides within an RNA molecule (called a codon) specifies the amino acid to be incorporated into a specific site in the protein being assembled. A cell's population of mRNA molecules is very diverse, as these molecules are responsible for the synthesis of the many different proteins found in the cell. However, mRNA makes up only 5 percent of total cellular RNA.

Ribosomal RNA (rRNA) is the most abundant intracellular RNA, making up 80 percent of total RNA. The **eukaryotic** ribonucleoprotein particle (ribosome) is composed of many proteins and four rRNA molecules (which are classified according to size). Ribosomes reside in the cytoplasm and are the "molecular platform" (the actual physical site of) for protein synthesis.

eukaryotic: relating to organized cells of the type found in animals and plants

Transfer RNA (tRNA) molecules contain between seventy-four and ninety-five nucleotides and all tRNAs have similar overall structures. There are twenty individual tRNAs; each one binds to a specific amino acid in the cytoplasm and brings its "activated amino acid" to a ribosome—part of the translational machinery that carries out protein synthesis. Transfer RNA makes up the remaining 15 percent of cellular RNA.

All nucleic acids are polynucleotides, with each nucleotide being made up of a base, a sugar unit, and a phosphate. The composition of DNA differs from that of RNA in two major ways (see Figure 1). Whereas DNA contains the bases guanine (G), cytosine (C), adenine (A), and thymine (T), RNA contains G, C, and A, but it contains **uracil** (U) in place of thymine. Both DNA and RNA contain a five-membered cyclic sugar (a pentose). RNA contains a ribose sugar. The sugar in DNA, however, is 2′-deoxyribose.

In DNA, each base is linked by a β-glycosidic bond to the C1′ position of the 2′-deoxyribose, and each phosphate is linked to either the C3′ or C5′ position. The linkages are essentially the same in RNA.

DNA is a right-handed, double-stranded helix, in which the bases essentially occupy the interior of the helix, whereas the phosphodi**ester** backbone (sugar-phosphate backbone) more or less comprises the exterior. The bases on the individual strands form intermolecular **hydrogen bonds** with each other (the complementary Watson–Crick base pairs). An adenine base on one strand interacts specifically with a thymine base on the other, forming two hydrogen bonds and an A–T base pair; while a G–C base pair contains three hydrogen bonds. These interactions possess a specificity that is pivotal to both DNA replication and transcription (see Figure 2).

DNA structure is also described in terms of primary, secondary, and tertiary structures. The primary structure is simply the sequence of nucleotides. The secondary structure refers to the **hydrogen bonding** between A–T and G–C base pairs. The tertiary structure refers to the larger twists and turns of the DNA molecule. Other features of DNA are the major and

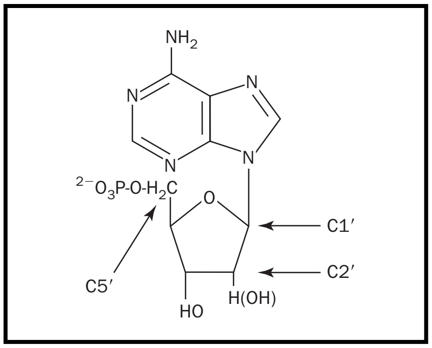

Figure 1.

uracil: heterocyclic, pyrimidine, amine base found in RNA

ester: organic species containing a carbon atom attached to three moieties: an O via a double bond, an O attached to another carbon atom or chain, and a H atom or C chain; the R(C=O)OR functional group

hydrogen bond: interaction between H atoms on one molecule and lone pair electrons on another molecule that constitutes hydrogen bonding

hydrogen bonding: intermolecular force between the H of an N–H, O–H, or F–H bond and a lone pair on O, N, or F of an adjacent molecule

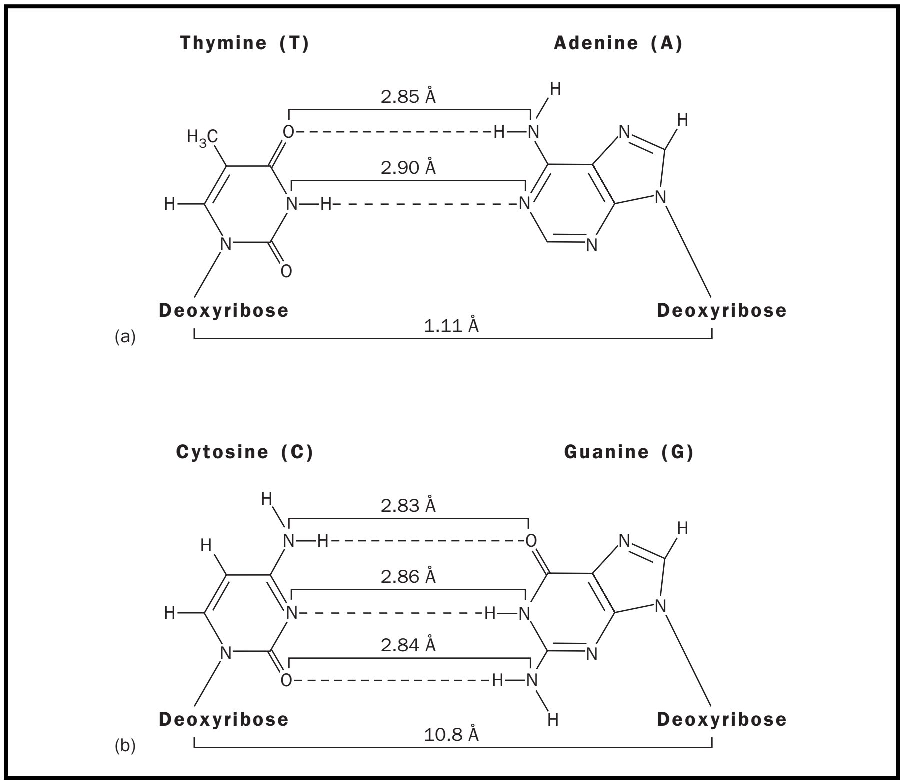

Figure 2.

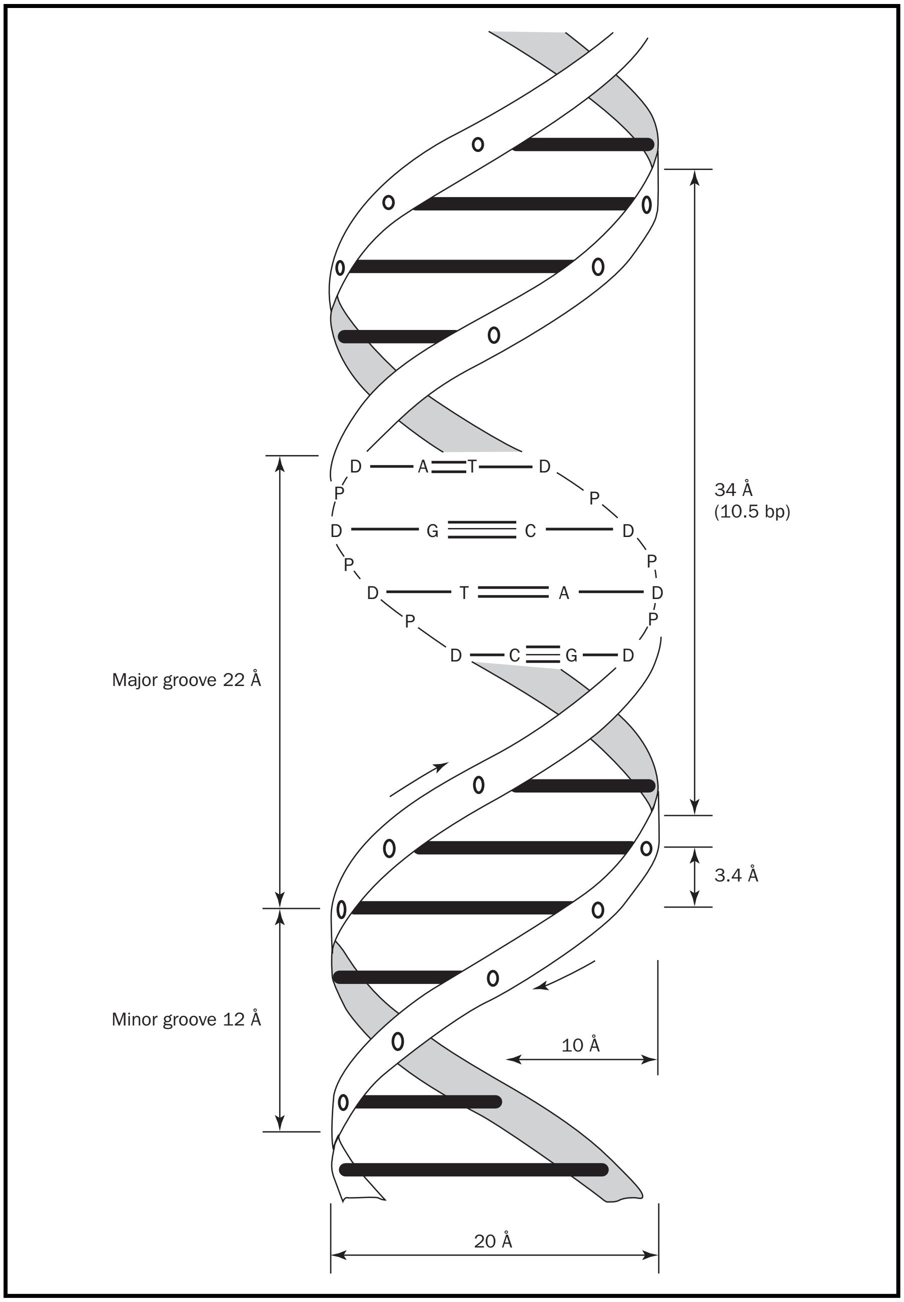

Figure 3.

minor grooves that run along the helix that are the target sites for DNA binding proteins involved in replication and transcription. Although DNA can exist in several alternate structures, the B-form of DNA (see Figure 3) is the biologically relevant form.

As stated previously, DNA is the genetic material in humans and in virtually all organisms, including viruses—with the exception of a few viruses that possess RNA as the genetic material.

In complex multicellular organisms (such as humans), DNA carries within itself the instructions for the synthesis and assembly of virtually all the components of the cell and (therefore) for the structure and function of tissues and organs. Within the approximately 3.2 × 10^9 base pairs (3.2 Gbps) in human DNA, the Human Genome Project has determined that there are a minimum of about 25,000 individual segments that correspond to individual genes. The genes collectively make up only about 2 to 3 percent of the total DNA, but encode the detailed genetic instructions for the synthesis of proteins. Proteins are the "workhorses" of the cell, and in one way or another are responsible for the functions that permit a cell to communicate with other cells and that define the character of the individual cell. A kidney cell is very different from a heart or eye cell. Although every cell contains the same DNA, different subsets of the 25,000 genes are expressed in the different organs or tissues. The expressed genes determine the type of cell that is produced and a cell's ultimate function in a multicellular organism.

Interestingly, there is only approximately a 0.1 percent difference in DNA among humans. The nucleotide sequences of DNA differs between organisms and is a fundamental difference between individuals and between species. For example, our closest (species) relative, the chimpanzee, has DNA that is 98.5 percent identical to that of humans. SEE ALSO DEOXYRIBONUCLEIC ACID; DOUBLE HELIX; WATSON, FRANCIS DEWEY.

William M. Scovell

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Nucleotides

Nucelotides are the repeating building blocks of nucleic acids (which are polynucleotides or polymers of nucleotides). A nucleotide is made up of a heterocyclic base (a purine or pyrimidine), a cyclic sugar unit (ribose or deoxyribose), and a phosphate group. A nucleotide is either a ribonucleotide, the repeating unit in ribonucleic acid (**RNA**), or a deoxyribonucleotide, the repeating unit in deoxyribonucleic acid (**DNA**). Table 1 below lists the names of purine and pyrimidine bases, the nucleosides (base + ribose), the corresponding 5′-nucleotides (base + ribose + phosphate), and the abbreviations.

RNA: ribonucleic acid—a natural polymer used to translate genetic information in the nucleus into a template for the construction of proteins

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

Nucleotides are sometimes abbreviated as 5′-NMP, in which N can stand for any of the bases.

Figure 1 illustrates two nucleotides, in which the phosphate is attached to the (ribose) sugar at either the 5′-carbon (5′-AMP) or the 3′-carbon (3′-TMP). The numbering systems for both purine (**guanine** shown here) and pyrimidine (**thymine** shown here) compounds are given, in addition to that for the sugar (ribose or deoxyribose). Note that the linkage between the

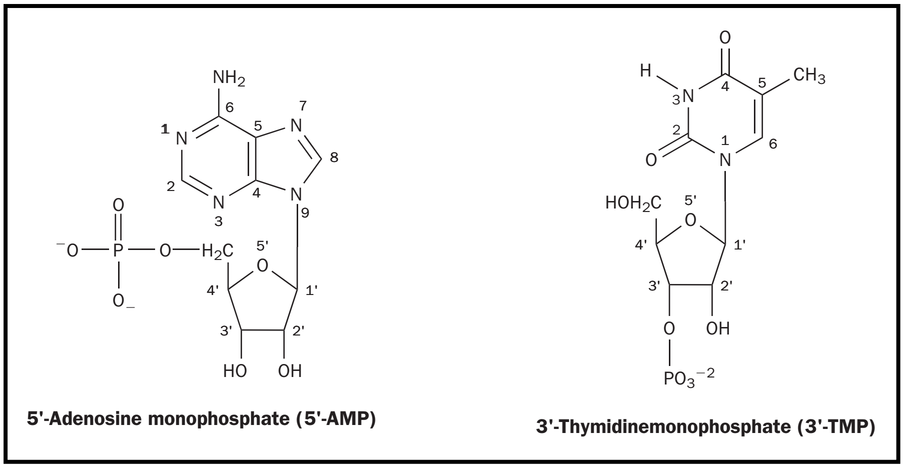
guanine: heterocyclic, purine, amine base found in DNA

thymine: one of the four bases that make up a DNA molecule

Base	Nucleoside	Nucleotide	Abbreviation
Adenine	Adenosine	Adenosine-5'-(mono)phosphate	5'-AMP
Guanine	Guanosine	Guanosine-5'-(mono)phosphate	5'-GMP
Cytosine	Cytidine	Cytidine-5'-(mono)phosphate	5'-CMP
Thymine	Thymidine	Thymidine-5'-(mono)phosphate	5'-TMP
Uracil	Uridine	Uridine-5'-(mono)phosphate	5'-UMP

(These nucleotides are generally abbreviated, 5'-NMP, where N can contain any of the bases.)

Table 1. Purine and pyrimidine bases, the nucleosides, nucleotides, and corresponding abbreviations.



5'-Adenosine monophosphate (5'-AMP)

3'-Thymidinemonophosphate (3'-TMP)

Figure 1.

(deoxy)ribose unit and the base, a β-glycosidic bond, has a different connectivity according to whether the link is to a purine or a pyrimidine. Although the linkage involves a C1′ carbon in both cases, the β-glycosidic bond in the case of a purine nucleotide is a link to the N-9 of the **purine base**, but to the N-1 of the **pyrimidine base**.

purine base: one of two types of nitrogen bases found in nucleic acids

pyrimidine base: one of two types of nitrogen bases found in nucleic acids

Nucleotides are also found in which two or three phosphate groups are linked together, the chain of phosphate groups bonded to the sugar's 5′-position. In these cases, they are nucleoside diphosphates (5′-NDP) and nucleoside triphosphates (5′-NTP).

The bases have very limited solubilities in water, whereas the nucleosides and nucleotides have greater solubilities, due to the presence of polar sugars, or of both sugars and charged phosphate groups, respectively.

The nucleoside triphosphates are of special interest for at least two reasons. First, they are the actual precursor molecules used in the **biosynthesis** of nucleic acids. Second, ATP is a high-energy molecule, produced primarily in mitochondria during oxidative **phosphorylation**. It stores energy, which is released (dG° = −7.3 kcal/mol) during the hydrolysis of ATP to ADP and phosphate (Pi), as shown, and then utilized to power cell reactions.

biosynthesis: formation of a chemical substance by a living organism

phosphorylation: the process of addition of phosphates into biological molecules

$$ATP + H_2O \longrightarrow ADP + Pi$$

SEE ALSO Deoxyribonucleic Acid (DNA); Restriction Enzymes.

William M. Scovell

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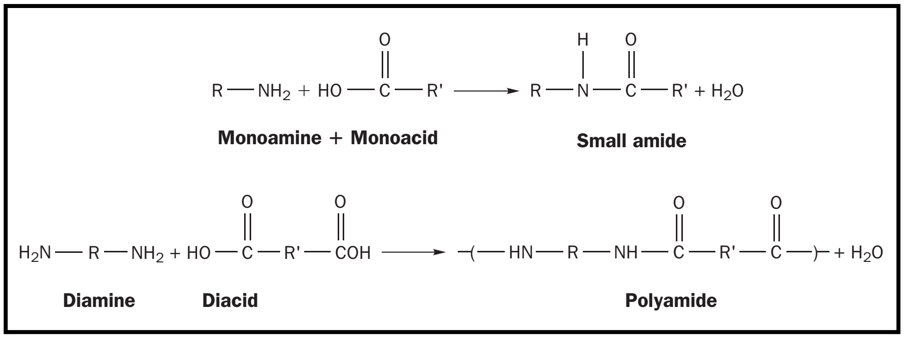
Nutrition *See Ascorbic Acid; Retinol; Riboflavin; Thiamin.*

Nylon

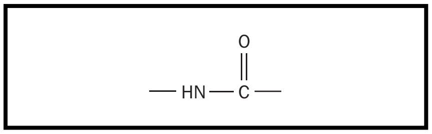
In 1928 E. I. du Pont de Nemours & Company (Du Pont) launched one of its first basic research programs and hired Wallace Hume Carothers to run it. He was brought to Du Pont in part because his fellow researchers at Harvard University and the University of Illinois had called him the best

Figure 1.



$$R-NH_2 + HO-\overset{O}{\overset{\|}{C}}-R' \longrightarrow R-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-R' + H_2O$$

$$H_2N-R-NH_2 + HO-\overset{O}{\overset{\|}{C}}-R'-\overset{O}{\overset{\|}{C}}OH \longrightarrow -\!\!(-HN-R-NH-\overset{O}{\overset{\|}{C}}-R'-\overset{O}{\overset{\|}{C}}-)\!\!- + H_2O$$



$$-HN-\overset{O}{\overset{\|}{C}}-$$

Figure 2. An amide unit.

synthetic chemist they knew. The program he supervised was designed to investigate the composition of natural polymers such as silk, cellulose, and rubber. Many of Carothers's efforts related to condensation polymers were based on his deduction that if a monofunctional reactant reacted in a certain manner in forming a small molecule, then similar reactions that employed a comparable reactant, but with two reactive groups, would form polymers. (See Figure 1.)

The amide unit (found in polyamides) shown in Figure 2 is the same connective grouping that is found in proteins.

Although the Carothers group had worked with both polyesters and polyamides, they initially emphasized their work on the polyesters, as polyesters were more soluble and easier to work with. Julian Hill, a member of the Carothers team, noticed that he could form fibers if he separated a portion of a soft polyester material using a glass stirring rod and pulled it away from the clump. But because the polyesters had softening points that were too low for their use as textiles, the group returned to its work with the polyamides. The researchers found that fibers could also be formed from the polyamides, similar to those formed from the polyesters. The strength of these fibers approached, and in some cases surpassed, the strengths of natural fibers. This new miracle fiber (nylon) was introduced at the 1939 New York World's Fair, in an exhibit that announced the **synthesis** of a wonder fiber from "coal, air, and water"—an exaggeration but nevertheless eye-catching. When the nylon stockings were first offered for sale in New York City, on May 15, 1940, over four million pairs were sold in the first few hours. Nylon stocking sales took a large drop during World War II when it became publicized that nylon was needed to make parachutes.

The polyamides (nylons) were given a special naming system. Nylons made from **diamines** and dicarboxylic acids are designated by two numbers, the first representing the number of carbons in the diamine chain *(a)* and the second the number of carbons in the di**carboxylic acid** *(b)*. (See Figure 3.)

The nylon developed by Carothers at Du Pont was nylon 6,6. Because of the importance of starting out with equal amounts of the two reactants, salts of the diamine and of the diacid are made and then used in the commercial synthesis of nylon 6,6. (See Figure 4.)

Nylon 6,6 (or simply nylon 66) is the largest volume nylon used as fiber, film, and plastic. About 1,134 million kilograms (2,500 million pounds) of nylon 66 were produced for fiber applications in 2000. Nylon 66 is used to make tire cord, rope, clothing, thread, hose, undergarments, rug filament,

synthesis: combination of starting materials to form a desired product

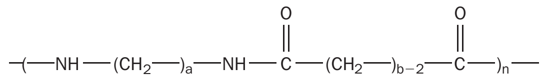
diamine: compound, the molecules of which incorporate two amino groups ($-NH_2$) in their structure, such as 1,2 diamino ethane (sometimes called ethylenediamine) and the three diamine benzene compounds

carboxylic acid: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the $-CO_2H$ functional group

STEPHANIE KWOLEK (1923–)

Stephanie Kwolek has seventeen patents, the first of which is for Kevlar. After creating a new polymer, she would spin them into fibers for strength and flexibility testing. Material for fibers of Kevlar was cloudy white instead of molasses brown, the first indication that she had uncovered an exceptional polymer.

—Valerie Borek



$$-(-NH-(CH_2-)_a-NH-\overset{O}{\overset{\|}{C}}-(CH_2-)_{b-2}-\overset{O}{\overset{\|}{C}}-)_n-$$

Nylon a,b

Figure 3.

socks, dresses, and more. Because of the presence of polar units in nylons, similar to the presence of polar units in proteins, materials made from nylon have a nice “feel” to them. Nylon materials also attract odors (many everyday odors are polar in nature) and are easily stained. Most textile and fabric products are treated to repel unwanted odors and stainmaking materials.

Nylon 66 was the first engineering thermoplastic, and up until 1953 represented all of engineering thermoplastic sales. The term “thermoplastic” denotes a material that can be melted through heating. The term “engineering thermoplastics” describes a plastic material that can be cut, drilled, or machined. About 680.4 million kilograms (1,500 million pounds) of nylons were produced in the United States in 2000 for thermoplastic use. Nylon 66 plastic is tough and rigid. It has a relatively high use temperature (to about 270°C or 518°F), and is used in the manufacture of products ranging from automotive gears to hairbrush handles. Molded nylon 66 is used to make skate wheels, motorcycle crank cases, bearings, tractor hood extensions, skis for snowmobiles, lawnmower blades, bicycle wheels, and so on.

Most polymers, when heated, progress from a glasslike solid to a softer solid, and then to a viscous “taffylike” material that is most amenable to heat-associated fabrication. In the case of nylon 66, the transition from the solid to the soft stage is abrupt, requiring that fabrication be closely watched.

The presence in nylons of polar groups results in materials that have a relatively high glass transition temperature (T_g, the point at which segmental mobility begins) and high **melting point** (the point at which entire polymer chain mobility begins), so that, unlike many vinyl polymers such as polyethylene and polypropylene (which must be at temperatures above their glass transition temperatures to possess needed flexibility), nylons, and many other condensation polymers, function best in contexts in which strength, and not flexibility, is the desired attribute.

melting point: temperature at which a substance in the solid state undergoes a phase change to the liquid state

Figure 4.

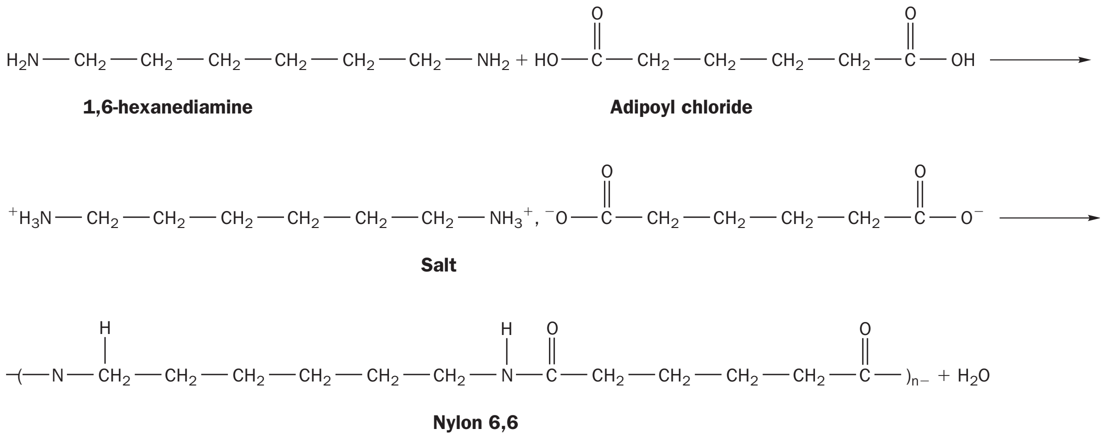
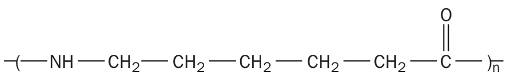


Figure 5.



$$-\!\!(\!-NH-CH_2-CH_2-CH_2-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-)_{n}-$$

Nylon 6

hydrogen bonding: intermolecular force between the H of an N–H, O–H, or F–H bond and a lone pair on O, N, or F of an adjacent molecule

Because they have these polar groups that also allow for **hydrogen bonding**, nylons and most condensation polymers are also stronger, more rigid and brittle, and tougher in comparison to most vinyl polymers. Nylons are also "lubrication-free," meaning they do not need lubricant for easy mobility; thus they can be used to make mechanical bearings and gears that do not need periodic lubrication.

During the early 1950s George deMestral, after walking in the Swiss countryside, noticed that he had cockleburs caught in his jacket. He examined the cockleburs and noticed that they had tiny "hooks." His cotton jacket had loops that "held" the cockleburs. He began playing with his observations and making combinations of materials—one having rigid hooks and the other having flexible loops or eyes. Today, Velcro, the name given to the nylon-based hook-and-eye combination, uses nylon as both the hook material and the eye material. Polyester is sometimes blended with the nylon to make it stronger. (Polyesters have also been used to make hook-and-eye material.) Velcro is used to fasten shoes, close space suits, and it has many other applications.

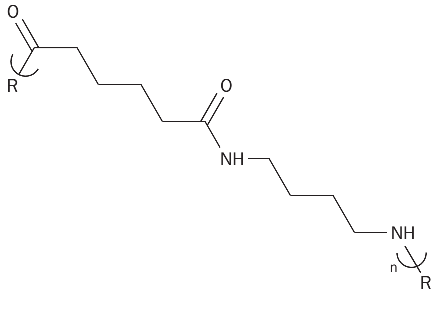
Nylon 6, produced via the ring-opening reaction of the compound caprolactam is structurally similar to nylon 66 and has similar properties and uses. It is widely used in Europe in place of nylon 66, but not in the United States. (See Figure 5.)

hydrophobic: part of a molecule that repels water

ductile: property of a substance that permits it to be drawn into wires

Nylon 6,10 and nylon 6,12 are also commercially available. Because of the presence of the additional methylene ($-CH_2-$) groups that are **hydrophobic** (water-hating), these nylons are more resistant to moisture and more **ductile** than nylon 66.

DSM (once called Dutch State Mines) introduced nylon 4,6 (Stanyl) in 1990. It is produced via the condensation reaction between adipic acid and 1,4-diaminobutane, produced from renewable resources. Stanyl can withstand temperatures up to about 300°C (570°F), allowing it to occupy a niche position—between conventional nylons and high-performance materials. (See Figure 6.)



Nylon 4, 6

Figure 6.

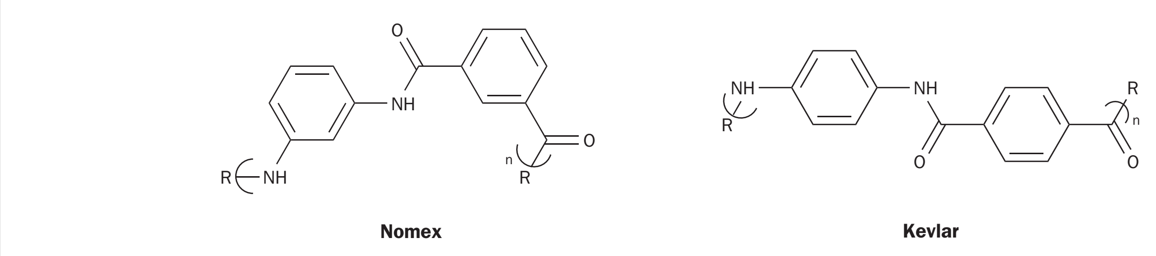


Figure 7.

Several new commercial ventures are based on using natural, renewable starting materials (instead of petrochemicals). These products are known as "green" products because they are made from renewable resources and can be composted. The compound 1,4-butanediamine, used to produce nylon 4,6 from natural material, is such a green product.

In general, more crystalline nylons are fibrous whereas less crystalline nylon materials are more plastic in behavior.

Several aromatic polyamides, called aramids, have been produced. These materials are strong, are stable at high temperatures, and have good flame-resistance properties. Nomex (made from *m*-diaminobenzene and isophthalic acid) is used to make flame-resistant clothing and the thin pads used in space shuttles to protect sintered silica-fiber mats from stress and vibration during flight. Kevlar (made from *p*-diaminobenzene and terephthalic acid) is structurally similar to Nomex and by weight is stronger than steel. It is used in the manufacture of so-called bullet-resistant clothing. Because of its outstanding strength to weight ratio, it was used as the skin covering of the human-powered Gossamer Albatross, flown over the English Channel.

Aramids are also widely used as the fibers that are part of space-age composites and in the manufacture of tire cord and tread. (See Figure 7.) SEE ALSO CAROTHERS, WALLACE; MATERIALS SCIENCE; POLYMERS, SYNTHETIC.

Charles E. Carraher Jr.

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Oil ***See Fossil Fuels.***

Oppenheimer, Robert

AMERICAN PHYSICIST
1904–1967

The son of a wealthy New York City textile importer (Julius) and a painter (Elle Friedman), Julius Robert Oppenheimer enjoyed an affluent childhood. He graduated from the Ethical Culture School of New York at the top of his class in 1921 and summa cum laude from Harvard in 1925. He then studied at the Cavendish Laboratory in Cambridge, England, and with Max Born at the University of Göttingen, in Germany, where he earned a doctorate in 1927. Although a rising star, he often was plagued by deep self-doubts and dark moods.

theoretical physics: branch of physics dealing with the theories and concepts of matter, especially at the atomic and subatomic levels

fissionable: of or pertaining to unstable nuclei that decay to produce smaller nuclei

In 1929 Oppenheimer moved to California and for many years taught at both the California Institute of Technology (Caltech) and the University of California, Berkeley. He made several contributions to subatomic physics, including (with his former mentor) the Born–Oppenheimer approximation, which posited that the spin and vibration of protons could be ignored in theoretical calculations. Thin, wiry, enigmatic, and charismatic, Oppenheimer was associated with several leftist groups, which he helped fund. In 1940 he married biologist Katherine Harrison, a former member of the Communist Party.

American physicist Robert Oppenheimer, scientific director of the Manhattan Project in which the atomic bomb was developed.

Oppenheimer declared his leftist ties severed soon after he joined a secret group of elite scientists working with Ernest O. Lawrence at Berkeley's radiation laboratory to develop an atomic bomb. In spite of continuing suspicions about his loyalty, the U.S. Army appointed him director of the bomb design unit in October 1942. Oppenheimer's team of hundreds of gifted young scientists was secluded at a facility in Los Alamos, New Mexico. One of the brightest, Edward Teller, became a disaffected rival of Oppenheimer, but most found him a brilliant and inspiring leader.

Pushing the boundaries of **theoretical physics**, Oppenheimer's Los Alamos scientists followed two technological paths simultaneously. One was a "gun assembly" designed to fire two masses of uranium at each other to initiate a chain reaction. But because **fissionable** uranium was exceedingly difficult to refine, other scientists worked on a design using more readily available but less stable plutonium, imploding a hollow sphere of the fuel with high explosives. Both designs worked, and they were used against

EDWARD TELLER (1908–2003)

Edward Teller was a physical chemist and an important, if controversial, voice in the politics of nuclear science. His work contributed to an understanding of both fusion and fission bombs. Regarded as the "father of the H-bomb," he was an ardent anticommunist and cold war warrior and he staunchly advocated the development and stockpiling of nuclear weapons. He opposed treaties limiting nuclear arsenals and testing, and he supported the development of space-based weapons.

—Valerie Borek

Japan—a uranium bomb was dropped over Hiroshima, a plutonium one over Nagasaki—in early August 1945 to end World War II.

Initially, Oppenheimer was elated over these technical achievements, but he quickly be came regretful and despondent about a nuclear future. As director of the prestigious Center for Advanced Study at Princeton (1947–1952) and chair of the General Advisory Committee of the Atomic Energy Commission (AEC), he was an outspoken advocate for the international sharing of nuclear technology and for international arms control, and he opposed further development of the hydrogen bomb. After a 1954 hearing, the AEC security board affirmed his loyalty but revoked his security clearance. Although there is little hard evidence that Oppenheimer ever passed atomic secrets to the former Soviet Union, the controversy surrounding this claim continues. Oppenheimer spent his final years sailing in the Virgin Islands and writing about science and Western culture. He died in Princeton, New Jersey, on February 18, 1967. SEE ALSO LAWRENCE, ERNEST; MANHATTAN PROJECT.

David B. Sicilia

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Organic Chemistry

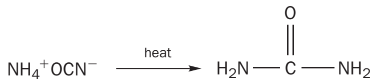
Organic chemistry is the chemistry of carbon compounds. All organic compounds contain carbon; however, there are some compounds of carbon that are not classified as organic. For example, salts such as carbonates (e.g., Na_2CO_3, $CaCO_3$) and cyanides (e.g., NaCN, KCN) are usually designated as inorganic. Perhaps a more useful description might be: Organic compounds are compounds of carbon that usually contain hydrogen and that may also contain other elements such as oxygen, nitrogen, sulfur, phosphorus, or **halogen** (F, Cl, Br, or I). In any case, there are very few carbon compounds that are not organic, while there are millions that are.

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

History

Prehistoric civilizations obtained many useful chemicals from plants and animals. They were familiar with sugar, which they learned to ferment to make wine. Then they found that the wine could turn into vinegar. Ancient Egyptians used blue dye made from the indigo in madder root, and a royal purple dye extracted from a rare kind of mollusk. Soap was made by heating animal fat with base from wood ashes.

During the Middle Ages dry distillation of wood yielded mixtures of methyl alcohol, acetone, and acetic acid. Alchemists isolated cholesterol from gallstones, morphine from opium, and drugs such as quinine, strychnine, and brucine from various plants. Two hundred years ago chemists such as Antoine Lavoisier determined the elemental composition of many of these substances and noted that they all contained carbon and hydrogen, and that many also contained oxygen and nitrogen. It also appeared that there were two classes of materials: the mineral type (generally hard, high-melting, and noncombustible), and the organic type (often soft, liquid or low melting solids, and frequently easily combustible materials). Most organic chemicals could be burned to produce carbon dioxide; and any hydrogen present was converted to water (H_2O). Because organic compounds had for centuries been isolated only from plants and animals, it was commonly believed that some "vital force" in living things was necessary to produce them. This belief persisted until 1828, when Friedrich Wöhler was able to make urea, a chemical found in the urine of animals, from the inorganic salt ammonium cyanate.



$$NH_4^+OCN^- \xrightarrow{\text{heat}} H_2N-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$$

(inorganic)

urea
(organic)

Since that time organic chemistry has grown into a vast and ever expanding field that encompasses millions of chemical compounds.

Scope of Organic Chemistry

The field of organic chemistry includes more than twenty million compounds for which properties have been determined and recorded in the literature. Many hundreds of new compounds are added every day. Much more than half of the world's chemists are organic chemists. Some new organic compounds are simply isolated from plants or animals; some are made by modifying naturally occurring chemicals; but most new organic compounds are actually synthesized in the laboratory from other (usually smaller) organic molecules. Over the years organic chemists have developed a broad array of reactions that allow them to make all kinds of complex products from simpler starting materials.

Singular Attributes of Carbon

When one considers the millions of chemical compounds that are known and notes that more than 95 percent of them are compounds of carbon, one realizes that carbon is unique. Why are there so many carbon compounds? It turns out that atoms of carbon are quite remarkable in a number of ways.

Carbon atoms form very strong bonds with other carbon atoms. The bonds are so strong that carbon can form long chains, some containing thousands of carbon atoms. (Carbon is the only element that can do this.)

A carbon atom forms four bonds, therefore carbon not only can form long chains, but it also forms chains that have branches. It is a major reason why carbon compounds exhibit so much isomerism. The simple compound decane ($C_{10}H_{22}$), for example, has 75 different **isomers**.

isomer: molecules with identical compositions but different structural formulas

Carbon atoms can be bonded by double or triple bonds as well as single bonds. This multiple bonding is much more prevalent with carbon than with any other element.

Carbon atoms can form rings of various sizes. The rings may be saturated or unsaturated. The unsaturated 6-membered ring known as the benzene ring is the basis for an entire subfield of "aromatic" organic chemistry.

Carbon atoms form strong bonds not only with other carbon atoms but also with atoms of other elements. In addition to hydrogen, many carbon compounds also contain oxygen. Nitrogen, sulfur, phosphorus, and the halogens also frequently occur in carbon compounds.

Various kinds of **functional groups** occur widely among carbon compounds, and many different kinds of isomers are possible.

functional group: portion of a compound with characteristic atoms acting as a group

Hydrocarbons

Compounds of carbon and hydrogen only are called *hydrocarbons*. These are the simplest compounds of organic chemistry. The most basic group of hydrocarbons are the *alkanes*, which contain only single bonds. The simplest member of the alkane series is methane, CH_4, the main component of natural gas. The names of some alkanes are listed in Table 1. Alkanes sometimes

ALKANES

Formula		Name	
CH_4	CH_4	methane	gases
C_2H_6	CH_3CH_3	ethane	
C_3H_8	$CH_3CH_2CH_3$	propane	
C_4H_{10}	$CH_3CH_2CH_2CH_3$	butane	
C_5H_{12}	$CH_3(CH_2)_3CH_3$	pentane	liquids
C_6H_{14}	$CH_3(CH_2)_4CH_3$	hexane	
C_7H_{16}	$CH_3(CH_2)_5CH_3$	heptane	
C_8H_{18}	$CH_3(CH_2)_6CH_3$	octane	
C_9H_{20}	$CH_3(CH_2)_7CH_3$	nonane	
$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	decane	
$C_{11}H_{24}$	$CH_3(CH_2)_9CH_3$	undecane	
$C_{12}H_{26}$	$CH_3(CH_2)_{10}CH_3$	dodecane	
$C_{13}H_{28}$	$CH_3(CH_2)_{11}CH_3$	tridecane	
$C_{14}H_{30}$	$CH_3(CH_2)_{12}CH_3$	tetradecane	
$C_{15}H_{32}$	$CH_3(CH_2)_{13}CH_3$	pentadecane	
$C_{16}H_{34}$	$CH_3(CH_2)_{14}CH_3$	hexadecane	
$C_{17}H_{36}$	$CH_3(CH_2)_{15}CH_3$	heptadecane	
$C_{18}H_{38}$	$CH_3(CH_2)_{16}CH_3$	octadecane	solids
$C_{19}H_{40}$	$CH_3(CH_2)_{17}CH_3$	nonadecane	
$C_{20}H_{42}$	$CH_3(CH_2)_{18}CH_3$	eicosane	

Table 1.

have ring structures. Since a 4-carbon chain of the alkane series is called *butane*, a ring of 4 carbon atoms is called *cyclobutane*.

butane (C_4H_{10}) **cyclobutane (C_4H_8)**

Simple hydrocarbons that contain one or more double bonds are called *alkenes.* They are named like alkanes, but their names end in "−ene." The simplest alkene has two carbon atoms and is called *ethene.* A 3-carbon chain that has a double bond is called *propene.*

$H_2C{=}CH_2$ ethene (C_2H_4)

$H_2C{=}CHCH_3$ propene (C_3H_6)

$CH_3CH{=}CHCH_2CH_2CH_3$ 2-pentene (C_5H_{10})

A 5-carbon hydrocarbon chain with a double bond is called *pentene*, and if the double bond links the second and third carbons, it is 2-*pentene.* Like cycloalkanes, alkenes have the general formula C_nH_{2n}. Alkenes having ring structures are called *cycloalkenes.* A 5-carbon ring with a double bond is called *cyclopentene.*

Hydrocarbons that contain one or more triple bonds are called *alkynes*, and is the name ending is "−yne." A 2-carbon alkyne is therefore named *ethyne.* (However, the compound is often referred to by its common name, which is *acetylene.*)

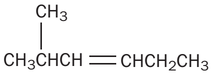
catalyst: substance that aids in a reaction while retaining its own chemical identity

Compounds that contain double or triple bonds are said to be "unsaturated"—because they are not "saturated" with hydrogen atoms. Unsaturated compounds are reactive materials that readily add hydrogen when heated over a **catalyst** such as nickel. The reverse reaction also occurs. Heating ethane with steam is an important commercial process for making ethene (or ethylene). This is an important commercial process called "steam cracking."

$$H_3C-CH_3 \xrightarrow[\text{heat}]{H_2O} H_2C=CH_2 + H_2$$

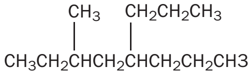
When a 6-carbon ring contains 2 double bonds, it is called *cyclohexadiene*, but when it has 3 double bonds, it is not called cyclohexatriene; this is because a 6-carbon ring with three double bonds takes on a special kind of stability. The double bonds become completely conjugated and no longer behave as double bonds. The ring, known as a "benzene ring," is said to be aromatic.

The removal of a hydrogen atom from a hydrocarbon molecule leaves an alkyl group that readily attaches to a functional group, or forms a branch on a hydrocarbon chain. The groups are named after the corresponding hydrocarbons. For example, CH_3- is named *methyl;* CH_3CH_2-, *ethyl;* $CH_2{=}CH-$, *ethenyl;* $CH_3CH_2CH_2-$, *propyl;* and so on. A benzene ring from which a hydrogen atom has been removed is often referred to as a *phenyl.* The branched molecules shown here would be given names as follows



$CH_3CH(CH_3)CH{=}CHCH_2CH_3$

2-methyl-3-hexene



$CH_3CH_2CH(CH_3)CH_2CH(CH_2CH_2CH_3)CH_2CH_2CH3$

3-methyl-5-propyloctane

In a conjugated system, there are alternating double and single bonds, allowing electrons to flow back and forth. Molecules that contain such conjugated systems are said to be stabilized by "resonance." In the benzene ring every other bond is a double bond, all the way around the ring. This results in a special kind of stabilization called "aromaticity," in which the electrons are delocalized and free to travel all around the ring. Certain ring compounds, like benzene, that contain such a conjugated system of double and single bonds are described as "aromatic."

Theoretically there is no limit to the length of hydrocarbon chains. Very large hydrocarbon molecules (polymers) have been made containing as many as 100,000 carbon atoms. However, such molecules are hard to make and very difficult to melt and to shape into useful products.

Hydrocarbons are obtained primarily from fossil fuels—especially petroleum and natural gas. Natural gas is a mixture that is largely methane mixed with varying amounts of ethane and other light hydrocarbons, while petroleum is a complex mixture of many different hydrocarbons. Coal, the other fossil fuel, is a much more complicated material from which many kinds of organic compounds, some of them hydrocarbons, can be obtained.

Functional Groups

Alkane molecules are rather unreactive (except for being very flammable), but alkenes react with many other substances. When a drop of bromine is added to an alkene, for example, the deep orange color of the bromine immediately disappears as the bromine adds across the double bond to form a dibromo derivative. The double bond is called a "functional group" because its presence in a molecule causes reactivity at that particular site. There are a dozen or so functional groups that appear frequently in organic compounds. Some of the most common ones are listed in Table 2. The same molecule may contain several functional groups. Aspirin, for example, is both a **carboxylic acid** and an **ester**, and cholesterol is an alkene as well as an alcohol.

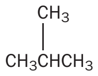
carboxylic acid: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the –CO_2H functional group

ester: organic species containing a carbon atom attached to three moieties: an O via a double bond, an O attached to another carbon atom or chain, and a H atom or C chain; the R(C═O)OR functional group

Isomerism

Isomers are molecules with the same molecular formula but different structures. There is only one structure for methane, ethane, or propane; but butane, C_4H_{10}, can have either of two different structure:

$CH_3CH_2CH_2CH_3$ or



$CH_3CH(CH_3)CH_3$

(1) **(2)**

The linear molecule (1) is called butane, or *normal* butane (*n*-butane), whereas the branched molecule (2) is methylpropane (rather than 2-methylpropane, as the methyl group has to be in a 2-position). If the methyl group of (2) were attached to a terminal carbon, the resultant molecule would be the same as (1). Methylpropane (2) is also called *iso*butane.

Pentane has 3 isomers: pentane (or *n*-pentane), methylbutane (or *iso*pentane), and dimethyl propane (or *neo*pentane). Hexane has 5 isomers:

hexane, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane. Heptane has 9 different isomers, octane has 18, nonane has 35, and decane has 75. An increase in the number of carbon atoms greatly increases the possibilities for isomerism. There are more than 4,000 isomers of $C_{15}H_{32}$ and more than 366,000 isomers of $C_{20}H_{42}$. The formula $C_{30}H_{62}$ has more than 4 billion. Of course, most of them have never been isolated as pure compounds (but could be, if there were any point in doing it).

For molecules other than hydrocarbons, still other kinds of isomers are possible. The simple formula C_2H_6O can represent ethyl alcohol or dimethyl ether; and C_3H_6O could stand for an alcohol, an ether, an **aldehyde**, or a **ketone** (among other things). The larger a molecule is, and the greater the variety of atoms and functional groups it contains, the more numerous its isomers.

aldehyde: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the RC(O)H functional group

ketone: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the FC(O)R functional group

There is still another kind of isomerism that stems from the existence of “right-” and “left-handed” molecules. It is sometimes referred to as *optical* isomerism because the molecules that make up a pair of these isomers usually differ only in the way they rotate plane polarized light.

Nomenclature

There are so many millions of organic compounds that simply finding names for them all is a major challenge. It was not until the late nineteenth century that chemists developed a logical system for naming organic compounds. Compounds had often been named according to their sources. The 1-carbon carboxylic acid, for example, was first obtained from ants, and so it was called *formic* acid, from the Latin word for ants (*formicae*). The 2-carbon acid was obtained from vinegar (*acetum* in Latin), and was called *acetic* acid.

To bring some order to the naming process an international meeting was held in 1892 at Geneva, Switzerland. The group later became known as the International Union of Pure and Applied Chemistry (IUPAC). Its objective was to establish a naming process that would provide each compound with a unique and systematic name. An initial set of rules was adopted at that first meeting in Geneva, and IUPAC has continued that work. Its systematic naming rules are used by organic chemists all over the world. The names of the alkanes form the basis for the system, with functional groups usually being indicated with appropriate suffixes. Some examples are given in Table 2.

Organic Reactions

Organic chemistry is concerned with the many compounds of carbon, their names, their isomers, and their properties, but it is mostly concerned with their reactions. Organic chemists have developed a huge array of chemical reactions that can convert one organic compound to another. Some reactions involve addition of one molecule to another; some involve decomposition of molecules; some involve substitution of one atom or group by another; and some even involve the rearrangement of molecules, with some atoms moving into new positions. Some reactions require energy in the form of heat or radiation; and some require a special kind of catalyst or some sort

NAMING ORGANIC COMPOUNDS

Functional Group		Type Compound	Example	IUPAC Name	Common Name
$C{=}C$	double bond	alkene	$H_2C{=}CH_2$	ethene	ethylene
$C{\equiv}C$	triple bond	alkyne	$HC{\equiv}CH$	ethyne	acetylene
$-OH$	hydroxyl	alcohol	CH_3OH	methanol	methyl alcohol
$-O-$	oxy	ether	H_3COCH_3	methoxymethane	methyl ether
$-\overset{H}{\overset{\vert}{C}}{=}O$	carbonyl	aldehyde	$H_2C{=}O$	methanal	formaldehyde
$-\overset{\vert}{C}{=}O$	carbonyl	ketone	CH_3COCH_3	propanone	acetone
$-\overset{O}{\overset{\Vert}{C}}-OH$	carboxyl	carboxylic acid	$HCOOH$	methanoic acid	formic acid
$-\overset{O}{\overset{\Vert}{C}}-O-$	carboxyl	ester	$HCOOCH_2CH_3$	ethyl methanoate	ethyl formate
$-NH_2$	amino	amine	CH_3NH_2	aminomethane	methylamine
$-CN$	cyano	nitrile	CH_3CN	ethanenitrile	acetonitrile
$-X$	halogen	haloalkane	CH_3Cl	chloromethane	methyl chloride

Table 2.

of solvent. Of course, not all organic reactions are highly successful. One reaction might be a very simple one giving essentially 100 percent of the desired product; but another might be a complex multistep process yielding less than 5 percent overall of the wanted product.

Organic reactions can often give remarkable control as to what products should be formed. Adding water to propene for example, produces 2-propanol in the presence of acid, but it yields 1-propanol if treated first with B_2H_6 and then H_2O_2 in the presence of base.

Future Sources of Organic Chemicals

Fossil fuels have been our primary natural source for many organic chemicals for more than a century, but our fossil fuel resources are finite, and they are being rapidly depleted (especially oil and gas). What will be our sources of organic materials in the future? Since fossil fuels are nonrenewable resources, it is believed that the twenty-first century will see a shift toward greater dependence on renewable raw materials. The largest U.S. chemical company has a goal of becoming 25 percent based on renewable resources by 2010. It is already producing 1,3-propanediol from cornstarch using a gene-tailored *E. coli* bacterium. This diol is used in Du Pont's fiber Sorona, which is said to combine the best features of both polyester and nylon fibers. Succinic acid and polyhydroxybutyrate are also obtainable from renewable crops, and the list of such renewable raw materials is destined to grow. For example, ethylene (or ethene), $CH_2{=}CH_2$, which is a highly important commercial chemical used in making many industrial chemicals and polymers, is presently made by steam cracking of ethane obtained from oil or natural gas; but ethylene can also be made by dehydration of ethyl alcohol made by fermentation of sugar. Efforts are even being made to use biowaste materials, such as corn husks, nutshells, and wood chips as industrial raw materials.

Analytical Tools

Organic chemists often need to examine products for identification, purity analysis, or structure determination. There are some marvelous tools available

chromatography: the separation of the components of a mixture in one phase (the mobile phase) by passing it through another phase (the stationary phase) making use of the extent to which the components are absorbed by the stationary phase

spectroscopy: use of electromagnetic radiation to analyze the chemical composition of materials

to help them do these things. **Chromatography**, **spectroscopy**, and crystallography are especially widely used in organic chemistry.

Column chromatography, gas chromatography, and liquid chromatography are all important methods for separating mixtures of organic compounds. Spectroscopic tools include ultraviolet (UV), infrared (IR), nuclear magnetic resonance (NMR), and mass spectroscopy (MS), each capable of providing a different kind of information about an organic compound. Although it is limited to substances that can be prepared as pure crystals, x-ray crystallography is probably the ultimate tool for determining molecular structure.

Careers in Organic Chemistry

Some organic chemists are involved in basic research at government or academic institutions, but most have careers in industry. The industries vary from oil and chemical companies to industries producing food, pharmaceuticals, cosmetics, detergents, paints, plastics, pesticides, textiles, or other kinds of products. Many organic chemists work in laboratories, where they do various kinds of analysis or research, but many others do not. Some are teachers, or writers, or science librarians. Some study law and become patent attorneys; some study medicine and become medical researchers; and some study business and become administrators of companies, colleges, or other institutions. Organic chemistry is an enormous field full of many kinds of career possibilities. SEE ALSO FOSSIL FUELS; LAVOISIER, ANTOINE; ORGANIC HALOGEN COMPOUNDS; WÖHLER, FRIEDRICH.

Kenneth E. Kolb

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Organic Halogen Compounds

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

tetrachloride: term that implies a molecule has four chlorine atoms present

Organic **halogen** compounds are a large class of natural and synthetic chemicals that contain one or more halogens (fluorine, chlorine, bromine, or iodine) combined with carbon and other elements. The simplest organochlorine compound is chloromethane, also called methyl chloride (CH_3Cl). Other simple organohalogens include bromomethane (CH_3Br), chloroform ($CHCl_3$), and carbon **tetrachloride** (CCl_4). Some examples of organohalogens are shown in Figure 1.

Synthesis

Organohalogens can be made in various ways. Direct halogenation of hydrocarbons with chlorine gives organochlorines; with bromine, organobromines. Alcohols can be converted into organohalogens by reaction with hydrogen halides.

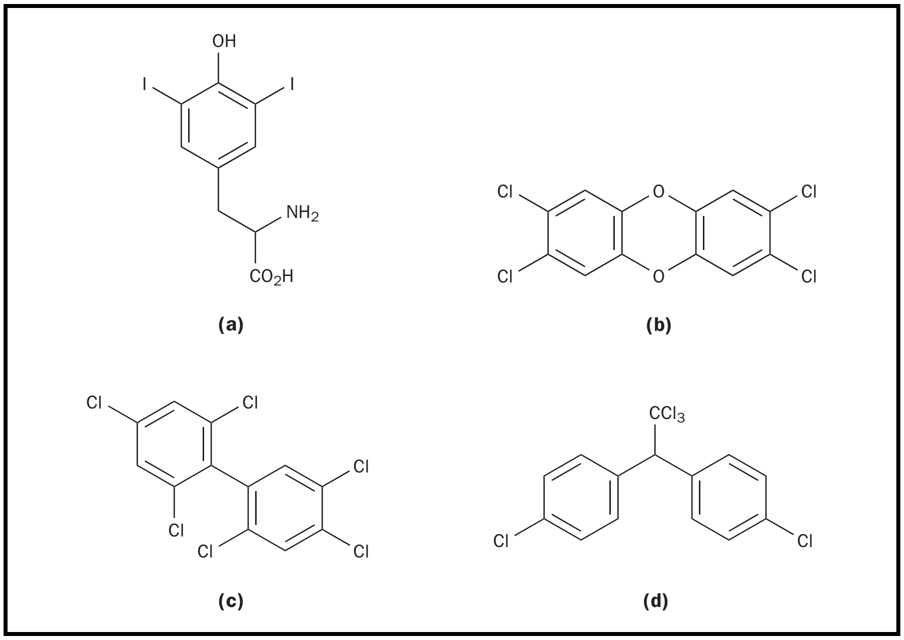
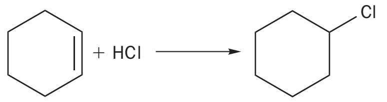


Figure 1. Four representative organohalogens: (a) a thyroid hormone; (b) "dioxin" (2,3,7,8-tetrachlorodibenzo-p-dioxin); (c) a polychlorinated biphenyl (PCB); (d) DDT (dichlorodiphenyltrichloroethane).

Aromatic organohalogens such as chlorobenzene are synthesized by treatment of benzene with halogen and a Lewis acid **catalyst** such as aluminum chloride.

catalyst: substance that aids in a reaction while retaining its own chemical identity

Organohalogen compounds are also produced by adding halogen or hydrogen halide to alkenes and alkynes.



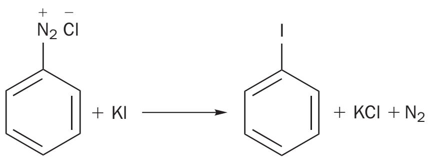
(1)

$$CH_2{=}CH_2 + Br_2 \longrightarrow BrCH_2CH_2Br \qquad (2)$$

$$HC{\equiv}CH + 2Cl_2 \longrightarrow Cl_2CHCHCl_2 \qquad (3)$$

Organoiodines and organofluorines are prepared by displacement reactions.

$$CH_3CH_2Br + KF \longrightarrow CH_3CH_2F + KBr \qquad (4)$$

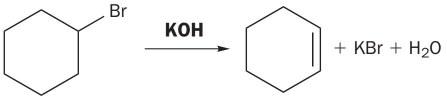


(5)

Reactivity

The reactivity of organohalogens varies enormously. The war gases phosgene (ClCOCl) and mustard ($ClCH_2CH_2SCH_2CH_2Cl$) are very reactive and highly toxic, whereas most other organohalogen compounds are relatively **inert**. Nevertheless, organohalogens undergo many chemical transformations. One common reaction is elimination, induced by the action of a strong base.

inert: incapable of reacting with another substance



(6)

Toxicity

combustion: burning, the reaction with oxygen

As with all chemicals, "the dose makes the poison." The chlorine-containing insecticide dichlorodiphenyltrichloroethane (DDT) is highly effective in killing disease-ridden mosquitoes, ticks, and fleas, but it is virtually nontoxic to mammals. The fluorine-containing pesticide "1080," or fluoroacetic acid (FCH_2CO_2H), is highly toxic and often lethal to all mammals. The industrial and **combustion** by-product dioxin is highly toxic to some animals but not to others; in humans, dioxin causes the skin disease chloracne.

Use

Organohalogens are widely used in industry and society. Chloromethane is used as a solvent in rubber polymerization. Bromomethane is an important fumigant; the related halons ($CBrClF_2$ and $CBrF_3$) are better fire extinguishants than carbon dioxide.

vitamins: organic moleculs needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

Eighty-five percent of all pharmaceutical agents and **vitamins** involve chlorine chemistry; many drugs require chlorine, fluorine, or bromine to be effective. Ceclor and Lorabid are used to treat ear infections, Toremifene is a breast-cancer drug, and the natural antibiotic vancomycin is used to fight penicillin-resistant infections. Benzyl chloride is used to synthesize the drugs phenobarbital, benzedrine, and demerol. Inhalation anesthetics include the organofluorines desflurane, sevoflurane, and enflurane ($CHClFCF_2OCHF_2$). Perfluorocarbons, such as perfluorotributylamine ($[CF_3CF_2CF_2CF_2]_3N$), are used as blood substitutes or blood extenders ("artificial blood") and are used for coronary angioplasty. The insecticide DDD (mitotane), related to DDT, is used to treat inoperable adrenal cancer. The chemical advantages to some of these halogenated drugs are shown in Figure 2.

Vinyl chloride ($CH_2{=}CHCl$), a carcinogenic gas, is polymerized to polyvinyl chloride (PVC), a plastic of great versatility and safety. PVC is an invaluable component of building materials, consumer goods, medical equipment, and many other everyday products. More than 2.2 billion kilograms (5 billion pounds) of PVC are used annually for wire, cable, and other electrical applications. The chlorine in PVC makes this plastic flame retardant and ideal for construction and furnishing applications. Polytetrafluoroethylene (Teflon) is the polymer of tetrafluoroethylene ($CF_2{=}CF_2$). Because of its chemical stability (very strong carbon-fluorine bonds), it has many diverse applications in our society; best known perhaps are the coatings used to make "nonstick" cookware. Trichloroethylene ($CHCl{=}CCl_2$) and tetrachloroethylene ($CCl_2{=}CCl_2$, "Perc") are widely used solvents in the dry cleaning industry.

Organohalogens are essential for crop production and protection as herbicides and insecticides. Ninety percent of grain farms utilize these chemicals in food production. The chemical structures of some of these organohalogens are shown in Figure 3.

Polychlorinated biphenyls (PCBs) were introduced in 1929 as insulators in capacitors and transformers in the electric power industry, as lubricants

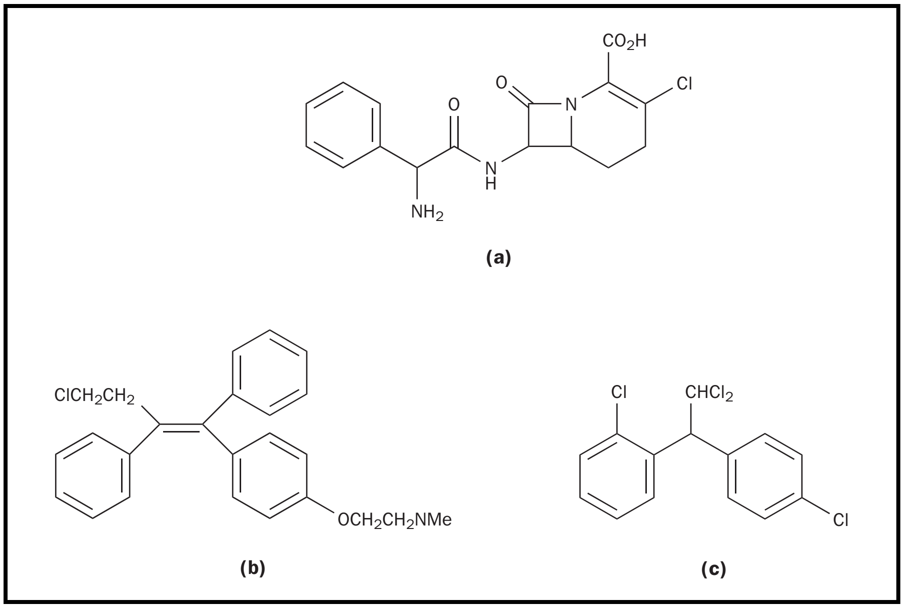


Figure 2. Organohalogens as drugs: (a) Lorabid, antibiotic; (b) toremifene, a breast cancer drug; (c) mitotane, a cancer drug.

and coolants in vacuum pumps, as paint additives, and in food packaging. The manufacture and use of PCBs were discontinued in 1977 because of their adverse effects on the environment. Their effect on humans is still unknown. An example of a PCB is shown in Figure 1.

Chlorofluorocarbons (CFCs or freons) are strongly implicated in causing the ozone hole, and are being phased out of use as refrigerants, dry cleaning solvents, propellants, fire extinguishants, and foam-blowing agents. These chemicals include CFC-11 (CCl_3F), CFC-13 ($CClF_3$), and CFC-112 (CCl_2FCCl_2F). Replacements for CFCs are the hydrochlorofluorocarbons (HCFCs) and the hydrofluorocarbons (HFCs), both of which have no impact on stratospheric ozone and have low global warming potential. Examples include HCFC-21 ($CHCl_2F$) and HFC-152 (FCH_2CH_2F).

chlorofluorocarbon (CFC): compound that contains carbon, chlorine, and fluorine atoms, which remove ozone in the upper atmosphere

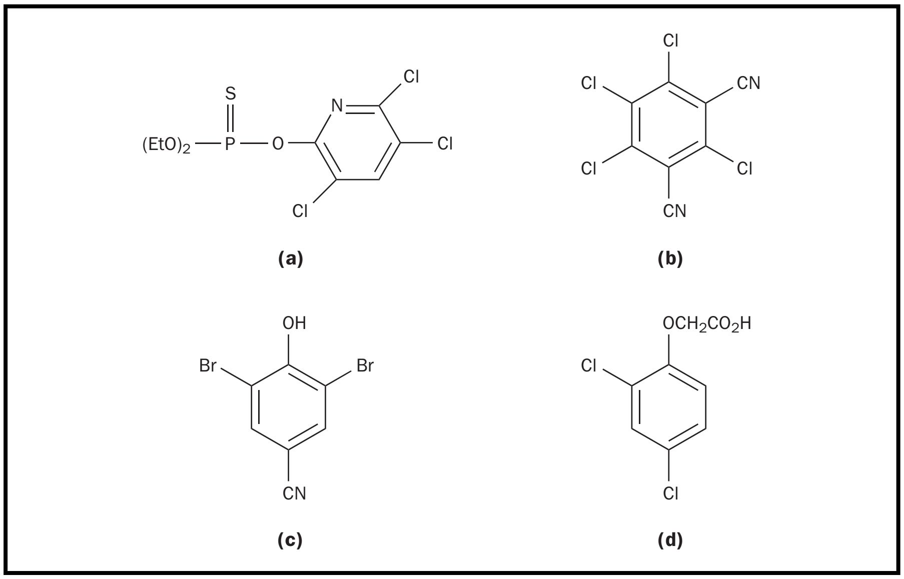


Figure 3. Organohalogens used as pesticides: (a) Dursban, an insecticide; (b) Daconil, a fungicide; (c) Bromoxynil, an herbicide; (d) 2,4-D, an herbicide.

Natural Occurrence

The number of known natural organohalogens has grown from thirty in 1968 to nearly 3,900 during the early 2000s. Many are the same as synthetic chemicals. They are biosynthesized by marine organisms, bacteria, fungi, plants, insects, and some mammals, including humans. Algae, wood-rotting fungi, mushrooms, several trees, phytoplankton, and even potatoes produce chloromethane. Termites are a major producer of chloroform, and several vegetables produce bromomethane. One hundred organohalogens have been found in the favorite edible seaweed of native Hawaiians.

biomass: collection of living matter

Chloride and bromide salts are normally present in plants, wood, soil, and minerals; as a result, forest fires and volcanoes produce organohalogens. Meteorites contain organochlorines. Global emissions of chloromethane from the **biomass** are 5 million tons per year, whereas synthetic emissions are only 26,000 tons per year. Volcanoes also emit hydrogen chloride (3 million tons/year) and hydrogen fluoride (11 million tons/year), both of which can react with organic compounds to produce organohalogens. Chlorofluorocarbons have been detected in volcanic emissions in Guatemala and Siberia, but a study of volcanoes in Italy and Japan indicates that they may not be a major source of environmental CFCs.

volatile: low boiling, readily vaporized

Seaweeds contain hundreds of organohalogens (see Figure 4). Telfairine, like the synthetic insecticide lindane, is a powerful insecticide. These organohalogens are used by marine life in chemical defense (natural pesticides). The "smell" of the ocean is likely due to the myriad **volatile** organohalogens produced by seaweeds.

Organohalogens also serve as hormones. Vegetables such as lentils, beans, and peas synthesize the growth hormone 4-chloro-3-indoleacetic acid. A cockroach produces two chlorine-containing steroids as aggregation pheromones. Female ticks use 2,6-dichlorophenol as a sex attractant. Thyroid hormones (see Figure 1) contain iodine, and an organobromine is involved in the mammalian sleep phenomenon.

metabolites: products of biological activity that are important in metabolism

Just as iodine is used to treat cuts and chlorine (bleach) to disinfect bathrooms, our white blood cells generate chlorine and bromine to kill germs and fight infection. The sponge **metabolite** spongistatin and the blue-green

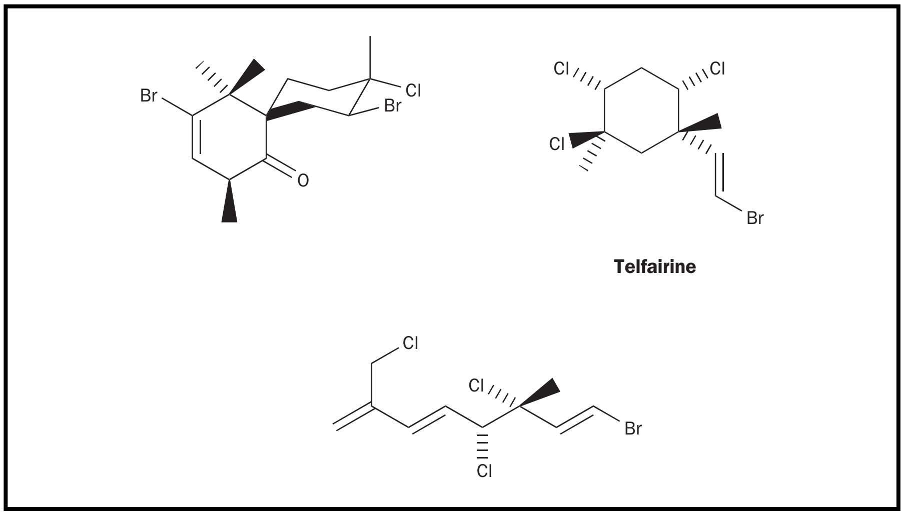


Figure 4. Three of the halogenated terpenes found in red algae, including (at top right) the natural insecticide telfairine.

alga cryptophycin, both of which contain a chlorine atom essential for biological activity, are powerful anticancer drugs. Ambigol, found in terrestrial blue-green alga, is active against human immunodeficiency virus (HIV). An Ecuadorian frog produces an organochlorine that is 500 times more potent than morphine; a synthetic analog is under development as a new anesthetic.

Although some synthetic organohalogens are toxic contaminants that need to be removed from the environment, the vast majority of organohalogens have little or no toxicity. Organic halogen compounds continue to play an essential role in human health and well being as chemists pursue the study of these fascinating chemicals. SEE ALSO Organic Chemistry.

Gordon W. Gribble

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Organometallic Compounds

Organometallic compounds have at least one carbon to metal bond, according to most definitions. This bond can be either a direct carbon to metal bond (σ bond or sigma bond) or a metal complex bond (π bond or pi bond). Compounds containing metal to **hydrogen bonds** as well as some compounds containing nonmetallic (**metalloid**) elements bonded to carbon are sometimes included in this class of compounds. Some common properties of organometallic compounds are relatively low melting points, insolubility in water, solubility in ether and related solvents, toxicity, oxidizability, and high reactivity.

hydrogen bond: interaction between H atoms on one molecule and lone pair electrons on another molecule that constitutes hydrogen bonding

metalloid: elements that exhibit properties that are between those of metals and nonmetals; generally considered to include boron, silicon, germanium, arsensic, antimony, tellurium, and polonium

An example of an organometallic compound of importance years ago is tetraethyllead (Et$_4$4Pb) which is an antiknock agent for gasoline. It is presently banned from use in the United States.

The first metal complex identified as an organometallic compound was a salt, $K(C_2H_4)PtCl_3$, obtained from reaction of ethylene with platinum (II) chloride by William Zeise in 1825. It was not until much later (1951–1952) that the correct structure of Zeise's compound (see Figure 1) was reported in connection with the structure of a metallocene compound known as ferrocene (see Figure 2).

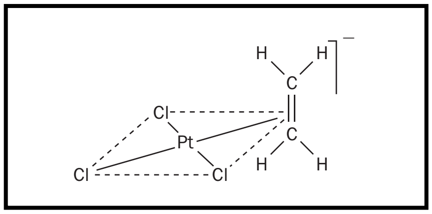

Figure 1. Anion of Zeise's compound

Preparation of ferrocene was reported at about the same time by two research groups, and a sandwich structure was proposed, based on ferrocene's physical properties (Kauffman, pp. 185–186). The sandwich structure was confirmed by x-ray diffraction studies. Since then, other metallocenes composed of other metals and other carbon ring molecules, such as dibenzenechromium (see Figure 3) and uranocene (see Figure 4), have been prepared.

Possibly the first scientist to synthesize an organometallic compound was Edward Frankland, who prepared diethylzinc by reaction of ethyl iodide with zinc metal in 1849 (Thayer 1969b, pp. 764–765).

$$2\ CH_3CH_2I + 2\ Zn \rightarrow CH_3CH_2ZnCH_2CH_3 + ZnI_2$$

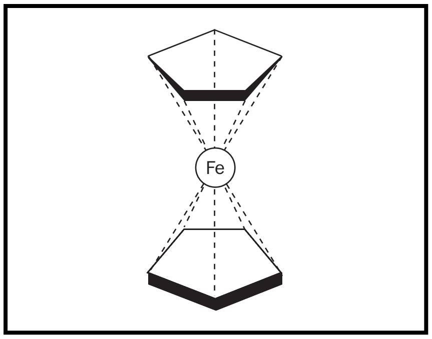

Figure 2. Ferrocene

transition metals: elements with valence electrons in d-sublevels; frequently characterized as metals having the ability to form more than one cation

ligand: molecule or ion capable of donating one or more electron pairs to a Lewis acid

In organometallic compounds, most p-electrons of **transition metals** conform to an empirical rule called the 18-electron rule. This rule assumes that the metal atom accepts from its **ligands** the number of electrons needed in order for it to attain the electronic configuration of the next **noble gas**. It assumes that the **valence** shells of the metal atom will contain 18 electrons. Thus, the sum of the number of d electrons plus the number of electrons supplied by the ligands will be 18. Ferrocene, for example, has 6 d electrons from Fe(II), plus 2 × 6 electrons from the two 5-membered rings, for a total of 18. (There are exceptions to this rule, however.)

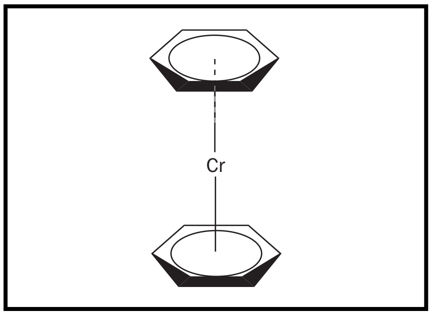

Figure 3. Dibenzenechromium

Possibly the earliest biomedical application of an organometallic compound was the discovery, by Paul Ehrlich, of the organoarsenical Salvarsan, the first antisyphilitic agent. Salvarsan and other organoarsenicals are sometimes listed as organometallics even though **arsenic** is not a true metal. **Vitamin** B_{12} is an organocobalt complex essential to the diet of human beings. Absence of or deficiency of B_{12} in the diet (or a body's inability to absorb it) is the cause of pernicious anemia.

Use as Reagents or Catalysts

Organometallic compounds are very useful as catalysts or reagents in the **synthesis** of organic compounds, such as pharmaceutical products. One of the major advantages of organometallic compounds, as compared with organic or inorganic compounds, is their high reactivity. Reactions that cannot be carried out with the usual types of organic reagents can sometimes be easily carried out using one of a wide variety of available organometallics. A second advantage is the high reaction selectivity that is often achieved via the use of organometallic catalysts. For example, ordinary free-radical polymerization of ethylene yields a waxy low-density polyethylene, but use of a special organometallic **catalyst** produces a more ordered linear polyethylene with a higher density, a higher **melting point**, and a greater strength. A third advantage is that many in this wide range of compounds are stable, and many of these have found uses as medicinals and pesticides. A fourth advantage is the case of recovery of pure metals. Isolation of a pure sample of an organometallic compound containing a desired metal can be readily accomplished, and the pure metal can then be easily obtained from the compound. (This is generally done via preparation of a pure metal carbonyl, such as $Fe[CO]_5$ or $Ni[CO]_4$, followed by thermal decomposition.) Other commonly used organometallic compounds are organolithium, organozinc, and organocuprates (sometimes called Gilman reagents).

The name "ferrocene" was coined by one of Harvard University professor R. B. Woodward's postdoctoral students, Mark Whiting. The entire class of transitional metal dicyclopentadienyl compounds quickly became known as "metallocenes" and this has since been expanded for compounds $[(H_5\text{-}C_5H_5)\ 2M]$ in general. G. Wilkinson and Woodward published their results on ferrocene in 1952.

Grignard Reagents

One of the most commonly used classes of organometallic compounds is the organomagnesium halides, or Grignard reagents (generally RMgX or ArMgX, where R and Ar are alkyl and aryl groups, respectively, and X is a **halogen** atom), used extensively in synthetic organic chemistry. Organomagnesium halides were discovered by Philippe Barbier in 1899 and subsequently developed by Victor Grignard. They are usually prepared by reaction of magnesium metal with alkyl or aryl halides. Other commonly used organometallic compounds are the organolithium and organozinc compounds.

Carbenes

Carbenes are the electrons of free carbenes that have two spin states, singlet and triplet. The electrons are paired as a sp^2 lone pair in the singlet (:CH_2); there is one electron in each of the sp^2 and p orbitals in the triplet (·CH_2). Carbenes are generally unstable in the free state, but are stable when bonded to metal atoms. Metal-carbene complexes have the general structure $L_nM{=}CXY$, where L_nM is the metal fragment with *n* ligands, and X and Y are alkyl groups, aryl groups, hydrogen atoms, or heteroatoms (O, N, S, or halogens). The first carbene complex [$(CO)_5W{=}CPh(OMe)$] was reported by E. O. Fischer and A. Maasbol in 1964 (Dunitz, Orgel, and Rich, pp. 373–375). In 1974 Richard R. Schrock prepared compounds in which the substituents attached to carbon were hydrogen atoms or alkyl groups; these complexes are known as Schrock-type carbene complexes. The two types of carbene complexes differ in their reactivities. Fischer-type complexes tend to undergo attack at carbon atoms by nucleophiles (negatively charged species) and are electrophilic (electron-attracting). Schrock-type complexes undergo attack at carbon atoms by electrophiles and are considered to be nucleophilic species. SEE ALSO CATALYSIS AND CATALYSTS; CHIRALITY; EHRLICH, PAUL.

A. G. Pinkus

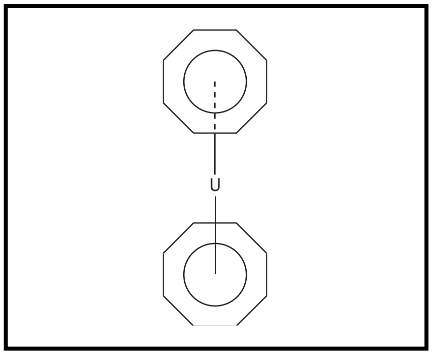

Figure 4. Uranocene

noble gas: element characterized by inert nature; located in the rightmost column in the Periodic Table

valence: combining capacity

arsenic: toxic element of the phosphorus group

vitamins: organic molecules needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

synthesis: combination of starting materials to form a desired product

catalyst: substance that aids in a reaction while retaining its own chemical identity

melting point: temperature at which a substance in the solid state undergoes a phase change to the liquid state

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

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Opiate Peptides *See Endorphins.*

76
Os
OSMIUM
190.23

Osmium

MELTING POINT: 3,127°C
BOILING POINT: 5,303°C
DENSITY: 22.590 g/cm^3
MOST COMMON IONS: $OsCl_6^{3-}$, $OsCl_6^{2-}$

The element osmium was discovered in 1804 by English chemist Smithson Tennant (1761–1815) in the black residue that remained after crude platinum was dissolved in aqua regia. The average abundance in Earth's crust is very low, about 0.005 grams (0.00018 ounces) per metric ton, and only four osmium-containing minerals, all extremely rare, are known: erlichmanite, OsS_2; omeiite, $(Os,Ru)As_2$; and osarsite and anduoite, $(Os,Ru)AsS$. Osmium also occurs in natural **alloys** with iridium and/or ruthenium (e.g., iridosmium). Osmium is obtained as a by-product of refining nickel and the more common platinum group **metals**. Worldwide production is very small, approximately 500 kilograms (1,102 pounds) per year (versus 2,500,000 kilograms, or 5,512,000 pounds, per year for gold). Despite its rarity, osmium is only 30 percent more expensive than gold because it has few commercial uses. Osmium metal is lustrous, bluish-white, hard, and brittle; it melts at 3,127°C (5,661°F) and boils at 5,303°C (9,577°F). It is the densest element known: Its density is 22.59 grams (0.8 ounces) per cubic centimeter (twice that of lead). Osmium is combined with other platinum group elements to yield extremely hard alloys, which find limited use as electrical contacts, wear-resistant instrument pivots and bearings, and tips for high-priced ink pens. Osmium forms compounds in all of its **oxidation** states, from +8 to −2. Its chemistry closely resembles that of ruthenium. The most important compound is osmium tetroxide, OsO_4, a pale yellow solid used as a stain in microscopy, in fingerprint detection, and as a **catalyst** in the production of some pharmaceuticals. Osmium tetroxide has an unpleasant chlorinelike odor, which prompted Tennant to name the element using the Greek word *osme*, "a smell."

alloy: mixture of two or more elements, at least one of which is a metal

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

catalyst: substance that aids in a reaction while retaining its own chemical identity

Gregory S. Girolami

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COFOUNDER OF MODERN PHYSICAL CHEMISTRY
1853–1932

Friedrich Wilhelm Ostwald, born in Riga, Latvia, Russia, almost single-handedly established physical chemistry as an acknowledged academic discipline. In 1909 he was awarded the Nobel Prize in chemistry for his work on **catalysis**, chemical equilibria, and reaction velocities.

Ostwald graduated with a degree in chemistry from the University of Dorpat (now Tartu, Estonia) and was appointed professor of chemistry at Riga in 1881, before he moved from Russia to Germany to become chair of the physical chemistry department at the University of Leipzig in 1887. For about twenty years he made Leipzig an international center of physical chemistry: by establishing an instruction and research laboratory that attracted virtually the entire next generation of physical chemists; by editing the first journal in the field (*Zeitschrift für physikalische Chemie*); and by writing numerous textbooks. In 1906 he retired from the university and devoted the rest of his life to various topics, including the history and philosophy of science, color theory, painting, the writing of textbooks and popular books about science, the international organization of science, and the formation of an artificial language for the international exchange of ideas.

German chemist Friedrich Ostwald, recipient of the 1909 Nobel Prize in chemistry, "in recognition of his work on catalysis and for his investigations into the fundamental principles governing chemical equilibria and rates of reaction."

Throughout his career as a chemist Ostwald followed the general approach of applying physical measurements and mathematical reasoning to chemical issues. One of his major research topics was the chemical affinities of acids and bases. To that end, he studied the points of equilibria in reaction systems where two acids in an **aqueous solution** compete with each other for a reaction with one base and vice versa. Because chemical analysis would have changed the equilibria, he skillfully adapted the measurement of physical properties, such as volume, refractive index, and electrical conductivity, to that problem. From his extensive data he derived for each acid and base a characteristic affinity coefficient independent of the particular acid–base reactions.

catalysis: the action or effect of a substance in increasing the rate of a reaction without itself being converted

aqueous solution: homogenous mixture in which water is the solvent (primary component)

To understand different chemical affinities, Ostwald drew on a new, but then hardly accepted and not yet fully developed, theory advanced by the Swedish physical chemist Svante Arrhenius. According to this theory of electrolytic dissociation, electrolytes such as acids, bases, and salts dissociated in solution into oppositely charged ions to a certain degree, such that at infinite dilution dissociation was complete. Ostwald recognized that if all acids contained the same active ion, their specific chemical affinities must correspond to the number of these active ions in solution, which depended on their specific degree of dissociation at each concentration, and which could be measured through electric conductivity studies. By applying the law of mass action to the dissociation reaction, a simple mathematical relation was derived between the degree of dissociation α, the concentration of the acid c, and an **equilibrium** constant specific for each acid K:

$$K = \frac{\alpha^2}{(1 - \alpha)c}$$

equilibrium: condition in which two opposite reactions are occurring at the same speed, so that concentrations of products and reactants do not change

This is Ostwald's famous dilution law from 1888, which he proved by measuring the electric conductivities of more than 200 organic acids at various concentrations. He substantiated the dissociation theory not only to explain the different activity of acids, but also as a general theory of electrolytes in solution. The theory gained further support from the Dutch physical chemist Jacobus Hendricus van't Hoff who, at the same time, advanced it on a general thermodynamic basis to explain his law of osmotic pressure of solutions as well as Raoult's laws of vapor pressure lowering and freezing point depression. Thus, the new physical chemistry grew to a comprehensive theory of solutions, based on both thermodynamics and dissociation theory.

propagating: reproducing; disseminating; increasing; extending

Ostwald was particularly successful in systematizing and **propagating** these new ideas, applying them to other fields, and organizing a school of physical chemistry. Many chemists rejected the dissociation theory because it predicted wrong values at high concentrations and for strong electrolytes. Despite his concessions about its restricted validity, Ostwald provided numerous proofs of its broad usefulness in his textbooks on general, inorganic, and, particularly, analytical chemistry.

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

Originally, and incorrectly, Ostwald studied reaction velocities as a measure of chemical affinity. Later, he broadly investigated the time (or kinetic) aspects of chemical reactions and provided a system for the study of chemical kinetics. He first recognized catalysis as the change of reaction velocity by a foreign compound, which allowed him to measure catalytic activities. He distinguished catalysis from triggering and from autocatalysis, which he considered essential to biological systems. His most famous contribution to applied chemistry was on the catalytic **oxidation** of ammonia to nitric acid, which became widely used in the industrial production of fertilizers. SEE ALSO Acid-Base Chemistry; Arrhenius, Svante; Equilibrium; Physical Chemistry; van't Hoff, Jacobus.

Joachim Schummer

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8
O
OXYGEN
15.9994

Oxygen

MELTING POINT: −218.4°C
BOILING POINT: −182.96°C
DENSITY: 1.429 g/L
MOST COMMON IONS: OH^-, OH_2^-, O^{2-}

Joseph Priestley and Carl Scheele (each working independently) are credited with the isolation and "discovery" in 1774 of the element oxygen. A few years later Antoine Lavoisier showed that oxygen is a component of the atmosphere. Oxygen is the most abundant element on Earth, constituting about half of the total material of its surface (47 percent by weight of the lithosphere and 89 percent by weight of the ocean) and about 21 percent by volume of the air. Under ordinary conditions (STP) on Earth, oxygen is a colorless, odorless, tasteless gas that is only slightly soluble in water. Oxygen has a pale blue color in the liquid and the solid phases. Ordinary oxygen gas (O_2) exists as diatomic molecules. It also exists in another allotropic form, the triatomic molecule ozone (O_3). Although eight **isotopes** of oxygen are known, atmospheric oxygen is a mixture of only three: those having mass numbers 16, 17, and 18.

isotope: form of an atom that differs by the number of neutrons in the nucleus

A patient is undergoing hyperbaric oxygen therapy.

Oxygen is very reactive. Its reaction with another substance to form an oxide is called **oxidation**. It is a constituent of a number of compound groups, such as acids, hydroxides, carbonates, chlorates, nitrates and nitrites, and phosphates and phosphites—as well as carbohydrates, proteins, fats, and oils. The respiration of animals and plants is actually a form of oxidation, essential to the production of energy within these organisms. The burning of substances in air is a rapid form of oxidation called **combustion**. In the eighteenth century the idea of combustion replaced the idea (phlogiston theory) that a colorless, odorless, tasteless, and weightless substance named phlogiston was given off during the burning of a substance. SEE ALSO Lavoisier, Antoine; Priestley, Joseph; Scheele, Carl.

Ágúst Kvaran

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

combustion: burning, the reaction with oxygen

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Ozone

stratosphere: layer of the atmosphere where ozone is found; starts about 10 km (6.2 mi) above ground

Earth's ozone layer plays a critical role in protecting Earth's surface from the Sun's harmful ultraviolet (UV) radiation. Every ozone molecule, which consists of three oxygen atoms, has the ability to absorb a certain amount of UV radiation. Under normal circumstances, the ozone layer, which is located in the **stratosphere** between 15 and 50 kilometers (9 and 31 miles) above Earth, remains in a continuous balance between natural processes that both produce and destroy ozone.

Ozone is produced in the upper atmosphere through a two-step chemical process that involves oxygen and UV radiation.

$$O + \text{UV radiation} \rightarrow O + O$$

$$O + O_2 \rightarrow O_3$$

The process begins with UV radiation breaking apart molecular oxygen (O_2), thus producing two oxygen (O) atoms. In the second step, an oxygen atom (O) recombines with an oxygen molecule (O_2) to form an ozone (O_3) molecule.

Ozone can also be naturally destroyed through reactions with chlorine, nitrogen, and hydrogen. For example, chlorine can be a very effective destroyer of ozone via the following set of reactions.

$$Cl + O_3 \rightarrow ClO + O_2$$

$$ClO + O \rightarrow Cl + O_2$$

In this process, a chlorine atom (Cl) reacts with ozone (O_3) to produce chlorine monoxide (ClO) and an oxygen molecule (O_2). ClO can then combine with an oxygen atom (O) to reform Cl and O_2. In this reaction set, because chlorine is reformed after destroying ozone, the cycle can repeat itself very quickly.

chlorofluorocarbon (CFC): compound that contains carbon, chlorine, and fluorine atoms, which remove ozone in the upper atmosphere

In recent years global chlorine levels have increased due to the use of **chlorofluorocarbons (CFCs)**, a large class of chemicals useful in a variety of industries. Under certain circumstances, even a single chlorine atom released from a CFC's molecule can destroy many thousands of ozone molecules through a chemical chain reaction. Current declines in global ozone levels and the development of the Antarctic ozone hole have both been linked to CFC use.

Although ozone concentrations in the upper atmosphere play an important role in protecting Earth's surface from harmful UV radiation, ozone at its surface is a pollutant harmful to human health. Enhanced levels of surface ozone are often the result of automobile exhaust and pose a serious health risk. Fortunately, current levels of surface ozone (also known as smog) over most major cities have declined to healthier levels due in part to domestic and international governmental regulations. SEE ALSO ATMOSPHERIC CHEMISTRY.

Eugene C. Cordero

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Palladium

MELTING POINT: **1,552°C**
BOILING POINT: **3,760°C**
DENSITY: **12.0 g/cm^3**
MOST COMMON IONS: **Pd^{2+}**

46
Pd
PALLADIUM
106.42

The element palladium was isolated and identified by William Wollaston in 1803. Its name comes from the asteroid Pallas. (Pallas was another name for Athena, the Greek goddess of wisdom.) Palladium in pure form is not found in nature. The preparation of the element is via a series of reactions. Platinum **metal** ore concentrates (65% of which come from the Merensky Reef in South Africa) are treated with aqua regia (giving copper and nickel as by-products). The solutions, containing H_2PdCl_4 with platinum and gold complexes, are treated with $FeCl_2$ (which precipitates gold) and then with excess of NH_4OH followed by HCl to precipitate the impure $[Pd(NH_3)_2Cl_2]$. This compound is purified by dissolution in NH_4OH and precipitation with HCl. The pure $[Pd(NH_3)_2Cl_2]$ is ignited to palladium metal.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Palladium metal, like platinum metal, is silvery-white and lustrous and has malleable and **ductile** properties. It has the face-centered cubic crystal structure. It forms a fluoride, PdF_4 (brick-red), and other halides: PdF_2 (pale violet), α-$PdCl_2$ (dark red), $PbBr_2$ (red black), and PdI_2 (black). Pd metal can absorb up to 935 times its own volume of hydrogen molecules. When the composition reaches about $PdH_{0.5}$, the substance becomes a semiconductor.

ductile: property of a substance that permits it to be drawn into wires

Palladium can form complexes in a variety of **oxidation** states. Table 1 contains some examples.

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

Palladium has extensive use as a **catalyst** in hydrogenation and dehydrogenation reactions, due to its capacity of combination with hydrogen. Palladium films are used as electrical contacts in connectors. Palladium-silver and palladium-nickel **alloys** are used to substitute for gold in jewelry.

catalyst: substance that aids in a reaction while retaining its own chemical identity

alloy: mixture of two or more elements, at least one of which is a metal

Oxidation states	Complexes
(O)	$K_4[Pd(CN)_4]$ (yellow)
(I)	$[PdCl(CO)]_x$ (reddish-violet)
(II)	$Na_2[PdCl_4]$
(IV)	$K_2[PdF_6]$ (bright yellow)

Table 1. Some palladium complexes.

Lea B. Zinner

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Paracelsus

GERMAN PHYSICIAN, ALCHEMIST, AND SCIENTIST
1493–1541

Paracelsus was born Theophrastus Bombastus von Hohenheim. He was a contemporary of Martin Luther and Nicolaus Copernicus. He adopted his

A woodcut from *Works* of the German alchemist Paracelsus.

pseudonym based on his assertion that he was a better physician than Celsus, the first century C.E. Roman author on medicine acclaimed in Renaissance Europe (he was "Para-Celsus," or beyond Celsus). His self-promotion as "The Most Highly Experienced and Illustrious Physician . . . " has given us the word "bombastic," derived from his birth name.

Paracelsus gained his early medical knowledge from his father, who was a physician. He followed this education with formal medical training at the University of Ferrara in Italy. Finding his formal training disappointing, Paracelsus embarked on a life of travel and study combined with medical practice. According to Paracelsus, he collected medical knowledge anywhere he could find it without regard to academic authority. He acknowledged his consultations with peasants, barbers, chemists, old women, quacks, and magicians. Paracelsus developed his notions of disease and treatment away from any established medical faculty and promoted the idea that academic medical training had reached a state deeply in need of reform.

Paracelsus believed in the four "Aristotelian" elements of earth, air, fire, and water. His medical theory was based on the notion that earth is the fundamental element of existence for humans and other living things. Paracelsus believed that earth generated all living things under the rule of three "principles": salt, sulfur, and mercury. He therefore believed these substances to be very potent as chemical reactants, as poisons, and as medical treatments. (Indeed, salt and sulfur can yield strong mineral acids, for example, hydrochloric acid and sulfuric acid, and mercury is a strong poison.) Finally, Paracelsus believed in the "Philosopher's Stone." The Philosopher's Stone (which he sometimes claimed to possess) was supposed to cure all ills and to enable the transformation of any **metal** into gold. Such a stone, it was believed, would be the strongest chemical reactant and the strongest medicine possible.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Paracelsus advocated the direct observation of a patient's medical condition and the assessment of his or her surroundings. He was one of the first physicians to describe occupational diseases. He described several lung diseases of miners and recommended improved ventilation as a means of their prevention. He emphasized that the legitimacy of a treatment was whether or not it worked, not its recommendation by an ancient authority in an ancient text. Paracelsus promoted the use of mineral treatments. Because small amounts of mercury salts were effective against some illnesses, these medicines were judged to be very strong.

Paracelsus's exalted claims for himself and his abrasive personality often brought him into conflict with civil authorities. His methods of trial and error and observation led him to reject the use of sacred relics as medical treatment. It brought him into conflict with religious authorities. His calls for reformation of the medical profession offended medical authorities. As a consequence he was on the move often. Paracelsus held an academic post only once, and it lasted only a year. Although he wrote a great deal, only one of his manuscripts was published in his lifetime. Most of his manuscripts were left in a variety of cities and were published several years after his death. Within these manuscripts are inconsistencies and contradictions. Paracelsus never established any one strong school of thought or medical practice. He did, however, influence future generations of iatrochemists (physician-chemists, *iatro* being Greek for "physician"), who continued to apply chemistry to questions of medical practice. SEE ALSO ALCHEMY.

David A. Bassett

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Particles, Fundamental

Fundamental particles are the elementary entities from which all matter is made. They have no known smaller parts. As recently as 1900 most people believed that atoms were the tiniest particles in the universe.

By the 1930s, however, it was clear that atoms were made up of even smaller particles—protons, neutrons, and electrons, then considered to be the fundamental particles of matter. (A proton is a positively charged particle that weighs about one atomic mass unit [1.0073 AMU]; a neutron has about the same mass [1.0087 AMU] but no charge; and an electron has a much smaller mass [0.0005 AMU] and a negative charge.) Protons and neutrons make up the tiny nucleus of an atom, while electrons exist outside the atomic nucleus in discrete energy levels within an electron “cloud.”

By 1970 it began to appear that matter might contain even smaller particles, an idea suggested in 1963 by American physicist Murray Gell-Mann (who called the particles *quarks*) and independently by American physicist George Zweig (who called them *aces*). There are in actuality hundreds of subatomic particles that have been observed, but many of them are unstable.

Fermions

At the start of the twenty-first century, scientists believe that all matter is made up of tiny particles called fermions (named after American physicist Enrico Fermi). Fermions include quarks and leptons. Leptons include electrons (along with muons and neutrinos); they have no measurable size, and they are not affected by the strong nuclear force. Quarks, on the other hand, are influenced by the strong nuclear force. They are the fundamental particles that make up protons and neutrons (as well as mesons and some other particles). Both protons and neutrons are classified as baryons, composite particles each made up of three quarks.

Quarks come in six different types, or “flavors”: up and down, top and bottom, and charm and strange. Protons and neutrons are made of up (u) quarks (which have a charge of $+\frac{2}{3}$) and down (d) quarks (which have a charge of $-\frac{1}{3}$). A proton is made from two u quarks $(+\frac{2}{3})(+\frac{2}{3})$ and one d quark $(-\frac{1}{3})$, giving a total charge of +1. A neutron contains one u quark $(+\frac{2}{3})$ and two d quarks $(-\frac{1}{3})(-\frac{1}{3})$ for a total charge of zero.

Fundamental Forces

There are also fundamental forces acting on matter; these have their own sets of fundamental particles. The forces are the strong nuclear force (or strong interaction), the weak nuclear force (or weak interaction), and electromagnetism (which includes light, x rays, and all the other electromagnetic forces). All these forces are transmitted by particles called *fundamental bosons* (named after Indian physicist S. N. Bose).

Fundamental bosons differ from fermions in spin and the number of quarks they contain. Fermions have spins measured in half numbers, and they contain an odd number of quarks. Bosons have whole integer spins, and they contain an even number of quarks. The bosons that transmit the strong nuclear force are called *gluons*, those that transmit electromagnetic forces are *photons*, and those transmitting the weak force are known as *weak bosons*. A fourth force, the gravitational force, is believed to be transmitted by particles called gravitons; however, the particles have not yet been observed. Still another kind of boson, called a *Higgs boson*, is thought to be the source of mass in other particles, but this particle also has not actually been observed.

Particle Accelerators

The study of fundamental particles often involves speeding up charged particles, such as protons or electrons, and then letting them collide with targets so as to produce other particles for further study. The particle accelerators used to do this are devices that force the charged particles to jump over longer and longer space gaps per unit of time, until the particles are moving at speeds approaching the speed of light.

The earliest of such devices were the linear Cockcroft-Walton accelerator (1929), the circular cyclotron (1930), and the Van de Graaff generator (1931). Modern *synchrotrons* are large machines that have both linear and curved sections. The most powerful synchrotron is the *Tevatron* proton accelerator at the Fermilab located near Batavia, Illinois (just outside of Chicago); it lies inside an underground circular tunnel that measures almost 6.4 kilometers (4.0 miles) around. The longest accelerator is the collider at the CERN research center in Geneva, Switzerland—it has a circumference of about 27.3 kilometers (17.0 miles).

Particle Detectors

Detection of fundamental particles is difficult because the particles are so extremely tiny. The earliest detector was just photographic film, since particles passing through would expose the film and become evident when it was developed. The first device designed for the purpose of detecting tiny particles was the "cloud chamber" (invented by Scottish physicist Charles Wilson in 1911). It was a glass container filled with air saturated with water (or alcohol) vapor. Charged particles passing through the chamber formed ions leaving fog tracks—the heavier the particles, the wider their tracks.

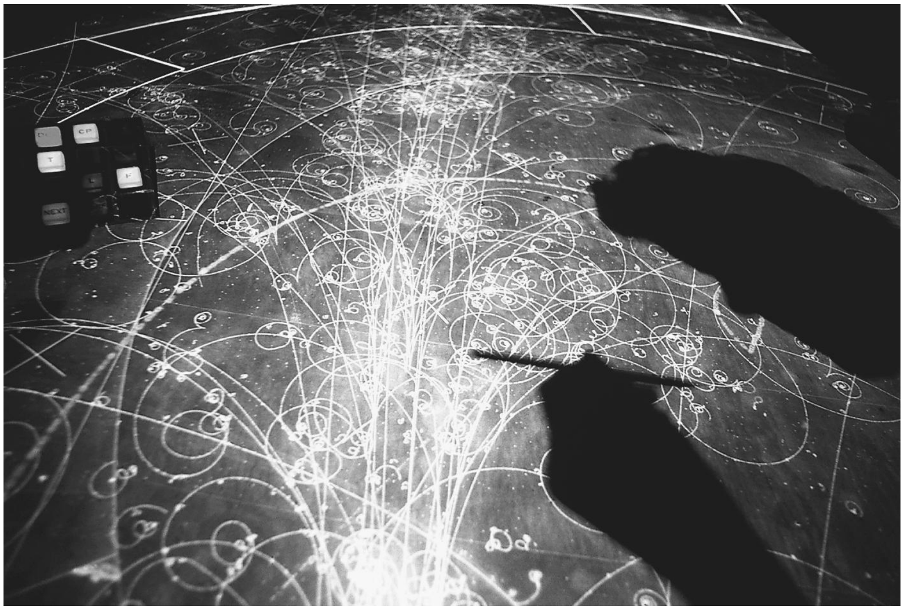
The "bubble chamber" (invented by American physicist Donald Glaser in 1952) was similar to a cloud chamber, except that it was filled with a liquid (usually liquefied helium or hydrogen) held at a temperature just below its boiling point. Moving particles would disturb the liquid, causing bubbles to form along their paths. There was also a "spark chamber" (invented in Japan in 1959) that contained a series of parallel metal plates and produced an electrical discharge along the ion trail left by a charged particle. Although all of these devices were once important for detecting subatomic particles, they have largely been replaced by more modern detectors.

In the twenty-first century fundamental particles are studied using detectors such as tracking chambers (which trace the path of a particle with electrical signals), sampling calorimeters (which track the particle's path by its energy of motion), scintillators (which give off light when particles strike them), or magnetic detectors (which cause charged particles to move in curved paths). Many instruments use combinations of these various kinds of detectors.

C. T. R. WILSON (1869–1959)

The inspiration for C. T. R. Wilson's expansion, or cloud, chamber came from his interest in meteorological sciences. His initial intention was to recreate cloud formations. This led to an interest in studying atmospheric electric fields and the vapor trail of ions. For his work he shared the Nobel Prize in 1927.

—Valerie Borek



As high-energy particles pass through a bubble chamber, bubbles are formed, which leave tracks as they move. This is important in the study of subatomic collisions, which normally are not visible to the naked eye.

Antimatter

To further complicate the subject of subatomic particles, each kind of particle has an antiparticle. For example, for each kind of quark there is an antiquark of the same mass and spin, but of opposite charge. The first antiparticle to be observed was the positron, an electron with a positive charge. An antiproton is like a proton, but it has a negative charge. Antiparticles can be observed, and molecules of antimatter can even be generated. A positron orbiting an antiproton, for example, is an antihydrogen atom.

Many scientists believe that there must be some areas of the universe that are completely made up of antimatter, the exact opposite of the kind of matter found on Earth. If that is true, such areas would not be very compatible with areas made of matter—when a particle and its antiparticle make contact, they destroy each other and are converted into energy. According to Einstein's special theory, $E = mc^2$, which means that energy is equivalent to mass times the speed of light, squared. In other words, a tiny speck of matter can be converted to a considerable amount of energy.

The conversion can also go the other way. Large releases of energy that occur when high-energy particles collide can produce new particles and antiparticles of matter. Much modern research in particle physics involves high-energy collisions between beams of particles, such as protons, so as to generate other kinds of particles. Some collisions involve interactions of particles with antiparticles (e.g., electrons with positrons). Particle accelerators have been turned into giant colliders in which beams of particles moving at speeds approaching the speed of light collide with each other, producing other kinds of particles.

By the early 2000s several hundred subatomic particles were known, almost all of them being made of quarks. The few remaining ones are the leptons, the electron being the best known. The other leptons are still rather mysterious. The muons and tau particles are negatively charged like the electron, while the neutrinos (which have no detectable mass but often pair up with the heavier leptons) have no charge. The electron was discovered in 1897, but there is still much to learn about other fundamental particles. SEE ALSO Atomic Structure; Fermi, Enrico.

Doris K. Kolb

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Pasteur, Louis

FRENCH CHEMIST AND MICROBIOLOGIST
1822–1895

Louis Pasteur was born in 1882 in Dole, France. Many people are unaware of the fact that he was a chemist. Pasteur received his schooling at the École Normale Supérieure in Paris—a school specifically designed to foster the development of students in the sciences and letters. He was, perhaps, the most accomplished of these students.

Pasteur's first major contribution to chemistry occurred when he was only 26 years old, working with French Chemist Antione Balard (1802–1876) in the new field of crystallography. Organic molecules—at the time thought to be made exclusively by living beings—were a particularly important area of study and Pasteur was both fortunate and perceptive when working with a compound called tartaric acid—a chemical found in the sediments of fermenting wine.

Pasteur, as well as other scientists of his time, used the rotation of plane-polarized light as one means for studying crystals. Polarized light can be thought of as occupying a single plane in space. If such light is passed through a solution with dissolved tartaric acid, the angle of the plane of light is rotated. Many organic acids display this feature. What made Pastuer's work with tartaric acid and polarized light so important was his careful observation of crystals.

In addition to tartaric acid another compound named paratartaric acid was found in wine sediments. Chemical analysis showed this compound to have the same composition as tartaric acid, so most scientists assumed the two compounds were identical. Strangely enough, however, paratartaric acid did not rotate plane-polarized light. Pasteur would not accept the idea that such an experimental result could be an accident or unimportant. He guessed that even though the two compounds had the same chemical composition, they must somehow have different structures—and he set out to find evidence to prove his hypothesis.

French chemist Louis Pasteur.

First, Pasteur carefully observed the paratartaric acid under a microscope. Looking at the tiny crystals, he noticed two different types. While almost identical, they were actually mirror images of each other as depicted in Figure 1. Pasteur's next step required incredibly meticulous work. Again, working with the microscope, he separated the two types of crystals into two piles. After separating the crystals, Pasteur made two solutions—one with each of the piles—and tested how they interacted with polarized light. He found that both solutions rotated the light—*but in opposite directions.* When the two types of crystals were together in the solution of paratartaric acid the effect of rotation of the light was canceled.

stereochemistry: the study of the three dimensional shape of molecules and the effects of shape upon the properties of molecules

Most importantly for the development of chemistry, these experiments by Pasteur established that composition alone does not provide all the information needed to understand how a chemical behaves. His work allowed chemists to start thinking about the structure of molecules in terms of their **stereochemistry**, a field that remains important in chemistry research.

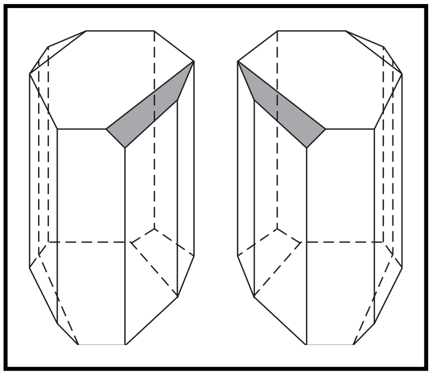

Figure 1. Structure of paratartaric crystals.

The discovery of stereochemistry was not the last chemical work carried out by Pasteur. Seven years after he first started working in crystallography (in 1854) he was became a professor of chemistry in Lille, France. Among the main commercial interests in Lille was the production of alcohol in distilleries. One of Pasteur's students was the son of a distillery owner who was encountering troubles with his factory. Too often the product of their efforts was lactic acid rather than alcohol. Once again, Pasteur would need to contradict current scientific beliefs to answer a chemical question.

At the time of his work in Lille, the scientific community knew that the alcohol produced by fermentation came from the breakdown of sugars (found in grapes for wine-making). However, they believed that the breakdown was caused by something in the sugar itself that they called unstabilizing vibrations. These unstabilizing vibrations could be transferred from one vat to a new batch of freshly squeezed grapes to make more wine. What this notion did not explain, however, was why some batches of grapes produced lactic acid rather than alcohol.

Pasteur approached this problem much like the earlier crystallography dilemma—by using his microscope to make careful observations. He observed microbes in the wines and noticed that different shaped microbes were present when lactic acid was formed versus when alcohol was formed. He also observed that some of the compounds rotated plane-polarized light, so Pasteur concluded that the microbes were living (because it was thought that stereochemistry was related to living systems only.) Ultimately he was able to help isolate the yeast that was responsible for good fermentation and he solved the chemical problem of lactic acid formation and at the same time invented the field of microbiology.

Pasteur went on to make many more advances in microbiology. He also realized the importance of making science an international endeavor and advocated for a scientific approach to the betterment of the human condition. He once remarked, "Do not put forward anything that you cannot prove by experimentation." Pasteur died in 1893, two years after the first international Pasteur Institute was established in Saigon in what was then French Indochina (now Ho Chi Min City in Vietnam). SEE ALSO CHIRALITY; COORDINATION CHEMISTRY; ISOMERISM; ORGANIC CHEMISTRY.

Thomas A. Holme

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Pauli, Wolfgang

AMERICAN THEORETICAL PHYSICIST
1900–1958

Wolfgang Ernst Pauli was born in Vienna, Austria, where his father, regarded as one of the founders of colloid chemistry, was employed at the University of Vienna. His godfather was Ernst Mach, a famous physicist, philosopher, and one of the founders of logical positivism; he had a significant influence on Pauli's thinking. In high school Pauli was an outstanding student with a special talent for mathematics and physics. His parents fostered Pauli's appetite for science by hiring a private tutor. The tutor was so successful that within twelve months of beginning his studies at the University of Munich in 1918, Pauli had submitted three original papers on the theory of relativity to a leading physics periodical; all were published before his twentieth birthday.

Pauli received his doctorate in 1921 for theoretical work on the hydrogen molecule ion. He then became an assistant to Max Born at Göttingen. While at Göttingen, Pauli met Niels Bohr, who invited him to work for a year with his group in Copenhagen, Denmark. Once there, Pauli began work on the problem of the anomalous Zeeman effect (how the energy levels of a multielectron atom are split in a magnetic field), work that he continued when in 1923 he moved to a new position at the University of Hamburg. By 1924 he had decided that the current model of atomic structure used by Bohr, which assumed only two numbers and which allowed many electrons to have identical quantum numbers, needed to be modified. He also found that the currently accepted idea that it was the magnetic moment of the core of the atom that was responsible for the splitting of the electron energy levels of the outer electrons, was incorrect. Instead, Pauli proposed a new model that had as its consequence his famous **exclusion principle**.

exclusion principle: principle that states that no two electrons can have the same four quantum numbers

The new model had its origins in a new classification of electron levels published in 1924 by Edmond C. Stoner, an English physicist at the University of Leeds who was an expert on the magnetic properties of matter. This classification divides the electrons of an atom into electronic shells using three quantum numbers (n, k1, k2). The first two number are the same as those used by Bohr, and the third one, the inner quantum number k2, was chosen so that twice the sum of the individual k2 numbers became the number of electrons in a subgroup. It was Pauli's genius that allowed him to extend this classification by adding a fourth quantum number (m1), which could have only two values (+1/2 and −1/2). As a result, Pauli was able in 1925 to arrive at the first statement of his exclusion principle, that stated that there cannot be two or more equivalent electrons in an atom for which in strong fields the values of all quantum numbers n, k1, k2, and m1 are the same. Initially, Pauli rejected the notion that the two-valuedness of m1 was due to spin, but after discussing the matter of electron spin with fellow physicists Samuel Goudsmit and George Uhlenbeck, he accepted the idea. The term "exclusion principle" had its origin in Pauli's insistence on each electron having a unique set of quantum numbers. This requirement immediately solved many problems in the interpretation of observed atomic spectra, because it prevented many lines that, according to prior theories, should be seen but never were, to become forbidden.

theoretical physics: branch of physics dealing with the theories and concepts of matter, especially at the atomic and subatomic levels

In 1928 Pauli became professor of **theoretical physics** at the Federal Institute of Technology, Zurich; largely through his efforts it became a leading center for research in theoretical physics. In 1931 he observed that when an electron was emitted from a nucleus, a loss of energy occurred that could not be explained by then-current theories. He proposed that it was due to the existence of another particle which carried no charge and had very low mass. The American physicist Enrico Fermi named this particle the "neutrino"; it was eventually discovered some twenty-five years later.

During World War II Pauli worked at the Institute for Advanced Studies at Princeton in New Jersey; he then returned to Zurich, where he died in 1958. SEE ALSO BOHR, NIELS; FERMI, ENRICO.

John E. Bloor

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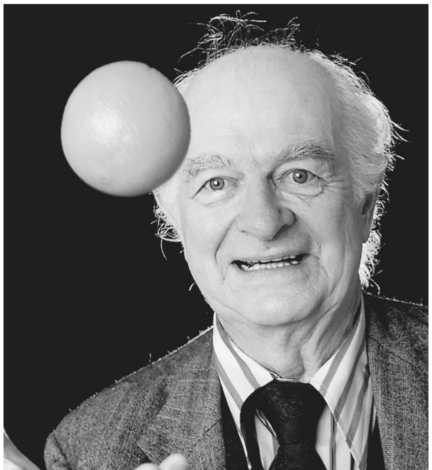
Pauling, Linus

AMERICAN CHEMIST
1901–1994

Linus Carl Pauling was born in Portland, Oregon, on February 28, 1901, the first of three children of pharmacist Herman W. Pauling and Lucy Isabelle Pauling (née Darling). An internationally acclaimed scientist, educator, humanitarian, and political activist, the only person to have received two unshared Nobel Prizes (for chemistry in 1954; for peace in 1962), Pauling was once characterized by *New Scientist* as one of the twenty greatest scientists of all time, on a par with Isaac Newton, Charles Darwin, and Albert Einstein. His magnum opus, *The Nature of the Chemical Bond* (1939), was one of the most influential and frequently cited scientific books of the twentieth century. His advocacy of megadoses of **vitamin** C for the common cold, cancer, and AIDS is still controversial, and the work for which he is best known. His life and career were characterized by controversy, and almost everything about him was larger than life.

vitamins: organic molecules needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

Pauling majored in chemical engineering at Oregon Agricultural College (now Oregon State University), where he developed the belief that would guide his lifetime of research: Atomic arrangements must be responsible for the chemical and physical properties of material substances. He received his B.S. degree in 1922 and entered the California Institute of Technology (Caltech) at Pasadena, where he worked with Roscoe G. Dickinson and adopted the relatively new technique of x-ray crystallography to explore the structure of crystals. In 1925 Pauling received his Ph.D. and was awarded a Guggenheim fellowship to pursue postgraduate research in Europe with the seminal atomic theorists Arnold Sommerfeld, Niels Bohr, and Erwin Schrödinger. The first to realize the ramifications of the new quantum mechanics within chemistry, he used this body of ideas to explain and predict the properties of atoms and ions, and thus to revolutionize chemistry. In 1927 Pauling returned to Pasadena to join the faculty of Caltech, where he stayed until 1963. There he used x-ray diffraction to measure the lengths and angles of atomic bonds in the three-dimensional structures of, first, inorganic crystals and, later, organic compounds.



American chemist Linus Carl Pauling, recipient of the 1954 Nobel Prize in chemistry, "for his research into the nature of the chemical bond and its application to the elucidation of the structure of complex substances," and the 1962 Nobel Peace Prize.

One of the key concepts of Pauling's quantum theory of chemical bonding, introduced in 1931, was resonance: In many cases an ion or molecule could not be represented, conceptually or on paper, as one classical structure, but required what he called a "hybridization" of two or more of these structures. The single classical structure simply did not describe the chemical bond(s). In less than a decade he had transformed the earlier, somewhat simplistic theory of the chemical bond into a powerful, highly sophisticated theory and research tool.

During the mid-1930s Pauling turned his attention to molecules present in living things. His interest in the binding of oxygen to hemoglobin (the protein molecule that carries oxygen via the bloodstream to cells throughout the body) provoked a more general interest in proteins, the nitrogen-containing organic compounds required in all of animal **metabolism**. In 1948, while in bed with influenza, Pauling occupied himself with making a paper model of linked amino acids, the basic building blocks of proteins. In this way he received the inspiration that led to his discovery of the α-**helix**—a crucial concept that helped James Watson and Francis Crick to determine the structure of **DNA**, one of the discoveries of the century. And this landmark discovery of Watson and Crick led, ultimately, to the Human Genome Project and the current revolution in genetic engineering.

metabolism: the complete range of biochemical processes that take place within living organisms; comprises processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those that break down complex food molecules, thus liberating energy (catabolism)

helix: form of a spiral or coil such as a corkscrew

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

After World War II Pauling studied sickle cell anemia, and theorized that it was the result of a genetically based defect in the patient's hemoglobin molecules. In 1949 he and Harvey Itano confirmed this theory; they had identified what they called a "molecular disease," one that could be defined by a molecular abnormality. In 1954 Pauling received the Nobel Prize in chemistry "for his research on the chemical bond and its application to the elucidation of the structure of complex substances."

Less well-known is the record of Pauling's evolution from ivory tower scientist to ardent and articulate advocate of nuclear disarmament and of the social responsibility of scientists. His eventual clashes with political and ideological adversaries, including the U.S. government, which denied him research grants and a passport, consumed much of his time and energy. His being chosen for the 1962 Nobel Peace Prize was criticized by many, and the American Chemical Society, which he had served as president in 1949, at around this time chose to slight him.

In 1963 Pauling left Caltech to become research professor at the Center for the Study of Democratic Institutions at Santa Barbara, California, at which time he began to divide his time between chemistry and world peace. In Santa Barbara he became greatly interested in what he called "orthomolecular medicine"—a biochemical approach to human health that included the central idea that large amounts of some chemical compounds normally present in the body could be used to treat or prevent disease. In 1973, following professorships at the University of California, San Diego (1967–1969) and Stanford University (1969–1974), he founded the Institute of Orthomolecular Medicine (later named the Linus Pauling Institute of Science and Medicine), an organization of which he was director of research at the time of his death. He died of cancer at his Deer Flat Ranch near Big Sur, California, on August 19, 1994, at the age of ninety-three.

Pauling has been called one of the two greatest scientists of the twentieth century (the other being Einstein) and the greatest chemist since Antoine-Laurent Lavoisier, the eighteenth-century founder of modern chemistry. Pauling's multifaceted life and activities, scientific and personal, spanned almost the entire twentieth century. SEE ALSO Bohr, Niels; Einstein, Albert; Hemoglobin; Lavoisier, Antoine; Newton, Isaac; Proteins; Schrödinger, Erwin; Watson, James Dewey.

George B. Kauffman

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Penicillin

Penicillin was discovered accidentally in 1929 when Sir Alexander Fleming observed bacterial **cultures** contaminated with a mold that inhibited bacterial growth. The antibiotic penicillin was subsequently isolated from cultures of the *Penicillium* mold. In 1938 two other British scientists, Howard

culture: living material developed in prepared nutrient media

Penicillin is a mold used to treat bacterial infections.

GRAM-POSITIVE AND GRAM-NEGATIVE BACTERIA

Bacteria can be broadly classified into two groups; the gram-positive bacteria, which are stained purple after the gram staining procedure, and the gram-negative bacteria, which are stained red. The difference in staining reflects differences in the structure of the cell walls between gram-positive and gram-negative bacteria. Pathogenic gram-positive bacteria include *Staphylococcus aureus* and *Bacillus anthracis*, and pathogenic gram-negative bacteria include *Escherichia coli* and *Neisseria gonorrhoeae.*

Florey and Ernst Chain, first used purified preparations of penicillin to treat bacterial infections. Penicillin may have been present in folk remedies used as early as 600 B.C.E., at around which time molded soybean curd was used by the Chinese to treat boils and carbuncles, and moldy cheese was used by Chinese and Ukrainian peasants to treat infected wounds.

Initially it was thought that penicillin was a pure substance, but further studies revealed that a number of closely related compounds were present in *Penicillium* cultures. Naturally occurring penicillins, such as penicillin G, are most effective against gram-positive bacteria, but much less effective against gram-negative bacteria. A further limitation to the use of Penicillin G is that it is not well absorbed when administered orally. Research programs to produce chemically modified penicillins with improved properties have resulted in a large number of clinically useful penicillin derivatives. Examples of such penicillin derivatives include ampicillin and amoxicillin, which have much greater efficacy against gram-negative bacteria than penicillin, retain good activity against gram-positive bacteria, and are well absorbed when administered orally. The principal adverse reaction associated with the penicillins is the occurrence of allergic response.

biosynthesis: formation of a chemical substance by a living organism

lysis: breakdown of cells; also the favorable termination of a disease

The molecular targets for the antibacterial activity of the penicillin and related β-lactam antibiotics such as the cephalosporins are a group of bacterial enzymes known as *penicillin-binding proteins* (PBPs). The PBPs are essential to the final stages of bacterial cell wall **biosynthesis**. Penicillin and other β-lactam antibiotics inhibit PBPs, thereby inhibiting bacterial cell wall biosynthesis, which eventually results in bacterial cell **lysis**. (Vancomycin and cycloserine are nonpenicillin antibiotics that also inhibit bacterial cell wall biosynthesis through other mechanisms.)

cleave: split

The penicillins and related antibiotics have been among the most widely used therapeutic agents since their introduction into clinical practice in the 1940s. However, the widespread use of these antibiotics has resulted in the emergence and spread of bacteria that are resistant to these agents. A major mechanism of resistance to the penicillin and other β-lactam antibiotics is the bacterial production of β-lactamases, enzymes that **cleave** the β-lactam antibiotics and render them inactive before they can inhibit their PBP targets. Significant efforts have been made to develop β-lactam antibiotics resistant to the β-lactamases, and toward finding inhibitors of the β-lactamases to allow β-lactam antibiotics to be useful antibacterial agents against β-lactamase producing bacteria. SEE ALSO ANTIBIOTICS; ENZYMES; FLEMING, ALEXANDER; INHIBITORS.

William G. Gutheil

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Peptide Bond

A peptide bond is a linkage between the building blocks of proteins called amino acids (shorter strings of linked amino acids are known as peptides). A peptide bond forms when the **carboxylic acid** group (R-C[O]OH) of one amino acid reacts with the amine group (R-NH_2) of another. The resulting molecule is an amide with a C–N bond (R-C(O)-NH-R).

carboxylic acid: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the –CO_2H functional group

While drawn as a single bond, the peptide bond has partial double bond character that enforces a well-defined flat structure. The O atom of the amide has a partial negative charge and is a good **hydrogen bond** acceptor, while the NH is partially positive and a good hydrogen bond donor. Hydrogen bonds between amides are critical to protein folding, as well as to the structure of deoxyribonucleic acid (**DNA**).

hydrogen bond: interaction between H atoms on one molecule and lone pair electrons on another molecule that constitutes hydrogen bonding

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

The **synthesis** of proteins involves the formation of many peptide bonds. Cleavage of peptide bonds, involved in digestion of proteins and in many regulatory processes, is carried out by enzymes known as proteases. One such protease is subtilisin, the enzyme frequently added to laundry detergent to **cleave** many protein contaminants. **Angiotensin**-converting enzyme (ACE) is an enzyme that targets a specific peptide bond, forming a chemical signal that increases blood pressure. Some blood pressure medications act by blocking ACE. SEE ALSO PRIMARY STRUCTURE; PROTEINS.

synthesis: combination of starting materials to form a desired product

cleave: split

angiotensin: chemical that causes a narrowing of blood vessels

Alan Schwabacher

Periodicity ***See Meyer, Lothar; Periodic Table.***

Periodic Table

The Periodic Table places the symbols of chemical elements, sequenced by **atomic number**, in rows and columns that align similar properties.

atomic number: the number assigned to an atom of an element that indicates the number of protons in the nucleus of that atom

Antiquity through the Renaissance

A few thousand years ago, primitive chemistry focused mostly on converting one substance into another. The word "chemistry" itself is arguably traced to the name of a region of ancient Egypt where such transformation attempts were practiced. Over the centuries, philosophers tried to come to terms with the growing variety of known substances. They postulated the role of fundamental entities that could not be broken down further but formed simple materials when combined. By the time of ancient Greece, Democritus, Leucippus, and Empedocles expounded the nature of matter in terms of constituent elements, the simple substances—earth, air, fire, and water—of which all materials were compounded. The term "atom" first appears in this context.

A millennium or so later, Arab civilizations made great strides in laboratory techniques. Subsequently, during the Renaissance period, these techniques were adopted in trying to transform one element into another, most notably into gold from less costly substances like lead. This gave the Arabic term **"alchemy"** its modern mystical connotation.

alchemy: medieval chemical philosophy having among its asserted aims the transmutation of base metals into gold

Post-Renaissance

By the mid-1700s about twenty elements were known. Science was beginning to get more sophisticated as measurements and instrumentation improved rapidly and theories based on observation grew more advanced and more compelling. Chemists, however, continued to anguish over the inability to easily categorize the elements.

What was likely the first attempt at sorting the elements was a table of simple substances, prepared in 1772 by French chemist Louis-Bernard Guyton de Morveau. French chemist Antoine-Laurent Lavoisier was most influential in developing an experimental approach, which is acknowledged to have laid the foundation for modern chemistry. In 1789, Lavoisier published a list of pure substances that included the known elements but also some compounds and light and heat. By the early 1800s, following the introduction of English chemist John Dalton's **atomic theory** and the concept of atomic weights, the number of known elements had grown. Although properties were carefully measured, confusion held sway when it came to agreeing on the composition of compound substances and the related assignment of atomic weights.

atomic theory: physical concept that asserts that matter is composed of microscopically tiny particles called atoms and that various elements differ from each other by having different atoms

In 1829 German chemist Johann Döbereiner noted that there were triplets of elements in which the central species' properties were almost exactly midway between the outer two. The first example of such a triplet included chlorine, bromine, and iodine. Properties such as atomic weights, color, and reactivity followed this "law of triads" for several such groupings, but not for the entire collection of known elements.

alloy: mixture of two or more elements, at least one of which is a metal

In 1860 Italian chemist Stanislao Cannizzaro presented analyses at an international chemistry meeting that, when merged with previously ridiculed hypotheses by fellow Italian Amedeo Avogadro, yielded unambiguous atomic weights. These eliminated most of the disharmony among property determinations. In attendance were German chemist Lothar Meyer and Russian chemist Dimitri Mendeleev, both of whom were inspired to give the presentation further thought.

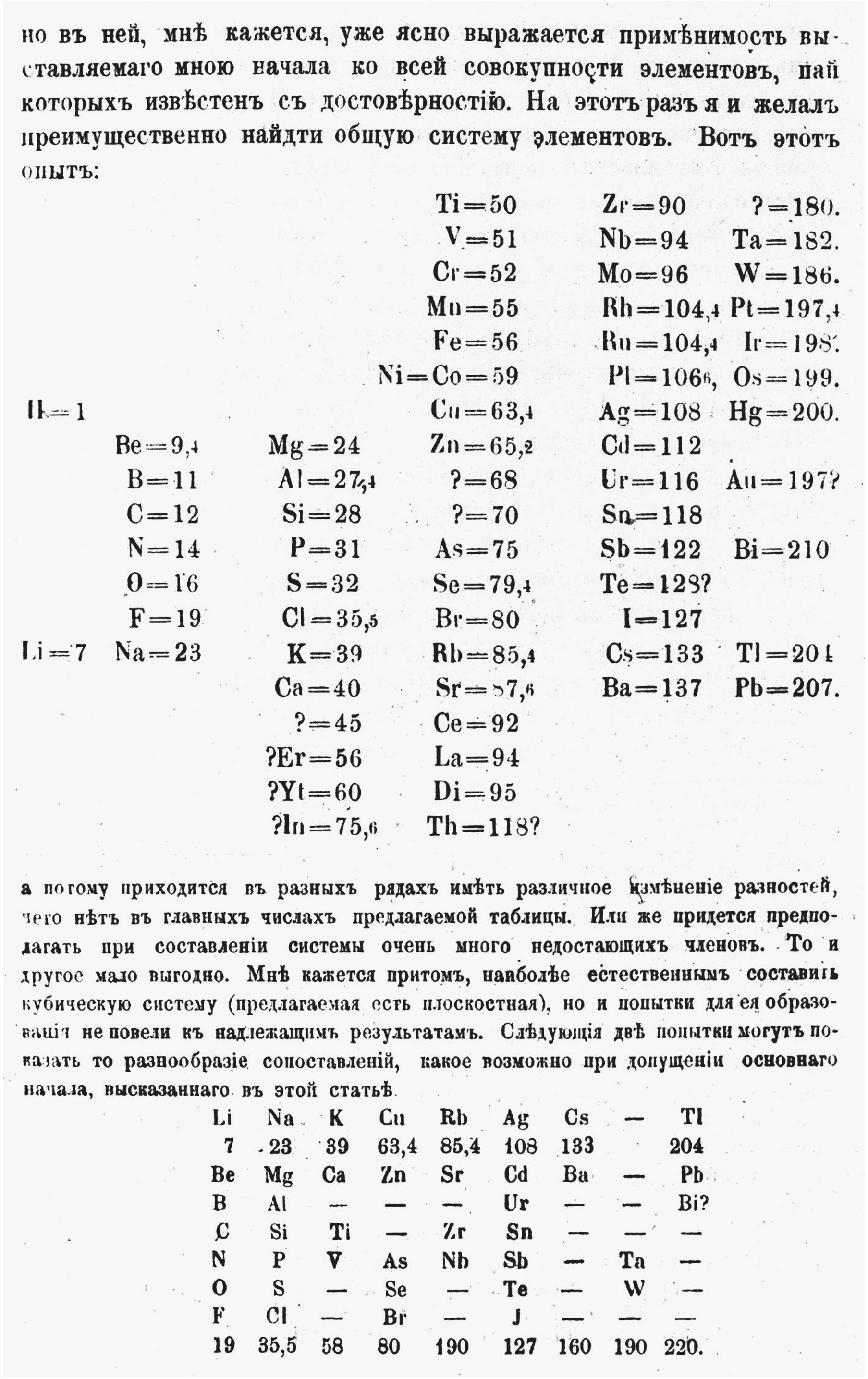
JOHN NEWLANDS (1837–1898)

John Newlands compared elements to musical notes with his law of octaves. As on a scale, every eighth element would share similar properties when arranged by increasing atomic weight. Newlands did not account for exceptions, however, and it was only upon establishment of the Periodic Table that his theory gained credibility.

—Valerie Borek

Industrial Age

In 1862 French geologist Alexandre-Émile Beguyer de Chancourtois arranged the elements in order of increasing atomic weights, wrapping the series around a cylinder in a helical display. He noted that elements with similar properties lined up, one over the other. His idea was obscured by its publication in a nonchemistry journal, the inclusion of compounds and **alloys** in the discussion, and the publisher's decision not to include an essential diagram.



The first Mendeleev periodic table, 1869.

но въ ней, мнѣ кажется, уже ясно выражается примѣнимость выставляемаго мною начала ко всей совокупности элементовъ, пай которыхъ извѣстенъ съ достовѣрностію. На этотъ разъ я и желалъ преимущественно найдти общую систему элементовъ. Вотъ этотъ опытъ:

			Ti=50	Zr=90	?=180.
			V=51	Nb=94	Ta=182.
			Cr=52	Mo=96	W=186.
			Mn=55	Rh=104,4	Pt=197,4
			Fe=56	Ru=104,4	Ir=198.
			Ni=Co=59	Pl=106,6,	Os=199.
H=1			Cu=63,4	Ag=108	Hg=200.
	Be=9,4	Mg=24	Zn=65,2	Cd=112	
	B=11	Al=27,4	?=68	Ur=116	Au=197?
	C=12	Si=28	?=70	Sn=118	
	N=14	P=31	As=75	Sb=122	Bi=210
	O=16	S=32	Se=79,4	Te=128?	
	F=19	Cl=35,5	Br=80	I=127	
Li=7	Na=23	K=39	Rb=85,4	Cs=133	Tl=204
		Ca=40	Sr=87,6	Ba=137	Pb=207.
		?=45	Ce=92		
		?Er=56	La=94		
		?Yt=60	Di=95		
		?In=75,6	Th=118?		

а потому приходится въ разныхъ рядахъ имѣть различное измѣненіе разностей, чего нѣтъ въ главныхъ числахъ предлагаемой таблицы. Или же придется предполагать при составленіи системы очень много недостающихъ членовъ. То и другое мало выгодно. Мнѣ кажется притомъ, наиболѣе естественнымъ составить кубическую систему (предлагаемая есть плоскостная), но и попытки для ея образованія не повели къ надлежащимъ результатамъ. Слѣдующія двѣ попытки могутъ показать то разнообразіе сопоставленій, какое возможно при допущеніи основнаго начала, высказаннаго въ этой статьѣ.

Li	Na	K	Cu	Rb	Ag	Cs	—	Tl
7	23	39	63,4	85,4	108	133		204
Be	Mg	Ca	Zn	Sr	Cd	Ba	—	Pb
B	Al	—	—	—	Ur	—	—	Bi?
C	Si	Ti	—	Zr	Sn	—	—	—
N	P	V	As	Nb	Sb	—	Ta	—
O	S	—	Se	—	Te	—	W	—
F	Cl	—	Br	—	J	—	—	—
19	35,5	58	80	190	127	160	190	220.

A few years later, British chemist John Newlands also arranged the elements in order of increasing atomic weights. He was apparently the first to assign hydrogen the weight of "1." Newlands noted that properties repeated when the sequence was broken into periods of seven and referred to his system as the "law of octaves."

During the mid-1860s Meyer took the newly established atomic weights of many elements and arranged them into families that bore similarities in properties, including the ability of an atom to combine with other atoms (valency).

In 1869 Mendeleev presented his table of the elements (sixty-three by now) arrayed in periods of seven for the lighter elements and opening up to seventeen for the heavier elements. Furthermore, Mendeleev had the foresight and confidence to break the **atomic weight** sequence by occasionally forcing elements out of order so as to fall in an appropriate location as determined by their properties. He left gaps in the arrangement at several places and used implied trends to predict characteristics of undiscovered elements needed to complete the table.

atomic weight: weight of a single atom of an element in atom ic mass units (AMU)

Mendeleev's Periodic Table was not well received at first, but was shortly helped by the discovery of the element gallium, which filled such a gap and had nearly exactly the atomic weight, density, and valency predicted. Other affirmations followed. It is for these reasons that Mendeleev is given most of the credit for the invention of the Periodic Table.

In 1892 Scottish chemist William Ramsay discovered two more elements, argon and helium. These unreactive gases did not fit into the Periodic Table. In short order, Ramsay also discovered three more unreactive gases. These gases represented a new family of elements that had to be inserted as an eighth main column in Mendeleev's table.

The Modern Periodic Table

As the twentieth century approached, elements of similar properties were arranged in eight main vertical columns referred to as chemical families. The first such family, or Group I, is collectively termed the "alkali metals," commencing with lithium. The next column, Group II, is designated the "alkaline earths," commencing with beryllium. Groups III through V are commonly referred to as the boron, carbon, and nitrogen families, respectively. The next group, the oxygen family, is technically called the "chalcogens." Group VII, the **"halogens,"** begins with fluorine. Finally, the elements of Group VIII, starting with helium, are called the **"noble gases."** Because of their relative unreactivity, they had once also been termed **inert** gases, a label no longer acceptable.

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

noble gas: element characterized by inert nature; located in the rightmost column in the Periodic Table

inert: incapable of reacting with another substance

In the absence of any understanding as to why the periodic arrangement appeared as it did, or whether or not there were yet more surprises, the science of chemistry remained incomplete, although very important and practical. At almost exactly this time, just before the start of the twentieth century, three findings were announced that changed the course of science: x rays were discovered by German physicist Wilhelm Röntgen in 1895, radioactivity by French physicist Antoine-Henri Becquerel in 1896, and the electron by British physicist Joseph John Thomson in 1897.

First Model

What soon emerged was a nuclear model of the atom, first proposed by New Zealand-born physicist Ernest Rutherford. In this view, an element's identity was determined by its atomic number, the amount of positive charge in the very small core nucleus that also contained almost all of the atom's mass. The light electrons were held in orbits by electrostatic **attraction** to the positive core.

attraction: force that brings two bodies together, such as two oppositely charged bodies

Rutherford's view was extended by Danish physicist Niels Bohr in 1913. Bohr modeled that electrons moved in fixed orbits around the nucleus, much as planets orbit the Sun. Furthermore, not only were the locations of these orbits fixed, but so were the speeds of the electrons in each orbit and the number of electrons that could be accommodated in each orbit, a description called the electron configuration. By explaining the quota of electrons allowed in each fixed orbit, Bohr resorted to a new physical idea called quantization. As a consequence, Bohr was able to reproduce the Periodic Table, adding one electron at a time as one stepped to the next higher element. Bohr argued that orbits of increasing radius could accommodate up to a maximum number of electron numbers that, when reached, corresponded to observed horizontal periods of two, eight, eight, eighteen, eighteen, and thirty-two. Bohr acknowledged the unattractiveness of this approach in that it was merely mimicking an observed pattern rather than addressing the underlying science.

Modern Theory

The mid-1920s witnessed a necessary breakthrough. The revolutionary wave concept of matter was incorporated into a mathematical framework, a new quantum theory, that explained all the properties of a bound electron: its energy, the description of where it could be found, and configuration restraints.

An electron could have only certain energies determined by the value of an integer (a whole number), traditionally symbolized by n with values 1, 2, 3, and so on. Electron energy with $n = 1$ is the lowest possible, $n = 2$ being the next lowest, and so on. The region of space where the electron might be found—called an orbital because it replaced Bohr's planetary fixed orbit idea—could be characterized by its size, shape, and orientation (how the shape might be tilted). For each n, there was a determined set of shapes and orientations with letters used to indicate the shapes. For $n = 1$, only a spherical shape is allowed, symbolized by *s*; since a sphere has no orientation, that is the only $n = 1$ orbital. It is abbreviated as *1s*. For $n = 2$, there are larger orbitals: another *s*, the *2s*, and also dumbbell-shaped orbitals with opposing lobes. These are symbolized as *p* orbitals and have three possible orientations for the *2p* and all other *p* orbitals. By the time $n = 3$ is considered, there is a third shape, *d*, with five orientations. For $n = 4$ there is a fourth shape, *f*, with seven orientations in addition to the *4s*, *4p* and *4d*. The sequence of filling follows a relatively simple pattern shown by arrows in Figure 1.

Very early in the development of modern quantum mechanics, German physicist Wolfgang Pauli realized that each of the substates characterized by *n*, shape, and orientation was permitted to have no more than two electrons, a feature sometimes pictured as if the electron were spinning and where only two spin orientations were allowed: clockwise and counterclockwise.

The predicted sequence of electron filling might be best illustrated by looking at some examples. Hydrogen is $1s^1$, the superscript referring to the number of electrons in the *1s* substate. Lithium (three electrons) and sodium (eleven electrons) are $1s^2 2s^1$ and $1s^2 2s^2 2p^6 3s^1$, respectively. The latter configuration, for example, corresponds to one pair of *1s*-electrons, one pair of

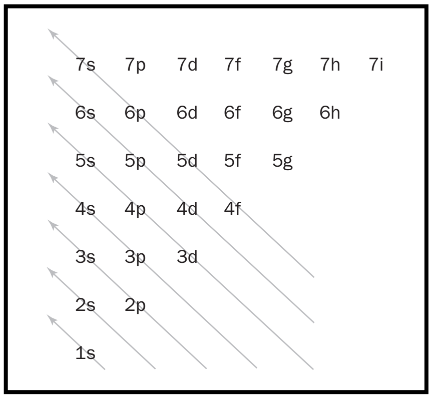


Figure 1. The sequence of substates, indicated by arrows, normally followed in determining electron configurations of the elements. Example: *1s* then *2s* then *2p* then *3s*, etc.

$2s$-electrons, three pairs of $2p$-electrons (six total), and a final $3s$-electron. Neon and argon are $1s^2 2s^2 2p^6$ and $1s^2 2s^2 2p^6 3s^2 3p^6$, respectively. They complete the horizontal periods of length eight.

The periods in which the *d* substates are filling are known as the *d*-block elements or **transition metals**. These ten elements increase the period length to eighteen elements. Some new Periodic Tables have adopted the convention of numbering the columns one through eighteen as a result.

transition metals: elements with valence electrons in d-sublevels; frequently characterized as metals having the ability to form more than one cation

The *f*-block, whose existence was recognized by American chemist Glenn Seaborg, has two rows containing nearly one-quarter of all the elements. The first row is known as the **rare earth elements** or **lanthanides**. The second *f*-block row is referred to as the actinides. The most common form of the Periodic Table, the Mendeleev-Seaborg form, has the *f*-elements at the bottom. Fourteen *f*-block elements increase the period length to thirty-two.

rare earth elements: older name for the lanthanide series of elements, from lanthanum to lutetium

lanthanides: a family of elements (atomic number 57 through 70) from lanthanum to lutetium having from 1 to 14 4f electrons

For nearly three centuries, a new element has been discovered every two-and-one-half years, on average. Undoubtedly, more will be found. Although their names and their discoveries will likely involve controversies, their place at the table is already set. SEE ALSO Alchemy; Avogadro, Amedeo; Becquerel, Antoine-Henri; Bohr, Niels; Cannizzaro, Stanislao; Dalton, John; Lavoisier, Antoine; Mendeleev, Dimitri; Meyer, Lothar; Pauli, Wolfgang; Ramsay, William; Röntgen, Wilhelm; Rutherford, Ernest; Seaborg, Glenn Theodore; Thomson, Joseph John.

Paul J. Karol

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Perkin, William Henry

ENGLISH CHEMIST AND CHEMICALS MANUFACTURER
1838–1907

William Henry Perkin was an entrepreneur and a self-made millionaire at an early age, long before the era of personal computers and dot-coms. His serendipitous **synthesis** of the purple dye mauve (also known as mauveine or aniline purple) in 1856 brought brightly colored clothing to the masses and laid the foundation for today's chemical and pharmaceutical industries.

synthesis: combination of starting materials to form a desired product

Perkin was born on March 12, 1838, in London, England. He was a curious boy who liked to play with instruments, tools, and paint. Perkin saw something wonderful in chemistry and dropped his other pursuits after a friend performed for him chemical experiments that yielded crystalline products. A few years later he enrolled at the City of London School and attended chemistry lectures given by Thomas Hall, an instructor at the school. Hall recognized Perkin's ability and arranged for him to enroll at the Royal College of Science, where the German chemist August von Hofmann was a teacher.

Hofmann appointed the seventeen-year-old Perkin as his personal assistant and guided him to work on the synthesis of the antimalarial drug quinine. Perkin had his own ideas for the synthesis of quinine and pursued them in his lab at his parents' home. During Easter break 1856 Perkin ran a reaction with aniline (a compound derived from coal tar) and potassium dichromate that produced a black sludge. Dissolving the sludge in ethyl alcohol, Perkin found that the solution took on an intense purple color. Instead of synthesizing quinine, Perkin had made the first synthetic dye derived from coal tar: mauve.

Perkin undoubtedly appreciated the significance of his discovery, as the worldwide dye and textile industry was the largest chemical industry at that time. Most dyes were derived from natural sources (plants or insects), and chemists were only just beginning to investigate synthetic dyes. Purple was an especially desired color, as expensive natural purple dyes made purple-dyed cloth too expensive for most people. Perkin's discovery was also especially timely, as mauve mania had hit the world a year earlier. Demand for the natural purple dye derived from lichen hit manic proportions (and a cheap, synthetic substitute would be worth vast sums of money).

Perkin left school after patenting his discovery, but promised himself that he would return to research one day. He and members of his family soon formed a company to mass-produce mauve from coal tar, and in 1859 the Perkin and Sons factory commenced production. Mauve mania, however, was short-lived, and within a few years the red dyes fuchsia (or magenta) and alizarin were the craze. Perkin was quick to capitalize on these manias, and made an immense fortune in the process.

But Perkin was not alone: Dye companies quickly sprang up in Austria, England, France, Germany, and Switzerland, and competition became intense. Companies created research subsidiaries that employed hundreds of chemists and found new uses for the flood of compounds being synthesized in their labs. Some of the subsidiaries eventually manufactured pharmaceuticals and explosives.

In 1874 Perkin retired from manufacturing and returned to chemical research. He discovered a reaction (the Perkin reaction) for producing unsaturated carboxylic acids. He also synthesized coumarin, an accomplishment that laid the foundation for the synthetic perfume industry. Perkin died on July 14, 1907, at the age of sixty-nine. SEE ALSO DYES.

Thomas M. Zydowsky

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Pesticides

Pesticides are chemicals that kill pests, and are categorized by the types of pests they kill. For example, insecticides kill insects, herbicides kill weeds, bactericides kill bacteria, fungicides kill fungi, and algicides kill algae.

A worker is spraying pesticides on ferns in order to eradicate insects and other pests.

Approximately 90 percent of all pesticides used worldwide are used in agriculture, food storage, or shipping. Because of a growing world population, there is pressure to increase and preserve the food supply by using pesticides and other agricultural chemicals.

History of Pesticides

Throughout history, various types of pests, such as insects, weeds, bacteria, rodents, and other biological organisms, have bothered humans or threatened human health. People have been using pesticides for thousands of years to try to control these pests. The Sumerians used sulfur to control insects and mites 5,000 years ago. The Chinese used mercury and arsenic compounds to control body lice and other pests. The Greeks and Romans used oil, ash, sulfur, and other materials to protect themselves, their livestock, and their crops from various pests. And people in various cultures have used smoke, salt, spices, and insect-repelling plants to preserve food and keep pests away.

Classes of Pesticides

Although the use of pesticides is not new, the types of substances people have used as pesticides have changed over time. The earliest pesticides were inorganic substances such as sulfur, mercury, lead, arsenic, and ash. Some of these inorganic pesticides are still used today. For example, sulfur is still used as a fungicide, copper is used as an algicide, lead and arsenic were used as insecticides until World War II, and chromium, copper, and arsenic have been used as wood preservatives to prevent microorganisms from causing wood decay. Even though many of these substances are effective pesticides, the use of some of these materials has been banned or restricted because of health and environmental concerns. Lead and arsenic are no longer used as insecticides, the use of mercury as a fungicide has been restricted, and the U.S. Environmental Protection Agency (EPA) is phasing out the use of arsenic as a wood preservative.

The modern era of chemical pest control began around the time of World War II, when the synthetic organic chemical industry began to develop. The first synthetic organic pesticides were organochlorine compounds, such as dichlorodiphenyltrichloroethane (DDT). Commercial production of DDT began in 1943. At that time, DDT was considered to be a wonderful invention. It was cheap to produce, very toxic to insects, and much less toxic to mammals. DDT and other organochlorine insecticides were used for many years to control mosquitoes and as a broad-spectrum insecticide against insect pests that damaged food and crops. Unfortunately, scientists learned later that many organochlorine insecticides were persistent in the environment (they did not **degrade** readily) and were bioaccumulating in birds, humans, and other animals. In 1962 Rachel Carson wrote the book *Silent Spring*, in which she reported that DDT was causing eggshell thinning in bird eggs and thus was leading to the near extinction of bird species such as peregrine falcons and bald eagles. Today most of the organochlorine pesticides have been banned in the United States by the EPA because of the tendency of these compounds to persist in the environment and bioaccumulate in animals.

degrade: to decompose or reduce to complexity of a chemical

Other classes of insecticides include the organophosphates, carbamates, pyrethroids, and biopesticides. These other classes of pesticides are not as persistent in the environment as the organochlorine pesticides. The organophosphate and carbamate pesticides affect the nervous system by disrupting the enzyme that regulates **acetylcholine**, a neurotransmitter. However, carbamate pesticides are less toxic to humans because their interactions with important enzymes are reversible. As a group, the organophosphate and carbamate pesticides are probably the most widely used insecticides, although many are being restricted by the EPA because of their toxicity.

acetylcholine: neurotransmitter with the chemical forumula $C_7H_{17}NO_3$; it assists in communication between nerve cells in the brain and central nervous system

Pyrethroid pesticides were developed as synthetic versions of the naturally occurring pesticide pyrethrin, which is found in chrysanthemums. Most pyrethroids are safer than the organochlorines, organophosphates, and carbamates, although some synthetic pyrethroids are toxic to the nervous system. Pyrethroids have been modified to increase their stability in the environment, and many different pyrethroids are being used today.

Biopesticides are substances that are derived from such natural materials as animals, plants, bacteria, and certain minerals. For example, canola oil and baking soda have pesticidal applications and are considered biopesticides. Biopesticides fall into three major classes, including microbial pesticides, plant-incorporated protectants, and biochemical pesticides. Microbial pesticides contain microorganisms, such as bacteria, fungi, and viruses, as their active ingredient. The most widely used microbial pesticides are strains of *Bacillus thuringiensis*, or Bt. Plant-incorporated protectants are pesticidal substances that plants produce from genetic material that has been added

RACHEL CARSON (1907–1964)

The role of chemistry became irreversibly intertwined with the environment in 1962 when the term "ecosystem" was introduced in Rachel Carson's *Silent Spring.* One of four works written by Carson, it targeted the now banned pesticide dichlorodiphenyltrichloroethane (DDT), spawning a movement that resulted in the formation of the U.S. Environmental Protection Agency (EPA).

—Valerie Borek

to the plant. Biochemical pesticides are naturally occurring substances that control pests by nontoxic mechanisms. Conventional pesticides, by contrast, are generally synthetic materials that directly kill or inactivate the pest. Biochemical pesticides include substances, such as insect sex pheromones, that interfere with mating, as well as various scented plant extracts that attract insect pests to traps. Because it is sometimes difficult to determine whether a substance meets the criteria for classification as a biochemical pesticide, the EPA has established a special committee to make such decisions.

Pesticide Residues

Pesticide residues are the materials that remain on plants and food when a crop is treated with a pesticide. The U.S. government establishes safe residue levels, called tolerances or maximum residue levels, for each food commodity. However, the presence of pesticide residues in food has been a public concern. There has also been a concern about pesticide residues in water, air, and soil. In response to this concern, the U.S. Congress passed the Food Quality Protection Act in 1996, which has had an impact on safety standards for pesticides.

Approaches to pest management have changed significantly since the 1950s and will continue to change as scientists learn more about the toxicity and environmental behavior of pesticides. Scientists will continue to develop newer approaches to insect pest management that are considered to be safer than the use of broad-spectrum pesticides. The most effective strategy for controlling pests may be to combine methods in an approach known as integrated pest management (IPM), which emphasizes preventing pest damage. In IPM information about pests and available pest control methods is used to manage pest damage by the most economical means and causing the least possible hazard to people, property, and the environment. Methods for pest management will continue to evolve as scientists conduct research and develop new information. SEE ALSO HERBICIDES; INSECTICIDES.

Cynthia Atterholt

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Petroleum

Petroleum is a naturally occurring complex mixture made up predominantly of carbon and hydrogen compounds, but also frequently containing significant amounts of nitrogen, sulfur, and oxygen together with smaller amounts of nickel, vanadium, and other elements. Solid petroleum is called asphalt; liquid, crude oil; and gas, natural gas. Its source is biological. Organic matter buried in an oxygen-deficient environment and subject to elevated temperature and pressure for millions of years generates petroleum as an **intermediate** in the transformation that ultimately leads to methane and graphite. The first successful drilled oil well came in 1859 in Pennsylvania. This is considered to be the beginning of the modern oil industry. Continuous distillation of crude oil began in Russia in 1875.

intermediate: molecule, often short-lived, that occurs while a chemical reaction progresses but is not present when the reaction is complete

Occurrence

Oil is the largest segment of our energy raw materials use, being 40 percent, while coal use accounts for 27 percent, gas 21 percent, and hydroelectric/nuclear 12 percent. Although there are 20,000 petroleum fields known worldwide, more than half of the known reserves are contained in the 51 largest fields. The Middle East has 66 percent of the known world reserves. The United States has only 2 percent of the known world reserves. Hence the need for imports. The Organization of Petroleum Exporting Countries (OPEC) is important to the international trade and distribution of this crude oil. There is a growing dependence of the United States on imports. Although U.S. domestic production has not grown since the 1950s, imports have grown dramatically, from 0.3 billion barrels of oil in 1955 to 3.0 billion barrels in 1997. The United States has increased its percentage of imports, from approximately 13 percent in 1970 to 55 percent in 2000. It uses approximately 18 million barrels of oil per day. Worldwide production is about 56 million barrels per day. With known reserves, this level of worldwide production could remain constant for only 43 years. But there are large volumes of unconventional petroleum reserves, such as heavy oil, tar sands, and oil shale. These are located in the Western Hemisphere. Improvements in recovery methods must be made, and the cost of production must decrease, for these sources to become more important providers of energy.

The world's first oil well, near Titusville, Pennsylvania, 1863.

Composition

Crude oils vary dramatically in color, odor, and flow properties. There are light and heavy crude oils; they are sweet or sour (i.e., have high or low sulfur content, with an average of 0.65%). Several thousand compounds are present in petroleum. The number of carbon atoms in these compounds can vary from one to over a hundred. Few are separated as pure substances. Many of the demands for petroleum can be served by certain fractions obtained from the distillation of crude oil. Typical distillation fractions and their uses are given in Table 1. The complexity of the molecules, their molecular weights, and their carbon numbers increase with the boiling point. The higher-boiling fractions are usually distilled in vacuo at temperatures lower than their atmospheric boiling points to avoid excessive decomposition to tars.

Each fraction of distilled petroleum is a complex mixture of chemicals, but these mixtures can be somewhat categorized. A certain sample of straight-run gasoline (light naphtha) might contain nearly 30 aliphatic (containing no benzene ring), noncyclic hydrocarbons; nearly 20 cycloaliphatic hydrocarbons (mainly cyclopentanes and cyclohexanes), sometimes called

Table 1.

FRACTIONS OF PETROLEUM

Approximate bp (˚C)	Name	Uses
<20˚C	Gases	Similar to natural gas and useful for fuel and chemicals.
20–150˚C	Light naphtha (C_5–C_6)	Fuel and chemicals, especially gasoline.
150–200˚C	Heavy naphtha (C_7–C_9)	Fuel and chemicals.
175–275˚C	Kerosene (C_9–C_{16})	Jet, tractor, and heating fuel.
200–400˚C	Gas oil (C_{15}–C_{25})	Diesel and heating fuel. Catalytically cracked to naphtha and steam-cracked to alkenes.
>350˚C	Lubricating oil	Lubrication. May be catalytically cracked to lighter fractions.
>350˚C	Heavy fuel oil	Boiler fuel. May be catalytically cracked to lighter fractions.
	Asphalt	Paving, coating, and structural uses.

SOURCE: Wittcoff, Harold A., and Reuben, Bryan G. (1996). *Industrial Organic Chemicals.* New York: John Wiley.

naphthenes; and 20 aromatic compounds (such as benzene, toluene, and xylene). Examples of compounds found or used in petroleum and mentioned in this article are given in Figure 1.

When any fraction of petroleum is used as a source of energy and burned to CO_2 and H_2O, the sulfur is converted into SO_2 in the air. The SO_2 is a major air contaminant, especially in larger cities. With air moisture it can form H_2SO_4 and H_2SO_3. Much of the sulfur-containing material must be taken out of petroleum before it can be used as fuel. The current maximum percentage allowable in gasoline is 0.10 percent S.

Octane Number

One cannot talk about the chemistry of gasoline without understanding octane numbers. When gasoline is burned in an internal **combustion** engine to CO_2 and H_2O, there is a tendency for many gasoline mixtures to burn unevenly. Such nonconstant and unsmooth combustion creates a "knocking" noise in the engine. Knocking signifies that the engine is not running as efficiently as it could. It has been found that certain hydrocarbons burn more smoothly than others in a gasoline mixture. In 1927 a scale that attempted to define the "antiknock" properties of gasolines was created. At that time, 2,2,4-trimethylpentane (commonly called "isooctane") was the hydrocarbon that, when burned pure in an engine, gave the best antiknock properties (caused the least knocking). This compound was assigned the number 100, meaning it was the best hydrocarbon to use. The worst hydrocarbon researchers could find in gasoline (which when burned pure gave the most knocking) was *n*-heptane, assigned the number 0. When isooctane and heptane were mixed, they gave different amounts of knocking depending on their ratio: The higher the percentage of isooctane in the mixture, the lower was the amount of knocking. Gasoline mixtures obtained from petroleum were burned for comparison. If a certain gasoline has the same amount of knocking as a 90 percent isooctane, 10 percent heptane (by volume) mixture, we now say that its "octane number" is 90. Hence, the octane number of a gasoline is the percent isooctane in an isooctane-heptane

combustion: burning, the reaction with oxygen

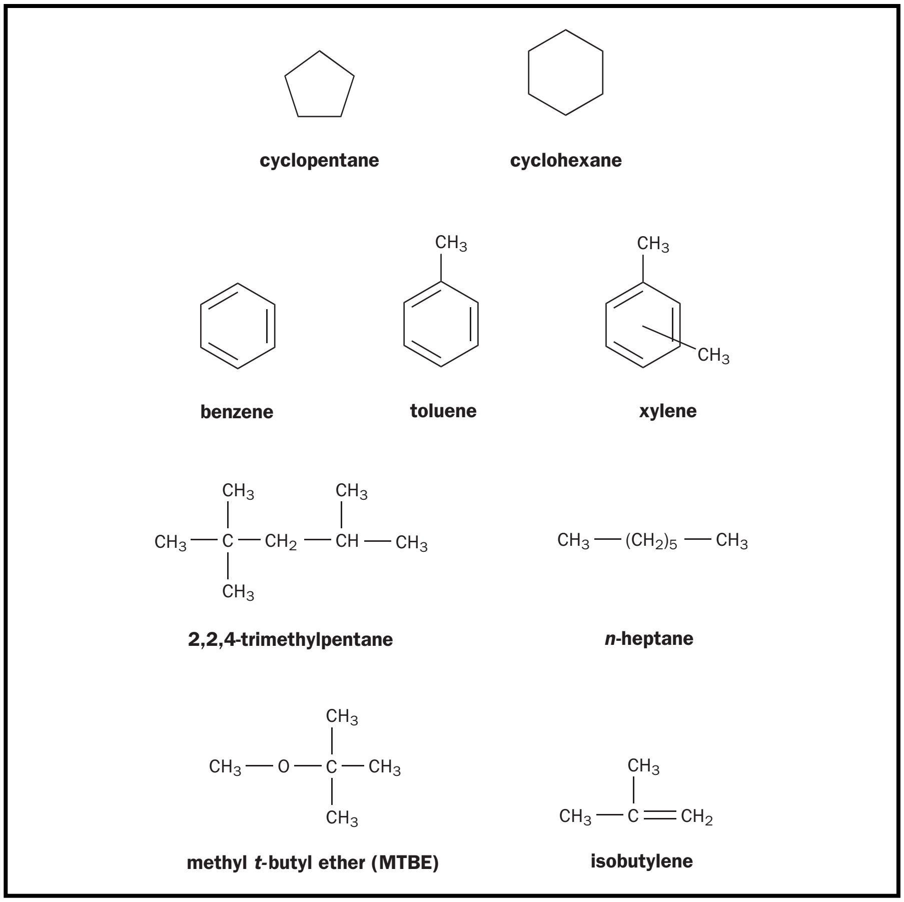


Figure 1. Some compounds found or used in petroleum.

cyclopentane

cyclohexane

benzene

toluene

xylene

2,2,4-trimethylpentane

***n*-heptane**

methyl *t*-butyl ether (MTBE)

isobutylene

mixture that gives the same amount of knocking as the gasoline being measured. Thus, a high octane number means a low amount of knocking.

Presently there are two octane scales, a research octane number (RON) and a motor octane number (MON). RON values reflect performance at 600 rpm, 148.8°C (125°F), and low speed. MON is a performance index of driving with 900 rpm, 51°C (300°F), and high speed. The station pumps now give the (R + M)/2 value. Regular is usually 87 to 89 and premium about 92 on this scale.

Certain rules have been developed for predicting the octane number of different types of gasoline, depending on the ratio of different types of hydrocarbons in the mixtures:

1. The octane number increases as the amount of branching or the number of rings increases.
2. The octane number increases as the number of double and triple bonds increases.

Additives

In 1922 two chemists working at General Motors, Midgley and Boyd, were looking at different substances that would aid the combustion of gasoline and help the knocking problems of engines. In other words, they were seeking methods of increasing the octane rating of gasoline without altering the

An oil refinery at Cap Bon, Tunisia.

hydrocarbon makeup. They were also interested in cleaning up the exhaust of automobiles by eliminating pollutants such as unburned hydrocarbons and carbon monoxide through more complete combustion. By far the best substance that they found was tetraethyllead. Lead in this form aids in breaking carbon-carbon and carbon-**hydrogen bonds**. But the lead oxide formed in the combustion is not **volatile** and would accumulate in the engine if dibromoethane and dichloroethane were not added. In the environment the lead dihalide formed undergoes reaction by sunlight to elemental lead and **halogen**, both of which are serious pollutants.

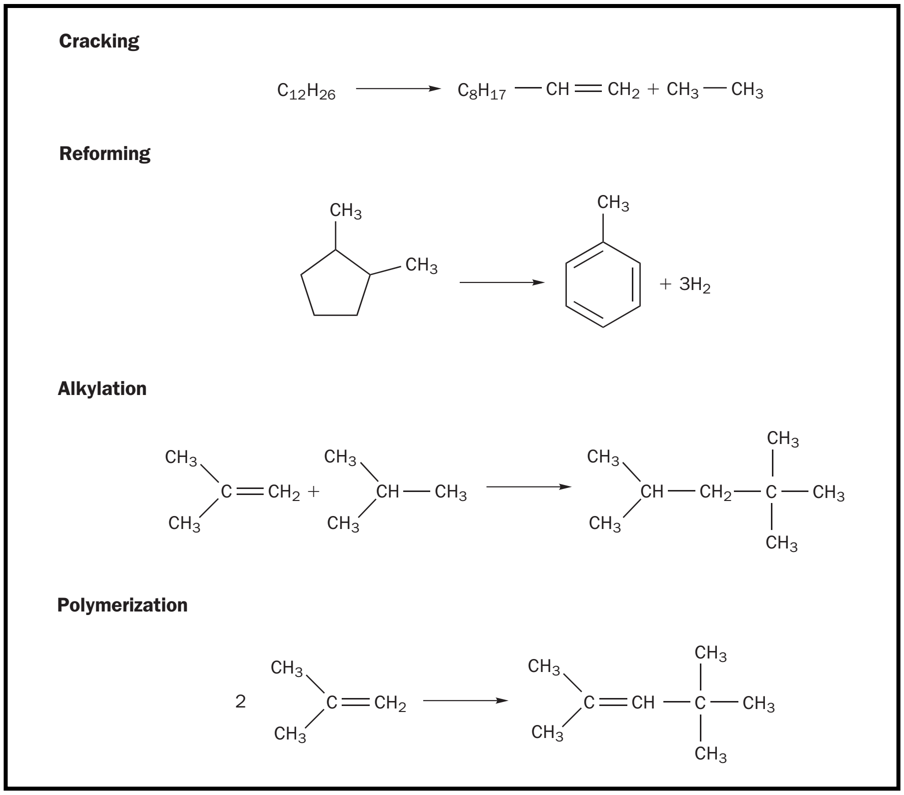
For the past several years other additives have been tried. Ethyl alcohol has become popular. When 10 percent ethyl alcohol is mixed with gasoline it is called gasohol and it is popular in states with good corn crops, as the alcohol can be made from corn fermentation. An attractive alternative to tetraethyllead is now methyl *t*-butyl ether (MTBE). MTBE has been approved at the 7 percent level since 1979. From 1984 to 1995 its production grew by 25 percent per year, the largest increase of any of the top chemicals. The Clean Air Act of 1991 specifies that the gasoline must be at the 2.0 percent oxygen level. Thus, MTBE, ethyl *t*-butyl ether (ETBE), ethanol, methanol, and other ethers and alcohols had to be added to gasoline at higher levels. The product is called reformulated gasoline (RFG), and it may cut carbon monoxide levels and may help to alleviate ozone depletion. But improved

hydrogen bond: interaction between H atoms on one molecule and lone pair electrons on another molecule that constitutes hydrogen bonding

volatile: low boiling, readily vaporized

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

Figure 2. Petroleum refining processes.



emission control systems may make this high-level input unnecessary. Currently MTBE accounts for 85 percent of the additive market, with 7 percent being ethanol and the remaining 8 percent split by other chemicals. In 1999 California took steps toward banning MTBE. In 2000 some factions called for a U.S. ban on MTBE and for increased use of ethanol to meet the oxygenate requirement. MTBE has been found in drinking water. But ethanol cannot be blended into gasoline at the refinery because it is hygroscopic and picks up traces of water in pipelines and storage tanks. Also, ethanol shipped away from the Midwest, where it is made by corn fermentation, would add to the cost of gasoline. Gasohol may increase air pollution because gasoline containing ethanol evaporates more quickly. Studies and debate continue.

Refinery Processes

There are processes that are used to refine petroleum into useful products. These are important processes for the gasoline fraction because they increase the octane rating. Some of these processes are used to increase the percentage of crude oil that can be used for gasoline. They were developed in the 1930s when the need for gasoline became great with the growing automobile industry. These processes are also keys in the production of organic chemicals. An example of each of these processes is given in Figure 2. One process is cracking. In **catalytic** cracking, as the name implies, petroleum fractions of higher molecular weight than gasoline can be heated with a **catalyst** and cracked into smaller molecules. This material can then be blended into the refinery gasoline feed.

Catalytic reforming leaves the number of carbon atoms in the **feedstock** molecules usually unchanged, but the resultant mixture contains a higher

catalysis: the action or effect of a substance in increasing the rate of a reaction without itself being converted

catalyst: substance that aids in a reaction while retaining its own chemical identity

feedstock: mixture of raw materials necessary to carry out chemical reactions

number of double bonds and aromatic rings. Reforming has become the principal process for upgrading gasoline. High temperatures with typical catalysts of platinum and/or rhenium on alumina and short contact times are used. A typical example is the reforming of dimethylcyclopentane to toluene. Straight-run gasoline can be reformed to as high as 40 to 50 percent aromatic hydrocarbons, of which 15 to 20 percent is toluene.

Although cracking and reforming are by far the most important refinery processes, especially for the production of petrochemicals, two other processes deserve mention. In alkylation, alkanes (hydrocarbons with no double or triple bonds) react with alkenes (hydrocarbons with double bonds) in the presence of an acid catalyst to give highly branched alkanes. In polymerization an alkene can react with another alkene to generate dimers, trimers, and tetramers of the alkene. As an example, isobutylene (C_4) reacts to give a highly branched C_8 alkene dimer.

Natural Gas

Natural gas can be as high as 97 percent methane, the remainder being hydrogen, ethane, propane, butane, nitrogen, hydrogen sulfide, and heavier hydrocarbons. A typical mixture contains 85 percent methane, 9 percent ethane, 3 percent propane, 1 percent butanes, and 1 percent nitrogen. Uses of natural gas by all industry include fuel (72%) and the manufacture of: inorganic chemicals including ammonia (15%), organic chemicals (12%), and carbon black (1%). The ethane and propane are converted to ethylene and propylene. The methane is purified and used to make a number of other chemicals. SEE ALSO Energy Sources and Production; Fire, Fuels, Power Plants; Fossil Fuels; Gasoline; Industrial Chemistry, Organic.

Philip J. Chenier

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Pharmaceutical Chemistry

Pharmaceutical chemists are involved in the development and assessment of therapeutic compounds. Pharmaceutical chemistry encompasses drug design, drug **synthesis**, and the evaluation of drug efficacy (how effective it is in treating a condition) and drug safety. Prior to the nineteenth century, schools of pharmacy trained pharmacists and physicians how to prepare medicinal remedies from natural organic products or inorganic materials. Herbal medications and folk remedies dating back to ancient Egyptian, Greek, Roman, and Asian societies were administered without any knowledge of their biological mechanism of action. It was not until the early 1800s that scientists began extracting chemicals from plants with purported therapeutic properties to isolate the active components and identify them. By discovering and structurally characterizing compounds with medicinal activity, chemists are able to design new drugs with enhanced potency and decreased adverse side effects.

synthesis: combination of starting materials to form a desired product

Drug discovery is the core of pharmaceutical chemistry. The drug discovery process includes all the stages of drug development, from targeting a disease or medical condition to toxicity studies in animals, or even, by some definitions, testing the drug on human subjects. Typically, conditions that affect a larger percentage of the population receive more attention and more research funding. Antiulcer drugs and cholesterol-**reducing agents** are currently the therapeutic areas of greatest emphasis. To develop a drug to target a specific disease, researchers try to understand the biological mechanism responsible for that condition. If the biochemical pathways leading up to the disease are understood, scientists attempt to design drugs that will block one or several of the steps of the disease's progress. Alternatively, drugs that boost the body's own defense mechanism may be appropriate.

reducing agent: substance that causes reduction, a process during which electrons are lost (or hydrogen atoms gained)

How do chemists "discover" drugs? Often there is an existing remedy for a condition, and scientists will evaluate how that drug exerts its actions. Once the drug's structure is known, the drug can serve as a prototype or "lead compound" for designing more effective therapeutic agents of similar chemical structure. Lead compounds are molecules that have some biological activity with respect to the condition under investigation. However, the lead compound may not be effective in combating the disease, or it may produce undesirable side effects. Lead optimization involves chemical modifications to the lead compound to produce a more potent drug, or one with fewer or decreased adverse effects.

Computers have transformed the drug discovery process. Rational drug design involves computer-assisted approaches to designing molecules with desired chemical properties. Rational drug design is based on a molecular understanding of the interactions between the drug and its target in biological systems. Molecular modeling software depicts three-dimensional images of a chemical. Mathematical operations adjust the positions of the atoms in the molecule in an attempt to accurately portray the size and shape of the drug, and the location of any charged groups. Chemists can vary the atoms or groups within the model and predict the effect the transformation has on the molecular properties of the drug. In this way, new compounds can be designed.

Advances in technology have made it possible for medicinal chemists to synthesize a vast number of compounds in a relatively short time, a process referred to as combinatorial chemistry. In this technique, one part of a molecule is maintained, as different chemical groups are attached to its molecular framework to produce a series of similar molecules with distinct structural variations. Combinatorial libraries of these molecular variants are thus created.

Every chemical that is synthesized must be tested for biological activity. **In vitro** testing involves biological assays outside a living system. For example, if the desired effect of a drug is to inhibit a particular enzyme, the enzyme can be isolated from an organ and studied in a test tube. New technologies have made it possible to assay large numbers of compounds in a short period. High-throughput drug screening allows pharmaceutical chemists to test between 1,000 and 100,000 chemicals in a single day! A compound that demonstrates some biological activity will undergo further tests, or it may be chemically modified to enhance its activity. As a consequence, chemical libraries consisting of potentially therapeutic compounds are developed. Each of these compounds can then serve as leads for the development of new drugs to be screened.

in vitro: Latin, meaning "in glass" and applied to experiments done under artificial conditions, that is, in a test tube

Once a drug shows promise in vitro as a therapeutic agent, it must also be screened for toxic properties. Adverse drug side effects are often due to the interaction of the drug with biological molecules other than the desired target. It is very rare that a drug interacts with only one type of molecule in a living system. Drug selectivity refers to the ability of the compound to interact with its target, not with other proteins or enzymes in the system. To investigate drug toxicity, animal studies are performed. These studies also estimate mutagenicity, that is, whether the compound under investigation damages genetic material.

Rarely does a drug pass through a biological system unchanged. Most drugs undergo chemical transformations (in a process known as drug **metabolism**) before they are **excreted** from the body. The drug transformation products (**metabolites**) must be identified so that their toxicological profiles can be determined.

metabolism: the complete range of biochemical processes that take place within living organisms; comprises processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those that break down complex food molecules, thus liberating energy (catabolism)

excrete: to eliminate or discharge from a living entity

metabolites: products of biological activity that are important in metabolism

Since the 1970s more attention has been given to drug formulation and methods of drug delivery. Historically, drugs have been administered orally, as a pill or a liquid, or in an injectable form. The goal of drug-delivery systems is to enable controlled and targeted drug release. Today, many medications are commonly introduced as inhalants or in a time-release formulation, either encapsulated in a biodegradable polymer or by means of a transdermal patch.

Once scientists and government regulatory agencies have determined the drug candidate to be relatively safe, it can enter into clinical trials. The clinical stage involves four phases of testing on human volunteers. Animal studies and in vitro testing continue during clinical investigations of a drug. Drug-therapy evaluation is very costly and time consuming. Phase I clinical trials evaluate drug tolerance and safety in a small group of healthy adult volunteers. Phase II trials continue to assess the drug's safety and effectiveness in a larger population. Volunteers participating in phase I trials understand that they are receiving experimental therapy. While those patients involved in phase II clinical trials are made aware of the medication and any known side effects, some of the volunteers may be administered a placebo (a compound with no pharmacological activity against the condition being treated) rather than the drug being studied. In a blind study, only the physician administering therapy knows whether the patient is receiving the drug or a placebo. Both groups of patients are monitored, and physicians or clinicians evaluate whether there is significant improvement in the condition of the group receiving the experimental drug, compared with those individuals who were administered a placebo. In a double-blind study, neither the physician nor the patient knows whether the drug, a placebo, or a related remedy has been administered. Therapy is monitored by an outside group.

Phase III and phase IV clinical trials involve larger populations. During phase III trials, which can last two to eight years, a drug is often brought to market. Phase IV studies continue after the drug is being marketed.

The field of pharmaceutical chemistry is diverse and involves many areas of expertise. Natural-product and analytical chemists isolate and identify active components from plant and other natural sources. Theoretical chemists construct molecular models of existing drugs to evaluate their properties.

These computational studies help medicinal chemists and bioengineers design and synthesize compounds with enhanced biological activity. Pharmaceutical chemists evaluate the bioactivity of drugs and drug metabolites. Toxicologists assess drug safety and potential adverse effects of drug therapy. When a drug has been approved for human studies, clinicians and physicians monitor patients' response to treatment with the new drug. The impact of pharmaceutical chemistry on the normal human life span and on the quality of life enjoyed by most people is hard to overestimate. SEE ALSO COMBINATORIAL CHEMISTRY; COMPUTATIONAL CHEMISTRY; MOLECULAR MODELING.

Nanette M. Wachter

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Phospholipids

Phospholipids are an important class of biomolecules. Phospholipids are the fundamental building blocks of cellular membranes and are the major part of **surfactant**, the film that occupies the air/liquid interfaces in the lung. These molecules consist of a polar or charged head group and a pair of **nonpolar** fatty acid tails, connected via a glycerol linkage. This combination of polar and nonpolar segments is termed amphiphilic, and the word describes the tendency of these molecules to assemble at interfaces between polar and nonpolar phases.

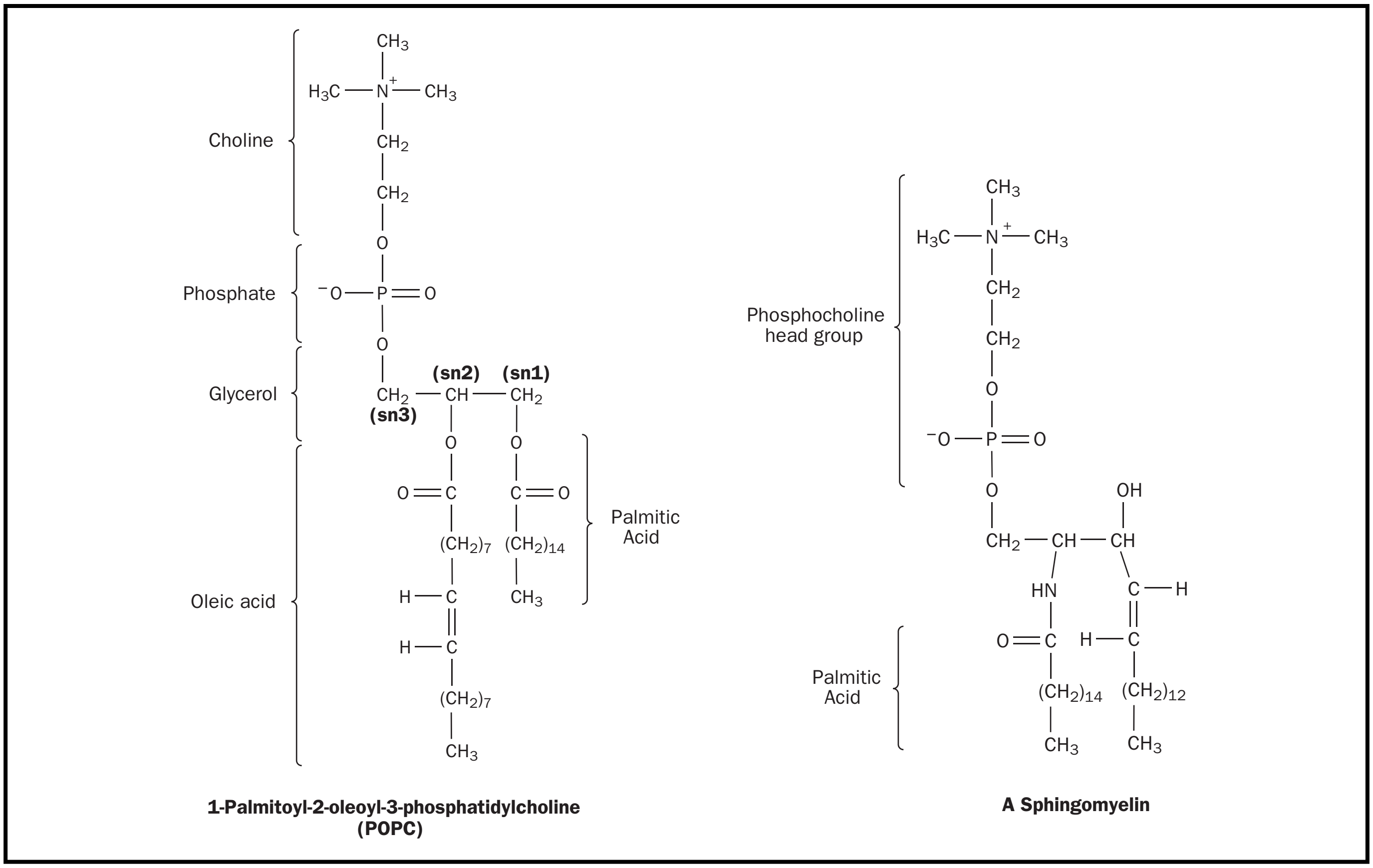
surfactants: surface-active agents that lower the surface tension of water; e.g., detergents, wetting agents

nonpolar: molecule, or portion of a molecule, that does not have a permanent, electric dipole

The structure of the most common class of phospholipids, phosphoglycerides, is based on glycerol, a three-carbon alcohol with the formula $CH_2OH–CHOH–CH_2OH$. Two fatty acid chains, each typically having an even number of carbon atoms between 14 and 20, attach (via a dual **esterification**) to the first and second carbons of the glycerol molecule, denoted as the sn1 and sn2 positions, respectively. The third hydroxyl group of glycerol, at position sn3, reacts with phosphoric acid to form phosphatidate. Common phospholipids, widely distributed in nature, are produced by further reaction of the phosphate group in phosphatidate with an alcohol, such as serine, ethanolamine, choline, glyercol, or inositol. The resulting lipids may be charged, for example, phosphatidyl serine (PS), phosphatidyl inositol (PI), and phosphatidyl glyercol (PG); or dipolar (having separate positively and negatively charged regions), for example, phosphatidyl choline (PC), and phosphatidyl ethanolamine (PE). The term "lecithin" refers to PC-type lipids. A typical phospholipid arrangement is the presence of a saturated fatty acid, such as palmitic or stearic acid, at the sn1 position, and an unsaturated or polyunsaturated fatty acid, such as oleic or arachodonic acid, at sn2 (see Figure 1 for the structure of a phosphoglyceride).

esterification: chemical reaction in which esters (RCO_2R') are formed from alcohols (R_1OH) and carboxylic acids (RCO_2H)

Another class of phospholipids is the sphingolipids. A sphingolipid molecule has the phosphatidyl-based headgroup structure described above, but (in contrast to a common phospholipid molecule) contains a single fatty acid



and a long-chain alcohol as its **hydrophobic** components. Additionally, the backbone of the sphingolipid is sphingosine, an **amino alcohol** (rather than glyercol). The structure of a representative sphingolipid, sphingomyelin, is also shown in Figure 1. Sphingolipids, occurring primarily in nervous tissue, are thought to form cholesterol-rich domains within lipid bilayer membranes that may be important to the functions of some membrane proteins.

Figure 1. The structures of two phospholipids. Structure A represents a classic glycerophospholipid, POPC, and it is composed of choline, phosphate, glycerol, and two fatty acids. Structure B is an example of a sphingomyelin, and it is composed of choline, phosphate, sphingosine, and only one fatty acid.

Phospholipids have many functions in biological systems: as fuels, as membrane structural elements, as signaling agents, and as surfactants. For example, **pulmonary surfactant** is a mixture of lipids (primarily dipalmitoyl phosphatidyl choline [DPPC]) and proteins that controls the surface tension of the fluid lining of the inner lung (the site of gas exchange), allowing rapid expansion and compression of this lining during the breathing cycle. Phospholipids are the major lipid constituent in cell membranes, thus maintaining structural integrity between the cell and its environment and providing boundaries between compartments within the cell. SEE ALSO Lipids; Membrane; Triglycerides.

Scott E. Feller
Ann T. S. Taylor

hydrophobic: part of a molecule that repels water

amino alcohol: an organic molecule that contains both an amino ($-NH_3$) and an alcohol (−OH) functional group.

pulmonary surfactant: The protein-lipid mixture that prevents the collapse of alveoli during expir ation.

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15
P
PHOSPHORUS
30.9738

Phosphorus

MELTING POINT: 44.1°C
BOILING POINT: 280°C
DENSITY: 1.82 g/cm^3
MOST COMMON IONS: PH_4^+, P^{3-}, $H_2PO_3^-$, PO_4^{3-}

The element phosphorus is essential to living organisms. It is part of the backbone of **DNA** (deoxyribonucleic acid), the carrier and transmitter of genetic information in cells. The element and its compounds have many commercial applications.

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

Phosphorus was first isolated by the alchemist Hennig Brand of Hamburg around 1670. He prepared white phosphorus, one of two common forms (allotropes) of the element, by evaporating human urine and strongly heating the residual solids. White phosphorus distilled and was collected under water.

The two common forms of phosphorus are white, which is made up of P_4 molecules, containing four atoms of phosphorus arranged in a regular tetrahedral formation, and red, which is a noncrystalline polymer. White phosphorus glows in the dark and bursts into flame in air. Red phosphorus does not react rapidly with air.

Phosphorus makes up about 0.12 percent of Earth's crust. It is extracted from minerals that contain phosphate (PO_4^{3-}) groups. Large deposits of such minerals, of which the most important is fluorapatite, $Ca_5F(PO_4)_3$, are found in the United States, Morocco, Russia, and Tunisia. At the present rate of extraction, the known deposits of phosphate rock would be sufficient to supply the world's demand for phosphorus for the next 1,000 years.

More than 90 percent of commercial phosphorus production is in the form of calcium salts of phosphoric acid, H_3PO_4, used as fertilizers. Other significant uses of phosphorus compounds are in the manufacture of matches (phosphorus sulfides), food products and beverages (purified phosphoric acid and its salts), detergents (sodium polyphosphates), plasticizers for polymers (**esters** of phosphoric acid), and pesticides (derivatives of phosphoric acid). Related to the phosphorus pesticides are nerve gases, poisonous compounds that rapidly attack the central nervous system, initially developed during World War II. SEE ALSO Deoxyribonucleic Acid (DNA); Fertilizer; Pesticides.

ester: organic species containing a carbon atom attached to three moieties: an O via a double bond, an O attached to another carbon atom or chain, and a H atom or C chain; the R(C═O)OR functional group

Harold Goldwhite

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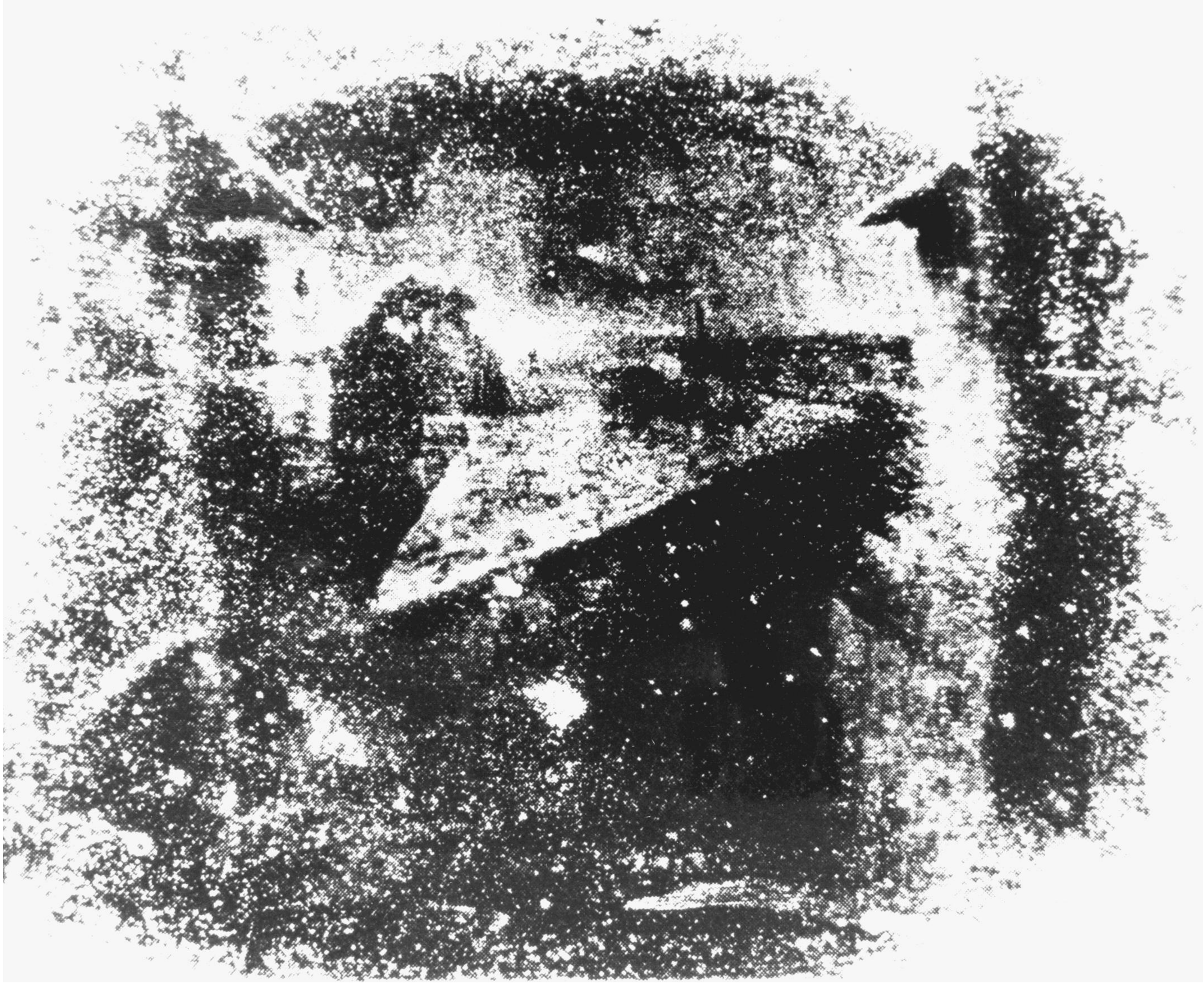
Photography

It has long been known that certain substances, when illuminated, undergo permanent visible changes. In the early part of the nineteenth century, these materials were sometimes used to make "photogenic drawings," for exam-



The first known photograph, made in 1826. It shows the courtyard outside the room of Joseph-Nicéphore Niepce.

ple, by exposing them to sunlight through patterned masks. The most light-sensitive compounds are silver salts, and the photography that prospered in the second half of the nineteenth and throughout the twentieth century was based almost entirely on the use of silver halides.

Early Photography

Practical photographic processes were devised in the 1830s by Louis-Jacques-Mandé Daguerre in France and by William Henry Fox Talbot in England. In Daguerre's method, a silver iodide-coated silver plate was exposed to light in a camera, whereby the exposed silver iodide was decomposed to metallic silver and iodine. A clear image was obtained by treating the plate with mercury vapor (which amalgamated the silver) and by rinsing it in a strong salt solution to remove the remaining silver iodide. A positive image could be viewed by holding this "Daguerreotype" in oblique lighting with a dark background, so that the amalgamated silver zones appeared bright and the silver plate appeared dark.

Talbot's procedure consisted of washing paper successively in baths of saltwater and silver nitrate solution, thus depositing silver chloride in the fibers of the paper. The still wet paper was then exposed in a camera until a dark silver image appeared in the light-struck regions, and the remaining silver chloride was removed by washing with a concentrated salt solution or a sodium thiosulfate solution. By waxing or oiling the negative sheet, Talbot made the paper transparent, and then by making an exposure of diffuse light through the negative onto another sensitized sheet, he produced a positive image. An unlimited number of copies of a photograph could thus be made from any one negative.

Improvements in Talbot's Method

Both Daguerre's and Talbot's methods were inconvenient because they required long exposures in the camera—sometimes as long as 60 minutes. In 1840 Talbot greatly improved his process. He found that a very short camera exposure (about 1/60 of that required to give a visible image) left an invisible "latent" image on the sensitized paper. The latent image was then "developed" into a visible image by treatment with a solution of gallic acid and silver nitrate. This modification, together with the negative/positive feature, made Talbot's process so superior that it has survived, in its general form, to the present day. The main difference between Talbot's process and modern photographic practice is that now the silver halide, in the form of approximately micron-sized crystals or "grains," is suspended in gelatin. The gelatin emulsion is coated as a thin film on glass plates or flexible sheets of plastic or paper.

Mechanism of the Photographic Process

When a photon is absorbed by a silver halide grain, an electron is ejected from a halide ion and temporarily held at some site in the crystal. A silver ion can migrate to the site and combine with the electron to form a silver atom. The atom is not stable; it can decompose back into a silver ion and a free electron. However, during its lifetime, the atom can trap a second electron if one becomes available. If this second electron remains trapped until the arrival of a second silver ion, a two-atom cluster forms. This buildup of a silver cluster can continue as long as photoelectrons are available. The smallest cluster corresponding to a stable latent image speck is believed to consist of three or four silver atoms. Specks of this size or greater on the crystal surface can catalyze the subsequent action of a developer.

Classic Processing

A common, well-established procedure for making photographic prints is as follows:

1. Exposure of the sensitive material, usually a gelatin emulsion of silver halides on a cellulose acetate film, in the camera.

2. Development in the darkroom by treating the film with a solution of organic reducing agents such as hydroquinone and N-methyl paraaminophenol. The reagents reduce to metallic silver those silver halide crystals that acquired latent-image silver clusters. The brighter the subject of a photograph, the

darker is the image that forms in this development, so that one obtains a negative picture.

3."Fixing" the image so that the film will not darken on further exposure to light. This is accomplished by dissolving the undeveloped silver halide grains in a solution of sodium thiosulfate:

$$AgBr + 2S_20_3{}^{2-} \longrightarrow Ag(S_20_3)_2{}^{3-}\ Br^-$$

4. Washing away the dissolved silver salts and drying the negative.

5. Printing, that is, shining diffuse light through the negative onto a sheet of sensitive photographic paper (a gelatin emulsion on paper).

6. Darkroom development of the exposed paper using developer solution much like that used in the film development step. This step produces a positive image, in which the tones are like those in the original scene.

7. Fixing, washing, and drying the print as in the analogous film processing steps.

Reversal Processing

Transparencies, or photographic prints on a transparent base, can be produced essentially as paper prints are, but with replacement of the photographic paper by photographic film. This procedure can be used for making motion picture films. However, positive transparencies are more easily prepared by reversal processing, in which the final image is formed on the same film as that used in the original exposure. Typical reversal processing is as follows:

1. Exposure of the film in the camera.
2. Development of the negative image.
3. Dissolution of the developed silver image by treatment with an oxidizing agent.
4. Exposure of the remaining silver halide to light or to a chemical fogging agent.
5. Development of the silver halide, producing a positive image.
6. Washing and drying of the film.

Reversal processing can also be accomplished using the Sabatier effect, in which the emulsion is given a brief exposure to diffuse light in the midst of development. Some emulsions, when subjected to very intense camera exposure, will yield a positive image by ordinary development—a process referred to as overexposure solarization.

Spectral Sensitization

The silver halides are sensitive mainly to blue, violet, and ultraviolet light; hence, without sensitization, positive photographs reproduce all other colors as dark grays or blacks. However, by the addition of certain dyes to the emulsion, increased sensitivity to the other colors is obtained. Thus, "panchromatic" films, in which sensitivity is extended throughout the visible spectrum, are possible, and the resulting photographs are much more realistic than those obtained using old-fashioned red-insensitive films.

Color Photography

The sensitization of emulsions to the three primary colors (blue, green, and red) is essential to conventional color photography. A common method for producing color prints uses a film containing three superimposed layers, each sensitive to one of the three primary colors. In the initial development, the deposition of silver is accompanied by the formations of a dye color complementary to the color sensitivity of the film layer. After removal of the silver and silver halides from all three layers, the image seen through the three layers is complementary in color to that of the original scene, that is, a color negative. This negative is then used to print a positive copy onto paper with similar layered emulsions, and development proceeds analogously to that of the film.

Instant Photography

In 1947 Edwin H. Land devised a diffusion transfer process for obtaining positive paper prints rapidly in the Polaroid Land camera. The negative is developed in the presence of a solvent for silver halides, which not only develops the negative, but also dissolves the nondeveloped silver halides. The silver halides dissolved out of the negative sheet are developed into an adjacent sheet (containing nuclei for development) to give a positive image. This principle was applied to color photography in the 1960s.

Digital Photography

Silver halide-based photography is being rapidly displaced by so-called digital photography, involving special cameras that contain no film, but rather charge-coupled devices (CCDs), consisting of rectangular arrays of millions of minute light sensors. Under exposure to light, each sensor produces an electric charge, and the enormous amount of information thereby produced (charge as a function of sensor position) is stored electronically as digital data in the camera. The CCD array can be reused indefinitely, the only limitation on the number of possible exposures being the amount of information that can be stored in the camera. However, this information can be downloaded from the memory bank of the camera to a computer, and the image can later be manipulated and printed out, for example, with an ink jet printer, a laser printer, or a dye sublimation printer. The CCD arrays are monochrome devices, but when combined with color filter arrays, they provide blue, green, and red data and thus yield color pictures.

W. L. Jolly

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Photosynthesis

No chemical process is more important to life on Earth than **photosynthesis**—the series of chemical reactions that allow plants to harvest sunlight and create carbohydrate molecules. Without photosynthesis, not only would there be no plants, the planet could not sustain life of any kind. In plants, photosynthesis occurs in the **thykaloid membrane** system of chloroplasts. Many of the enzymes that allow photosynthesis to occur are transmembrane proteins embedded in the thykaloid membranes. What then is the chemistry involved?

photosynthesis: process by which plants convert carbon dioxide and water to glucose

thykaloid membrane: part of a plant that absorbs light and passes the energy on to where it is needed

The most basic summary of the photosynthesis process can be shown with a net chemical equation

$$6CO_2(g) + 6\ H_2O(l) + h\nu \longrightarrow C_6H_{12}O_6(s) + 6O_2(g)$$

The symbol $h\nu$ is used to depict the energy input from light (in the case of most plants, sunlight). This chemical equation, however, is a dramatic simplification of the very complicated series of chemical reactions that photosynthesis involves. It also implies that the only product is **glucose**, $C_6H_{12}O_6$ (s), which is also a simplification.

glucose: common hexose monosaccharide; monomer of starch and cellulose; also called grape sugar, blood sugar, or dextrose

Still, take a moment to look at this chemical equation. If one were to guess where the various atoms in the reactants end up when products are produced, it would be reasonable to suggest that the oxygen atoms in the O_2 (g) were those originally associated with carbon dioxide. Most scientists believed this to be true until the 1930s when experiments by American biologist Cornelius van Niel suggested that oxygen-**hydrogen bonds** in water must be broken in photosynthesis. Further research confirmed his hypothesis and ultimately revealed that many reactions are involved in photosynthesis.

hydrogen bond: interaction between H atoms on one molecule and lone pair electrons on another molecule that constitutes hydrogen bonding

There are two major components of photosynthesis: the light cycle and the dark cycle. As implied by these names, the reactions in the light cycle require energy input from sunlight (or some artificial light source) to take place. The reactions in the dark cycle do not have to take place in the dark, but they can progress when sunlight is not present.

The critical step of the light cycle is the absorption of electromagnet radiation by a pigment molecule. The most famous pigment is **chlorophyll**, but other molecules, such as β-carotene, also absorb light (see Figure 1). Together, these pigment molecules form a type of light harvesting antennae that is more efficient at interacting with sunlight than would be possible with

chlorophyll: active molecules in plants undergoing photosynthesis

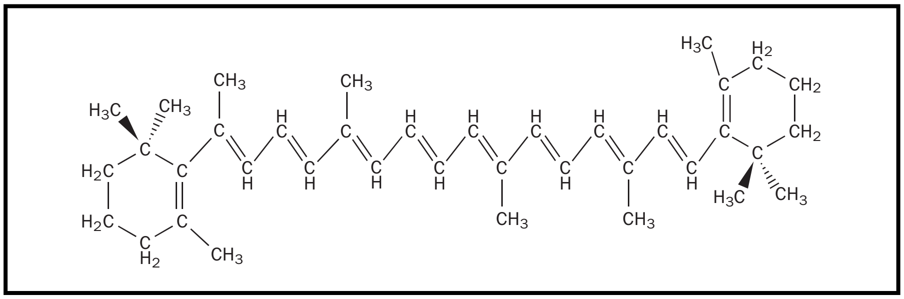

Figure 1a. Structure of β-carotene.

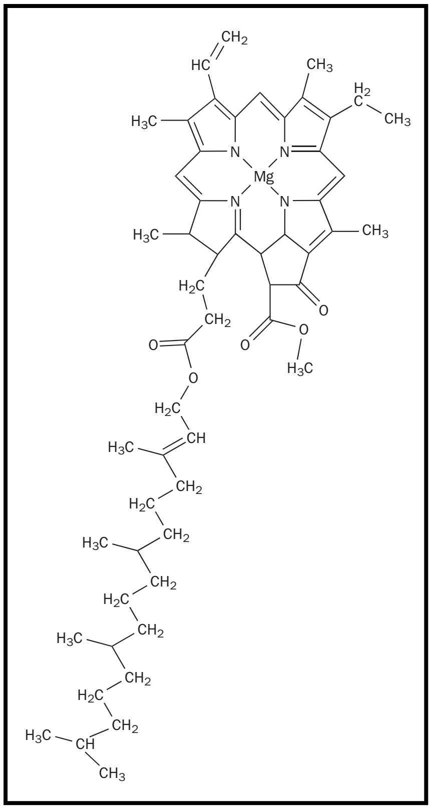

Figure 1b. Structure of GAP.

adenine: one of the purine bases found in nucleic acids, $C_5H_5N_5$

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

photon: a quantum of electromagnetic energy

synthesis: combination of starting materials to form a desired product

the pigments acting alone. When the light is absorbed, electrons in the pigment molecule are excited to high energy states. A series of enzymes called electron transport systems help channel the energy present in these electrons into reactions that store it in chemical bonds.

For example, one major chemical reaction that results from the absorbed light energy (and excited electrons) involves water and nicotinamide **adenine** dinucleotide phosphate ($NADP^+$). The net reaction is shown by the chemical equation

$$2\ NADP^+ + 2\ H_2O \rightarrow NADPH + O_2 + 2H^+$$

This is an example of an **oxidation**–reduction reaction, and it shows that the light cycle is the stage of photosynthesis when water breaks up. The amount of energy required to make this reaction proceed is greater than what can be provided by a single **photon** of visible light. Therefore, there must be at least two ways that plants harvest light energy in photosynthesis. These two systems are referred to as photosystem I (PSI) and photosystem II (PSII), although the numbers associated with these names do not imply which one happens “first.”

At the same time that NADPH is being produced, the combination of the photo systems also produces a concentration gradient of protons. Enzymes in the cell use this proton gradient to produce ATP from ADP. Thus, the light cycle produces two “high energy” molecules: NADPH and ATP.

With the high energy products provided by the light cycle, plants then use reactions that do not require light to actually produce carbohydrates. The initial steps in the dark cycle are collectively called the Calvin cycle, named after American chemist Melvin Calvin who along with his coworkers determined the nature of these reactions during the late 1940s and early 1950s.

The Calvin cycle essentially has two stages. In the first part of the cycle, several enzymes act in concert to produce a molecule called glyceraldehyde-3-phosphate (GAP). (See Figure 2). Note in the illustration that this molecule has three carbon atoms. Each of these carbon atoms comes originally from carbon dioxide molecules—so photosynthesis completes the amazing task of manufacturing carbohydrates out of air (the source of the carbon dioxide). This stage of the Calvin cycle is sometimes called carbon fixing. In order to carry out this **synthesis** of GAP, the Calvin cycle consumes some of the NADPH and ATP that was produced during the light cycle.

The carbon dioxide needed for this step enters through pores in the photosynthetic leaf (called stromata). Plants close these pores during hot, dry times of the day (to prevent water loss) so the details of carbon fixing vary for plants from different climates. In hot climates, where stomata are closed for a higher percentage of time, the trapping of carbon dioxide has to be more efficient than in cooler climates. This biochemical difference in photosynthesis helps explain why plants from one climate do not grow as well in warmer (or cooler) places.

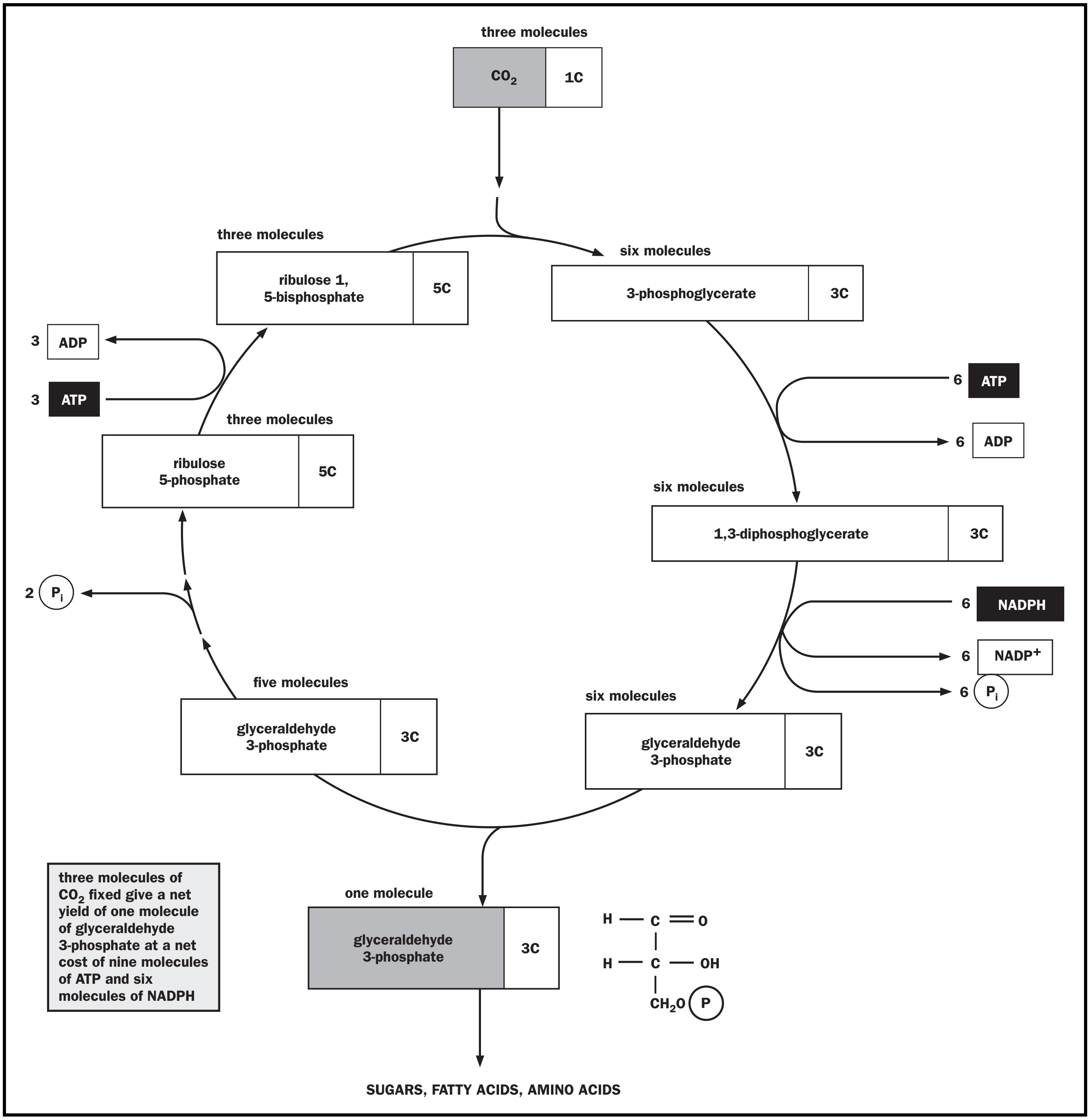

Figure 2. The Calvin cycle.

The second stage of the cycle builds even larger carbohydrate molecules. With more than half a dozen enzyme-catalyzed reactions in this portion of the dark cycle, five- and six-carbon carbohydrates are produced. The five-carbon molecules continue in the cycle to help produce additional GAP, thus perpetuating the cyclic process.

Photosynthesis is central to all life on the planet and has been for many thousands of years. As a result, there are numerous variations in the way it occurs in different cells. The efficient collection of carbon dioxide mentioned earlier is one example of variation in photosynthesis. Other differences occur when the process takes place in bacteria rather than plants. Nonetheless, the description provided here outlines the basic concepts that would be noted in all photosynthesis. These differences pose the research questions that continue to challenge scientists today. SEE ALSO CALVIN, MELVIN; CONCENTRATION GRADIENT.

Thomas A. Holme

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Physical Chemistry

Physical chemistry is the branch of chemistry concerned with the interpretation of the phenomena of chemistry in terms of the underlying principles of physics. It lies at the interface of chemistry and physics, inasmuch as it draws on the principles of physics (especially quantum mechanics) to account for the phenomena of chemistry. It is also an essential component of the interpretation of the techniques of investigation and their findings, particularly because these techniques are becoming ever more sophisticated and because their full potential can be realized only by strong theoretical backing. Physical chemistry also has an essential role to play in the understanding of the complex processes and molecules characteristic of biological systems and modern materials.

Hot water is vaporizing as it is thrown into air that is −37.2°C (−35°F).

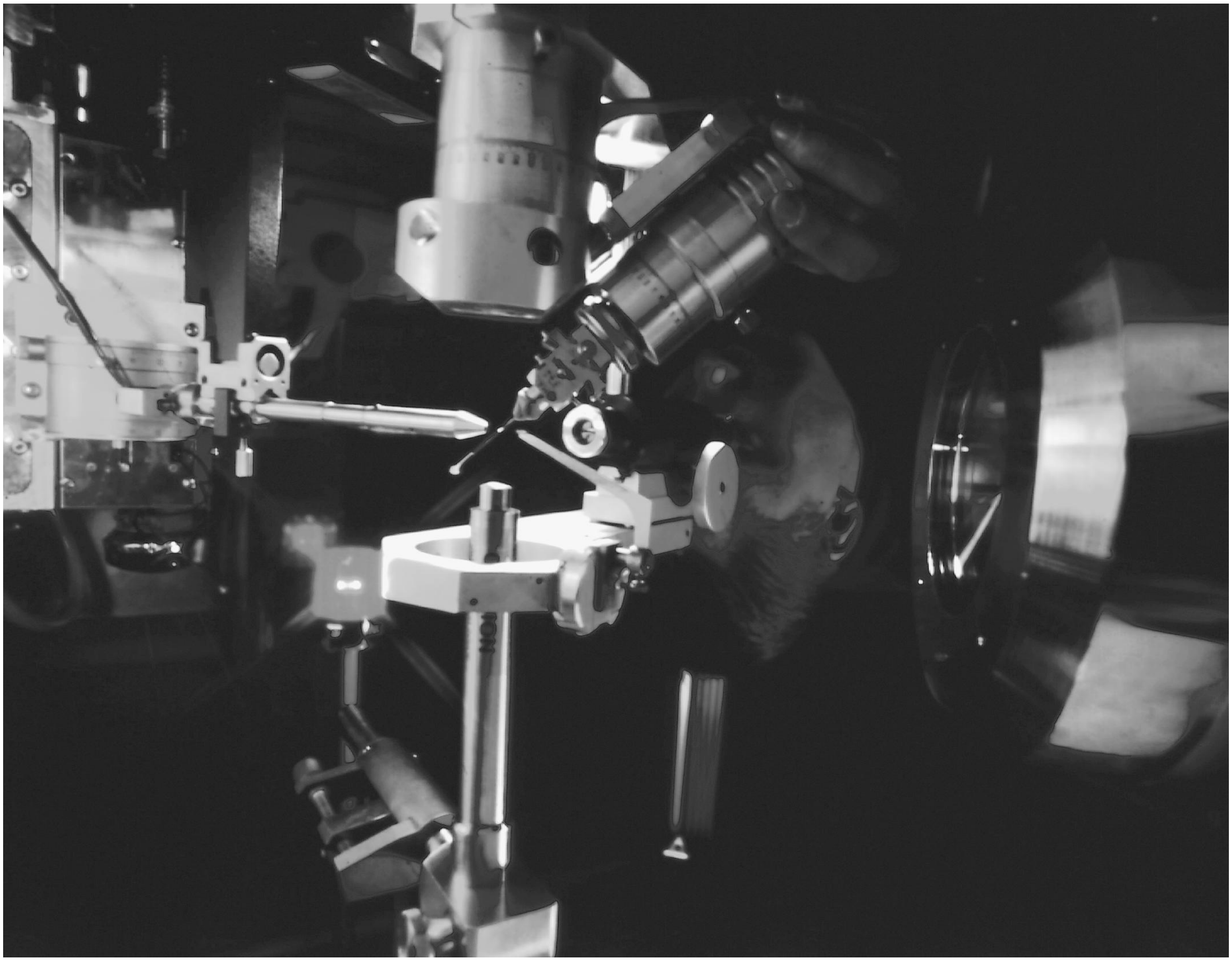
Physical chemistry is traditionally divided into a number of disciplines, but the boundaries between them are imprecise. Thermodynamics is the study of transformations of energy. Although this study might seem remote from chemistry, in fact it is vital to the study of how chemical reactions yield work and heat. Thermodynamic techniques and analyses are also used to elucidate the tendency of physical processes (such as vaporization) and chemical reactions to reach **equilibrium**—the condition when there is no further net tendency to change. Thermodynamics is used to relate bulk properties of substances to each other, so that measurements of one may be used to deduce the value of another. **Spectroscopy** is concerned with the experimental investigation of the structures of atoms and molecules, and the identification of substances, by the observation of properties of the electromagnetic radiation absorbed, emitted, or scattered by samples. Microwave spectroscopy is used to monitor the rotations of molecules; infrared spectroscopy is used to study their vibrations; and visible and ultraviolet spectroscopy is used to study electronic transitions and to infer details of electronic structures. The enormously powerful technique of nuclear magnetic resonance is now ubiquitous in chemistry. The detailed, quantitative interpretation of molecular and solid-state structure is based in quantum theory and its use in the interpretation of the nature of the chemical bond. Diffraction studies, particularly x-ray diffraction and neutron diffraction studies, provide detailed information about the shapes of molecules, and x-ray diffraction studies are central to almost the whole of molecular biology. The scattering of neutrons, in inelastic neutron scattering, gives detailed information about the motion of molecules in liquids. The bridge between thermodynamics and structural studies is called statistical thermodynamics, in which bulk properties of substances are interpreted in terms of the properties of their constituent molecules. Another major component is chemical kinetics, the study of the rates of chemical reactions; it examines, for example, how rates of reactions respond to changes in conditions or the presence of a **catalyst**. Chemical kinetics is also concerned with the detailed mechanisms by which a reaction takes place, the sequences of elementary processes that convert reactants into products, including chemical reactions at solid surfaces (such as electrodes).

equilibrium: condition in which two opposite reactions are occurring at the same speed, so that concentrations of products and reactants do not change

spectroscopy: use of electromagnetic radiation to analyze the chemical composition of materials

catalyst: substance that aids in a reaction while retaining its own chemical identity

There are further subdivisions of these major fields. Thermochemistry is a branch of thermodynamics; its focus is the heat generated or required by chemical reactions. Electrochemistry is the study of how chemical reactions can produce electricity and how electricity can drive chemical reactions in "reverse" directions (electrolysis). Increasingly, attention is shifting from equilibrium electrochemistry (which is of crucial importance in interpreting the phenomena of inorganic chemistry) to dynamic electrochemistry, in which the rates of electron-transfer processes are the focus. Chemical kinetics has divisions that are based on the rates of reaction being studied. Special techniques for studying atomic and molecular processes on ever shorter time scales are being developed, and physical chemists are now able to explore reactions on a femtosecond (10^{-15} second) timescale. Chemical kinetics studies are theoretical as well as experimental. One goal is to understand the course of reactions in step-by-step (and atomic) detail. Techniques are available that allow investigators to study collisions between individual molecules.



X-ray diffraction gives detailed information about shapes of molecules and is the basis of molecular biology.

Physical chemistry is essential to understanding the other branches of chemistry. It provides a basis for understanding the thermodynamic influences (principally, the entropy changes accompanying reactions) that drive chemical reactions forward. It provides justifications for the schemes proposed in organic chemistry to predict and account for the reactions of organic compounds. It accounts for the structures and properties of **transition metal** complexes, **organometallic compounds**, the microporous materials known as zeolites that are so important for **catalysis**, and biological macromolecules, such as proteins and nucleic acids (including **DNA**). It is fair to say that there is no branch of chemistry (including biochemistry) that can be fully understood without interpretations provided by physical chemistry.

There is a distinction between physical chemistry and chemical physics, although the distinction is hard to define and it is not always made. In physical chemistry, the target of investigation is typically a bulk system. In chemical physics, the target is commonly an isolated, individual molecule.

Theoretical chemistry is a branch of physical chemistry in which quantum mechanics and statistical mechanics are used to calculate properties of

transition metals: elements with valence electrons in d-sublevels; frequently characterized as metals having the ability to form more than one cation

organometallic compound: compound containing both a metal (transition) and one or more organic moieties

catalysis: the action or effect of a substance in increasing the rate of a reaction without itself being converted

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

molecules and bulk systems. The greater part of activity in quantum chemistry, as the former is commonly termed, is the computation of the electronic structures of molecules and, often, their graphical representation. This kind of study is particularly important to the screening of compounds for potential pharmacological activity, and for establishing the mode of action of enzymes. SEE ALSO Catalysis and Catalysts; Electrochemistry; Equilibrium; Kinetics; Quantum Chemistry; Spectroscopy; Theoretical Chemistry; Thermodynamics.

Peter Atkins

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Pigments

Pigments and dyes are called colorants. The ways in which colorants are used determines whether they are pigments or dyes. Pigments are water- and oil-insoluble natural and synthetic products that impart color to materials such as paper and plastics. Dyes, by contrast, are water-soluble colorants, although some are converted into insoluble lake pigments by coprecipitating onto an inorganic base. Artists' colors are pigments that are spread on a surface suspended in a suitable medium, such as oil. The mass coloration of textile fibers, polymers, plastics, and rubber takes place when pigments exist in the form of dispersions. A convenient way of classifying pigments is into organic and inorganic pigments.

Pigments are used in the production of paint to add color.

Organic Pigments

Natural organic pigments were used in cave paintings and for decoration from the earliest times. The ancient Britons obtained indigo from the woad plant *Isatis tinctoria*, and used the extract to color their bodies. Here the insoluble blue is used as a pigment rather than as a dye. Other organic pigments found in nature include **chlorophyll**, the green coloring matter of leaves responsible for **photosynthesis**, and heme, which gives blood its red color and, when bound to proteins in hemoglobin, transports oxygen around the body. These biochemical pigments are members of the **porphyrin** family.

chlorophyll: active molecules in plants undergoing photosynthesis

photosynthesis: process by which plants convert carbon dioxide and water to glucose

porphyrin: common type of heterocyclic ligand that has four five-member rings with a nitrogen, all of which lie in a plane; nitrogen atom lone pairs are available for coordinate covalent bonds

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

During the early 1930s synthetic organic pigments, called phthalocyanines, were developed in Britain and manufactured by Imperial Chemical Industries (ICI). Academic researchers showed that phthalocyanines are coordination complexes that mimic the structures of porphyrins. The coordination concept, involving groups of atoms called chelates attached to a central **metal**, was developed beginning in 1893 by the Swiss chemist Alfred Werner and confirmed in 1911, when he collaborated in Zurich with Victor L. King, later a leading technical expert in the U.S. colorant industry. Phthalocyanines represent the only structurally novel class of synthetic colorants invented in the twentieth century. Copper phthalocyanine, known as Monastral blue, and its congeners are used in automobile finishes, printing inks, and plastics.

Lake pigments made from the first synthetic dyes, such as mauve, were used during the 1860s for printing postage stamps and wallpaper. Red lake pigments, such as that derived from the madder dye, or after 1870 from synthetic dyes, were highly regarded by the Impressionist painters. Other synthetic organic pigments are made from azo dyes, those containing the $-N{=}N-$atomic grouping, introduced during the 1870s. The use of synthetic organic pigments in printing inks increased perhaps threefold in the last two decades of the twentieth century, as color became the norm in newspapers, magazines, advertising, and packaging. Careful standardization of the **microcrystalline** form, the crystal habit, is required for pigments employed in printing inks and paints. In order to add color to synthetic polymers, the plastics and resins, pigments are mixed in bulk with other chemicals during the manufacturing process.

microcrystalline: relating to the structure of crystals of very small size, typically a micron (μm) in a dimension

Inorganic Pigments

Ultramarine, or lazurite, is a natural blue pigment derived from lapis lazuli, a semiprecious mineral of the sodalite group, found in Afghanistan. From around 1000 C.E. it was used as a pigment for illumination and later in murals and paintings. In 1271, the explorer Marco Polo visited the site where it was found. Artificial ultramarine, a blue pigment of variable composition, became available in Europe during the late eighteenth and nineteenth centuries. The German poet and dramatist Johann Wolfgang von Goethe, who was interested in color, visited one of the factories in 1787. Although the natural and synthetic forms of ultramarine are chemically similar, they differ in their particle forms. Prussian blue, iron hexacyanoferrate (III) or **ferric** ferrocyanide, is a synthetic dark blue pigment discovered in Berlin in 1704. It was originally made from animal matter, including blood, and the salts of iron.

ferric: older name for iron in the +3 oxidation state

Chromium pigments followed the discovery of the element in a rare Siberian mineral by the French chemist Louis-Nicolas Vauquelin in 1797. Lead chromate gives yellows and oranges, including chrome yellow, invented in 1809, and extensively used by artists, though often modified by addition of other ingredients. Also in 1809 George Field in England produced the dye lemon yellow, based on barium chromate.

Lead has been known and used since ancient times, in part because of the ease with which it can be isolated in the free state. It was converted into the dense pigment white lead (lead carbonate), an essential component of artists' palettes, including the Italian masters of the Renaissance. In the past lead was often used in white paint for the external protection of homes. However, lead is a toxic metal that induces swelling of the brain (lead encephalophy), and causes madness and death. Young children are particularly susceptible to its scourge. In 1910 the pioneer of American industrial hygiene, Alice Hamilton, selected as her first assignment at the Bureau of Labor an investigation of conditions in the white lead industry. Lead-based paints fell out of favor during the 1950s and were banned by the federal government during the 1970s. In modern paints, the toxic lead has been replaced by titanium dioxide.

Theories of Color

Color arises from the way in which colorants interact with light. Colored organic compounds contain groups of atoms whose bonds are unsaturated, such as C=C, C=O, and N=N. These are part of an extended **delocalized** system of electrons called a **chromophore**. A sequence of alternating double bonds through which the electrons are spread is termed a conjugated system. The presence of salt-forming groups of atoms such as −OH and NH_2 modify the color. They are called auxochromes and contain lone pairs of electrons that become part of the delocalized electron system. The nomenclature is based on the first successful theory of color and constitution, that of German chemist Otto N. Witt.

delocalized: of a type of electron that can be shared by more than one orbital or atom

chromophore: part of the molecule that yields characteristic colors

Colored inorganic compounds often contain **transition metals** in which the *d* **subshell** of electrons is split by attached groups, the **ligands**. The extent of this splitting is responsible for the color. The **oxidation** state of metals also affects the *d* electrons and determines color. When absorbed light brings about the transfer of an electron from the ground state of an atom to the excited state of a nearby atom, the process is electron or charge transfer. This accounts for the colors of Prussian blue and chrome yellow.

transition metals: elements with valence electrons in d-sublevels; frequently characterized as metals having the ability to form more than one cation

subshell: electron energy sublevel, of which there are four: s, p, d, and f

ligand: molecule or ion capable of donating one or more electron pairs to a Lewis acid

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

Although pigments have been associated with artists' paints, printing inks, and the coloration of synthetic polymers, they are also used in electronics and telecommunications, for the absorption of light, especially at semiconductor wavelengths, and in ink-jet printers, in addition to xerography (electrophotography) and thermography. SEE ALSO DYES; PERKIN, WILLIAM HENRY; WERNER, ALFRED.

Anthony S. Travis

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Planck, Max

GERMAN PHYSICIST
1858–1947

German physicist Max Karl Ernst Ludwig Planck, recipient of the 1918 Nobel Prize in physics, "in recognition of the services he rendered to the advancement of Physics by his discovery of energy quanta."

Max Karl Ernst Ludwig Planck was born into a family of lawyers and clergymen, and he became the fourth generation of university professors from his family. As a child, he exhibited considerable talent in mathematics, music, and philology (the scientific study of language). By 1874, when he entered the University of Munich, the sixteen-year-old Planck had decided to study mathematics. Very quickly, however, he became interested in physics and the application of mathematics to the physical world. The university's professor of physics, Philip von Jolly, discouraged the young student from studying physics because—as Jolly told him—it was very nearly a closed subject with little left to discover. Luckily, Planck disregarded his professor's advice.

Planck also studied at the University of Berlin with such notable physicists as Gustav Kirchhoff, whom he thought brilliant, but a dry and boring teacher. He also became familiar with the thermodynamics research of Rudolf Clausius, and in 1879 Planck received his Ph.D. from the University of Munich, only three months after his twenty-first birthday. His dissertation explored the second law of thermodynamics.

After holding posts at the universities of Munich and Kiel, Planck succeeded Kirchhoff at the University of Berlin in 1888 after the latter's death. Planck continued his research in thermodynamics, including attempts to connect heat with the Scottish physicist James Clerk Maxwell's theory of electromagnetic radiation. He also addressed a problem suggested by Kirchhoff, who had earlier established that the energy of radiation emitted by a blackbody depends on temperature and the frequency of the radiation.

A blackbody is any object that absorbs all the radiation falling on its surface. Thus, it appears black. A perfect absorber, a blackbody is also a perfect emitter of radiation, and Kirchhoff had challenged physicists to find the mathematical equation relating the energy to temperature and frequency.

The German physicist Wilhelm Wien had proposed such an equation, which worked well only for high frequencies, and Lord Rayleigh (born John William Strutt) proposed another equation, which worked well only at low frequencies. In 1900 Planck was able to develop a single expression that combined these two earlier equations and accurately predicted the energy over the entire range of frequencies.

Subsequently, Planck tried to provide a theoretical basis for his equation. He found that to do so, it was necessary to reject the idea from classical physics that electromagnetic radiation is wavelike and continuous and instead to make the bold assumption that it is particle-like and discrete. Planck assumed that radiation can occur in discrete packets of energy, which Albert Einstein called "quanta." This radical idea is expressed in the equation

$$E = h\nu$$

in which the energy E is directly proportional to the frequency v, and the proportionality constant h, now known as Planck's constant, has the value 6.62×10^{-34} joule per second.

Planck's revolutionary idea about energy provided the basis for Einstein's explanation of the photoelectric effect in 1906 and for the Danish physicist Niels Bohr's atomic model of the hydrogen atom in 1913. Their success, in turn, lent support to Planck's theories, for which he received the Nobel Prize in physics in 1918. In the mid-1920s the combination of Planck's ideas about the particle-like nature of electromagnetic radiation and French physicist Louis de Broglie's hypothesis of the wavelike nature of electrons led to the formulation of quantum mechanics, which is still the accepted theory for the behavior of matter at atomic and subatomic levels.

By the second decade of the twentieth century, Planck was less active in quantum theory research, taking on, in addition to his teaching responsibilities, various administrative duties, including the presidency of the Kaiser Wilhelm Gesellschaft during the years 1930 through 1937 and again after World War II from 1945 until 1946. Planck suffered many personal losses during this part of his life. His first wife died in 1909; his elder son was killed in World War I; and his two daughters both died in childbirth during the early part of the century. In World War II his younger son was executed after being accused of helping plot the assassination of Adolf Hitler, and his home and library were destroyed by Allied bombing. Planck spent the last few years of his life in Göttingen, living long enough to witness the establishment of the Max Planck Gessellschaft from the earlier Kaiser Wilhelm Gesellschaft, to which he had devoted so much of his professional life. SEE ALSO Bohr, Niels; de Broglie, Louis; Einstein, Albert; Maxwell, James Clerk.

Richard E. Rice

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Plastics

The term "plastic" can be broadly defined as any inherently formless material that can be molded or modeled under heat and/or pressure. It is derived from the Greek word *plastikos*, meaning a shaped or molded substance.

The term "plastics" first included only natural polymers—usually animal proteins (horn and tortoise shell), tree resins, or insect secretions called shellac—that were subsequently mixed with fillers such as wood flour to yield substances having better molding properties. (A polymer, from the Greek word *poly*, meaning "many," and *mer* meaning "unit," is a molecule with an extremely high molecular weight.)

The use of natural polymers to make plastic products started as early as 1760, when Enoch Noyes opened a business making combs out of keratin and albuminoid organic proteins derived from animal horns and horse hoofs. However, the first commercially successful plastic material, celluloid, would not come about for another hundred years.

In the 1840s German chemist Christian Schönbein developed cellulose nitrate from a mixture of cotton, nitric acid, and sulfuric acid. Cellulose nitrate is a highly flammable doughlike substance primarily used in the manufacture of explosives. Schönbein's innovation represents the beginning of the modification of natural polymers by chemists so as to increase their processibility and functionality. Cellulose nitrate's properties as a molding substance interested other scientists of the time, and in 1855 an Englishman named Alexander Parkes developed a form of cellulose nitrate he named Parkesine. From this material, Parkes manufactured a number of buttons, pens, medallions, and combs. In 1862 he displayed this material officially at the Great International Exhibit in London. Parkes made small commercial gains with Parkesine and eventually sold the rights to Daniel Spill, who subsequently began production of the substance under the names Xylonite and Ivoride, around 1865. Spill received British patents for Xylonite and Ivoride in 1867 and 1869, respectively.

At around the same time in the United States, a billiard ball company advertised a $10,000 reward for the discovery of an alternate material to ivory. John Wesley Hyatt developed collodion, a mixture of cellulose nitrate and alcohol. Like cellulose nitrate, collodion was highly flammable and would produce a small explosion upon agitation. Hyatt reported: "[W]e had a letter from a billiard saloon proprietor in Colorado mentioning this fact . . . saying he did not care so much about it, but that instantly every man in the room pulled a gun." To avoid melee, camphor, a derivative of the laurel tree, was added, and in 1870 Hyatt received a U.S. patent for celluloid. In 1871 Hyatt and his brother Isaiah formed the American Celluloid Company, which is today the Plastics Division of the Celanese Corporation.

A more common perception of plastic is that it is a synthetic or man-made material, with highly engineered properties and product designs. Dr. Leo Baekeland engineered the first totally synthetic plastic in 1907. Patented in 1909 and named Bakelite after its inventor, the material was the first thermoset plastic. The term "thermoset" refers to a plastic that under initial heat and pressure can be molded into form. After cooling, the material sets and cannot be remelted or re-formed. This setting is due to the cross-linking of polymer chains, wherein strong covalent bonds form between separate oligomers, short chains of polymer units called monomers. The most common thermoset resin is vulcanized rubber, created by Charles Goodyear in the United States in 1839. Vulcanized rubber utilizes natural hevea rubber made from the gutta percha tree, and therefore is not totally synthetic (like Bakelite). Ironically, the first use of Bakelite was as a replacement for

HERMAN MARK (1895–1992)

The influence of Herman Mark, the so-called father of polymer science, on the plastics industry still echoes today in a legacy of education and research. His work in the 1920s on the structure of cellulose opened the door for the development of synthetic fibers such as acrylic, nylon, polyester, polystyrene, and PVC.

—Valerie Borek

natural rubber in electrical insulations. Bakelite is formed via the reaction of phenol and formaldehyde under high heat. Initially, formaldehyde is added to the reaction mixture in small amounts (forming a resin); the mixture is then poured into a mold, into which more formaldehyde is added; and pressure is applied to create the final product.

Over the next several decades, many varieties of synthetic thermoplastic materials would be developed in Germany, England, and the United States. Thermoplastic materials such as vinyls, nylons, and acrylics are polymers that can be molded or formed under heat and pressure, and if necessary can be reheated and re-formed (and will retain most of their original mechanical properties).

Eugen Baumann created today's most common vinyl, polyvinyl chloride (PVC), in 1872. However, Friedrich Heinrich August Klatte did not patent it until 1913. At that time PVC was not well received, as illustrated by Waldo Semon's comment, "People thought of PVC as worthless back then; they would throw it in the trash." Semon was responsible for creating plasticized PVC. He had been attempting to dehydrohalogenate PVC in a high boiling solvent when he realized that the molten material was exhibiting greater flexibility and elasticity. The exposure of PVC to a boiling solvent introduced a plasticizer, or low molecular weight molecule, to the PVC matrix. Today plasticizers are commonly added to polymers (especially PVC) to enhance flexibility, prevent stress cracking, and enhance processability. This has enabled the use of PVC in diverse commercial applications, including the manufacture of rigid tubing and flexible car seats.

In 1920 German scientist Hermann Staudinger published his theories on polyaddition polymerization, the formation of long-chain molecules. (Previously, the manner in which long-chain molecules were formed was unexplained.) Nine years later, in a publication that detailed the polymerization of styrene, this method of chain formation would be laid out. During this time period Staudinger developed polystyrene into a commercial product. A division of the German chemical company IG Farben, known as Badische Anilin- und Soda-Fabrik, or BASF, produced polystyrene in 1930. The Dow Chemical Company introduced the American public to polystyrene in 1937.

In 1928 directors at E. I. du Pont de Nemours & Company (Du Pont) placed Dr. Wallace H. Carothers in charge of fundamental research into what are now classic studies on the formation of polymer chains. During his years at Du Pont, Carothers published his theory on polycondensation, and discovered both neoprene and nylon.

Nylon, not publicly announced until 1938, was first used for bristles on combs, but made headlines in 1939 when nylon stockings debuted at the World's Fair in New York City. Nylon is known by its chemical name, poly(hexamethylene) adipamide, but more often simply as nylon. The first nylon manufacturing plant went into production at Seaford, Delaware, in 1940. Commercial production of nylon 6 by IG Farben in Germany began in 1941. These two plants would go on to produce millions of pounds of nylon annually. This mass production was essential to the World War II effort, as nylon was used for everything from belts, ropes, and straps to tents and parachutes.

Another polymer that came into use during World War II was polytetrafluoroethylene (PTFE), which received the trademark Teflon. Dr. Roy J. Plunkett and his assistant Jack Rebock at Du Pont discovered PTFE accidentally on April 6, 1938. They had been conducting research on alternate refrigeration methods when they discovered the polymerization of tetrafluoroethylene. Plunkett received a patent for PTFE in 1941. It was found that the material was resistant to corrosion by all the solvents, acids, and bases that were available for testing at that time. This led to the U.S. military's interest in PTFE, and its subsequent use as a cover for proximity fuses on the nose cones of artillery shells. It was not until the material was declassified in 1946 that the public learned of the material Du Pont had named Teflon two years earlier. Teflon has since become a household name; its best-known use being its contribution to nonstick surfaces on pots and pans.

Today's most widely produced and perhaps most versatile plastic, polyethylene, was discovered at the Imperial Chemical Industries (ICI) in England in 1933. E. W. Fawcett and R. O. Gibson set off a reaction between ethylene and benzaldehyde under 2,000 atmospheres of pressure, resulting in the polymerization of ethylene and the birth of polyethylene. By 1936, ICI had developed a larger volume compressor that made the production of useful quantities of polyethylene possible. Among polyethylene's first applications were its uses as underwater cable coatings and as insulation for radar during World War II.

In 1943, Karl Ziegler began work that would drastically alter the production of polyethylene. Ziegler used organometallic compounds, which have both metallic and organic components, as catalysts. At very modest pressures, these catalysts generated a linear, more rigid, high molecular weight polyethylene, and the innovation increased the number of the polymer's applications. Today polyethylene is used in the production of detergent bottles and children's toys, and is even replacing Kevlar as a bulletproof material.

In 1957, at the Montecatini Laboratories in Italy, Giulio Natta continued the work of Ziegler and used what is now termed Ziegler–Natta polymerization to create polypropylene. When Natta reported the polymerization of ethylene with a titanocene catalyst, it became clear that polymer chains with specific tacticities, or specific ordered structures, were possible. Polypropylene rose to become a substitute for polyethylene in products in which slightly higher temperature stability was necessary, for example, dishwasher-safe cups and plates.

Polycarbonate, a popular plastic used originally to make eyeglass lenses, was first discovered by A. Einhorn in 1898. But it would be more than fifty years before further research was performed on the material. In the 1950s Dr. Herman Schnell, working at Bayer, a division of IG Farben, along with Daniel Fox of General Electric's Corporate Laboratory in Schenectady, New York, conducted concurrent research on the synthesis of polycarbonate. Schnell and Fox each achieved a polymerization that produced polycarbonate via different methods, and received patents in 1954 and 1955, respectively. Upon his achievement of polymerization, Fox described his attempts to remove the newly formed polymer from the reaction vessel: "The remnants of the glass were broken away to yield a hemispherical, glass fragment embedded, glob of plastic on the end of a steel stirrer shaft. The glob was pounded on the cement floor and struck with a hammer in abortive attempts to remove the remaining glass, and/or, shatter the plastic. The pseudo plastic mallet was even used to drive nails into wood." That glob would eventually be developed into bulletproof glass and provide General Electric and Bayer with billions of dollars in revenue.

Means to improve the material properties of plastics have been sought for decades. Improvement has sometimes come in the form of compounds such as mineral fillers, antioxidants, and flame-retardants. One of the first searches for an improved material was centered on cellulose nitrate. Cellulose nitrate is colorless and transparent, which enabled it to be used as photographic film. However, it is extremely flammable, and its early use in motion picture film and concomitant exposure to hot lights led to numerous fires. In 1900, Henri Dreyfus substituted acetic acid for nitric acid in the synthesis of cellulose nitrate, and created instead a less flammable material, cellulose acetate. Today, polymers are often halogenated in order to achieve flame-retardation.

Plastics have been designed to be chemically resistant, stable compounds, and have been extremely successful in these regards. In fact, they have been so successful that an environmental problem has been created. Plastic products discarded in landfills decay slowly. They sometimes contain heavy metal additives. In addition, the millions of pounds of plastic discarded annually have engendered a crisis over landfill space. In the early 1980s plastic recycling programs began to spring up across the United States in response to the large number of polyethylene terephthalate (PET or PETE) bottles being discarded. In 1989, 235 million pounds of PET bottles were recycled. The number rose to 1.5 billion pounds in 1999.

Most plastics can be recycled. Even mixed plastic waste can be recycled into artificial lumber or particleboard. Plastic "wood" is easy to saw, and it has better resistance to adverse weather and insects than real wood. SEE ALSO Baekeland, Leo; Carothers, Wallace; Goodyear, Charles; Staudinger, Hermann; Nylon; Polymers, Synthetic.

Paul E. Koch

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metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Platinum

MELTING POINT: **1,739°C**
BOILING POINT: **4,170°C**
DENSITY: **21.45 g/cm^3**
MOST COMMON IONS: **Pt^{2+}, $Pt(Cl)_6^{2-}$, $Pt(CN)_4^{2-}$, $Pt(CN)_6^{2-}$**

78
Pt
PLATINUM
195.09

The first reports of the discovery of platinum were the papers of Antonio de Ulloa, who found an unworkable **metal**, *platina* (Spanish for "little silver"), in the gold mines of Colombia in 1736. Charles Wood provided the first samples in 1741. Platinum has a concentration of approximately 10^{-6} percent in Earth's crust. Platinum crystallizes in the face-centered cubic structure. The pure metal is malleable and **ductile**, and lustrous and silvery in appearance. It is capable of absorbing gaseous hydrogen. Platinum is found in nature in alluvial deposits and in association with copper, iron, and nickel sulfide ores. The metal is soluble in aqua regia, isolated as $(NH_4)_2PtCl_6$ from aqua regia, and obtained as a sponge or powder by ignition of $(NH_4)_2PtCl_6$.

ductile: property of a substance that permits it to be drawn into wires

catalyst: substance that aids in a reaction while retaining its own chemical identity

catalysis: the action or effect of a substance in increasing the rate of a reaction without itself being converted

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

Platinum is used as a **catalyst** in a wide variety of chemical reactions. Some of the more common **catalytic** uses are the **oxidation** of organic vapors in automobile exhaust, the oxidation of ammonia in the production of nitric acid, and the rearrangement of atoms in petroleum reforming. Most of the halides are formed by direct combination of the **halogen** elements with platinum, resulting in PtF_6, $[PtF_5]_4$, PtX_4 (where X = F, Cl, Br, or I), and PtX_3 and PtX_2 (where X = Cl, Br, or I). The two oxides, PtO and PtO_2, are unstable and decompose upon heating. In the +2 and +3 oxidation states, platinum forms coordination complexes bonded to carbon, nitrogen, phosphorous, oxygen, and sulfur donor atoms. Perhaps the most well known coordination complex is *cis*-platin, $Pt(NH_3)_2Cl_2$, used in chemotherapy treatments of cancer.

D. Paul Rillema

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94
Pu
PLUTONIUM
244

Plutonium

MELTING POINT: 640°C
BOILING POINT: 3,228°C
DENSITY: 19.84g/cm^3
MOST COMMON IONS: Pu^{3+}, Pu^{4+}, PuO_2^{+}, PuO_2^{2},$^{+}$ PuO_5^{3-}

Plutonium was discovered by Glenn Seaborg, Edwin McMillan, Joseph Kennedy, and Arthur Wahl in 1940. They prepared a new **isotope** of neptunium, ^{238}Np, which decayed by β-emission to ^{238}Pu.

isotope: form of an atom that differs by the number of neutrons in the nucleus

Manhattan Project: government project dedicated to creation of an atomic weapon; directed by General Leslie Groves

$$^{238}U(d,2n)^{238}Np \xrightarrow{\beta-} {}^{238}Pu(t_{1/2} = 87.7y)$$

Their work as part of the **Manhattan Project** was kept secret and was finally reported in 1946, after World War II, although the existence of plutonium had been revealed to the world earlier, when the atomic bomb was dropped over Nagasaki, Japan. There are sixteen isotopes of plutonium, having mass numbers ranging from 232 to 247. The principal isotopes of Pu are those having mass numbers 238, 239, 240, 241, 242, and 244. Ton quantities of ^{239}Pu (having a half-life of 2.4×0^4 y) are available. The isotope ^{239}Pu is the source material for nuclear weapons and is produced via neutron capture reactions on ^{238}U in nuclear reactors.

$$^{238}U(n,\gamma)^{239}U \xrightarrow{\beta-} {}^{239}Np \xrightarrow{\beta-} {}^{239}Pu$$

About 110 tons of ^{239}Pu are generated in nuclear power plants each year, with approximately 40 percent of the energy produced in the nuclear fuel cycle coming from ^{239}Pu. About three times as much electricity is generated from ^{239}Pu in the United States as from oil-fired electrical generating plants. The ground state (outer orbital) electronic configuration of Pu is [Rn]$5f^6 7s^2$. The most stable **oxidation** state for plutonium ions in solution is +4, although appreciable amounts of plutonium in its +3, +5, and +6 oxidation states can exist. The aqueous chemistry of plutonium is further complicated by the successive, stepwise hydrolysis of Pu(IV) compounds to form polymers of colloidal dimensions. Plutonium is the transuranium element that is most abundant in the environment, due to the atmospheric testing of nuclear weapons during the 1950s and 1960s that deposited approximately 4.2 tons of plutonium in the environment. Most of this plutonium is in the soil, in which it has no discernable effects. SEE ALSO Actinium; Berkelium; Einsteinium; Fermium; Lawrencium; Mendelevium; Neptunium; Nobelium; Protactinium; Rutherfordium; Seaborg, Glenn Theodore; Thorium; Uranium.

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

Walter Loveland

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Volume 1

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Volume 2

p. 2: Dalton, John, engraving. The Library of Congress, Prints and Photographs Division; p. 3: Davy, Sir Humphrey, portrait. Corbis-Bettmann. Reproduced with permission; p. 6: Broken egg, photograph by Arthur Beck. Corbis. Reproduced by permission; p. 7: Sunny side up egg, photograph by Japack Company/Corbis. Reproduced by permission; p. 12: Dewar, Sir James, portrait. The Library of Congress; p. 14: A female patient undergoing a cerebral angiography, photograph by Laurent. Photo Researchers. Reproduced by permission; p. 18: Baby wearing a disposable diaper, photograph by Elizabeth Thomason. Copyright © 2003 Elizabeth Thomason. Reproduced by permission; p. 23: DNA, computer graphics, photograph by Clive Freeman. Photo Researchers, Inc. Reproduced by permission; p. 25: Dupont, Eleuthere Irenee, engraving. Archive Photos, Inc. Reproduced by permission; p. 27: Textiles, fabric dyes, photograph by Randy Duchaine. Stock Market. Reproduced by permission; p. 31: Ehrlich, Paul, in laboratory, 1908, photograph. Liaison Agency/Hulton Getty. Reproduced by permission; p. 32: Einstein, Albert, photograph. Archive Photos. Reproduced by permission; p. 40: Hitchings, George, Gertrude Elion, photograph. AP/Wide World. Reproduced by permission; p. 43: Wheelchair racers participating in a marathon in Washington, D.C., photograph by Joe Sohm. Chromosohm/Stock Connection/PictureQuest. Reproduced by permission; p. 45: Electronic display (concentric octagons) of energies from subatomic particles, photograph. Newman Laboratory of Nuclear Science, Cornell University, National Audubon Society Collection/Photo Researchers, Inc. Reproduced by permission; p. 51: Leachate from the Dowelanco plant in Lafayette, Indiana, photograph by Sandra Marquardt. Greenpeace. Reproduced by permission; p. 52: Chemicals being sprayed on agricultural land on the Everglades Park border, Florida, photograph. Earth Scenes/© Arthur Gloor. Reproduced by permission; p. 55: Enzyme, lock-and-key model of interaction, drawing by Hans & Cassidy. Gale Research; p. 58: Chemical reaction, nitric acid, photograph. © LevyYoav/Phototake NYC. Reproduced by permission; p. 69: Reed, Ken and Peter Mckay, taking part in a demonstration against embryonic stem cell research outside of George Washington University Hospital, photograph by Kamenko Pajic. AP/Wide World Photos. Reproduced by permission; p. 70: Harman, Jane, holding up a support sign of stem cell research, at a press conference, outside the Capitol building, in Washington D.C., photograph by Shawn Thew. Getty Images. Reproduced by permission; p. 75: Nuclear explosion at sea, photograph by PHOTRI. Stock Market. Reproduced by permission; p. 78: Engraving of Professor Faraday delivering a lecture at the Royal Institution, London, photograph. © Corbis. Reproduced by permission; p. 86: Fermi, Enrico, photograph. © Bettmann/Corbis. Reproduced by Corbis Corporation; p. 88: Truck applying fertilizer in rice field, photograph by Thomas Del Brase. Stock

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Volume 3

p. 1: Kekule, Friedrich, photograph. Photo Researchers, Inc. Reproduced by permission; p. 3: Kelsey, Frances Oldham, photograph. The Library of Congress; p. 5: Khorana, Har Gobind, photograph. AP/Wide World Photos. Reproduced by permission; p. 8: Acid dehydration of sugar, photograph by David Taylor. Science Photo Library, National Audubon Society Collection/Photo Researchers, Inc. Reproduced by permission; p. 10: Krebs, Hans Adolf, photograph. The Library of Congress; p. 16: Lavoisier, Antoine-Laurent, photograph. The Library of Congress; p. 17: Instruments from Lavoisier's lab, portrait. The Library of Congress; p. 18: Lawrence, Ernest (with atom smasher), photograph. Corbis-Bettmann. Reproduced by permission; p. 23: Le Bel, Joseph Achille, photograph. Photo Researchers, Inc. Reproduced by permission; p. 24: Leblanc, Nicholas, photograph. Bettmann/Corbis. Reproduced by permission; p. 28: Leloir, Luis F., photograph. UPI/Corbis-Bettmann. Reproduced by permission; p. 29: Lewis, Gilbert N., photograph. Corbis-Bettmann. Reproduced by permission; p. 34: Liebig, Justes von, portrait. The Library of Congress; p. 40: Transmission electron micrograph of lipid droplets in a rat fat cell, magnified x 90,000, photograph by David M. Phillips, The Population Council/Photo Researchers, Inc. Reproduced by permission; p. 41: Woman holding a digital fishfinder, photograph. © AFP/Corbis. Reproduced by permission; p. 45: Waterstrider bug, photograph. © Hermann Eisenbeiss, National Audubon Society Collection/Photo Researchers, Inc. Reproduced by permission; p. 46: Liquids, viscosity, photograph. © Yoav Levy/Phototake NYC. Reproduced by permission; p. 48: Lister, Joseph, photograph. © Bettmann/Corbis. Reproduced by permission; p. 50: Lonsdale, Kathleen, photograph. AP/Wide World Photos. Reproduced by permission; p. 52: False-color angiogram showing stenosis in the carotid artery, photograph by Alfred Pasteka. © CNRI/ Science Photo Library, National Audubon Society Collection/Photo Researchers, Inc. Reproduced by permission. p. 56: Bar magnet with iron filings showing field of force (bright blue background), photograph. Grantpix/Photo Researchers, Inc. Reproduced by permission; p. 60: Oppenheimer, J. Robert, 1946, photograph. © Bettmann/Corbis. Reproduced by permission; p. 62: Martin, Archer, photograph by Nick Sinclair. Photo Researchers, Inc. Reproduced by permission; p. 63: Red sports car, photograph. © Royalty Free/Corbis. Reproduced by permission; p. 67: Maxwell, James Clerk, engraving. The Library of Congress; p. 69: Post-mounted sundial in a Bolivian town, photograph. © John Slater/Corbis. Reproduced by permission; p. 72: Teenage girl being weighed on large scale, photograph by Robert J. Huffman. Field Mark Publications. Reproduced by permission; p. 74: Hahn, Otto, standing with Lise Meitner, photograph. Photo Researchers, Inc. Reproduced by permission; p. 77: Mendeleev, Dmitri Ivanovich, in the chemical factory of the University of St. Petersburg, photograph. © Bettmann/Corbis. Reproduced by permission; p. 82: Landfill with aluminum drum for mercury waste, photograph. Recio/Greenpeace. Reproduced by permission; p. 83: Ritalin tablets, photograph. © Photo Researchers, Inc. Reproduced by permission; p. 85: Lothar von Meyer, Julius, photograph. Photo Researchers, Inc. Reproduced by permission; p. 86: Millikan, Robert A., photograph. The Library of Congress; p. 88: Stratas of banded liassic limestone and shale on a seacliff by

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Volume 4

p. 5: Travolta, John, with Karen Lynn Gorney in a scene from "Saturday Night Fever," photograph. The Kobal Collection. Reproduced by permission; p. 12: Ghost crab walking among a sandy shoreline, photograph. Sapelo Island National Estuarine Research Reserve. Reproduced by permission; p. 30: Priestley, Joseph, engraving. International Portrait Gallery; p. 38: Scientist adjusts equipment used in fast protein liquid chromatography, photograph. Photo Researchers, Inc. Reproduced by permission; p. 50: Spectrum of electromagnetic radiation, (chart) illustrations by Robert L. Wolke. Reproduced by permission; p. 52: Radioactive emission of alpha particles from radium, yellow sunburst, dark blue background, photograph. Photo Researchers, Inc. Reproduced by permission; p. 58: International mobile radiological radiologists measuring soil radioactivity levels near Ukraine's Chernobyl Nuclear Plant, wearing protective clothing, from International Mobile Radiological Laboratories, near Chernobyl, Ukraine, photograph. © Reuters NewsMedia Inc./Corbis. Reproduced by permission; p. 60: Radon test kit and carbon monoxide detector, photograph by Robert J. Huffman. Field Mark Publications. Reproduced by permission; p. 63: Ramsay, William, portrait. The Library of Congress; p. 65: Reaction rate, illustration. GALE Group. Studio: EIG; p. 74: Bragg, Kevin, photograph. © James A. Sugar/Corbis. Reproduced by permission; p. 80: Open electric oven showing the glowing red heating element, photograph by Robert J. Huffman. FieldMark Publications. Reproduced by permission; p. 86: Robinson, Robert, portrait. The Library of Congress; p. 89: Captured German V-2 rocket cuts through the clouds during experiment, 1947, photograph. AP/Wide World Photos. Reproduced by permission; p. 90: Full-scale operational model of the Mars Viking Lander, photograph by Lowell Georgia/Corbis. Reproduced by permission; p. 97: Rubidium, photograph. © Russ Lappa/Science Source, National Audubon Society Collection/Photo Researchers, Inc. Reproduced by permission; p. 99: Rutherford, Ernest, Walton (left to right), Ernest Rutherford, and J.D. Cockcroft, standing together outside, photograph. © Hulton-Deutsch Collection/Corbis; p. 103: Large pile of salt at a salt mine, October 29, 1996, Upington, South Africa, photograph. © Charles O'Rear/Corbis; p. 106: Sanger, Frederick looking up at model of DNA molecule, photograph. © Bettmann/Corbis. Reproduced by Corbis Corporation; p. 108: Scheele, Carl Wilhelm, portrait. The Library of Congress; p. 110: Schrodinger, Professor Erwin of Magdalen College, Oxford, winner of the 1933 Nobel Prize in Physics along with Professor P.H.M. Dirac of Cambridge University, England, November 18, 1933, photograph. © Bettmann/Corbis. Reproduced by permission; p. 111: Seaborg, Glenn T., photograph. © Roger Ressmeyer/Corbis. Reproduced by permission; p. 115: Seibert, Florence, photograph. AP/Wide World Photos. Reproduced by permission; p. 116: Dish of selenium, photograph. © Rich

Treptow, National Audubon Society Collection/Photo Researchers, Inc. Reproduced by permission; p. 117: Person holding a conventional tub amplifier, photograph. © Bettmann/Corbis. Reproduced by permission; p. 120: Micro wires, silicon chip, photograph by Andrew Syred. The National Audubon Society Collection/ Photo Researchers, Inc. Reproduced by permission; p. 122: Worker testing silicon wafers at the Matsushita Semiconductor plant in Puyallup, Washington, c. 1994, photograph. © Kevin R. Morris/Corbis. Reproduced by permission; p. 131: Soddy, Frederick, drawing. The Library of Congress; p. 132: Sodium acetate hot pack reacting, photograph by Charles D. Winters. Photo Researchers, Inc. Reproduced by permission; p. 149: Solution of water and oil, droplets are exposed to polarized light, magnification, photograph by David Spears. © Science Pictures Limited/Corbis; p. 154: Electron spectroscopy, chemical analysis, photograph by Joseph Nettis. Photo Researchers, Inc. Reproduced by permission; p. 157: Stanley, Wendell Meredith, photograph. The Library of Congress; p. 159: Staudinger, Hermann, portrait. The Library of Congress; p. 161: Steel worker sampling molten metal, photograph by John Olson. Stock Market. Reproduced by permission; p. 164: Steel Bridge, Portland, Oregon, photograph by James Blank. © James Blank. Reproduced by permission; p. 167: Hand holding 50 mg bottle of the injectable anabolic steroid Durabolin, photograph. Custom Medical Stock Photo. Reproduced by permission; p. 169: Razor blade cutting powder form of the drug Speed into lines for snorting, photograph. Science Photo Library. Reproduced by permission; p. 174: Germinating garden pea Pisum Sativum, showing embryonic root growing downward, macrophotograph, photograph. © J. Burgess/Photo Researchers. Reproduced by permission; p. 176: Rayleigh, 3rd Baron (John W. Strut, III), drawing. The Library of Congress; p. 179: Vat of sulfur, photograph by Farrell Grehan. Corbis. Reproduced by permission; p. 180: Sumner, James B., portrait. The Library of Congress; p. 182: Meissner effect, cube floating above a superconductor, photograph by Yoav Levy. Phototake NYC. Reproduced by permission; p. 187: Scanning tunneling microscope image of sulfur atoms on rhodium surface, photograph by Dr. James Batteas. National Institute of Standards and Technology; p. 187: Topographic image of a reconstructed silicon surface showing outermost atomic positions, photograph of Dr. James Batteas. National Institute of Standards and Technology. Reproduced by permission; p. 189: Infrared near-field scanning optical microscope (NSOM) image of blended polystyrene/polyethylacrylate film on silicon, photograph by f Dr. Chris Michaels and Dr. Stephan Stranick, National Institute of Standards and Technology. Reproduced by permission; p. 189: Nanowriting of a mercaptbenzoic acid layer into a background layer of dodecanethiol using nanografting, photograph by Dr. Jayne Gerano, National Institute of Standards and Technology. Reproduced by permission; p. 191: Tractor riding past wind generators, photograph. © AP/Wide World Photos. Reproduced by permission; p. 192: Cutaway of the ITER tokamak device, photograph. Photo Researchers, Inc. Reproduced by permission; p. 193: Svedberg, Theodor, portrait. The Library of Congress; p. 195: Synge, Richard L.M., photograph. The Library of Congress; p. 198: Organic chemist synthesizing chemotherapy agent, photograph by Geoff Tompkinson. Photo Researchers, Inc. Reproduced by permission; p. 200: Szent-Gyorgyi, Dr. Albert, Nobel Prize winner, discoverer of Vitamin C and bioflavinoids, photograph. © Bettmann/CORBIS. Reproduced by permission; p. 205: Photocopier in office, photograph by Robert J. Huffman. FieldMark Publications. Reproduced by permission; p. 207: © Royalty-Free/Corbis. Reproduced by permission; p. 209: Yendell, Thomas, a Thalidomide baby, picks up a toy with his feet, photograph. AP/Wide World Photos. Reproduced by permission; p. 215: Thallium heart scan, photograph by Peter Berndt, M.D. Custom Medical Stock Photo. Reproduced by permission; p. 226: Thomson, Sir Joseph John, photograph. UPI/Corbis-Bettmann.

Reproduced by permission; p. 227: Man, writing, being flanked by two other men watching. AP/Wide World Photos. Reproduced by permission; p. 228: Army medic, taking an x-ray of a fellow soldier simulating an injury, photograph. © Bettmann/Corbis. Reproduced by permission; p. 236: Stanford Linear Accelerator Center, photograph by David Parler. National Audubon Society Collection/Photo Researchers Inc. Reproduced by permission; p. 241: Alchemist (seated left wearing eyeglasses) and his assistants, engraving. The Granger Collection, New York. Reproduced by permission; p. 244: Computer generated graphic of a molecule of hemoglobin-carrier of oxygen in the blood, photograph. © Science Photo Library. Photo Researchers. Reproduced by permission; p. 249: Urey, Harold, photograph. The Library of Congress; p. 253: Van Der Waals, Johannes Diderik, photograph. Science Photo Library. Photo Researchers, Inc. Reproduced by permission; p. 255: Helmont, Jan (Baptise) Van (standing), print; p. 256: Hoff, Jacobus Henricus vant, photograph. Photo Researchers, Inc. Reproduced by permission; p. 258: Banded gila monster, photograph by Renee Lynn. The National Audubon Society Collection/Photo Researchers, Inc. Reproduced by permission; p. 261: Allesandro Volta, standing, body turned slightly to his left, painting. UPI/Corbis-Bettmann. Reproduced by permission; p. 263: Waksman, Selman A.(in laboratory), photograph. The Library of Congress.; p. 265: Molecular graphic of water molecules evaporating from a solution, photograph. © K. Eward/Photo Researchers. Reproduced by permission; p. 270: Dead fish, killed from water pollution, photograph. © U.S. Fish & Wildlife Service; p. 273: Newly treated water in the Orange County Water Treatment Works, Florida, photograph by Alan Towse. © Ecoscene/CORBIS. Reproduced by permission; p. 275: Watson, Dr. James Dewey, with DNA model, 1962, photograph. UPI/Corbis-Bettmann. Reproduced by permission; p. 277: Werner, Alfred, portrait. The Library of Congress; p. 279: Willstatter, Richard, photograph. Photo Researchers, Inc. Reproduced by permission; p. 280: Wohler, Friedrich, portrait. The Library of Congress; p. 282: Woodward, Robert Burns (standing with unknown man, viewing book), photograph. The Library of Congress; p. 284: Cylindrical map of the eastern half of the surface of Venus, as viewed from the spacecraft Magellan, photograph. NASA/JPL/CALTECH. Reproduced by permission; p. 285: Yalow, Rosalyn, 1978, photograph. Corbis-Bettmann. Reproduced by permission; p. 288: Yukawa, Hideki (holding chalk, pointing to writing on board), photograph. The Library of Congress; p. 293: Kangaroo on the beach in Australia, photograph. © Australian Picture Library/Corbis. Reproduced by permission; p. 294: Zsigmondy, Richard, portrait. The Library of Congress.

Glossary

acetylcholine: neurotransmitter with the chemical formula $C_7H_{17}NO_3$; it assists in communication between nerve cells in the brain and central nervous system

acid rain: precipitation that has a pH lower than 5.6; term coined by R. A. Smith during the 1870s

activation analysis: technique that identifies elements present in a sample by inducing radioactivity through absorbtion of neutrons

adenine: one of the purine bases found in nucleic acids, $C_5H_5N_5$

adenosine triphosphate (ATP): molecule formed by the condensation of adenine, ribose, and triphosphoric acid, HOP(O)OH–O–(O)OH–OP(O)OH–OH; it is a key compound in the mediation of energy in both plants and animals

adrenalin: chemical secreted in the body in response to stress

alchemy: medieval chemical philosophy having among its asserted aims the transmutation of base metals into gold

aldehyde: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the RC(O)H functional group

aliphatic: having carbon atoms in an open chain structure (as an alkane)

aliquot: specific volume of a liquid used in analysis

alkaloid: alkaline nitrogen-based compound extracted from plants

alloy: mixture of two or more elements, at least one of which is a metal

α subunit: subunit that exists in proteins that are composed of several chains of amino acids, the first unit in the "counting" of the units

α-particle: subatomic particle with 2+ charge and mass of 4; a He nucleus

amalgam: metallic alloy of mercury and one or more metals

amine functional group: group in which nitrogen is bound to carbon in an organic molecule in which two other groups or hydrogen atoms are bound to nitrogen; major component of amino acids

amino acid residue: in a protein, which is a polymer composed of many amino acids, that portion of the amino acid that remains to become part of the protein

amino acid sequence: twenty of the more than five hundred amino acids that are known to occur in nature are incorporated into a variety of proteins that are required for life processes; the sequence or order of the amino acids present determines the nature of the protein

amphetamine: class of compounds used to stimulate the central nervous system

anabolism: metabolic process involving building of complex substances from simpler ones, using energy

analgesic: compound that relieves pain, e.g., aspirin

androgen: group of steroids that act as male sex hormones

angiotensin: chemical that causes a narrowing of blood vessels

anhydrous compound: compound with no water associated with it

anion: negatively charged chemical unit, like $Cl-$, $CO_{32}-$, or NO_3-

anthcyanin: antioxidant flavanoid that makes raspberries red and blueberries blue

antibody: protein molecule that recognizes external agents in the body and binds to them as part of the immune response of the body

anticoagulant: molecule that helps prevent the clotting of blood cells

antiscorbutic: substance that has an effect on scurvy

apoenzyme: the protein part of an enzyme that requires a covalently bound coenzyme (a low molecular weight organic compound) or a cofactor (such as a metal ion) for activity

aqueous solution: homogenous mixture in which water is the solvent (primary component)

aromatic: having a double-bonded carbon ring (typified by benzene)

asparagine residue: amino acid asparagine unit as it occurs in a polypeptide chain

atomic mass units: unit used to measure atomic mass; 1/12 of the mass of a carbon-12 atom

atomic number: the number of protons in an atomic nucleus, expressed in terms of electric charge; it is usually denoted by the symbol Z

atomic orbital: mathematical description of the probability of finding an electron around an atom

atomic spectrum: electromagnetic array resulting from excitement of a gaseous atom

atomic theory: concept that asserts that matter is composed of tiny particles called atoms

atomic weight: weight of a single atom of an element in atomic mass units (amu)

attraction: force that brings two bodies together, such as two oppositely charged bodies

axial bond: covalent bond pointing along a molecular axis

azo dye: synthetic organic dye containing a –N=N– group

bacteriophage multiplication: process by which immune system cells responsible for battling bacterial infections reproduce

basal metabolism: the process by which the energy to carry out involuntary, life-sustaining processes is generated.

β subunit: subunit that exists when two or more polypeptide chains associate to form a complex functional protein, the chains are referred to as "subunits"; these subunits are often identified as α, β, etc.

biological stain: dye used to provide contrast among and between cellular moieties

biomass: collection of living matter

biosynthesis: formation of a chemical substance by a living organism

boat conformation: the arrangement of carbon atoms in cyclohexane, C_6H_{12}. In which the spatial placement of the carbon atoms resembles a boat with a bow and a stern

brine: water containing a large amount of salts, especially sodium chloride (NaCl)

Brownian motion: random motion of small particles, such as dust or smoke particles, suspended in a gas or liquid; it is caused by collisions of the particle with gas or solvent molecules which transfer momentum to the particle and cause it to move

calc: calcium carbonate

calcine: to heat or roast to produce an oxide (e.g., CaO from calcite)

capacitor plate: one of several conducting plates, or foils, in a capacitor, separated by thin layers of dielectric constant, an insulating material

carboxylate: structure incorporating the –COO– group

carboxyl group: an organic functional group, –C(O), found in aldehydes, ketones, and carboxyl acids.

carboxylic acid: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the $-CO_2H$ functional group

catabolism: metabolic process involving breakdown of a molecule into smaller ones resulting in a release of energy

catalysis: the action or effect of a substance in increasing the rate of a reaction without itself being converted

catalyst: substance that aids in a reaction while retaining its own chemical identity

catalytic conversion: catalytic oxidation of carbon monoxide and hydrocarbons in automotive exhaust gas to carbon dioxide and water

cell culture: artificially maintained population of cells, grown in a nutrient medium and reproducing by asexual division

cephalosporin C: family of antibiotics obtained from a fungus acting in a manner similar to penicillin

chain of custody: sequence of possession through which evidentiary materials are processed

chair conformation: arrangement of atoms in a cycle structure (usually a six-membered ring) that appears to be arranged like a chair (as opposed to the other conformation which is described as a "boat")

chemical-gated: of a membrane protein whose action to open a pore in the membrane occurs only after a substrate has been binded to the protein or a cofactor

chlorofluorocarbon (CFC): compound containing carbon, chlorine, and fluorine atoms that remove ozone in the upper atmosphere

chlorophyll: active molecules in plants undergoing photosynthesis

chromatography: the separation of the components of a mixture in one phase (the mobile phase) by passing in through another phase (the stationary phase) making use of the extent to which the components are absorbed by the stationary phase

chromophore: part of the molecule that yields characteristic colors

cladding: protective material surrounding a second material, which is frequently tubes filled with uranium dioxide pellets in a nuclear reactor

cleave: split

cobrotoxin: polypeptide toxin containing sixty-two residues that is found in the venom of cobras

code: mechanism to convey information on genes and genetic sequence

cofactor: inorganic component that combines with an apoenzyme to form a complete functioning enzyme

coherent mass: mass of particles that stick together

color fastness: condition characterized by retention of colored moieties from a base material

combustion: burning, the reaction with oxygen

competitive inhibitor: species or substance that slows or stops a chemical reaction

complementarity: basis for copying the genetic information, where each nucleotide base has a complementary partner with which it forms a base-pair

congener: an element or compound belonging to the same class

constitutional isomer: form of a substance that differs by the arrangement of atoms along a molecular backbone

contact activity: process involving the touching of different surfaces

contraction: the shortening of a normal trend of a quantity

coordinate covalent bond: covalent bond in which both of the shared electrons originate on only one of the bonding atoms

coordination chemistry: chemistry involving complexes of metal ions surrounded by covalently bonded ligands

corrosive gas: gas that causes chemical deterioration

covalent bond: bond formed between two atoms that mutually share a pair of electrons

crystal lattice: three-dimensional structure of a crystaline solid

crystallization: process of producing crystals of a substance when a saturated solution in an appropriate solvent is either cooled or some solvent removed by evaporation

culture: living material developed in prepared nutrient media

cyanobacterium: eubacterium sometimes called "the blue-green alga"; it contains chlorophyll (the pigment most abundant in plants), has very strong cell walls, and is capable of photosynthesis

cyclopentadienyl ring: five-membered carbon ring containing two C–C double bonds; formula C_5H_6

cysteine residue: sulfhydryl-containing cysteine unit in a protein molecule

cytosine: heterocyclic, pyrimidine, amine base found in DNA

dedifferentiation: the opposite of the biological process of differentiation by which a relatively unspecialized cell undergoes a progressive change to a more specialized form or function

degradative: relating to or tending to cause decomposition

degrade: to decompose or reduce the complexity of a chemical

delocalized: of a type of electron that can be shared by more than one orbital or atom

denitrification: process of removing nitrogen

density-functional theory: quantum mechanical method to determine ground states

depolarization: process of decreasing the separation of charge in nerve cells; the opposite of hyperpolarization

deterministic: related to the assumption that all events are based on natural laws

deuteron: nucleus containing one proton and one neutron, as is found in the isotope deuterium

dialcohol: organic molecule containing two covalently-bonded –OH groups

diamagnetic: property of a substance that causes it to be repelled by a magnetic field

diamine: compound, the molecules of which incorporate two amino groups (–NH_2) in their structure, such as 1,2 diamino ethane (sometimes called ethylenediamine) and the three diamine benzene compounds

dibasic acid: acidic substance that incorporates two or more acidic hydrogen atoms in one molecule, such as sulfuric (H_2SO_4) and phosphoric (H_3PO_4) acids

dihydroxy compound: compound with molecules that incorporate two hydroxyl groups (–OH) in their structure, such as 1,2 dihydroxy ethane (sometimes called glycol) and the three dihydroxy benzene compounds

directing effect: ability of a functional group to influence the site of chemical reaction, such as substitution, for a molecule

discharge display tube: glass tube containing gas at low pressure through which a beam of electrons is passed

disperse system: two-phase system in which one phase, the disperse phase, is distributed in the second phase, the dispersion medium

disulfide bond: bond in a complex substance that involves two bonding sulfur atoms, –S–S–

disulfide bridge: covalent –S–S– linkage that provides cross-links in protein molecules

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

dope: to add a controlled amount of an impurity to a very pure sample of a substance, which can radically change the properties of a substance

drug resistance: ability to prevent the action of a particular chemical substance

ductile: property of a substance that permits it to be drawn into wires

Eighteen Electron Rule: rule noting that coordination complexes with eighteen electrons are stable; electrons from both metal species and ligand donor species are counted

electrolyte solution: a liquid mixture containing dissolved ions

electron correlation error: quantum mechanical method for studying atoms, ions, or molecules

electronegative: capable of attracting electrons

electrophoresis: migration of charged particles under the influence of an electric field, usually in solution; cations, the positively charged species, will move toward the negative pole and anions, the negatively charged species, will move toward the positive pole

electrostatic interaction: force that arises between electrically charged particles or regions of particles

elemental analysis: determination of the percent of each atom in a specific molecule

emulsifier: substance that stabilizes the formation of an emulsion—normally it contains molecules with both polar and non-polar functional groups

emulsion: immiscible two-phase mixture in which one phase is dispersed (as small droplets) in the other phase

enantiomorphic shape: mixture of molecules with the same molecular formulas but different optical characteristics

endohedral: descriptive term for a point within a three-dimensional figure

endoplasmic reticulum: internal membrane system that forms a net-like array of channels and interconnections of organelles within the cytoplasm of eukaryotic cells

Equation of State for Ideal Gases: mathematical statement relating conditions of pressure, volume, absolute temperature, and amount of substance; $PV = nRT$

equatorial bond: covalent bond perpendicular to a molecular axis

equilibrium: condition in which two opposite reactions are occurring at the same speed, so that concentrations of products and reactants do not change

erythromycin: antibiotic used to treat infections

ester: organic species containing a carbon atom attached to three moieties: an O via a double bond, an O attached to another carbon atom or chain, and an H atom or C chain; the R(C=O)OR functional group

esterification: chemical reaction in which esters (RCO_2R_1) are formed from alcohols (R_1OH) and carboxylic acids (RCO_2R')

estrogen: female sex hormone

eukaryotic cell: cell characterized by membrane-bound organelles, most notably the nucleus, and that possesses chromosomes whose DNA is associated with proteins

excitatory: phenomenon causing cells to become active

excitatory neurotransmitter: molecule that stimulates postsynaptic neurons to transmit impulses

exclusion principle: principle that states that no two electrons can have the same four quantum numbers

excrete: to eliminate or discharge from a living entity

expressed: made to appear; in biochemistry—copied

extracellular matrix: entity surrounding mammalian tissue cells, also called connective tissue; composed of structural proteins, specialized proteins, and proteoglycans

face centered cubic structure: close-packed crystal structure having a cubic unit cell with atoms at the center of each of its six faces

feedstock: mixture of raw materials necessary to carry out chemical reactions

Fermi conduction level: vacant or partially occupied electronic energy level resulting from an array of a large number of atoms in which electrons can freely move

ferric: older name for iron in the +3 oxidation state

ferrous: older name for iron in the +2 oxidation state

fibril: slender fiber or filament

fission: process of splitting of an atom into smaller pieces

fissionable: of or pertaining to unstable nuclei that decay to produce smaller nuclei

5′ end: situation in nucleic acids in which the phosphate group is attached at the fifth carbon atom from where the base is attached

folic acid: pteroylglutamic acid; one of the B complex vitamins

formaldehyde: name given to the simplest aldehyde HC(O)H, incorporating the –C(O)H functional group

fractional distillation: separation of liquid mixtures by collecting separately the distillates at certain temperatures

fulcrum: prop or support to an item as in a lever

functional group: portion of a compound with characteristic atoms acting as a group

galactose: six-carbon sugar

galvanic: relating to direct current electricity, especially when produced chemically

galvanometer: instrument used to detect and measure the strength of an electric current

gas density: weight in grams of a liter of gas

glucocorticoid: class of hormones that promotes the breakdown of proteins to make amino acids available for gluconeogenesis; this elevates the blood sugar level and leads to glycogen synthesis in the liver

glucose: common hexose monosaccharide; monomer of starch and cellulose; also called grape sugar, blood sugar, or dextrose

golgi apparatus: collection of flattened stacks of membranes in the cytoplasm of eukaryotic cells that function in the collection, packaging, and distribution of molecules synthesized in the cell

gram negative: bacteria that do not retain their color when exposed to basic dyes such as crystal violet and then exposed to organic solvents; named after Danish bacteriologist Hans Christian Joachim Gram

gram positive: bacteria that retain their color when exposed to basic dyes such as crystal violet and then exposed to organic solvents; named after Danish bacteriologist Hans Christian Joachim Gram

Gray: unit of radiation dose per second; 1 Gray = 1 J/kg

greenhouse effect: presence of carbon dioxide in the atmosphere prevents heat from escaping, thereby raising Earth's temperature

Griess reagent: solution of sulfanilic acid and a-naphthylamine in acetic acid; reagent for nitrites

guanine: heterocyclic, purine, amine base found in DNA

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

heavy metal: by convention, a metal with a density greater than 5 g/cm^3; 70 elements are thus classified as heavy metals

helix: in the shape of a spiral or coil, such as a corkscrew

heme group: functional group formed by an iron atom interacting with a heterocyclic ligand called a porphyrin

hemiacetal: relating to organic compounds formed from an alcohol and a carbonyl-containing molecule

hemlock: poisonous herb of the genus Conium

Hippocrates: Greek physician of fifth century B.C.E. known as the "father of medicine"

homogeneous: relating to a mixture of the same materials

homogeneous solution: mixture of molecules that forms a single phase (solid, liquid, or gas)

hormonal signaling: collective processes by which hormones circulate in the blood stream to their target organs and trigger the desired responses

hydrogen bonding: intermolecular force between the H of an N–H, O–H or F–H bond and a lone pair on O, N or F of an adjacent molecule

hydrolyze: to react with water

hydrophilic: having an affinity with water

hydrophobic: water repelling

hyperbolic relationship: a geometric system in which two or more lines can be drawn through any point in a plane and not intersect a given line in that plane

hyperpolarization: process of causing an increase in charge separation in nerve cells; opposite of depolarization

hypertension: condition in which blood pressure is abnormally high

Ibn Sina: given name of an Islamic scientist known in the West as Avicenna (979–1037); reputed to be the author of more than 100 books that were Europe's most important medical texts from the 12th century until the 16th century

inert: incapable of reacting with another substance

inhibitory: preventing an action that would normally occur

integro-differential: complex mathematical model used to calculate a phase transition

interface tension: contractile force at the junction of two liquids

intermediate: molecule, often short-lived, that occurs while a chemical reaction progresses but is not present when the reaction is complete

intermolecular force: force that arises between molecules, generally it is at least one order of magnitude weaker than the chemical bonding force

internuclear: distance between two nuclei

intestinal epithelium: layer of cells in the intestines that allows the passage of water and solutes

intramolecular force: force that arises within molecules—essentially the force associated with chemical bonds

invertebrate: category of animal that has no internal skeleton

in vitro: Latin, meaning "in glass" and applied to experiments done under artificial conditions, that is, in a test tube

in vivo: Latin, meaning "in life" and applied to experiments conducted in a living cell or organism

ion exchange chromatography: form of liquid-solid chromatography based on the reversible formation of bonds between the fixed ions bound to an insoluble matrix of an ion exchanger and mobile counter ions present in the liquid phase passing over the insoluble matrix

ionization: dissociation of a molecule into ions carrying + or − charges

isolate: part of a reaction mixture that is separated and contains the material of interest

isomer: molecules with identical compositions but different structural formulas

isoprene: common name for 2-methyl-1,3butadiene, the monomer of the natural rubber polymer

isostructural: relating to an arrangement of atomic constituents that is geometrically the same although different atoms are present

isotope: form of an atom that differs by the number of neutrons in the nucleus

ketone: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the RC(O)R functional group

kinetic theory: theory of molecular motion

Kohlrausch drum: rotating cylinder used to mount a variable resistance slide wire for a polarograph

lanthanides: a family of elements (atomic number 57 through 70) from lanthanum to lutetium having from 1 to 14 4f electrons

lattice: systematic geometrical arrangement of atomic-sized units that describe the structure of a solid

ligand: molecule or ion capable of donating one or more electron pairs to a Lewis acid

lipid: a nonpolar organic molecule; fatlike; one of a large variety of nonpolar hydrophobic (water-hating) molecules that are insoluble in water

lipophilic: a molecule that tends to congregate in solution with lipids—it will be a nonpolar molecule or the nonpolar portion of a molecule

liposome: sac formed from one or more lipid layers that can be used for drug transport to cells in the body

liquefaction: process of changing to a liquid form

locomotor: able to move from place to place

Lucretius: Roman poet of first century B.C.E., also known as Titus Carus; author of *De Rerum Natura*

lysergic acid: one of the Ergot series of alkaloids, which constrict blood vessels so that the victim develops burning sensations in the limbs, gangrene, and, ultimately, convulsions; the diethylamide of this substance (LSD) induces visual perception disorders, delusion

lysis: breakdown of cells; also the favorable termination of a disease

macrolide: substance with a large ring lactone structure

macronutrient: one of a number of substances, needed in relatively large amounts, that provide nourishment for living organisms

macroscopic phenomena: events observed with human vision unassisted by instrumentation

mammalian toxicity: poisonous effect on humans and other mammals

Manhattan Project: government project dedicated to creation of an atomic weapon; directed by General Leslie Groves

manifold of ensemble states: a set of quantum states that meet the specific requirements (such as total energy) being considered in a calculation

mechanical energy: energy of an object due to its position or motion

mediate: to act as an intermediary agent

melting point: temperature at which a substance in the solid state undergoes a phase change to the liquid state

mentorship: the process by which a wise and trusted teacher guides a novice in the development of his/her abilities

metabolism: the complete range of biochemical processes that take place within living organisms; comprises processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those that break down complex food molecules, thus liberating energy (catabolism)

metabolites: products of biological activity that are important in metabolism

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

metal cation: positively charged ion resulting from the loss of one or more valence electrons

metalloenzyme: a protein enzyme that contains at least one metal atom, often in an active site of the protein

metalloid: elements that exhibit properties that are between those of metals and nonmetals; generally considered to include boron, silicon, germanium, arsensic, antimony, tellurium, and polonium

metallothionein: class of low molecular weight proteins and polypeptides with very high metal and sulfur content; thought to play a role in concentration and flow of essential elements, e.g., Cu and Zn, and in ameliorating the influence of toxic elements, e.g., Hg and Cd, in the body

metallurgy: the science and technology of metals

microchemistry: chemical investigation carried out on a microscopic level

microcrystalline: relating to the structure of crystals of very small size, typically a micron (μm) in dimension

micromolar: relating to a solution of a substance that is in the concentration range of micromoles per liter, or 10^{-6} moles per liter

mitochondrial matrix: soluble phase inside the inner mitochondrial membrane containing most of its enzymes

mitosis: process by which cells divide, particularly the division of the cell nucleus

molecular identity: "fingerprint" of a molecule describing the structure

monoclinic: one of several arrangements of atoms found in crystalline solids; characterized by a unit cell of three axes each of a differing length; two axes are mutually perpendicular while the third is at an oblique angle

monodentate: capable of donating one electron pair; literally, one-toothed

monosaccharide: one class of the natural products called carbohydrates with the general formula $C_x(H_2O)_y$; monosaccharides have a weak sweet taste, are readily soluble in water, and are called sugars

mordant dye: dye substance containing an acidic moiety, e.g., a carboxyl group, which binds metallic compounds, forming insoluble colored compounds

natural philosophy: study of nature and the physical universe

nesosilicate: any silicate in which the SiO_4 tetrahedra are not interlinked

net charge: total overall charge

neurologic: of or pertaining to the nervous system

neuropathy: degenerative state of the nerves or nervous system

neuropeptide: neurotransmitter released into the blood stream via nerve cells

neutron activation analysis: method for detecting traces of elements by bombardment with high-flux neutrons and then measuring the decay rate of the radioactive products

Newtonian: based on the physics of Isaac Newton

nicotine adenine dinucleotide (NAD): one compound of a group of coenzymes found in hydrogen-transferring enzymes

nitric oxide: compound, NO, which is involved in many biological processes; the drug Viagra enhances NO-stimulation of pathways to counteract impotence; may be involved in killing tumors

nitrotoluic acid: benzoic acid molecule with methyl and nitro groups attached

noble gas: element characterized by inert nature; located in the rightmost column in the Periodic Table

noncovalent: having a structure in which atoms are not held together by sharing pairs of electrons

noncovalent aggregation: non-specific interaction leading to the association of molecules

nonpolar: molecule, or portion of a molecule, that does not have a permanent, electric dipole

nuclear: (a) having to do with the nucleus of an atom; (b) having to do with the nucleus of a cell

nucleosynthesis: creation of heavier elements from lighter elements via fusion reactions in stars

octahedral: relating to a geometric arrangement of six ligands equally distributed around a Lewis acid; literally, eight faces

odd chain fatty acid: long chain carboxylic acid with an odd number of carbon atoms

oligomeric chain: chain that contains a few repeating units of a growing polymeric species

opioid: naturally produced opium-like substance found in the brain

optically active: capable of rotating the plane of plane-polarized light

organoleptic: effect of a substance on the five senses

organometallic compound: compound containing both a metal (transition) and one or more organic moieties

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

oxidation state zero: condition characterized by an atom having neither lost nor gained electrons

oxidation–reduction reaction: reaction, sometimes called redox, that involves the movement of electrons between reactants to form products

oxide ion conductor: series of oxides of various compounds in perovskite structure—especially of interest in high-temperature fuel cells

parabolic curve: planar curve each point of which is equidistant from a straight line (axis)

paraffin: saturated aliphatic hydrocarbon (alkane), or hydrocarbon wax

partial pressure: portion of a total pressure of a gas mixture contributed by a single type of gas in the sample

passive diffusion: mechanism of transporting solutes across membranes

pasteurization: process of heating foods such as milk to destroy bacteria

peerage: a body of peers; dignitaries of equal standing

perpendicular: condition in which two lines (or linear entities like chemical bonds) intersect at a 90-degree angle

pH effect: effect caused by a change in the concentration of hydrogen ions

phase: homogenous state of matter

phenol: common name for hydroxybenzene (C_6H_5OH)

phosphorylation: the addition of phosphates into biological molecules

photodiode assembly: grouping of electronic devices which includes a photodiode—a photodetector; useful in medical diagnostics, bar code readers, and guidance systems

photon: a quantum of electromagnetic energy

photosynthesis: process by which plants convert carbon dioxide and water to glucose

physostigmine: alkaloid derived from the leaves of the Calabar bean, formula $C_{15}H_{12}N_3O_2$; salts used for anticholinesterase activity

pilot plant: intermediate stage of testing for chemical process, between bench-top and production scale

planar complex: arrangement of atoms in which all atoms lie within a common two-dimensional plane

plane polorized light: electromagnetic radiation (light) in which the electric (or magnetic) vectors are all vibrating in the same plane

platelet: smallest noncellular component of human blood

pneumatic chemist: early chemist who studied primarily the properties of gases

polynucleotide synthesis: formation of DNA or RNA

polypeptide: compound containing two or more amide units—C(O)NH—produced by the condensation of two or more amino acids

porphyrin: common type of heterocyclic ligand that has four five-member rings with a nitrogen, all of which lie in a plane; nitrogen atom lone pairs are available for coordinate covelent bonds

postsynaptic neuron: receptor nerve cell

potash: the compound potassium oxide, K_2O

precipitation: process of separating a solid substance out of a solution

precursor molecule: molecule that is the chosen starting point for the preparation of another molecule; a starting molecule in a chemical synthesis; a reactant molecule

primary electrochemical cell: voltaic cell based on an irreversible chemical reaction

principal oxidation state: oxidation state that is most important

prism: triangular-shaped material made from quartz or glass used to diffract light

prodrug: precursor of a drug that is converted into an active form by a metabolic process

progesterone: steroid found in the female reproductive system; formula $C_{21}H_{30}O_2$

prokaryotic: relating to very simple cells of the type found in bacteria

propagating: reproducing; disseminating; increasing; extending

protecting group: substance added to a functional group of a molecule preventing further reaction until the substance is removed by subsequent reactions

proximate percent: nearest percent of a population (e.g. people, substances)

purine base: one of two types of nitrogen bases found in nucleic acids

putative: commonly believed or hypothesized

pyramidal: relating to a geometric arrangement of four electron-donating groups at the four vertices of a pyramid

pyrimidine base: one of two types of nitrogen bases found in nucleic acids

pyruvate: anion of pyruvic acid produced by the reaction of oxygen with lactic acid after strenuous exercise

quantum: smallest amount of a physical quantity that can exist independently, especially a discrete amount of electromagnetic energy

quantum mechanical: theoretical model to describe atoms and molecules by wave functions

quantum physics: physics based on the fact that the energy of an electron is equal to its frequency times Planck's constant

radioactive decay: process involving emission of subatomic particles from a nucleus, typically accompanied by emission of very short wavelength electromagnetic radiation

radioelement: a radioactive element; one in which the nucleus spontaneously decomposes (decays) producing α (alpha) and β (beta) particles and γ (gamma) rays

rare earth elements: older name for the lanthanide series of elements, from lanthanum to lutetium

rate-limiting step: slowest step in a complex reaction; it determines the rate of the overall reaction; sometimes called the rate-determining step

reagent: chemical used to cause a specific chemical reaction

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

reducing agent: substance that causes reduction, a process during which electrons are lost (or hydrogen atoms gained)

reducing potential: stored energy capable of making a chemical reduction occur

relativistic calculation: quantum mechanical model that includes the effects of relativity, particularly for core electrons

repulsive force: force that repels two bodies; charges of the same sign repel each other

reserpine: one of a group of alkaloids found naturally in the shrub *Rarewolfia serpentina*; has been used for centuries to treat hypertension, insomnia, and mental disorders; more recently it has been used to reduce blood pressure

retardation: to slow down a chemical reaction

retrosynthetic analysis: method of analyzing chemical reactions that starts with the product and works backward to determine the initial reactants

reverberator furnace: furnace or kiln used in smelting that heats material indirectly by deflecting a nearby flame downward from the roof

ribosome: large complex of proteins used to convert amino acids into proteins

RNA: ribonucleic acid, a natural polymer used to translate genetic information in the nucleus into a template for the construction of proteins

RNA polymerase: enzyme used to make RNA using DNA as a template

rough endoplasmic reticulum: regions of endoplasmic reticulum the outer surfaces of which are heavily studded with ribosomes, which make proteins for activities within membrane-bounded organelles

Royal Society: The U.K. National Academy of Science, founded in 1660

rutile: common name of TiO_2; also a common structural type for compounds with the general composition AB_2

saltpeter: potassium nitrate; chile saltpeter is sodium nitrate

screen: process of comparing multiple reagents simultaneously to provide information on reaction of one reagent with another

seed germination: beginning of the process by which a seed produces a new plant

selenium toxicity: condition created by intake of excess selenium (Se) from plants or seleniferous water; acute and chronic toxicity are known

semisynthetic: produced by synthesis from natural starting materials

serology: the study of serum and reactions taking place within it

sigma plus pi bonding: formation of a double bond within a molecule or ion

single Slater determinant: wave function used to describe atoms and molecules

size of the basis set: number of relatively simple mathematical functions (called the basis set) used to represent a more complicated mathematical function such as an atomic orbital

smelting: process by which ores are reduced in the production of metals

Socrates: Greek philosopher, c.470–399 B.C.E.

somatic cell: cells of the body with the exception of germ cells

spectral line: line in a spectrum representing radiation of a single wavelength

spectroscopy: use of electromagnetic radiation to analyze the chemical composition of materials

spinel: name given to a group of minerals that are double oxides of divalent and trivalent metals, for example, $MgO \cdot Al_2O_3$ or $MgAl_2O_4$; this mineral is called spinel; also a structural type

stacking interactions: one type of interaction that affects conformation of double-stranded DNA; caused by van der Waals forces

stereospecific: yielding one product when reacted with a given compound but the opposite product when reacted with its stereoisomer

steric repulsion: repulsive force that exists when two atoms or groups get too close together

sterol: steroid containing an alcohol group; derived from plants or animals; e.g., cholesterol

stigmasterol: sterol found in soybeans, $C_{29}H_{48}O$

stratosphere: layer of the atmosphere where ozone is found; starts about 6.2 mi (10 km) above ground

streptomycin: antibiotic produced by soil bacteria of genus *Streptomyces*

subcritical: mass of nuclear materials below the amount necessary to cause a chain reaction

subshell: electron energy sublevel, of which there are four: *s*, *p*, *d*, and *f*

sulfonamides: first of a series of drugs used for the prevention and cure of bacterial infections in humans; sulfanomides are amides of sulfuric acids and contain the $-SO_2NRR_1$ group

super-heavy elements: elements of atomic number greater than 103

superhelix: helical-shaped molecule synthesized by another helical-shaped molecule

surfactants: surface-active agents that lower the surface tension of water; e.g., detergents, wetting agents

synaptic cleft: tiny space between the terminal button of one neuron and the dendrite or soma of another

synthesis: combination of starting materials to form a desired product

synthon: in retrosynthesis, molecules are broken into characteristic sections called synthons

tetrachloride: term that implies a molecule has four chlorine atoms present

tetravalent oxidation state: bonding state of an atom that can form four bonds

theoretical physics: branch of physics dealing with the theories and concepts of matter, especially at the atomic and subatomic levels

3′ end: situation in nucleic acids in which the phosphate group is attached at the third carbon atom from where the base is attached

thykaloid membrane: part of a plant that absorbs light and passes the energy on to where it is needed

thymine: one of the four bases that make up a DNA molecule

toluic acids: methylbenzoic acids

torsion balance: instrument used to measure small forces (weights), based upon the resistance of a wire to be twisted

toxicology: division of pharmacology dealing with poisons, their identification, detection, effects on the body, and remedies

toxin: poisonous substance produced during bacterial growth

trace element: element occurring only in a minute amount

transcription: enzyme-catalyzed assembly of an RNA molecule complementary to a strand of DNA

transition metal complex: species formed when a transition metal reacts with ions or molecules, including water

transition metals: elements with valence electrons in d-sublevels; frequently characterized as metals having the ability to form more than one cation

translational process: transfer of information from codon on mRNA to anticodon on tRNA; used in protein synthesis

trigonal bipyramidal: geometric arrangement of five ligands around a central Lewis acid, with ligands occupying the vertices of two trigonal pyramids that share a common face; three ligands share an equatorial plane with the central atom, two ligands occupy an axial position

tropocollagen: fibers, or fibrils, consisting of three polypeptide sequences arranged in a helix

tyrosine: one of the common amino acids

ultraviolet radiation: portion of the electromagnetic spectrum with wavelengths shorter than visible but longer than x rays

uracil: heterocyclic, pyrimidine, amine base found in RNA

valence: combining capacity

vertabrates: animals that have a skeleton

vesicle: small compartment in a cell that contains a minimum of one lipid bilayer

vitamins: organic molecules needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

vitriol: sulfate of a metal; there are blue (Cu), white (Zn), green (Fe), and rose (Co) vitriols

volatile: low boiling, readily vaporized

voltage: potential difference expressed in volts

vulcanized rubber: chemical process of mixing rubber with other materials like sulfur; it strengthens rubber so it can be used under hot or cold conditions; discovered by Charles Goodyear

wetting agent: molecule that, when added to a liquid, facillitates the spread of the liquid across a surface

zoology: branch of biology concerned with the animal kingdom

zwitterion: molecule that simultaneously contains a positive and a negative charge

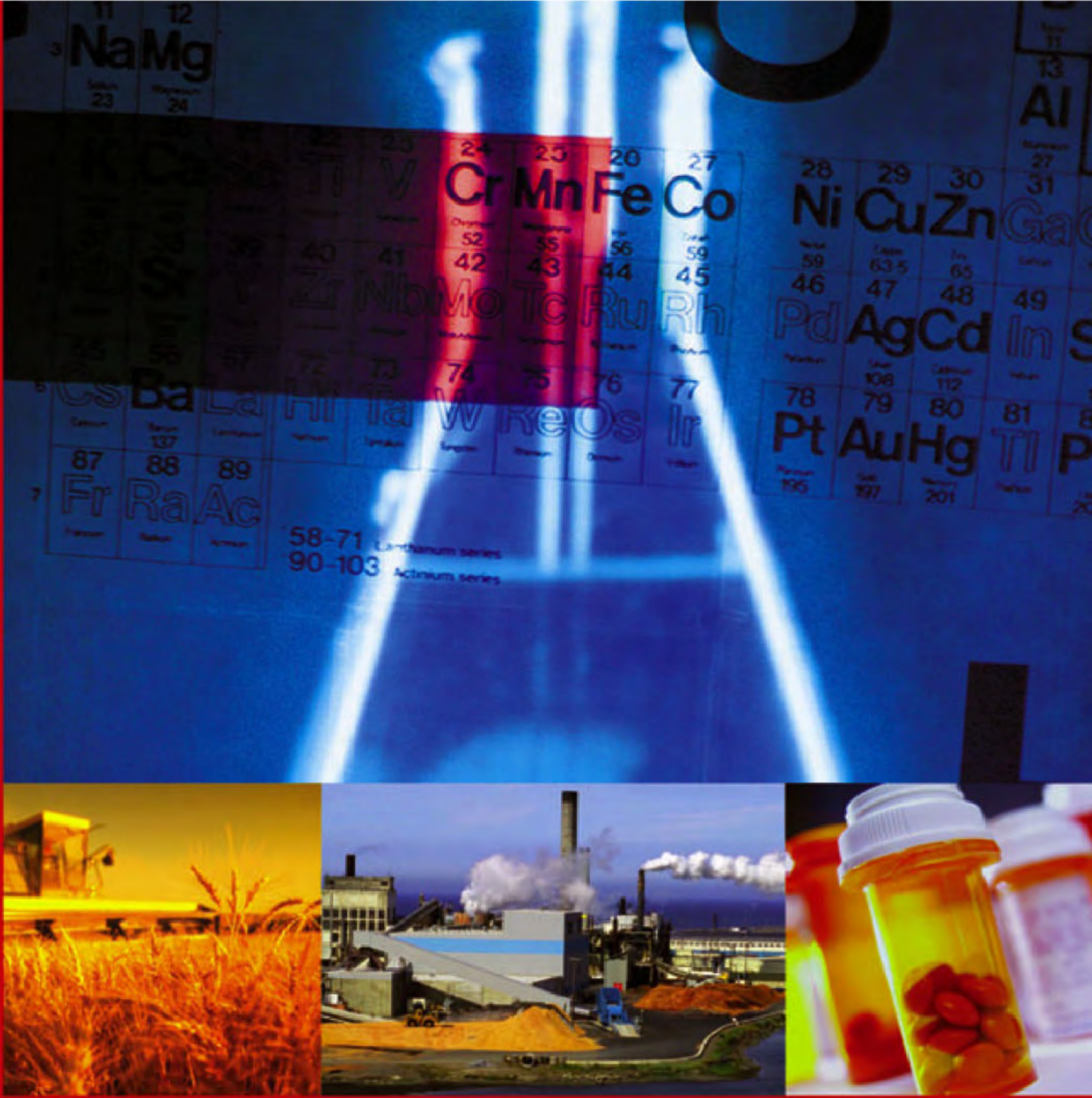

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Table of Contents

Volume 1

Volume 2

Volume 3

Volume 4

Preface

Chemistry. The word conjures up mystery—perhaps magic—smoke, fireworks, explosions, unpleasant odors. But it could evoke "smokeless burning," which would be invisible, fluorescent lights, "neon" signs, the quiet crumbling of rocks under the pressure of freezing water, the slow and quiet formation of caves in limestone, and the delightful scents of perfumes or fruit aromas. There is no magic, only knowledge and understanding. We offer this *Encyclopedia* as a contribution to help readers gain knowledge and understanding of chemistry.

Chemistry was manifested as an art at the beginnings of civilization. The early decorative chemical arts included the preparation of pigments such as the Egyptian blue applied to King Tutankhamen's golden death mask; the various bronze alloys that were used to make vases in the ancient world of the Middle East as well as in China; and the glass objects that have been found in Mesopotamia (now known as Iraq). Those chemical arts became a science in the eighteenth century when Antoine Laurent Lavoisier (1743–1794) led what has been called "the chemical revolution." Using accurate measurements of primarily mass, early chemists began to make order out of the myriad of substances that are found in the natural world. This order was eventually expressed in a number of chemical concepts that include the laws of chemical composition (constant composition, mass conservation, multiple proportions), periodicity, the nature of atoms, chemical bonding, and a variety of concepts involving chemical structures. The early symbiosis of chemistry with civilization remains. Chemistry is still a useful science in the advancement of civilization. Chemists have developed and refined the core concepts of chemistry to the point where they have become powerful tools to assist humankind in the acquisition of materials of practical use to extend and preserve civilization. Humans now have available a broader array of substances with a remarkable spectrum of properties than was available before chemistry became a science. Light emitting diodes (LEDs) produce more light than the individual torches, candles, and oil lamps of the distant past—indeed, than the incandescent light bulbs of the immediate past—more efficiently and with less pollution. Polymeric materials or composites can be produced with virtually any property desired—from stretching clingy Saran Wrap to Kevlar used in bullet proof vests; from nonstick Teflon to optical fibers; from rubber objects that are impervious to oil and gasoline to tires that can be used for 100,000 miles before needing replacement; from fibers that compete with (in some cases

surpass) natural materials to plastics that have more desirable optical properties than glass. In a word, chemistry is *everywhere*.

There is no magic, only knowledge and understanding.

These volumes are a contribution to assist readers in their understanding of chemistry and chemical ideas and concepts. The 509 articles have been carefully chosen to provide basic information on a broad range of topics. For those readers who desire to expand their knowledge of a topic, we have included bibliographic references to readily accessible sources.

The continual evolution of the discipline of chemistry is reflected in our treatment of the elements. The careful reader will note that we have included articles for the first 104 elements; the remainder of the elements are "recently" discovered or exist only as short-lived species and, accordingly, are not readily available for the usual chemical studies that reveal, for example, their bulk properties or reactivity and much of the "standard chemistry" that is of interest. Much of what little we know about the elements beyond 104 permits us to place these elements in their appropriate places in the periodic table, which nevertheless still turns out to be quite insightful from a chemical point of view.

Entries in the *Encyclopedia* are in alphabetic sequence. Cross-references appear in small capitals at the ends of the articles to help readers locate related discussions. Articles range from brief, but concise, definitions to extensive overviews that treat key concepts in larger contexts. A list of common abbreviations and symbols, and a list of the known elements, as well as a modern version of the periodic table are included in the For Your Reference section at the beginning of each volume. A glossary and a comprehensive index appear at the end of each volume. Contributors are listed alphabetically, together with their academic and professional affiliations, at the beginning of each volume.

Following this preface, we offer a topical arrangement of the articles in the *Encyclopedia*. This outline provides a general overview of the principal parts of the subject of chemistry and is arranged in alphabetical order.

Many individuals have contributed greatly and in many ways to this *Encyclopedia*. The associate editors—Alton J. Banks, Thomas Holme, Doris Kolb, and Herbert Silber—carried the major responsibility in shaping the intellectual content of the *Encyclopedia*. The authors of the articles executed that plan admirably and we thank them for that effort.

The staff at Macmillan Reference USA—Marie-Claire Antoine, Hélène Potter, Ray Abruzzi, Gloria Lam, and Christine Slovey—have been outstanding in their dedication and contributions to bring this *Encyclopedia* from its initial concept to the current reality. Without their considerable input, insightful guidance, and effort this *Encyclopedia* would never have seen the light of day. I take this opportunity to thank them personally and publicly. I am particularly grateful to Rita Wilkinson, my administrative assistant for her persistent and careful attention to details that kept the editorial office and my office connected for the smooth transmission of numerous critical details. I am especially grateful to Christine Slovey who, through her determined efforts and dedication, made a potentially difficult and tedious task far less onerous and, indeed, enjoyable.

J. J. Lagowski

Topical Outline

Analytical Chemistry Applications

Adhesives
Agricultural Chemistry
Analytical Chemistry
Bleaches
Ceramics
Chemical Engineering
Chemical Informatics
Coal
Cosmetics
Cryogenics
Detergents
Disposable Diapers
Dyes
Explosions
Fertilizer
Fibers
Food Preservatives
Forensic Chemistry
Formulation Chemistry
Freons
Gardening
Gasoline
Gemstones
Genetic Engineering
Glass
Hair Dyes and Hair Treatments
Herbicides
Industrial Chemistry, Inorganic
Industrial Chemistry, Organic
Insecticides
Irradiated Foods
Materials Science
Nanochemistry
Nylon
Pesticides
Pigments
Polymers, Synthetic
Recycling
Rocketry
Superconductors
Zeolites

Aqueous Chemistry

Acid-Base Chemistry
Bases
Bleaches
Chemical Reactions
Colloids
Corrosion
Equilibrium
Solution Chemistry
Water

Astrochemistry

Astrochemistry

Biochemistry

Acetylcholine
Active Site
Allosteric Enzymes
Amino Acid
Antibiotics
Artificial Sweeteners
Base Pairing
Bioluminescence
Caffeine
Carbohydrates
Cellulose
Chemiluminescence
Cholecalciferol
Cholesterol
Chromosome
Clones
Codon
Coenzyme
Cofactor
Collagen
Cortisone
Denaturation
Deoxyribonucleic Acid
Disaccharides
DNA Replication
Dopamine
Double Helix
Endorphins
Enzymes
Epinephrine
Estrogen
Fats and Fatty Acids
Fibrous Protein
Genes
Genetic Engineering
Genome
Globular Protein
Glycolysis
Glycoprotein
Hemoglobin
Hydrolase
Hydrolysis
Ion Channels
Kinase
Krebs Cycle
Lipid Bilayers
Lipids
Low Density Lipoprotein (LDL)
Membrane
Methylphenidate
Mutagen
Mutation
Neurochemistry
Neurotoxins
Neurotransmitters
Nicotinamide
Nicotinamide Adenine Dinucleotide (NAD)
Nicotine
Norepinephrine
Nucleic Acids
Nucleotide
Peptide Bond
Phospholipids

Photosynthesis
Polymerase Chain Reaction (PCR)
Polymers, Natural
Polysaccharides
Proteins
Primary Structure
Protein Solubility
Protein Synthesis
Protein Translation
Quaternary Structure
Residue
Restriction Enzymes
Retinol
Rhodium
Ribonucleic Acid
RNA Synthesis
Secondary Structure
Starch
Steroids
Stimulants
Storage Protein
Substrate
Taste Receptors
Teratogen
Tertiary Structure
Testosterone
Thiamin
Toxicity
Transmembrane Protein
Transport Protein
Triglycerides
Venom
Zwitterion

Biographies

Al Razi, Abu Bakr Muhammed ibn Zakariya
Anfinsen, Christian
Arrhenius, Svante
Avery, Oswald
Avogadro, Amedeo
Baekeland, Leo
Balmer, Johann Jakob
Bardeen, John
Becquerel, Antoine-Henri
Berg, Paul
Berthollet, Claude-Louis
Berzelius, Jöns Jakob
Black, Joseph
Bohr, Niels
Boltzmann, Ludwig
Boyle, Robert
Bragg, William Henry
Bragg, William Lawrence
Brønsted, Johannes Nicolaus
Bunsen, Robert
Caldwell, Mary
Calvin, Melvin
Cannizzaro, Stanislao
Carnot, Sadi
Carothers, Wallace
Carver, George Washington
Cavendish, Henry
Chadwick, James
Chappelle, Emmett
Chardonnet, Hilaire
Charles, Jacques
Chevreul, Michel
Cleve, Per Theodor
Cori, Carl and Gerty
Cottrell, Frederick
Coulomb, Charles
Curie, Marie Sklodowska
Dalton, John
Davy, Humphry
de Broglie, Louis
Dewar, James
du Pont, Éleuthère Irénée
Ehrlich, Paul
Einstein, Albert
Elion, Gertrude Belle
Fahrenheit, Gabriel
Faraday, Michael
Fermi, Enrico
Fischer, Emil Hermann
Fleming, Alexander
Franklin, Rosalind
Gadolin, Johan
Gay-Lussac, Joseph-Louis
Gibbs, Josiah Willard
Goodyear, Charles
Haber, Fritz
Hall, Charles
Heisenberg, Werner
Hess, Germain Henri
Heyrovsky, Jaroslav
Hodgkin, Dorothy
Julian, Percy
Kekulé, Friedrich August
Kelsey, Frances Kathleen Oldham
Khorana, Har Gobind
Krebs, Hans Adolf
Lavoisier, Antoine
Lawrence, Ernest
Le Bel, Joseph-Achille
Leblanc, Nicolas
LeChâtelier, Henri
Leclanché, Georges
Leloir, Luis
Lewis, Gilbert N.
Liebig, Justus von
Lister, Joseph
Lonsdale, Kathleen
Lucretius
Marsden, Ernest
Martin, Archer John Porter
Maxwell, James Clerk
Meitner, Lise
Mendeleev, Dimitri
Menten, Maud
Meyer, Lothar
Millikan, Robert
Morgan, Agnes Fay
Moseley, Henry
Nernst, Walther Hermann
Newton, Isaac
Nobel, Alfred Bernhard
Northrop, John
Oppenheimer, Robert
Ostwald, Friedrich Wilhelm
Paracelsus
Pasteur, Louis
Pauli, Wolfgang
Pauling, Linus
Perkin, William Henry
Planck, Max
Priestley, Joseph
Raman, Chandrasekhara
Ramsay, William
Remsen, Ira
Robinson, Robert
Röntgen, Wilhelm
Rutherford, Ernest
Rydberg, Johannes
Sanger, Frederick
Scheele, Carl
Schrödinger, Erwin
Seaborg, Glenn Theodore
Seibert, Florence
Soddy, Frederick
Stanley, Wendell
Staudinger, Hermann
Strutt, John (Lord Rayleigh)
Sumner, James
Svedberg, Theodor
Synge, Richard Laurence Millington
Szent-Györgyi, Albert
Thomson, Joseph John
Todd, Alexander
Travers, Morris
Urey, Harold
van der Waals, Johannes
Van Helmont, Johann Baptista
Van't Hoff, Jacobus Hendricus
Volta, Alessandro
Waksman, Selman
Watson, James Dewey
Weizmann, Chaim

Werner, Alfred
Willstätter, Richard
Wöhler, Friedrich
Woodward, Robert
Yalow, Rosalyn
Yukawa, Hideki
Zsigmondy, Richard

Chemical Substances

Coordination Compounds
Materials Science
Minerals
Nanochemistry
Nylon
Plastics
Rubber
Rydberg, Johannes
Silicone
Soap
Starch
Steel
Water

Computing

Chemical Informatics
Computational Chemistry
Digital X Ray
Molecular Modeling

Elements

Actinides
Actinium
Alkali Metals
Alkaline Earth Metals
Allotropes
Aluminum
Americium
Antimony
Argon
Arsenic
Astatine
Barium
Berkelium
Beryllium
Bismuth
Boron
Bromine
Cadmium
Calcium
Californium
Carbon
Cerium
Cesium
Chalcogens
Chlorine
Chromium
Cobalt
Copper
Curium
Dysprosium
Einsteinium
Erbium
Europium
Fermium
Fluorine
Francium
Fullerenes
Gadolinium
Germanium
Gold
Hafnium
Halogens
Helium
Holmium
Hydrogen
Indium
Iodine
Iridium
Iron
Lanthanides
Lanthanum
Lawrencium
Lead
Lithium
Lutetium
Magnesium
Manganese
Mendelevium
Mercury
Molybdenum
Neodymium
Neon
Neptunium
Nickel
Niobium
Nitrogen
Nobelium
Noble Gases
Osmium
Oxygen
Ozone
Palladium
Platinum
Plutonium
Polonium
Potassium
Praseodymium
Promethium
Protactinium
Radium
Radon
Rhenium
Rhodium
Rubidium
Ruthenium
Rutherfordium
Samarium
Scandium
Selenium
Silicon
Silver
Sodium
Sulfur
Tantalum
Technetium
Tellurium
Terbium
Thallium
Thorium
Thulium
Tin
Titanium
Transactinides
Tungsten
Uranium
Vanadium
Xenon
Ytterbium
Yttrium
Zinc
Zirconium

Energy

Chemistry and Energy
Energy
Energy Sources and Production
Explosions
Fire, Fuels, Power Plants
Fossil Fuels
Heat
Manhattan Project
New Battery Technology
Nuclear Fission
Nuclear Fusion
Petroleum
Solar Cells
Solid-State Devices
Storage Protein
Sustainable Energy Use
Temperature
Thermochemistry
Thermodynamics

Environmental Chemistry

Air Pollution
Atmospheric Chemistry
Environmental Pollution
Fertilizer

Freons
Global Warming
Green Chemistry
Herbicides
Insecticides
Pesticides
Recycling
Water Pollution
Water Quality

History

Alchemy

Inorganic Chemistry

Ceramics
Gemstones
Industrial Chemistry, Inorganic
Materials Science
Minerals
Nomenclature of Inorganic Chemistry

Medicine

Acetaminophen
Acetylsalicylic Acid
Acne Medication
Antibiotics
Ascorbic Acid
Carcinogen
Chemotherapy
CT Scans
Heavy Metal Toxins
Ibuprofen
Insulin
Interferon
Irradiated Foods
Neurotoxins
Neurotransmitters
Nuclear Medicine
Penicillin
Pharmaceutical Chemistry
Sulfa Drugs
Teratogen
Toxicity
Venom

Organic Chemistry

Aromaticity
Freons
Industrial Chemistry, Organic
Nylon
Organic Chemistry
Organic Halogen Compounds
Organometallic Compounds
Pesticides
Petroleum
Polyesters
Polymers, Synthetic
Rubber
Terpenes
Zwitterion

Physical Chemistry

Catalysis and Catalysts
Colloids
Concentration Gradient
Corrosion
Electrochemistry
International System of Units
Kinetics
Measurement
Nuclear Magnetic Resonance
Physical Chemistry
Quantum Chemistry
Spectroscopy
Surface Chemistry
Theoretical Chemistry

Radiation

Digital X Ray
Radiation
Radiation Exposure
Radioactivity

Reactions

Chemical Reactions
Combinatorial Chemistry
Equations, Chemical
Equilibrium
Inhibitors
Recombinant DNA
Synthesis, Chemical

States of Matter

Gases
Liquid Crystals
Liquids
Solid State

Structure

Chirality
Isomerism
Lewis Structures
Magnetism
Molecular Geometry
Molecular Modeling
Molecular Structure
Molecules
Periodic Table
Primary Structure
Quaternary Structure
Secondary Structure
Stoichiometry
Tertiary Structure

For Your Reference

TABLE 1. SELECTED METRIC CONVERSIONS

WHEN YOU KNOW	MULTIPLY BY	TO FIND
Temperature		
Celsius (˚C)	1.8 (˚C) +32	Fahrenheit (˚F)
Celsius (˚C)	˚C +273.15	Kelvin (K)
degree change (Celsius)	1.8	degree change (Fahrenheit)
Fahrenheit (˚F)	[(˚F) −32] / 1.8	Celsius (˚C)
Fahrenheit (˚F)	[(˚F −32) / 1.8] +273.15	Kelvin (K)
Kelvin (K)	K −273.15	Celsius (˚C)
Kelvin (K)	1.8(K −273.15) +32	Fahrenheit (˚F)

WHEN YOU KNOW	MULTIPLY BY	TO FIND
Distance/Length		
centimeters	0.3937	inches
kilometers	0.6214	miles
meters	3.281	feet
meters	39.37	inches
meters	0.0006214	miles
microns	0.000001	meters
millimeters	0.03937	inches

WHEN YOU KNOW	MULTIPLY BY	TO FIND
Capacity/Volume		
cubic kilometers	0.2399	cubic miles
cubic meters	35.31	cubic feet
cubic meters	1.308	cubic yards
cubic meters	8.107×10^{-4}	acre-feet
liters	0.2642	gallons
liters	33.81	fluid ounces

WHEN YOU KNOW	MULTIPLY BY	TO FIND
Area		
hectares (10,000 square meters)	2.471	acres
hectares (10,000 square meters)	107,600	square feet
square meters	10.76	square feet
square kilometers	247.1	acres
square kilometers	0.3861	square miles

WHEN YOU KNOW	MULTIPLY BY	TO FIND
Weight/Mass		
kilograms	2.205	pounds
metric tons	2205	pounds
micrograms (µg)	10^{-6}	grams
milligrams (mg)	10^{-3}	grams
nanograms (ng)	10^{-9}	grams

TABLE 2. ALPHABETIC TABLE OF THE ELEMENTS

Symbol	Element	Atomic Number	Atomic Mass*	Symbol	Element	Atomic Number	Atomic Mass*
Ac	Actinium	89	(227)	Mt	Meitnerium	109	(266)
Al	Aluminum	13	26.982	Md	Mendelevium	101	(258)
Am	Americium	95	(243)	Hg	Mercury	80	200.59
Sb	Antimony	51	121.75	Mo	Molybdenum	42	95.94
Ar	Argon	18	39.948	Nd	Neodymium	60	144.24
As	Arsenic	33	74.922	Ne	Neon	10	20.180
At	Astatine	85	(210)	Np	Neptunium	93	237.048
Ba	Barium	56	137.33	Ni	Nickel	28	58.69
Bk	Berkelium	97	(247)	Nb	Niobium	41	92.908
Be	Beryllium	4	9.012	N	Nitrogen	7	14.007
Bi	Bismuth	83	208.980	No	Nobelium	102	(259)
Bh	Bohrium	107	(262)	Os	Osmium	76	190.2
B	Boron	5	10.811	O	Oxygen	8	15.999
Br	Bromine	35	79.904	Pd	Palladium	46	106.42
Cd	Cadmium	48	112.411	P	Phosphorus	15	30.974
Ca	Calcium	20	40.08	Pt	Platinum	78	195.08
Cf	Californium	98	(251)	Pu	Plutonium	94	(244)
C	Carbon	6	12.011	Po	Polonium	84	(209)
Ce	Cerium	58	140.115	K	Potassium	19	39.1
Cs	Cesium	55	132.90	Pr	Praseodymium	59	140.908
Cl	Chlorine	17	35.453	Pm	Promethium	61	(145)
Cr	Chromium	24	51.996	Pa	Protactinium	91	231.036
Co	Cobalt	27	58.933	Ra	Radium	88	226.025
Cu	Copper	29	63.546	Rn	Radon	86	(222)
Cm	Curium	96	(247)	Re	Rhenium	75	186.207
Ds	Darmastadtium	110	(269)	Rh	Rhodium	45	102.906
Db	Dubnium	105	(262)	Rb	Rubidium	37	85.47
Dy	Dysprosium	66	162.50	Ru	Ruthenium	44	101.07
Es	Einsteinium	99	(252)	Rf	Rutherfordium	104	(261)
Er	Erbium	68	167.26	Sm	Samarium	62	150.36
Eu	Europium	63	151.965	Sc	Scandium	21	44.966
Fm	Fermium	100	(257)	Sg	Seaborgium	106	(263)
F	Fluorine	9	18.998	Se	Selenium	34	78.96
Fr	Francium	87	(223)	Si	Silicon	14	28.086
Gd	Gadolinium	64	157.25	Ag	Silver	47	107.868
Ga	Gallium	31	69.723	Na	Sodium	11	22.990
Ge	Germanium	32	72.61	Sr	Strontium	38	87.62
Au	Gold	79	196.967	S	Sulfur	16	32.066
Hf	Hafnium	72	178.49	Ta	Tantalum	73	180.948
Hs	Hassium	108	(265)	Tc	Technetium	43	(98)
He	Helium	2	4.003	Te	Tellurium	52	127.60
Ho	Holmium	67	164.93	Tb	Terbium	65	158.925
H	Hydrogen	1	1.008	Tl	Thallium	81	204.383
In	Indium	49	114.82	Th	Thorium	90	232.038
I	Iodine	53	126.905	Tm	Thulium	69	168.934
Ir	Iridium	77	192.22	Sn	Tin	50	118.71
Fe	Iron	26	55.847	Ti	Titanium	22	47.88
Kr	Krypton	36	83.80	W	Tungsten	74	183.85
La	Lanthanum	57	138.906	U	Uranium	92	238.029
Lr	Lawrencium	103	(260)	V	Vanadium	23	50.942
Pb	Lead	82	207.2	Xe	Xenon	54	131.29
Li	Lithium	3	6.941	Yb	Ytterbium	70	173.04
Lu	Lutetium	71	174.967	Y	Yttrium	39	88.906
Mg	Magnesium	12	24.305	Zn	Zinc	30	65.38
Mn	Manganese	25	54.938	Zr	Zirconium	40	91.224

*Atomic masses are based on the relative atomic mass of ^{12}C=12. These values apply to the elements as they exist in materials of terrestrial origin and to certain artificial elements. Values in parenthesis are the mass number of the isotope of the longest half-life.

TABLE 3. COMMON ABBREVIATIONS, SYMBOLS, AND ACRONYMS

′	minute (of arc); single prime
″	second (of arc); double prime
$+$	plus
$^+$	positive charge
$-$	minus
$^-$	negative charge
$\pm$	plus-or-minus
$\mp$	minus-or-plus
$\times$	multiplied by
$\cdot$	multiplied by
$\div$	divided by
$=$	equals
$\neq$	not equal to
$\backsim$	about, approximately
$\cong$	congruent to; approximately equal to
$\approx$	approximately equal to
$\equiv$	identical to; equivalent to
$<$	less than
$\leq$	less than or equal to
$>$	greater than
$\geq$	greater than or equal to
%	percent
°	degree (temperature; angle of arc)
@	at
—	single bond
═	double bond
: :	double bond
≡	triple bond
: : :	triple bond
∞	infinity
$\propto$	variation
∂	partial derivative or differential
α	proportional to, alpha
$\surd$	square root
Δ	delta; increment of a variable
ϵ_0	dielectric constant; permittivity
θ	plane angle
λ	wavelength
μ	magnetic moment; micro
μA	microampere
μC	microcoulomb
μF	microfarad
μg	microgram
μg/ml	microgram per milliliter
μK	microkelvin
μm	micrometer (also called micron)
μmol;	micromole
μs, μsec	microsecond
ν	frequency
υ	velocity
π or pi	ratio of the circumference of a circle to its diameter; double as in double bond
σ	single as in single bond; Stefan-Boltzmann constant
Σ	summation
ϕ	null set
ψ	amplitude of a wave (as in *wave,* or *psi, function)*
$\rightarrow$	reaction to right
$\leftarrow$	reaction to left
$\leftrightarrow$	connecting resonance forms
$\leftrightarrows$	equilibrium reaction beginning at right
$\rightleftarrows$	equilibrium reaction beginning at left
$\rightleftharpoons$	reversible reaction beginning at left
$\leftrightharpoons$	reversible reaction beginning at right
$\uparrow$	elimination
$\Downarrow$	absorption
a	acceleration
A	area
a_o	Bohr Unit
AAS	atomic absorption spectroscopy
ABS	alkylbenzene sulfate
ACS	American Chemical Society
ADH	alcohol dehydrogenase
ADP	adenosine diphosphate
AEC	Atomic Energy Commission
AES	atomic emission spectroscopy
AFM	atomic force microscope; atomic force microscopy
AFS	atomic fluorescence spectroscopy
ALDH	aldehyde dehydronase
amp	ampere
AMS	accelerator mass spectrometry
AMU	atomic mass unit
atm.	standard atmosphere (unit of pressure)
ATP	adenosine triphosphate
β	beta
b.p.	boiling point
Btu	British thermal unit
c	centi-; speed of light
C	carbon; Celsius; centigrade; coulomb
C	heat capacity; electric capacitance

TABLE 3. COMMON ABBREVIATIONS, SYMBOLS, AND ACRONYMS [continued]

Ci	Curies
cm	centimeter
CT	computed tomography
d	d-orbital
D	dipole moment
DC	direct current
deg	degree
dr	diastereomer ratio
e	elementary charge
E	electric field strength; energy
$\mathrm{E_a}$	activation energy
$\mathrm{E_g}$	bandgap energy
EA	electron affinity
er	enantiomer ratio
eV	electron volts
f	f-orbital
F	Fahrenheit; Faraday's constant; fluorine
F	force
g	gram
g	g-orbital; gas
h	hour
h	Planck's constant
Hz	hertz
i	i-orbital
IUPAC	International Union of Pure and Applied Chemistry
J	joule
J	electric current density
k	k-orbital
K	degrees Kelvin; Kelvin; potassium
$\mathrm{K_a}$	acidity constant for the dissociation of weak acid (the weaker the acid, the lower the $\mathrm{K_a}$ value
$\mathrm{k_B}$	Boltzmann's constant
Kg	kilogram
kHz	kilohertz
kJ	kilojoule
kJ mol	kilojoule mole
km	kilometer
$\mathrm{K_m}$	Michaelis constant
l	length; liquid
L	lambert; liter
L	length; Avogadro's constant
LD	lethal dose
L/mole	liters per mole
ln	natural logarithm
log	logarithm
m	meter; milli-; molal (concentration)
m	mass
M	molar (concentration)
m_e	electron mass
mA	milliamperes
mg	milligram
mg/L	milligrams per liter
MHz	megahertz
min	minute
ml	milliliter
MO	molecular orbital
p	p-orbital
ω	omega
ppb	parts per billion
ppm	parts per million
ppt	parts per trillion
psi	per square inch; English for ψ
q	quantity
REM	Roentgen Equivalent Man (radiation-dose unit of measure)
s	solid; s-orbital
S	entropy
sec	second; secant
SEM	scanning electron microscope
SI	Système Internationale (International System of Measurements)
SPM	scanning probe microscope
STM	scanning tunneling microscope
STP	standard temperature and pressue (˚C, 1 atm)
Sv	sievert unit (1 Sv = 100 REM; used to measure radiation dose)
t	time
T	moment of force, thermodynamic temperature (in degrees Kelvin); torque
$\mathrm{T_c}$	critical temperature
TEM	transmission electron microscope
u	unified atomic mass unit
U	electric potential
V	electric potential; vanadium; volume
V	volt
vap.	vaporization
VB	valence bond
vel.	velocity
VSEPR	valence shell electron pair repulsion
Z	atomic number

PERIODIC TABLE OF THE ELEMENTS*†

	I	II
s	3 LITHIUM **Li** 6.941	4 BERYLLIUM **Be** 9.012
	11 SODIUM **Na** 22.990	12 MAGNESIUM **Mg** 24.305
	19 POTASSIUM **K** 39.1	20 CALCIUM **Ca** 40.08
	37 RUBIDIUM **Rb** 85.47	38 STRONTIUM **Sr** 87.62
	55 CESIUM **Cs** 132.90	56 BARIUM **Ba** 137.33
	87 FRANCIUM **Fr** (223)	88 RADIUM **Ra** 226.025

					1 HYDROGEN **H** 1.008					
d	21 SCANDIUM **Sc** 44.966	22 TITANIUM **Ti** 47.88	23 VANADIUM **V** 50.942	24 CHROMIUM **Cr** 51.996	25 MANGANESE **Mn** 54.938	26 IRON **Fe** 55.847	27 COBALT **Co** 58.933	28 NICKEL **Ni** 58.69	29 COPPER **Cu** 63.546	30 ZINC **Zn** 65.38
	39 YTTRIUM **Y** 88.906	40 ZIRCONIUM **Zr** 91.224	41 NIOBIUM **Nb** 92.908	42 MOLYBDENIUM **Mo** 95.94	43 TECHNETIUM **Tc** (98)	44 RUTHENIUM **Ru** 101.07	45 RHODIUM **Rh** 102.906	46 PALLADIUM **Pd** 106.42	47 SILVER **Ag** 107.868	48 CADMIUM **Cd** 112.411
	71 LUTETIUM **Lu** 174.967	72 HAFNIUM **Hf** 178.49	73 TANTALUM **Ta** 180.948	74 TUNGSTEN **W** 183.85	75 RHENIUM **Re** 186.207	76 OSMIUM **Os** 190.2	77 IRIDIUM **Ir** 192.22	78 PLATINUM **Pt** 195.08	79 GOLD **Au** 196.967	80 MERCURY **Hg** 200.59
	103 LAWRENCIUM **Lr** (260)	104 RUTHERFORDIUM **Rf** (261)	105 DUBNIUM **Db** (262)	106 SEABORGIUM **Sg** (263)	107 BOHRIUM **Bh** (262)	108 HASSIUM **Hs** (265)	109 MEITNERIUM **Mt** (266)	110 DARMASTADTIUM **Ds** (269)	111 UNUNUNIUM **Uuu** (272)	112 (?)

	III	IV	V	VI	VII	VIII
						2 HELIUM **He** 4.003
p	5 BORON **B** 10.811	6 CARBOM **C** 12.011	7 NITROGEN **N** 14.007	8 OXYGEN **O** 15.999	9 FLUORINE **F** 18.998	10 NEON **Ne** 20.180
	13 ALUMINUM **Al** 26.982	14 SILICON **Si** 28.086	15 PHOSPHORIUS **P** 30.974	16 SULFUR **S** 32.066	17 CHLORINE **Cl** 35.453	18 ARGON **Ar** 39.948
	31 GALLIUM **Ga** 69.73	32 GERMANIUM **Ge** 72.61	33 ARSENIC **As** 74.922	34 SELENIUM **Se** 78.96	35 BROMINE **Br** 79.904	36 KRYPTON **Kr** 83.80
	49 INDIUM **In** 114.82	50 TIN **Sn** 118.71	51 ANTIMONY **Sb** 121.75	52 TELLURIUM **Te** 127.60	53 IODINE **I** 126.905	54 XENON **Xe** 131.29
	81 THALLIUM **Tl** 204.383	82 LEAD **Pb** 207.2	83 BISMUTH **Bi** 208.980	84 POLONIUM **Po** (209)	85 ASTATINE **At** (210)	86 RADON **Rn** (222)

f	57 LANTHANUM **La** 138.906	58 CERIUM **Ce** 140.15	59 PRAESEODYMIUM **Pr** 140.908	60 NEODYMIUM **Nd** 144.24	61 NEODYMIUM **Pm** (145)	62 SAMARIUM **Sm** 150.36	63 EUROPIUM **Eu** 151.965	64 GADOLINIUM **Gd** 157.25	65 TERBIUM **Tb** 158.925	66 DYSPROSIUM **Dy** 162.50	67 HOLMIUM **Ho** 164.93	68 ERBIUM **Er** 167.26	69 THULIUM **Tm** 168.934	70 YTTERBIUM **Yb** 173.04
	89 ACTINIUM **Ac** 227.03	90 THORIUM **Th** 232.038	91 PROTACTINIUM **Pa** 231.036	92 URANIUM **U** 238.029	93 NEPTUNIUM **Np** 237.048	94 PLUTONIUM **Pu** (244)	95 AMERICIUM **Am** (243)	96 CURIUM **Cm** (247)	97 BERKELIUM **Bk** (247)	98 CALIFORNIUM **Cf** (251)	99 EINSTEINIUM **Es** (252)	100 FERMIUM **Fm** (257)	101 MENDELEVIUM **Md** (258)	102 NOBELIUM **No** (259)

*Each element in the table is listed with (from top to bottom) its atomic number, its name, its symbol, and its atomic mass. Atomic mass numbers in parentheses are the mass numbers of the longest-lived isotope. Other atomic mass numbers are the average mass number of the naturally occurring isotopes.

†The names and labels for elements beyond number 103 are controversial. IUPAC initially ruled in favor of Latin names based on atomic number, but in 1994 a set of specific names and symbols was suggested. After considerable debate, a revised final list of names for elements 104-109 was issued on August 30, 1997. Temporary names were also assigned for elements 110 and 111. Various groups have suggested alternatives names for some of these elements. Additional elements continue to be synthesized, though with increasing difficulty, with no definite upper atomic-number limit yet established.

Contributors

Catalina Achim
Carnegie Mellon University
Pittsburgh, Pennsylvania

David T. Allen
University of Texas at Austin
Austin, Texas

Carolyn J. Anderson
Washington University School of Medicine
St. Louis, Missouri

Ronald D. Archer
Professor Emeritus
University of Massachusetts, Amherst
Amherst, Massachusetts

D. Eric Aston
University of Idaho
Moscow, Idaho

Peter Atkins
University of Oxford
Oxford, United Kingdom

Cynthia Atterholt
Western Carolina University
Cullowhee, North Carolina

Michèle Auger
Laval University
Quebec, Quebec, Canada

Karl W. Böer
Professor Emeritus
University of Delaware
Newark, Delaware

Catherine H. Banks
Peace College
Raleigh, North Carolina

Joseph Bariyanga
University of Wisconsin
Milwaukee, Wisconsin

Nathan J. Barrows
University of Northern Colorado
Greeley, Colorado

David A. Bassett
Brockton, Massachusetts

James D. Batteas
CUNY - College of Staten Island
Staten Island, New York

Bruce Beaver
Duquesne University
Pittsburgh, Pennsylvania

C. Larry Bering
Clarion University
Clarion, Pennsylvania

Bill Bertoldi
Kingsford, Michigan

W. E. Billups
Rice University
Houston, Texas

Koen Binnemans
Catholic University of Leuven
Leuven, Belgium

James P. Birk
Arizona State University
Tempe, Arizona

Jeffrey R. Bloomquist
Virginia Polytechnic Institute and State University
Blacksburg, VA

John E. Bloor
University of Tennessee
Knoxville, Tennessee

George Bodner
Purdue University
West Lafayette, Indiana

Paul W. Bohn
University of Illinois
Urbana, Illinois

Valerie Borek
Boothwyn, Pennsylvania

Erwin Boschmann
Indiana University
Indianapolis, Indiana

Wayne B. Bosma
Bradley University
Peoria, Illinois

Ole Bostrup
The Danish Society of The History of Chemistry
Fredensborg, Denmark

F. Javier Botana
University of Cadiz
Cadiz, Spain

Lawrence H. Brannigan
Southwestern Illinois College
Bellville, Illinois

Ronald Brecher
GlobalTox International Consultants Inc.
Guelph, Ontario, Canada

Jeffrey C. Bryan
University of Wisconsin-La Crosse
La Crosse, Wisconsin

Robert A. Bulman
National Radiological Protection Board
Oxfordshire, England

Jean-Claude Bunzli
Swiss Federal Institute of Technology
Lausanne, Switzerland

Douglas Cameron
Montana Tech of the University of Montana
Butte, Montana

Michael C. Cann
University of Scranton
Scranton, Pennsylvania

Charles E. Carraher Jr.
Florida Atlantic University
Boca Raton, Florida

Henry A. Carter
Augustana University College
Camrose, Alberta, Canada

John Castro
Huntington Station, New York

Lyman R. Caswell
Texas Woman's University
Denton, Texas

Raymond Chang
Williams College
Williamstown, Massachusetts

Philip J. Chenier
University of Wisconsin
Eau Claire, Wisconsin

Peter E. Childs
University of Limerick
Limerick, Ireland

Gregory R. Choppin
Florida State University
Tallahassee, Florida

Abraham Clearfield
Texas A&M University
College Station, Texas

Brian P. Coppola
University of Michigan
Ann Arbor, Michigan

Eugene C. Cordero
San José State University
San José, California

Paul A. Craig
Rochester Institute of Technology
Rochester, New York

M. J. Crawford
Ludwig-Maximilians-Universtät-München
Munich, Germany

Mary R. S. Creese
University of Kansas
Lawrence, Kansas
(retired)

Bartow Culp
Purdue University
West Lafayette, Indiana

Carlos Eduardo da Silva Cortes
Universidade Federal Fluminense
Rio de Janeiro, Brazil

G. Brent Dawson
University of North Carolina at Greensboro
Greensboro, North Carolina

Stephanie E. Dew
Centre College
Danville, Kentucky

Anthony Diaz
Central Washington University
Ellensburg, Washington

Diego J. Diaz
University of Illinois at Urbana-Champaign
Urbana, Illinois

James S. Dickson
Iowa State University
Ames, Iowa

David A. Dobberpuhl
Creighton University
Omaha, Nebraska

Daryl J. Doyle
Kettering University
Flint, Michigan

Michael Eastman
Northern Arizona University
Flagstaff, Arizona

Andrew Ede
University of Alberta
Edmonton, Canada

Edward M. Eyring
University of Utah
Salt Lake City, Utah

Scott E. Feller
Wabash College
Crawfordsville, Indiana

Kurt W. Field
Bradley University
Peoria, Illinois

Matthew A. Fisher
St. Vincent College
Latrobe, Pennsylvania

George Fleck
Smith College
Northampton, Massachusetts

Michael J. Fosmire
Purdue University
West Lafayette, Indiana

Mark Freilich
The University of Memphis
Memphis, Tennessee

Ken Geremia
Copper Development Association, Inc.
New York, New York

Gregory S. Girolami
University of Illinois, Champaign-Urbana
Urbana, Illinois

Carmen Giunta
Le Moyne College
Syracuse, New York

Harold Goldwhite
California State University, Los Angeles
Los Angeles, California

Barbara E. Goodman
University of South Dakota
Vermillion, South Dakota

Gordon W. Gribble
Dartmouth College
Hanover, New Hampshire

Robert K. Griffith
West Virginia University
Morgantown, West Virginia

Neena Grover
Colorado College
Colorado Springs, Colorado

William G. Gutheil
University of Missouri-Kansas City
Kansas City, Missouri

David G. Haase
North Carolina State University
Raleigh, North Carolina

Arthur M. Halpern
Indiana State University
Terre Haute, Indiana

R. Adron Harris
The University of Texas at Austin
Austin, Texas

John Harwood
Tennessee Technological University
Cookeville, Tennessee

Ian S. Haworth
University of Southern California
Los Angeles, California

James M. Helt
CUNY- College of Staten Island
Staten Island, New York

J. Carver Hill
Cary, North Carolina

Darleane C. Hoffman
Lawrence Berkeley National Laboratory, University of California
Berkeley, California

Thomas A. Holme
University of Wisconsin-Milwaukee
Milwaukee, Wisconsin

Chaim T. Horovitz
Emeritus Professor
Rehovot , Israel

John D. Hostettler
San José State University
San José, California

Brian R. James
University of British Columbia
Vancouver, British Columbia, Canada

Frank A. J. L. James
The Royal Institution
London, England

Mark Jensen
Argonne National Laboratory
Argonne, Illinois

Melvin D. Joesten
Vanderbilt University
Nashville, Tennessee

W. L. Jolly
University of California, Berkeley
Berkeley, California

Loretta L. Jones
University of Northern Colorado
Greeley, Colorado

David A. Juckett
Michigan State University
Lansing, Michigan
Barros Research Institute
Holt, Michigan

Paul J. Karol
Carnegie Mellon University
Pittsburgh, Pennsylvania

Vladimir Karpenko
Charles University
Prague, Czech Republic

George B. Kauffman
California State University, Fresno
Fresno, California

W. Frank Kinard
College of Charleston
Charleston, SC

Thomas M. Klapotke
Ludwig-Maximillians-Universität München
Munich, Germany

Kyle Knight
University of Tennessee at Chattanooga
Chattanooga, Tennessee

Paul E. Koch
Penn State, Behrend College
Erie, Pennsylvania

Doris K. Kolb
Bradley University
Peoria, Illinois

Kenneth E. Kolb
Bradley University
Peoria, Illinois

Daniel P. Kramer
Kramer & Asscociates, Ltd.
Centerville, Ohio

Ágúst Kvaran
University of Iceland
Reykjavik, Iceland

J. J. Lagowski
The University of Texas
Austin, Texas

Michael Laing
Professor Emeritus
University of Natal
Durban, South Africa

Rattan Lal
The Ohio State University
Columbus, Ohio

Thomas H. Lane
Dow Corning Coporation
Midland, Michigan

Alan B. G. Lansdown
Imperial College School of Medicine
London, United Kingdom

Amanda Lawrence
University of Illinois, Champaign-Urbana
Urbana, Illinois

Peter B. Leavens
University of Delaware
Newark, Delaware

G. J. Leigh
University of Sussex
Brighton, United Kingdom

H. Eugene LeMay, Jr.
University of Nevada
Reno, Nevada

Kenneth B. Lipkowitz
North Dakota State University
Fargo, North Dakota

Ingrid A. Lobo
University of Texas at Austin
Austin, Texas

Walter Loveland
Oregon State University
Corvallis, Oregon

Phyllis A. Lyday
U.S. Geological Survey
Reston, Virginia

Paul A. Maggard Jr.
North Carolina State University
Raleigh, North Carolina

Michael E. Maguire
Case Western Reserve University
Cleveland, Ohio

Keith L. Manchester
University of the Witwatersrand, Johannesburg
South Africa

Dean F. Martin
University of South Florida
Tampa, Florida

Barbara B. Martin
University of South Florida
Tampa, Florida

James D. Martin
North Carolina State University
Raleigh, North Carolina

Anthony F. Masters
University of Sydney
New South Wales, Australia

Seymour Mauskopf
Duke University
Durham, North Carolina

Sean McMaughan
Texas A&M University
College Station, Texas

Paul F. McMillan
University College London, Christopher Ingold Laboratories
London, United Kingdom

Edward A. Meighen
McGill University
Montreal, Canada

Louis Messerle
University of Iowa
Iowa City, Iowa

Donald E. Moreland
Professor Emeritus
North Carolina State University
Raleigh, North Carolina

Matthew J. Morra
University of Idaho, Soil & Land Resources Division
Moscow, Idaho

Richard Mowat
North Carolina State University
Raleigh, North Carolina

Frank Mucciardi
McGill University
Montreal, Quebec, Canada

Kathleen L. Neeley
University of Kansas
Lawrence, Kansas

John Michael Nicovich
Georgia Institute of Technology
Atlanta, Georgia

Robert Noiva
University of South Dakota School of Medicine
Vermillion, South Dakota

Charles E. Ophardt
Elmhurst College
Elmhurst, Illinois

Richard Pagni
University of Tennessee
Knoxville, Tennessee

Gus J. Palenik
University of Florida
Gainsville, Florida

Robert P. Patterson
North Carolina State University, Crop Science Department
Raleigh, North Carolina

Harry E. Pence
State University of New York, College at Oneonta
Oneonta, New York

Mark A. Pichaj
Biola University
La Marada, California

John Pickering
San José State University
Nuclear Science Facility
San José, California

Tanja Pietraß
New Mexico Tech
Socorro, New Mexico

A. G. Pinkus
Baylor University
Waco, Texas

Jennifer L. Powers
Kennesaw State University
Kennesaw, Georgia

Suzanne T. Purrington
North Carolina State University
Raleigh, North Carolina

Ray Radebaugh
National Institute of Standards and Technology, Cryogenics Technologies Group
Boulder, Colorado

Thomas B. Rauchfuss
University of Illinois, Champaign-Urbana
Urbana, Illinois

Geoffrey W. Rayner-Canham
Sir Wilfred Grenfell College

Corner Brook, Newfoundland, Canada

Marelene Rayner-Canham
Sir Wilfred Grenfell College
Corner Brook, Newfoundland, Canada

Jeffrey C. Reid
North Carolina Geological Survey
Raleigh, North Carolina

Richard E. Rice
Florence, Montana

D. Paul Rillema
Wichita State University
Wichita, Kansas

Frank Rioux
St. John's University
College of St. Benedict
St. Joseph, Minnesota

Robert Rittenhouse
Walla Walla College
College Place, Washington

Elizabeth S. Roberts-Kirchhoff
University of Detroit Mercy
Detroit, Michigan

Brett Robinson
Horticultural and Food Research Institute of New Zealand
Palmerston North, New Zealand

Herbert W. Roesky
University of Göttingen
Göttingen, Germany

Hiranya S. Roychowdhury
New Mexico State University
Las Cruces, New Mexico

Gordon Rutter
Royal Botanic Garden Edinburgh
Edinburgh, United Kingdom

Martin D. Saltzman
Providence College
Providence, Rhode Island

Jerry L. Sarquis
Miami University
Oxford, Ohio

Nancy N. Sauer
Los Alamos National Laboratory
Los Alamos, New Mexico

Wolf-Dieter Schubert
Vienna University of Technology
Vienna, Austria

Joachim Schummer
University of South Carolina
Columbia, South Carolina

Alan Schwabacher
University of Wisconsin-Milwaukee
Milwaukee, Wisconsin

A. Truman Schwartz
Macalester College
Saint Paul, Minnesota

William M. Scovell
Bowling Green State University
Bowling Green, Ohio

Lydia S. Scratch
Ottawa, Ontario, Canada

Peter Rudolf Seidl
Universidade Federal do Rio de Janeiro
Rio de Janeiro, Brazil

N. M. Senozan
California State University
Long Beach, California

James F. Shackelford
University of California at Davis
Davis, California

Stephanie Dionne Sherk
Westland, Michigan

Ben Shoulders
The University of Texas at Austin
Austin, Texas

David B. Sicilia
University of Maryland
College Park, Maryland

Herbert B. Silber
San José State University
San José, California

Robert J. Silva
Lawrence Berkeley National Laboratory, University of California
Berkeley, California

Sharron W. Smith
Hood College
Frederick, Maryland

C. Graham Smith
Penicuik, United Kingdom

Mary L. Sohn
Florida Institute of Technology
Melbourne, Florida

David Speckhard
Loras College
Dubuque, Iowa

Jonathan N. Stack
North Dakota State University
Fargo, North Dakota

Conrad L. Stanitski
University of Central Arkansas
Conway, Arkansas

Donald H. Stedman
University of Denver
Denver, Colorado

Anthony N. Stranges
Texas A&M University
College Station, Texas

Dan M. Sullivan
University of Nebraska at Omaha
Omaha, Nebraska

Tammy P. Taylor
Los Alamos National Laboratory
Los Alamos, New Mexico

Ann T. S. Taylor
Wabash College
Crawfordsville, Indiana

Sidney Toby
Rutgers University
Piscataway, New Jersey

Reginald P. T. Tomkins
New Jersey Institute of Technology
Newark, New Jersey

Anthony S. Travis
The Hebrew University
Jerusalem, Israel

Donald G. Truhlar
University of Minnesota
Minneapolis, Minnesota

Georgios Tsaparlis
University of Ioannina
Ioannina, Greece

Dennis G. Tuck
University of Windsor
Windsor, Ontario, Canada
(deceased)

Geraldo Vicentini
Instituto de Quimíca, University of São Paulo
São Paulo, Brazil

Nanette M. Wachter
Hofstra University
Hempstead, New York

George H. Wahl Jr.
North Carolina State University
Raleigh, North Carolina

Helen R. Webb
Monash University
Clayton, Victoria, Australia

Laurence E. Welch
Knox College
Galesburg, Illinois

J. Reed Welker
University of Arkansas
Fayetteville, Arkansas
(retired)

Guang Wen
Tottori University
Tottori, Japan

Todd W. Whitcombe
University of Northern British Columbia
Prince George, British Columbia, Canada

Vivienne A. Whitworth
Ryerson University
Toronto, Ontario, Canada

David A. Williams
University College London
London, United Kingdom

Robert K. Wismer
Millersville University
Millersville, Pennsylvania

Ronni Wolf
Kaplan Medical Center
Rechovot, Israel

Adele J. Wolfson
Wellesley College
Wellesley, Massachusetts

Burghard Zeiler
Wolfram Bergbau und Hüttenges m.b.H.
Austria, Germany

Lea B. Zinner
Departamento de Química
São Paulo, Brazil

Cynthia G. Zoski
Georgia State University
Atlanta, Georgia

Thomas M. Zydowsky
FMC Corporation
Princeton, New York

Poison *See Toxicity; Venom.*

Polonium

MELTING POINT: 254°C
BOILING POINT: 962°C
DENSITY: 9.32 g/cm^3
MOST COMMON IONS: Po^{2-}, Po^{2+}, PoO_3^{2-}

84
Po
POLONIUM
209

Polonium is a silver-grey, radioactive **metal**. Discovered by chemist Marie Curie in 1898, polonium was named after her country of origin (Poland). Curie discovered the element while analyzing samples of pitchblende, or uranium ore, from Bohemia. She found that unrefined pitchblende was more radioactive than the uranium extracted from it. Small amounts of polonium and another radioactive element, radium, were later obtained from the refined ore.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Polonium is found in the earth's crust at exceedingly low levels; its natural abundance is only 2 x 10^{-10} milligrams per kilogram. Polonium is produced in pitchblende when the bismuth **isotope** ^{210}Bi, which has a half-life of five days, decays into ^{210}Po. Approximately 100 micrograms of polonium are found in 1 ton of uranium ore. Polonium can also be produced by bombarding ^{209}Bi with neutrons to form ^{210}Bi, which in turn decays into ^{210}Po.

isotope: form of an atom that differs by the number of neutrons in the nucleus

Polonium has more isotopes than any other element. The most common isotope is ^{210}Po, which has a half-life of 138.4 days. Other isotopes have half-lives ranging from less than 1 second to 102 years (^{209}Po). Polonium burns in air to form polonium (IV) oxide (PoO_2) and reacts with **halogens** to form tetrahalides (e.g., $PoCl_4$, $PoBr_4$, PoI_4). It also dissolves readily in dilute acids.

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

Polonium is a strong emitter of **α-particles**; approximately 1 gram of ^{210}Po emits 140 watts of heat energy. For this reason, it is used as a source of thermoelectric power in satellites. It is also utilized as a source of neutrons (when mixed with beryllium), as an antistatic device in industrial equipment, and in brushes that remove dust from photographic film. SEE ALSO Curie, Marie Sklodowska; Halogens; Radioactivity; Radium; Uranium.

α-particle: subatomic particle with 2+ charge and mass of 4; an He nucleus

Stephanie Dionne Sherk

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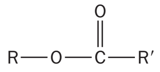
Polyesters

polymer: molecule composed of many similar parts

Polyesters are long chain synthetic **polymers** that have ester linkages. Polyester materials are used as fibers, plastics, and films; in composites and elastomers; and as coatings. They are truly versatile materials.



$R{-}O{-}\overset{\overset{O}{\|}}{C}{-}R'$

Ester linkage

aliphatic: having carbon atoms in an open-chain structure

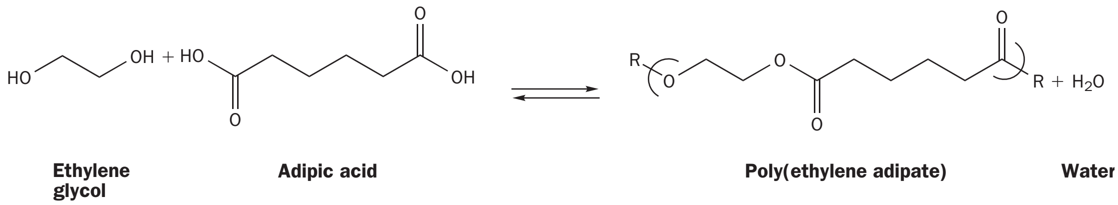
ester: organic species containing a carbon atom attached to three moieties: an O via a double bond, an O attached to another carbon atom or chain, and an H atom or C chain; the R(C–O)OR functional group

In the late 1920s American chemist Wallace Carothers and his research group at DuPont began to investigate the formation of polymers from the reaction of **aliphatic** diacids (having two acid groups) with diols (having two alcohol groups), in search of materials that would give them fibers. At first they were able to form only syrupy mixtures. But the Carothers group did make polyester fibers. They investigated a wide array of dialcohols, diacids, and w-hydroxy acids for use as starting points. Some of the polyesters that they achieved were solids, but they had rather low melting points and thus were not useful as fiber materials. The lack of success was due to the fact that the researchers had used only aliphatic diacids. In order to form long polymer chains, the reactive groups of the reactants must be present in approximately equal amounts. This is easily achieved via the use of amines and the subsequent formation of amine salts. (Diols do not easily form salts.) Carothers’s group understood the principle of “driving” an equilibrium reaction and so sought to remove water from their amine salt mixtures, thus forcing the reaction toward **ester** formation. For this they developed a so-called molecular still, which involved heating the mixture and applying a vacuum coupled with a “cold-finger” that allowed evacuated water to condense and be removed from the reaction system. Even with this understanding and lots of hard work, they achieved polymer chains with fewer than 100 repeat units. (See Figure 2.)

The DuPont research team turned from the synthesis of polyesters to tackle, more successfully, the synthesis of polyamides. The experience with polyesters was put to use in the making of polyamides.

Initial polyester formation actually occurred much earlier and is attributed to Gay Lussac and Théophile-Jules Pelouze in 1833 and Jöns Jakob

Figure 2. Wallace Carothers attempted to form polymers from the reaction of ethylene glycol (a diol) and apidic acid (an aliphatic diacid).



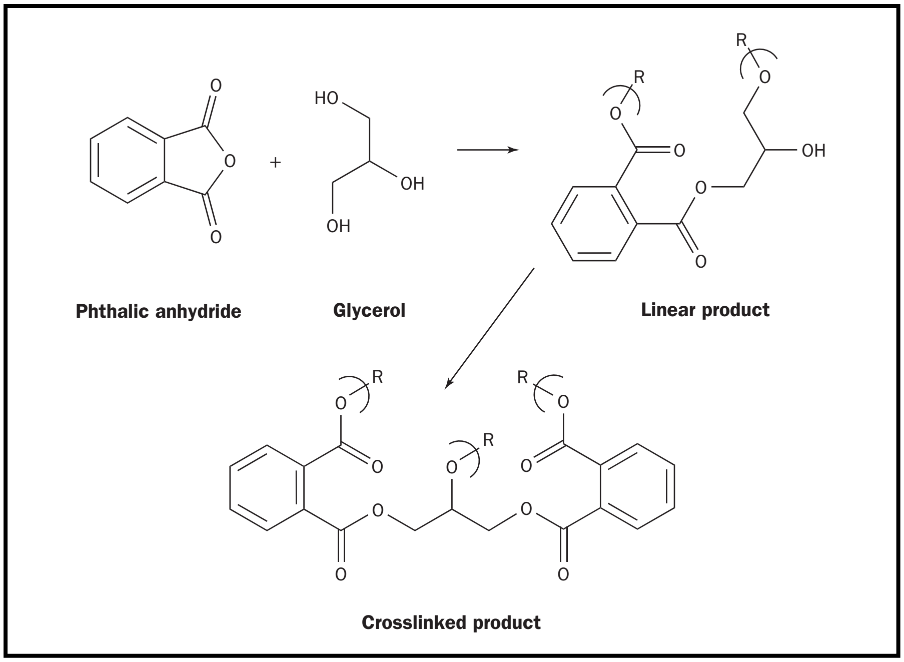


Figure 3. Glyptal polyester formation.

Berzelius in 1847. They did not realize what they had discovered, however, and so moved on to other work.

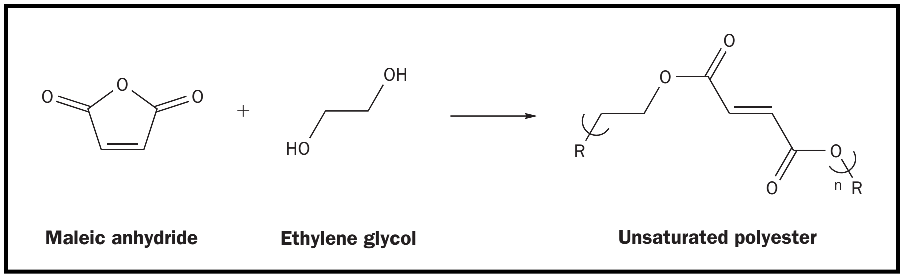
Glyptal polyesters were first produced in 1901 by heating glycerol and phthalic anhydride. (See Figure 3.) Because the secondary hydroxyl is less active than the terminal, primary hydroxyl in glycerol, the initial product formed is a linear polyester. A cross-linked product is produced by further heating through reaction the third alcohol.

Related compounds, alkyds, were synthesized by Kienle in the 1920s from trifunctional alcohols and dicarboxylic acids. Unsaturated oils (alcohols and anhydrides containing double bonds) were also reacted with phthalic anhydride, yielding polyesters that contained a double bond, which could be further reacted to produce cross-linked products. The extent of cross-linking or “drying” depends on the amount of unsaturated oil present.

Today, the term alkyd is often used to describe all polyesters produced from the reaction of a diacid or anhydride and a diol or triol resulting in a product that contains a double bond that can be further reacted, giving a cross-linked product. (See Figure 4.) These polyesters are called unsaturated polyesters. They are mainly used in the production of reinforced plastics (composites) and nonreinforced filled products for the marine, automotive, and other industries.

These glyptal and alkyd polyesters are useful as coating materials but not for fiber or plastic production. The first commercially available polyesters were made by GE in the 1920s. Called Glyptals™, they were used as sealing waxes. Out of the Glyptal™ research came alkyd paints. Although these reactions had low fractional conversions, they formed high molecular weight materials because they had functionalities (i.e., a number of reactive groups on a single reactant) greater than 2, resulting in cross-linking.

Figure 4. Reaction of an anhydride and a diol result in a double bonded product that can be further reacted to produce a cross-linked product called unsaturated polyester.



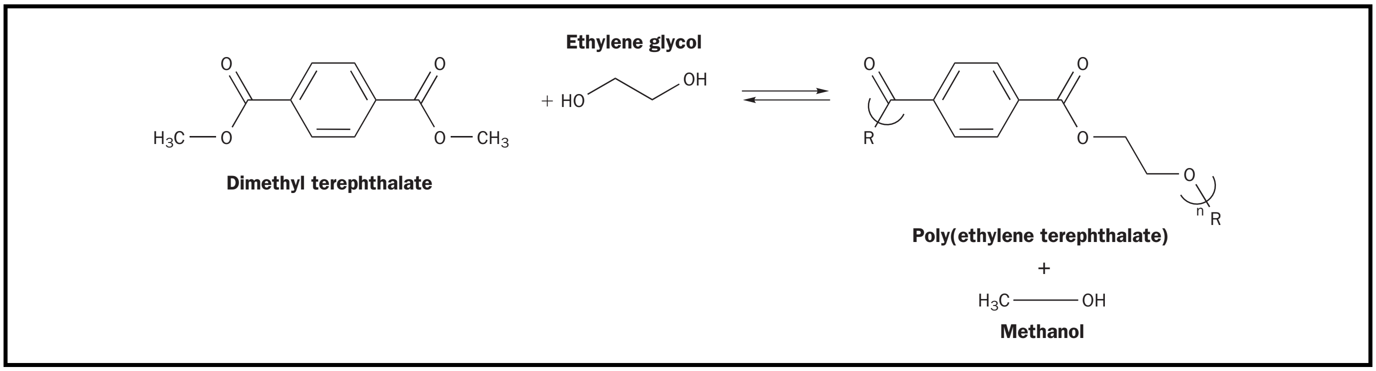
The heat resistance of Carothers's polyesters was not sufficient to withstand the temperature of the hot ironing process. Expanding on the work of Carothers and his coworkers on polyesters, Whinfield and Dickson, in England, overcame the problems of the Carothers group by using aromatic acids, especially terephthalic. This classic reaction, which produces plastics and fibers that are sold under a variety of tradenames, including Dacron, Fortrel, Trevira, and Terylene, and films sold under a variety of trade names that includes Mylar, is shown in Figure 5. All new plants now use pure acid for this reaction.

Methyl alcohol, or methanol, is lower boiling than water (65ºC compared with 100ºC) and is thus more easily removed, allowing the reaction to be forced toward polymer formation more easily. Although this poly(aryl ester), produced by Whinfield and Dickson, poly(ethylene terephthalate) or PET, met the specifications for a useful synthetic fiber, because of inferior molding machines and inadequate plastic technology, it was not possible to use it in injection molds. Until more recently PET was not a widely used plastic or film material.

aromatic: having a double-bonded carbon ring (typified by benzene)

Although aromatic polyesters had been successfully synthesized from the reaction of ethylene glycol with various **aromatic** diacids (almost always terephthalic acid or its ester), commercialization of polyester synthesis awaited an inexpensive source of aromatic diacids. In 1953 an inexpensive process for the separation of the various xylene isomers by crystallization was discovered. The availability of inexpensive xylene isomers enabled the formation of terephthalic acid through the air oxidation of the p-xylene isomer. Du Pont, in 1953, produced polyester fibers from melt spinning, but it was not until the 1970s that these polyester fibers became commercially available.

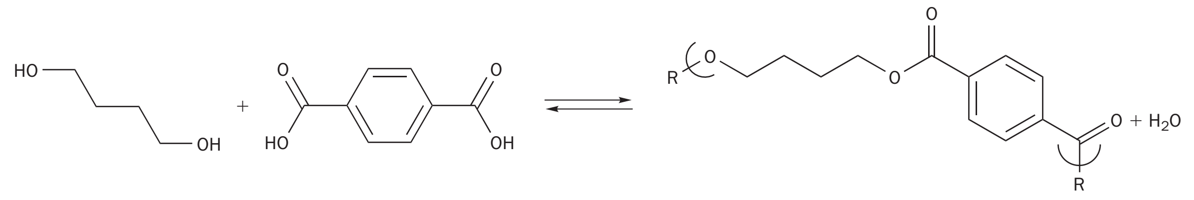
Figure 5. The classic reaction for producing plastics and fibers. New plants use pure acid for this reaction.



John Travolta and Karen Lynn Gorney in the 1970s hit film *Saturday Night Fever.* Polyester was a popular fabric used in clothing in the 1970s.

In 2000 about 3,900 million pounds of polyester fiber were used in the United States, making it the largest single fiber group material. As with nylon, polyester fibers are comparable to and/or surpass common natural fibers such as cotton and wool in heat stability, wash-and-wear properties, and wrinkle resistance. Textiles blended from polyester, cotton, and wool (in varying combinations) can also be made to be "permanent press" and wrinkle resistant. The fibers are typically formed from melt or solvent spinning. Chemical and physical modification can generate fibers of differing fiber appearances from the same basic fiber material. Self-crimping textiles are made by combining materials that have differing shrinkage properties. Different shaped dyes produce materials with varying contours and properties, including hollow fibers.

Along with the famous polyester suits and slacks, polyester fibers are widely used in undergarments, permanent press shirts, tire cord, and felts.



Poly(butylene terephthalate), PBT

Figure 6. Poly(butylene terephthalate), or PBT, has a lower melting point than PET, and it crystallizes more rapidly.

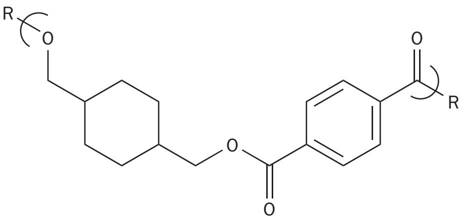
Because the ease of processing and fabricating polyesters is related to the number of methylene groups $(-CH_2-)$ in the repeat units, scientists turned to the use of diols with additional methylene units. Whereas PET is difficult to mold because of its high melting point, Tm 240ºC, poly(butylene terephthalate), or PBT, because of its two additional methylene units in the diol-derived portion (see Figure 6), is lower melting with a Tg of about 170ºC. PET also crystallizes relatively slowly, so extra care must be exercised to insure that PET molded products become fully crystallized. Otherwise, the partially crystallized portions will be preferred sites for cracking, crazing, shrinkage, and so on.

By comparison, PBT melts at a lower temperature (as noted above), crystallizes more rapidly, and is often employed as a molding compound. PBT has properties that represent a balance between those of nylons and acetals. It is characterized by low moisture absorption, good fatigue resistance, good solvent resistance, extremely good self-lubrication, and good maintenance of its physical properties even at relatively high use temperatures. Fiber-reinforced PBT molding compound is sold under the tradename Celanex. Another PBT molding compound was first sold under the tradename Valox. Today, there are many PBT molding compounds available.

In 2000 worldwide production of PET was 30 million tons. The manufacture of PET textiles is increasing at 5 percent a year, of PET bottles at 10 percent a year. China produces the most polyesters. PET is now used extensively as bottling material for soft drinks instead of glass because it is shatterproof and lightweight. Carbon dioxide permeability decreases with increasing film thickness and crystallinity. Glass has better CO_2 impermeability than PET in these respects. Therefore, to achieveoptimal crystallinity, partially crystalline PET is employed in the stretch blow molding process, carried out to promote further crystalline formation. It is also used for molded automobile parts. Over 500,000 tons of polyester engineering plastics are produced annually in the United States.

Poly(dihydroxymethylcyclohexyl terephthalate) was introduced by Eastman Kodak as Kodel in 1958. Here, the insertion of the cyclohexyl moiety gives a more **hydrophobic** material (in comparison to PET and PBT) as well as a more moldable product that can very readily be injected-molded. (See Figure 7.) The polymer's sole raw material is dimethyl terephthalate. Reduction of dimethyl terephthalate yields the dialcohol, cyclohexanedimethanol. Kodel, along with its blends and mixtures, is often extruded into film and sheeting for packaging. Kodel-type materials are used to pack-

hydrophobic: water repelling



Poly(dihydroxymethylcyclohexyl terephthalate)

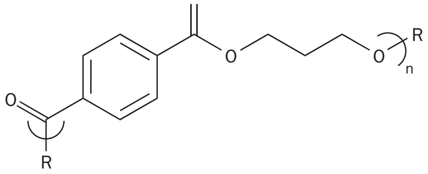
Figure 7. Materials made from Poly(dihydroxy methylcyclohexyl terephthalate) are used in shampoo and detergent bottles.

age hardware and other heavy items; they are also blow-molded to produce packaging for shampoos, liquid detergents, and so on.

Du Pont and Shell have developed a new polyester, poly(trimethylene terephthalate), or PTT, with the trademarks Sorona (Du Pont) and Corterra (Shell). It is structurally similar to poly(ethylene terephthalate), PET, except that 1,3-propanediol (PDO) is used as a reactant in place of ethylene glycol. (See Figure 8.) The extra methylene (CH_2) in PTT allows the fiber to be more easily colored, giving a material that is also softer to the touch and with greater stretch for textile use. Further, PTT offers good wear and stain resistance for carpet use. The ready availability of the monomer PDO is a major consideration, with current efforts underway to create PDO from the fermentation of sugar through the use of biocatalysts for this conversion. Corterra and Lycra blends have already been successfully marketed. Corterra is also targeted for use as a resin and film.

Du Pont first introduced microfibers in 1989. Microfibers have diameters that are less than typical fibers; they are about half the diameter of fine silk fiber, one-quarter the diameter of fine wool, and one hundred times finer than human hair. Denier, the weight in grams of 9,000-meter length of a fiber, is the term used to define the diameter or fineness of a fiber. Microfibers have a denier that is 0.9 denier or less. In comparison, nylon stockings are knit from 10- to 15- denier fiber.

Microfibers allow a fabric to be woven that is lightweight and strong. They can be tightly woven so that wind, rain, and cold do not easily penetrate. Rainwear manufactures use microfibers for this reason. They also have the ability to allow perspiration to pass through them. In addition, microfibers are very flexible because their small fibers can easily slide back and forth on one another. The first fabric made from microfiber was Ultrasuade, in which short polyester microfibers were imbedded into a polyurethane base. Today, microfibers are manufactured primarily from



Poly(trimethylene terephthalate), PTT

Figure 8. The extra methylene in poly(trimethylene terephthalate) (PTT) provides material that is easily colored and soft to the touch.

polyesters, nylon, and acrylic fibers. They are used under various tradenames to make a variety of products, such as clothing, hosiery, bedding, and scarves. SEE ALSO Polymers, Synthetic.

Charles E. Carraher Jr.

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Polymerase Chain Reaction

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information

The polymerase chain reaction (PCR) is used to make millions of copies of a section of deoxyribonucleic acid (**DNA**). Until the 1980s obtaining numerous copies of a section of DNA took one to two weeks and required isolation of the DNA, cloning the DNA into a viral or plasmid vector, growing the cloned DNA using living host cells, usually bacteria, and finally isolating the DNA again. With PCR a scientist can produce thirty million copies of a DNA section in a test tube overnight. In a series of early articles, PCR's inventor, Kary Mullis, described just how valuable he believed this tool would be. He could not have been more correct: PCR is now a mainstay of molecular biology. In 1993 Mullis received the Nobel Prize in chemistry in recognition of his discovery.

How PCR Works

PCR repeats the synthesis of a DNA segment through twenty-five to thirty cycles. The power of the technique resides in its ability to copy the products of each previous cycle along with the original sample. This results in exponential growth in the amount of product, as illustrated in Figure 1. The first stage or round of the process only involves copying the original sample. First, the DNA is separated into its two strands, and each strand acts as an instruction directing a new segment. The two products each contain one original strand and one new one. In the second round of the process, both of the DNA molecules manufactured in stage one are separated and each of the four strands is copied, producing four double-stranded products. The number of DNA segments doubles during each round. Twenty-five rounds can create millions of new segments from each original DNA.

To separate the double-stranded DNA products, the reaction is heated to near boiling, 95°C, for a few minutes. Originally, the catalyst, DNA polymerase, was killed by this treatment and manually replaced after each round. In 1988 Randall Saiki and coworkers dramatically improved the original concept of PCR by using a heat-stable catalyst, taq polymerase, isolated from the bacteria, *Thermis aquaticus*, found in hot springs. This catalyst survives the high temperature step and can start the next round of synthesis when cooled to the start temperature.

The specificity of PCR derives from the primers. Primers are short pieces of single-stranded DNA that are the starting point of the new DNA strands. The primers recognize the target DNA segment in the sample and

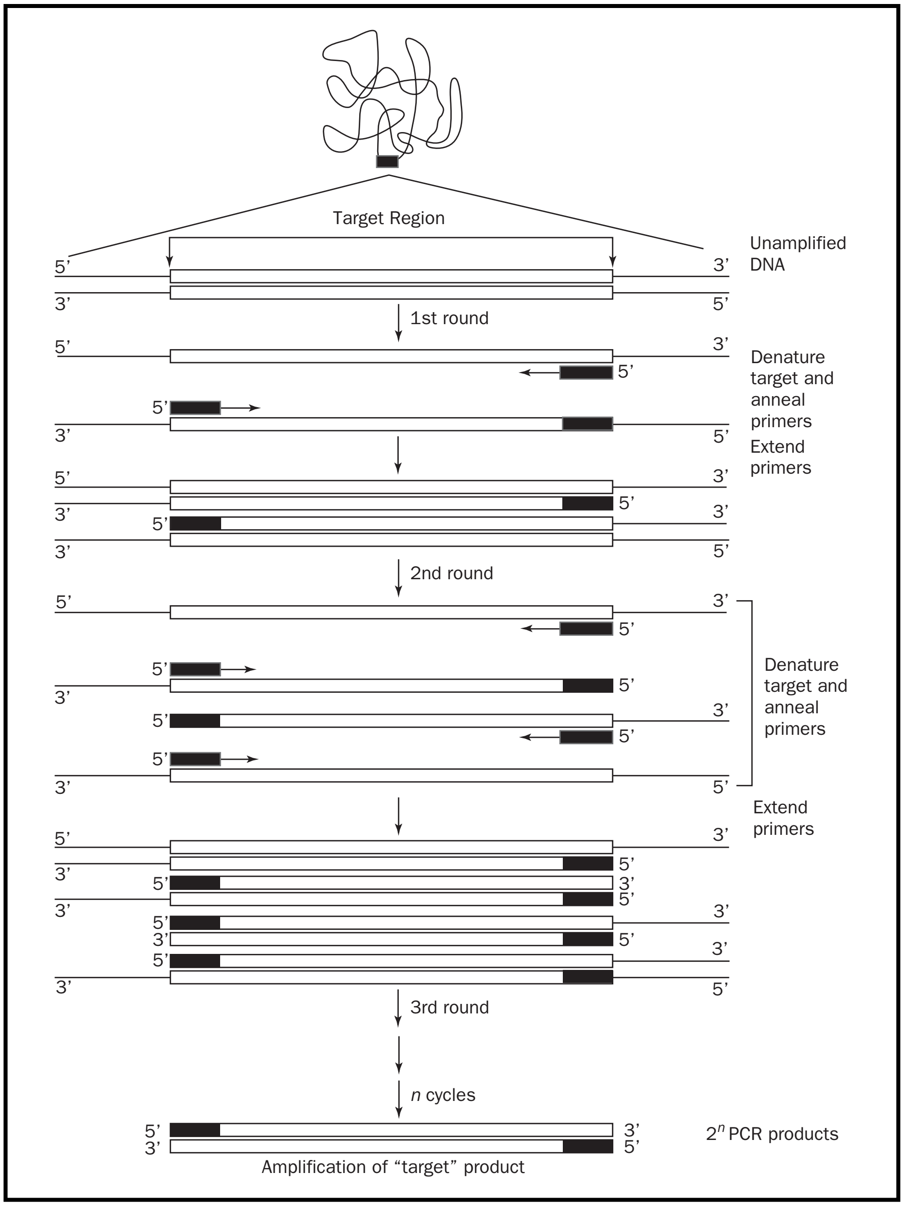

Figure 1. The polymerase chain reaction. PCR is a cycling process; with each stage the amount of target product is doubled.

bind to the target. Taq polymerase uses the primer as the beginning of the new product strand. Taq polymerase cannot synthesize DNA without a primer at the beginning, so the primers and not the catalyst determine what segment of the sample is copied.

Applications of PCR

Originally, PCR was employed to produce usable amounts of small- and medium-sized DNA segments. Many other important techniques quickly developed. PCR is used to identify bacteria and virus infections. It is not only very sensitive but is also selective enough to distinguish closely related strains. For example, this procedure has been adapted to detect genetically modified crops to help ensure they are utilized only in approved ways.

A widely known application of PCR is DNA fingerprinting. Certain regions of the human chromosome have short sections that are repeated up to several hundred times. Different individuals have different numbers of repeats in each section. If several sections are tested, a unique pattern is observed. Initially, these regions were cut out of sample DNA and tested for size. PCR allows the variable regions to be copied millions of times, greatly increasing the sensitivity and speed of the technique. Because of the technique's sensitivity, extreme care must be taken to avoid any contamination of the samples. Forensic scientists continue to make even greater use of this method.

One of the latest applications of PCR is the DNA microarray or gene chip. It allows medical personnel to test a cancer cell before and after chemotherapy with different drugs. If two patterns look the same, the two drugs administered are likely working on the same pathway and may not be as useful as treatment with two drugs that work by different pathways. SEE ALSO DEOXYRIBONUCLEIC ACID (DNA); FORENSIC CHEMISTRY.

David Speckhard

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Polymers, Natural

The word "polymer" means "many parts" (from the Greek *poly*, meaning "many," and *meros*, meaning "parts"). Polymers are giant molecules with molar masses ranging from thousands to millions. Approximately 80 percent of the organic chemical industry is devoted to the production of synthetic polymers, such as plastics, textiles fibers, and synthetic rubbers. A polymer is synthesized by chemically joining together many small molecules into one giant molecule. The small molecules used to synthesize polymers are called monomers. Synthetic polymers can be classified as addition polymers, formed from monomer units directly joined together, or condensation polymers, formed from monomer units combining such that a small molecule, usually water, is produced during each reaction.

Polymers are widely found in nature. The human body contains many natural polymers, such as proteins and nucleic acids. Cellulose, another natural polymer, is the main structural component of plants. Most natural polymers are condensation polymers, and in their formation from monomers water is a by-product.

glucose: common hexose monosaccharide; monomer of starch and cellulose; also called grape sugar, blood sugar, or dextrose

Starch is a condensation polymer made up of hundreds of **glucose** monomers, which split out water molecules as they chemically combine. Starch is a member of the basic food group carbohydrates and is found in cereal grains and potatoes. It is also referred to as a polysaccharide, because it is a polymer of the monosaccharide glucose. Starch molecules include two types of glucose polymers, amylose and amylopectin, the latter being the major starch component in most plants, making up about three-fourths of the total starch in wheat flour. Amylose is a straight chain polymer with an average of about 200 glucose units per molecule.

A typical amylopectin molecule has about 1,000 glucose molecules arranged into branched chains with a branch occurring every 24 to 30 glucose units. Complete hydrolysis of amylopectin yields glucose; partial hydrolysis produces mixtures called dextrins, which are used as food additives and in mucilage, paste, and finishes for paper and fabrics.

Glycogen is an energy reserve in animals, just as starch is in plants. Glycogen is similar in structure to amylopectin, but in a glycogen molecule a branch is found every 12 glucose units. Glycogen is stored in the liver and skeletal muscle tissues.

Cellulose is the most abundant organic compound on Earth, and its purest natural form is cotton. The woody parts of trees, the paper we make from them, and the supporting material in plants and leaves are also mainly cellulose. Like amylose, it is a polymer made from glucose monomers. The difference between cellulose and amylose lies in the bonding between the glucose units. The bonding angles around the oxygen atoms connecting the glucose rings are each 180° in cellulose, and 120° in amylose. This subtle structural difference is the reason we cannot digest cellulose. Human beings do not have the necessary enzymes to break down cellulose to glucose. On the other hand, termites, a few species of cockroaches, and ruminant mammals such as cows, sheep, goats, and camels, are able to digest cellulose.

Chitin, a polysaccharide similar to cellulose, is Earth's second most abundant polysaccharide (after cellulose). It is present in the cell walls of fungi and is the fundamental substance in the exoskeletons of crustaceans, insects, and spiders. The structure of chitin is identical to that of cellulose, except for the replacement of the OH group on the C-2 carbon of each of the glucose units with an $-NHCOCH_3$ group. The principal source of chitin is shellfish waste. Commercial uses of chitin waste include the making of edible plastic food wrap and cleaning up of industrial wastewater.

All proteins are condensation polymers of amino acids. An immense number of proteins exists in nature. For example, the human body is estimated to have 100,000 different proteins. What is amazing is that all of these proteins are derived from only twenty amino acids. In the condensation reaction whereby two amino acids become linked, one molecule of water forming from the **carboxylic acid** of one amino acid and the amine group of the other is eliminated. The result is a peptide bond; hence, proteins are **polypeptides** containing from approximately fifty to thousands of amino acid residues.

The primary structure of a protein is the sequence of the amino acid units in the protein. The secondary structure is the shape that the backbone of the molecule (the chain containing peptide bonds) assumes. The two most common secondary structures are the α-**helix** and the β-pleated sheet. An α-helix is held together by the intramolecular **hydrogen bonds** that form between the N-H group of one amino acid and the oxygen atom in the third amino acid down the chain from it.

The α-helix is the basic structural unit of hair and wool, which are bundles of polypeptides called α-keratins. The helical structure imparts some

carboxylic acid: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the $-CO_2H$ functional group

polypeptide: compound containing two or more amide units—C(O)NH—produced by the condensation of two or more amino acids

helix: form of a spiral or coil such as a corkscrew

hydrogen bond: interaction between H atoms on one molecule and lone pair electrons on another molecule that constitutes hydrogen bonding

Chitin, the earth's second most abundant polysaccharide, is the fundamental substance in the exoskeletons of crustaceans.

elasticity to hair and wool. The polypeptides in silk, on the other hand, are β-keratins with the β-sheet structure, in which several protein chains are joined side-to-side by intermolecular hydrogen bonds. The resulting structure is not elastic.

Nucleic acids are condensation polymers. Each monomer unit in these polymers is composed of one of two simple sugars, one phosphoric acid group, and one of a group of heterocyclic nitrogen compounds that behave chemically as bases. Nucleic acids are of two types: deoxyribonucleic acid (**DNA**), the storehouse of genetic information, and ribonucleic acid (RNA), which transfers genetic information from cell DNA to cytoplasm, where protein **synthesis** takes place. The monomers used to make DNA and RNA are called nucleotides. DNA nucleotides are made up of a phosphate group, a deoxyribose sugar, and one of four different bases: **adenine**, **cytosine**, **guanine**, or **thymine**. The nucleotides that polymerize to produce RNA differ from DNA nucleotides in two ways: they contain ribose sugar in place of deoxyribose sugar and **uracil** instead of thymine.

Natural rubber is an addition polymer made up of thousands of **isoprene** monomer repeating units. It is obtained from the *Hevea brasiliensis* tree in the form of latex. The difference between natural rubber and another natural polymer, gutta-percha (the material used to cover golf balls), is the geometric form of the polyisoprene molecules. The CH_2 groups joined by double bonds in natural rubber are all on the same sides of the double bonds (the *cis* configuration), whereas those in gutta-percha are on opposite sides of the double bonds (the *trans* configuration). This single structural difference changes the elasticity of natural rubber to the brittle hardness of gutta-percha. SEE ALSO Deoxyribonucleic Acid; Nucleic Acids; Polymers, Synthetic; Proteins.

Melvin D. Joesten

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

synthesis: combination of starting materials to form a desired product

adenine: one of the purine bases found in nucleic acids, $C_5H_5N_5$

cytosine: heterocyclic, pyrimidine, amine base found in DNA

guanine: heterocyclic, purine, amine base found in DNA

thymine: one of the four bases that make up a DNA molecule

uracil: heterocyclic, pyrimidine, amine base found in RNA

isoprene: common name for 2-methyl-1,3butadiene, the monomer of the natural rubber polymer

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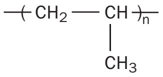
Polymers, Synthetic

Polymers are large molecules composed of repeated chemical units. The smallest repeating unit is called a mer. The term polymer is derived from the Greek words *poly* and *mers* meaning "many parts." Linear polymers are like ropes. For a polymer chain of 10,000 units (a typical length), a standard half-inch-thick rope would be about 128 meters (140 yards) long to represent the length-to-thickness ratio. Polymers are synthesized naturally and artificially to perform a wide variety of specialized tasks.

Basic Polymer Science

A polymer is generally described in terms of a single repeat unit, such as the following example:

Figure 1.

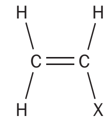


$$-(\mathrm{CH_2}-\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{CH}}})_n-$$

The number of repeat units in a chain is called the degree of polymerization (DP) or chain length. Thus, a poly(propylene) chain 5,000 units long would have a DP of 5,000 and an "n" value of 5,000. Because most polymer mixtures contain chains of varying lengths, the chain length is often referred to in terms of average chain length or average DP.

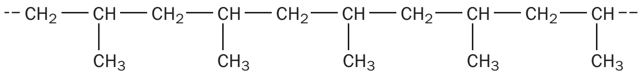
At either end of the polymer chain are end groups. (Because the chain is often thousands of units long, the end groups are usually omitted.) For (poly)propylene (shown in Figure 1) the repeating carbons (C-C-C-C-C-C-C-C) form the polymer backbone and represent the atoms that connect the chain together. In vinyl polymers, so called because they are generally derived from substituted vinyl reactants or monomers (Figure 2), the polymer backbone is composed of only carbon atoms. An example is poly(propylene), which has five mers represented (Figure 3).

Figure 2.



Vinyl Monomer

Figure 3.



$$--\mathrm{CH_2}-\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{CH}}}--$$

Poly(propylene)

Condensation polymer backbones include non-carbon atoms. For example, polyesters have oxygen atoms and nylons have nitrogen atoms in the backbone in addition to carbon atoms (Figure 4).

Figure 4.

$$-(\mathrm{O}-\mathrm{R}-\mathrm{O}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{R'}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}})_n-$$

Polyesters

$$-(\overset{\mathrm{H}}{\overset{|}{\mathrm{N}}}-\mathrm{R}-\overset{\mathrm{H}}{\overset{|}{\mathrm{N}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{R'}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}})_n-$$

Nylons

Unsymmetrical reactants, such as substituted vinyl monomers, react almost exclusively to give what are called "head-to-tail" products where the substituents occur on alternative carbon atoms:

Figure 5. $—CH_2—CHX—CH_2—CHX—CH_2—CHX—CH_2—CHX—$

Occasionally a "head-to-head, tail-to-tail" configuration occurs. For most vinyl polymers this structure occurs less than 1 percent of the time in a random manner throughout the chain.

Figure 6. $—CH_2—CHX—CHX—CH_2—CH_2—$

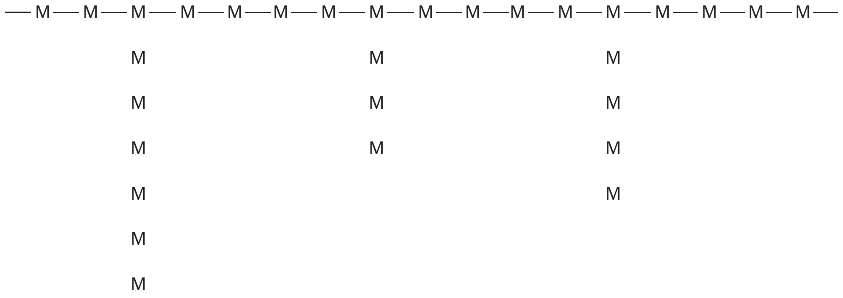
Even with the head-to-tail configuration, a variety of structures are possible. These include a simple linear homopolymer structure

Figure 7.

—M—M—M—M—M—M—M—M—M—M—M—M—M—M—M—M—M—

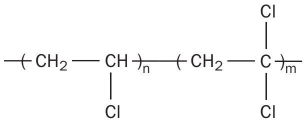
and branched structures with varying amounts and lengths of branching.

Figure 8.



Copolymers are polymers derived from two different monomers (M and N). Saran, a component of Saran Wrap, is one example (Figure 9). Other examples of copolymer structures are depicted in Figure 10.

Figure 9.



$$—\!(CH_2—\underset{Cl}{CH})_n\!—\!(CH_2—\overset{Cl}{\underset{Cl}{C}})_m\!—$$

Repeat units of vinyl chloride and vinylidene chloride, Saran copolymer

Figure 10.

—M—N—M—N—M—N—M—N—M—N—M—N—M—N—

Alternating

—N—N—M—N—M—M—N—M—N—N—M—N—M—M—N—

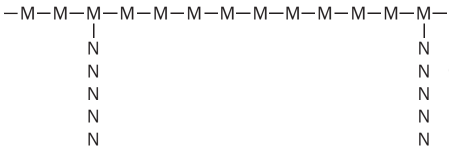
Random

—M—N—M—M—M—M—M—M—M—M—M—M—M—N—

Block in "M"

—N—N—N—N—N—N—M—M—M—M—M—M—M—N—N—

Block in both "M" & "N"

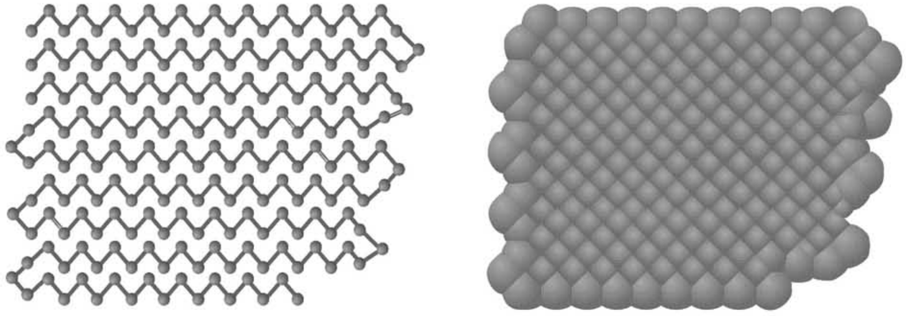


Graft

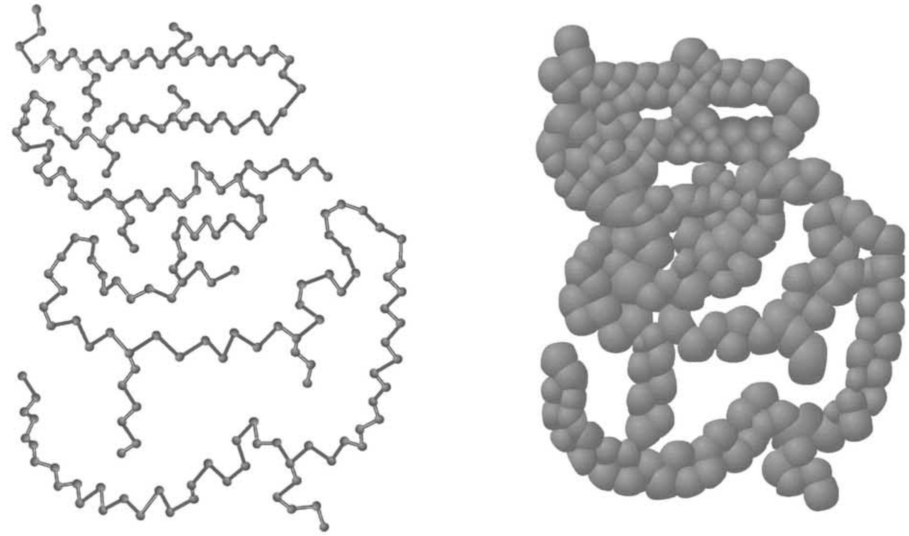
Some linear chains have extensions (beyond the substitution) coming off the polymer backbone. These extensions are called branches and influence a polymer's properties. Branches may be long or short, frequent or infrequent. For example, so-called low density polyethylene (LDPE) has between forty and one hundred short branches for every 1,000 ethylene units, whereas high density polyethylene (HDPE) has only one to six short branches for every 1,000 ethylene units (Figure 11). Branching discourages the chains from fitting close together so that the structure will be **amorphous** with relatively large amounts of empty space. Regular structures with little or no branching allow the polymer chains to fit close together, forming a crystalline structure. Crystalline structures are generally stronger, more brittle, of higher density, more resistant to chemical penetration and degradation, less soluble, and have higher melting points. For example, HDPE has a density of 0.97 gram per milliliter and a melting point of about 130°C (266°F), whereas LDPE has a density of about 0.92 gram per milliliter and a melting point of about 100°C (212°F).

amorphous: containing chains that are arranged in less than a well-ordered, crystalline manner

Figure 11.



High-density polyethylene, 200 units, without branching in a crystalline structure (ball-and-stick model to the left and space-filling model on the right. Only carbon atoms are shown.)

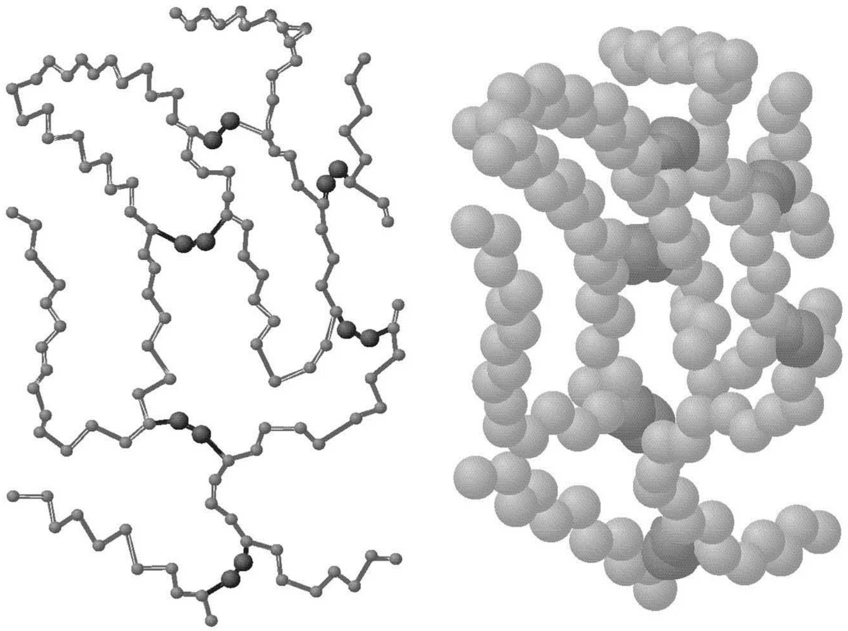


Low-density polyethylene, 200 units, with branching occurring about every 20 carbons, in an amorphous arrangement

Polymer chains can be connected to one another chemically or physically, much like a knot can connect two pieces of string. These connections are called crosslinks and cause the connected chains to act as a single unit

(Figure 12). Some materials can have only a few crosslinks, such as permanent press materials where the fabric contour is locked into place with crosslinks. Others materials such as Bakelite and ebonite are heavily crosslinked; these are hard, brittle, non-flexible materials.

Figure 12.



Low-density polyethylene, 200 repeat units, with crosslinks at 5 percent of the carbon atoms

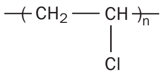
Physical Properties of Polymers

The properties of polymers are dependent on many factors including inter- and intrachain bonding, the nature of the backbone, processing events, presence/absence of additives including other polymers, chain size and geometry, and molecular weight distribution.

While most materials have melting/freezing and boiling/condensing points, polymers do not boil because the energy necessary to put a polymer into the vapor state is greater than the bond energies of the atoms that hold the polymer together, thus they degrade prior to boiling. In order for a polymer to be flexible, its various units or segments must be able to move. The glass transition temperature (T_g) is the temperature where polymer units or segments can move but the entire chain cannot. Most vinyl polymers have T_g values below room temperature so that they appear to be flexible and act as rubber and plastic materials. Most condensation polymers have T_g values above room temperature and are used as hard plastics and fibers. The temperature where entire chain movement occurs is called the melting point (T_m) and is greater than the T_g.

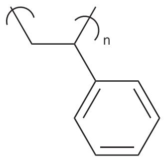
Many polymers are themselves brittle at room temperature. For these polymers to become more pliable, additives called plasticizers that allow segmental mobility, and consequently segmental flexibility, are added. For synthetic polymers such as poly(vinyl chloride) (PVC) and polystyrene (Figure 13), plasticizers are added that allow the polymers to be flexible.

Figure 13.



$$\left(CH_2 - \underset{\underset{\displaystyle Cl}{|}}{CH} \right)_n$$

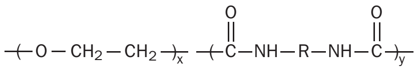
Poly(vinyl chloride), PVC



Polystyrene

The inflexible regions of a polymer, such as crystalline regions, are often referred to as “hard” regions. Conversely, the flexible regions of a polymer, where segmental mobility occurs, are referred to as “soft” regions. This combination of hard and soft can be illustrated with so-called segmented polyurethanes (Figure 14). The urethane portion of such polymers is involved in hydrogen bonding and is considered “hard,” while the polyether portion, flexible at room temperature, is considered “soft.” These segmented polyurethanes are sold under a number of trade names including Spandex.

Figure 14.



$$\left(O - CH_2 - CH_2 \right)_x \left(\overset{\overset{\displaystyle O}{\|}}{C} - NH - R - NH - \overset{\overset{\displaystyle O}{\|}}{C} \right)_y$$

Soft **Hard**

Segmented Polyurethane

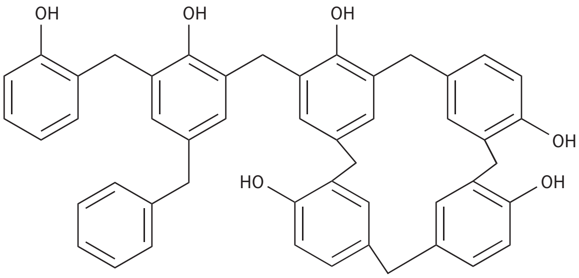
History of Synthetic Polymers

While polymers form the basis of life, the history of synthetic polymers is relatively recent. Some of the key polymers that have been developed since the early days of polymer science include:

Vulcanized rubber. In the mid-1800s, American scientist Charles Goodyear began working with rubber to try to make it more temperature stable. After many unsuccessful attempts, he accidentally allowed a mixture of sulfur and pre-rubber to touch a hot stove. The rubber did not melt but only charred a little. By 1844 Goodyear had been given a patent for a process he called “vulcanization” after the Roman god of fire, Vulcan. Vulcanization is the crosslinking reaction between the rubber chains and the sulfur.

Bakelite. After years of work in his chemistry lab in Yonkers, New York, Leo Baekeland announced in 1907 the synthesis of the first truly synthetic polymeric material, later dubbed “Bakelite.” It was generally recognized by leading organic chemists of the nineteenth century that phenol would condense with formaldehyde, but because they did not understand the principles of the reaction, they produced useless crosslinked materials. Baekeland’s main project was to make hard objects from phenol and formaldehyde and then dissolve the product to reform it again in a desired shape. He circumvented the problem by placing the reactants directly in a mold of the desired shape and then allowing the reactants to form a hard, clear solid—Bakelite (Figure 15). It could be worked (i.e., cut, drilled, and sanded), was resistant to acids and organic liquids, was stable at high temperatures, and did not break down when exposed to electrical charge. By adding dyes to the starting materials the objects became available in different colors. Bakelite was used to make bowling balls, phonograph records, telephone housings, cookware, and billiard balls. Bakelite also acted as a binder for textiles, sawdust, and paper, forming a wide range of composites including Formica laminates. Many of these combinations are still in use in the twenty-first century.

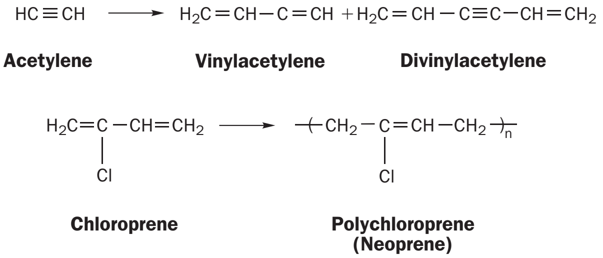
Figure 15.



Representative structure of the complex three-dimensional, highly crosslinked structure of Bakelite.

Neoprene. Chemist and Catholic priest Julius A. Nieuwland did extensive work in the 1920s on acetylene. He found that acetylene could be made to add to itself forming dimers and trimers. Arnold Collins, a chemist at the Dupont Company in the lab of Wallace Carothers, continued work on the project and in 1930 ran the reaction described by Nieuwland, purifying the reaction mixture. He found a small amount of material that was not vinylacetylene or divinylacetylene. After setting the liquid aside, it solidified into a material that seemed rubbery and even bounced. This new rubber was given the name Neoprene (Figure 16). Neoprene has outstanding resistance to gasoline, ozone, and oil in contrast to natural rubber and is used in a variety of applications including electrical cable jacketing, window gaskets, shoe soles, industrial hose, and heavy-duty drive belts.

Figure 16.

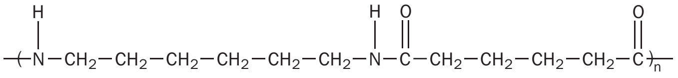


$$HC{\equiv}CH \longrightarrow H_2C{=}CH{-}C{=}CH + H_2C{=}CH{-}C{\equiv}C{-}CH{=}CH_2$$

$$H_2C{=}\underset{\displaystyle Cl}{\underset{|}{C}}{-}CH{=}CH_2 \longrightarrow {-}\!\!\left(CH_2{-}\underset{\displaystyle Cl}{\underset{|}{C}}{=}CH{-}CH_2\right)_{n}\!\!{-}$$

Nylon. In the early 1930s Wallace Carothers and his team of chemists at Dupont were investigating synthetic fibers in order to find a synthetic alternative to silk. One promising candidate was formed from the reaction of adipic acid with hexamethylenediamine and was called fiber 66 because each monomer-containing unit had six carbons. It formed a strong, elastic, largely insoluble fiber with a relatively high melting temperature. DuPont chose this material for production. Such polyamides were given the name “nylons”; thus was born nylon 6,6 (Figure 17).

Figure 17.



$$-\!\!\left(\overset{\displaystyle H}{\overset{|}{N}}{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}\overset{\displaystyle H}{\overset{|}{N}}{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}\overset{\displaystyle O}{\overset{\|}{C}}\right)_{n}\!\!-$$

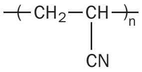
Nylon 6,6

Poly(vinyl chloride). While PVC was initially formed by German chemist Eugen Baumann in 1872, scientists at B. F. Goodrich discovered in 1926 how to make sheets and adhesives from it, starting the "vinyl age." PVC's many applications include water pipes and joints, building materials, food packaging, wire insulation, and medical components.

Polystyrene. While polystyrene was probably first formed by German apothecary Eduard Simon in 1839, it was almost 100 years later, in 1930, that the German chemical company I. G. Fraben placed polystyrene on the market. Polystyrene-molded parts became common place by 1935. Applications of polystyrene include loose-fill packaging "peanuts," shape-molded packaging, and disposable utensils.

Polyacrylonitrile. Rohm and Haas Company bought out Plexiglas (polyacrylonitrile [Figure 18]; also known as acrylic and as a fiber sold under tradenames such as Orlon) from a British firm in 1935 and began production of clear plastic parts and goods, including replacements for glass in camera lenses, aircraft windows, clock faces, and car tail lights.

Figure 18.

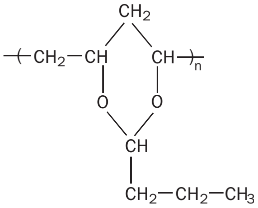


$$-\!\left(CH_2-\underset{\displaystyle CN}{\underset{|}{CH}}- \right)_n\!-$$

Polyacrylonitrile

Poly(vinyl butyral). The polymer poly(vinyl butyral) (PVB) was first used in automotive safety glass in 1938 to prevent flying glass resulting from automobile accidents and continues to be utilized in the twenty-first century for this purpose (Figure 19).

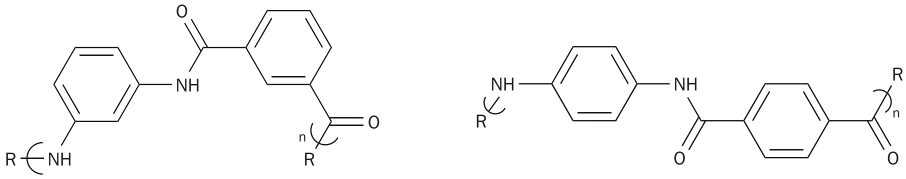
Figure 19.



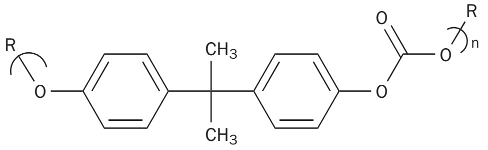
Poly(vinyl butyral), PVB

Other important synthetic polymers. World War II helped shape the future of polymers. Wartime demands and shortages encouraged scientists to seek substitutes and materials that exceeded currently available materials. During and after the war new materials were developed, spurred by needs in the electronics, medical, communications, food, aerospace, and other industries. The aromatic nylons (armids) Kevlar (capable of stopping a speeding bullet and used as tire cord) and Nomex (used in constructing fire-resistant garments) were developed. Polycarbonates sold under the trade names of Merlon and Lexon were developed that substituted for glass in many automotive products such as tail lights. Other key developments included polytetrafluoroethylene, a slick material also known as Teflon; polysiloxanes, also know as silicones, which have an extremely wide temperature-use range and were a component of the soles of the shoes that first touched the moon; and polyester fibers and plastics such as poly(ethylene terephthalate) (PET), used in carbonated drink bottles (Figure 20).

Figure 20.

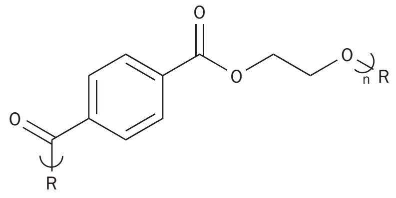


Nomex **Kevlar**



Polycarbonate

Polytetrafluoroethylene **Polydimethylsiloxane**



Even with this early commercial activity, little was actually known about polymers. German chemist Herman Staudinger studied the polymerization of isoprene (a five-carbon hydrocarbon containing a double bond that is obtained as a product of the degradation of natural rubber by heating) as early as 1910. Intrigued by the difference between this synthetic material and natural rubber he began to study giant molecules. Many of his fellow scientists told him there was no such thing as giant molecules and that he was wasting his time. By 1920 he published a summary of his studies and correctly proposed linear structures for polystyrene and polyoxymethylene. X-ray studies were used to support the concept of macromolecules.

Wallace Hume Carothers is considered to be the father of synthetic polymer science. In 1927 the DuPont Company began a program of fundamental research in the areas of colloid chemistry, catalysis, organic synthesis, and polymer formation. Carothers, then a Harvard instructor, was persuaded to join the DuPont group. Carothers looked at the construction of giant molecules from small molecules to form synthetic polymers. His intention was to prepare molecules of known structure through the use of known organic chemistry and to "investigate how the properties of these substances depended on constitution." Over the course of his career, Carothers filed for over fifty patents and was involved in the discovery of nylon and the synthetic rubber neoprene.

From his studies Carothers established several concepts. First, polymers could be formed by employing already known organic reactions but with reactants that had more than one reactive group per molecule. Second, the forces that bring together the individual polymer units are the same as those that hold together the starting materials: namely, primary covalent bonds. Much of the polymer chemistry names and ideas that permeate polymer science were standardized through his efforts.

MAJOR SYNTHETIC ELASTOMERS

Polychloroprene	Epichlorohydrin Copolymers
Styrene-Butadiene, SBR	Polybutadiene
Nitrile	Ethylene-Propylene
Neoprene	Polyfluorocarbon
Silicone	Polyurethane (Segmented)
Polyisoprene	Butadiene-Acrylonitrile
Styrene-Isoprene	

Table 1.

Types of Synthetic Polymers

Elastomers. Elastomers are polymers possessing chemical and/or physical crosslinks (Table 1 and 2). These crosslinks allow the stretched, deformed segments to return to their original locations after the force is removed. The “use” temperature must be above the T_g to allow ready chain slippage as the rubbery material is flexed and extended. The forces between the chains should be minimal to allow easy movement of these chain segments. Finally, the chains must be present in an amorphous, disorganized fashion. As force is applied and the material distorts or elongates, the randomly oriented chains are forced to align and take more ordered positions with the chains, forming crystalline regions that resist ready movement. As the force is removed the material has a tendency to return to its original disorganized state and therefore its pre-stretched shape. The formation of the crystalline regions as the material is stretched gives the material a greater tensile strength (i.e. an increased force is necessary for further elongation) at high extensions. Crosslinked vinyl polymers are ideal materials to be used in elastomers: the attractive forces between chains is low and their T_g is below room temperature.

Thermosets and thermoplastics. Thermosets are materials that have sufficient crosslinking present so that they are prevented from being soluble and melting when heated. Such materials are therefore difficult to recycle. Thermoplastics are materials that melt on heating and generally contain little or no crosslinking. They can be recycled more easily through heating and reforming. Linear polymers are thermoplastic materials.

Fibers. Fibers require materials with a high tensile strength and high modulus (high force required for elongation). This requires polymers with strong forces between the chains and chains that are symmetrical to allow for good crystalline formation. Condensation polymers exhibit these properties and so are most utilized as fibers. Fibers are normally linear and drawn (pulled) in one direction, producing higher mechanical properties in that direction. If the fiber is to be ironed, its T_g should be above 200°C. Branching and crosslinking are undesirable since they inhibit crystalline formation. Even so, some crosslinking may be present to maintain a given orientation, such as desired in permanent press clothing. While most fibers are made from condensation polymers, new treatments allow some fibers to be made from olefinic materials such as polypropylene (Table 3).

Plastics. Plastics require properties that are intermediate between elastomers and fibers. Engineering plastics can be readily machined, cut, and drilled. Condensation polymers are typically engineering plastics while vinyl polymers are typically plastics. Table 4 contains a listing of the most common engineering plastics and plastic materials and Table 5 the volume of engineering plastics and plastics produced in the United States.

U.S. PRODUCTION OF ELASTOMERIC MATERIALS IN 2000

Elastomer	Production (millions of pounds)
Ethylene-Propylene	700
Nitrile	180
Polybutylene	1,210
Styrene-Butadiene	1,750
Other	1,100

Source: International Institution of Synthetic Rubber Producers.

Table 2.

U. S. PRODUCTION OF FIBERS IN 2000

Fiber	Production (millions of pounds)
Cellulosic, Acetate and Rayon	350
Fiber Glass	2,000
Acrylics	340
Polyesters	3,870
Nylons	2,610
Olefins	3,180

Source: Fiber Economics Board

Table 3.

Coatings. Coatings and adhesives are generally derived from polymers that are considered to be plastics, although there are major groups that do not. For instance, silicone rubbers are elastomers that can be used as adhesives. Coatings, or coverings, are generally highly viscous (low flowing) materials. Coatings protect surfaces from the degradative effects of oils, oxidative chemical agents, extreme temperatures, rain, snow, and ionizing radiation. Coatings must adhere to the surface they are applied to. Coatings are typically a mixture of a liquid (vehicle or binder/adhesive) and one or more colorants (pigments). Coatings often also contain a number of so-called additives that can furnish added protection against ionizing radiation, increase the rate of drying and/or curing (crosslinking), and prevent microorganism growth. Coatings are specially formulated for specific purposes and locations and can be divided into five groups:

- Oil paints consist of a suspension of pigment (colorant) in a drying oil such as linseed oil.
- Oil varnishes consist of a polymer, either natural or synthetic, dissolved in a drying oil together with the necessary additives such as catalyst that promotes crosslinking of the drying oil.
- Enamels are oil varnishes with pigment added.
- Lacquers are polymer solutions to which pigments have been added.
- Latex paints are polymer latexes, often poly(methyl methacrylate) and polyacrylonitrile, to which pigments have been added. They account for well over one half of the commercial paint used.

Hardening or drying consists of removal of solvent (evaporation) and/or crosslinking of a drying oil that contains C=C units.

Adhesives. In contrast to coatings that must adhere to only one surface, adhesives are used to join two surfaces together (Table 6). Adhesion for both adhesives and coatings can occur through a number of mechanisms including physical interlocking, chemical adhesion where primary bonding occurs between the adhesive and the surfaces being joined, secondary bonding where hydrogen bonding or polar bonding occurs, and viscosity adhesion where movement is restricted because of the viscous nature of the adhesive material. Adhesives can be divided according to the type of delivery of the adhesive or by the type of polymer:

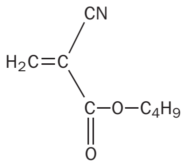
INDUSTRIALLY IMPORTANT ENGINEERING PLASTICS AND PLASTICS

Epoxies	Polyesters
Urea-Formaldehydes	Melamine-Formaldehydes
Phenolics (Phenol-Formaldehydes)	Polyethylenes
Polypropylene	Styrene-Acrylonitriles
Polystyrene	Polyamides
Poly(vinyl chloride) and Co-polymers	
Polytetrafluoroethylene	Poly(methyl methacrylate)
Polycarbonates	Silicons
Polysulphone	Poly(phenylene oxide)
Polyimides	

Table 4.

- Solvent-based adhesives like model airplane glue contain a volatile solvent that dissolves part of the plastic and when dry forms a solvent weld.
- Pressure-sensitive adhesives like those used on Post-It-Notes often contain the same adhesive material used in more permanent adhesives like Scotch Tape except in lesser amounts.
- Reactive adhesives are short chained polymers or monomers that solidify through polymerization or crosslinking after application.
- Plywood is formed from the impregnation of thin sheets of wood with resin that dries after the sheets are pressed together. Phenolic thermosets such as those developed by Bakelite are often used as the resins for plywood.
- Adhesives made from cyanoacrylates are among the best known adhesives, sold under trade names such as Super Glue and Crazy Glue. Monomers such as butyl-alpha-cyanoacrylate (Figure 16) polymerize spontaneously in the presence of moisture. The presence of the cyano and acrylate groups, both quite polar, makes this a particularly good adhesive; it is used in surgery and for mechanical assemblies.

Figure 21.



Butyl-alpha-cyanoacrylate

Sealants and caulks. Sealants and caulks provide a barrier to the passage of gases, liquids, and solids; maintain pressure differences; and moderate mechanical and thermal shock. While adhesives are used for "load transfer" and require high tensile and shear strengths, sealants act as insulators and shock attenuators and do not require high tensile and shear strengths.

Films and sheeting. Films are two-dimensional forms of plastic, thick enough to be coherent, but thin enough to be flexed, creased, or folded without cracking. Most films are produced from materials from the elastomeric and plastic categories. Sheeting is a two-dimensional form of plastic that is thicker (generally greater than 250 micrometers) than film and is generally not easily flexed, creased, or folded without cracking.

INDUSTRIALLY IMPORTANT ENGINEERING PLASTICS AND PLASTICS

Epoxies	Polyesters
Urea-Formaldehydes	Melamine-Formaldehydes
Phenolics (Phenol-Formaldehydes)	Polyethylenes
Polypropylene	Styrene-Acrylonitriles
Polystyrene	Polyamides
Poly(vinyl chloride) and Co-polymers	
Polytetrafluoroethylene	Poly(methyl methacrylate)
Polycarbonates	Silicons
Polysulphone	Poly(phenylene oxide)
Polyimides	

Table 6.

U.S. PRODUCTION OF PLASTICS AND ENGINEERING PLASTICS IN 2000

Plastic	Production (millions of pounds)
Nylons	1,400
Polyesters	4,400
Acrylonitrile-Butadiene-Styrene, ABS	3,100
Polyethylene, high density	15,400
Polyethylene, low density	17,900
Styrene-Acrylonitrile	125
Polystyrene	6,600
Polypropylene	15,400
Poly(vinyl chloride) & Copolymers	14,300

Source: C & E News

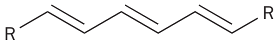
Table 5.

Composites. Composites are materials that contain strong fibers or reinforcement embedded in a continuous phase called a matrix. They are found in jet fighters such as stealth fighters and bombers, in the "reusable" space shuttle, in graphite golf clubs, in synthetic human body parts, and for many years in marine craft (fibrous glass).

Laminates. The combination of an adhesive and an adherent is a laminate, a type of composite. Commercial laminates are produced on a large scale with wood as the adherent and phenolic, urea, epoxy, resorcinol, or polyester resins as the adhesive. Plywood is an example of a laminate. Laminates of paper or textile include Formica and Micarta. Laminates of phenolic, nylon, or silicone resins with cotton, asbestos, paper, or glass textiles are used as mechanical, electrical, and general purpose structural materials.

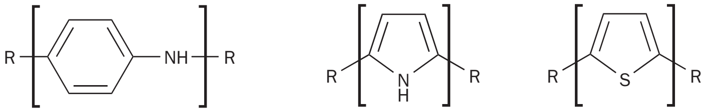
Conductive polymers. Most polymers are nonconductive and polymers such as polyethylene, polypropylene and polytetrafluoroethylene (Teflon) are used as insulators. Even so, some polymers have been found to conduct electricity. An example is polyacetylene; oxidation with chlorine, bromine, or iodine vapor makes polyacetylene film10^9 (1,000,000,000) times more conductive than the non-treated film (Figure 17). This treatment with a halogen is called "doping." Other polymers including polyaniline, polythiophene, and polypyrrole have been found to be conducting after doping and these materials are now being used in a variety of applications (Figure 18). Doped polyaniline is employed as a conductor and as an electromagnetic shielding for electronic circuits. Polythiophene derivatives are used in field-effect transistors. Polypyrrole is used in microwave-absorbing "stealth" screen coatings and in sensing devices. Poly(phenylene vinylidene) derivatives are used in the production of electroluminescent displays.

Figure 22.



Segment of trans-polyacetylene

Figure 23.



Polyaniline **Polypyrrole** **Polythiophene**

Polymer Synthesis

The process by which polymers are formed from monomers is called polymerization. Polymerization occurs by one of two basic reactions: addition or condensation. In addition polymerization, entire monomers are linked together to form long chains. In condensation polymerization, some small molecules (such as water) are released as polymer is formed.

Polymerization reactions may be divided into two major categories: step-wise processes and chain-type processes. In the step-wise process, reactants are brought together and heated. Initially short chains are formed and only at the end of the reaction are long chains formed. Reactions generally require hours to form the polymers. It is by this process that condensation polymers are generally made.

Vinyl polymers are formed using a chain-type process that involves three steps:

- Initiation. This first step requires that the monomer's double bond is broken. This can occur by means of heat or light, or by the addition of other chemical compounds that have less stable bonds. The decomposition products of these chemical compounds add to the vinyl monomer, causing the double bond to break. These materials are called initiators because they start the polymerization process.
- Propagation. This second step involves growth of the polymer chain by the addition of monomer units. This occurs rapidly, within fractions of a second.
- Termination. Finally, the growth of the chain is stopped (terminated).

The process of initiation, growth, and termination continues until the monomer is consumed. Reactions often occur at or below room temperature.

Synthetic Routes

Starting materials are often referred to as feedstocks. Most of the starting materials (monomers) employed in the synthesis of synthetic polymers like polystyrene, polyethylene, and nylons are derived indirectly from fossil fuels. The term fossil fuels refer to materials formed from the decomposition of once-living matter.

There are four basic routes by which polymers are synthesized industrially:

Melt process. Also referred to by other names including high melt, bulk melt, bulk, or neat. The melt process is an equilibrium-controlled process in which polymer is formed by driving the reaction toward completion, usually through removal of the byproduct or condensate. Thus, in the reaction of a diacid and a diol to form a polyester, water is removed, causing the reaction to proceed towards polymer formation. The reactants are employed "neat" (without solvent); any other needed materials such as catalysts are added to the reaction vessel. Heat is applied to melt the reactants, permitting them to come into contact with one another. Additional heat can be added and the pressure reduced, but heat control is important since most of these reactions are exothermic. These reactions typically take several hours to days before the desired polymer is formed. The product yield is necessarily high.

Solution process. Solution polymerizations are also equilibrium processes, with the reaction also often driven by removal of the small byproduct. The product may be recovered from the reaction system through addition of the reaction liquid to a non-solvent, removal of the solvent, or direct precipitation of the polymer from the reaction system. Because the reaction is often run at a lower temperature, more reactive reactants are generally required.

Suspension process. Water-insoluble monomers can be polymerized as suspended droplets in a process called suspension polymerization. Coalescing of the droplets is prevented by use of small amounts of water-soluble polymers such as poly(vinyl alcohol).

Emulsion process. The emulsion process differs from suspension polymerization in the size of the suspended particles and in the mechanism.

Polymer Companies

About 10,000 companies in the United States are active in synthetic polymers. These companies can be divided into three groupings:

Manufacturers. Over 200 companies produce the "bulk" polymers that are used by the other two groupings of companies. While most of these produce the bulk polymers in large quantities, some produce what are called "specialty polymers," those used in special applications on a small scale.

Processors. While some companies produce their own polymers, most purchase the raw polymer material from a manufacturing company. Processors may specialize in the use of selected polymers, such as polypropylenes, polyethylenes, or nylons; in a particular mode of processing; or in the production of particular markets such as films, sheets, laminates, adhesives, or coatings.

Fabricators and finishers. The large majority of companies are involved in the fabrication and finishing of polymer-containing products. Fabrication can be divided into three broad areas: machining, forming, and fashioning. SEE ALSO Adhesives; Fibers; Nylons; Plastics; Polyesters; Polymers, Natural.

Charles E. Carraher Jr.

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Polypeptide ***See Proteins.***

Polysaccharides

monosaccharide: one class of the natural products called carbohydrates with the general formula $C_x(H_2O)_y$; monosaccharides have a weak sweet taste, are readily soluble in water, and are called sugars

Polysaccharides are long polymers of **monosaccharides** and their derivatives. Unlike proteins or nucleic acids, these polymers can be either linear or branched, and they can contain only one type of monosaccharide (homopolysaccharides), or more than one (heteropolysaccharides). Polysaccharides can also be roughly divided into groups according to their two main functions: energy storage and their contributions to structural components of cells.

Starch is the main energy reserve in plants; glycogen is the main energy reserve in animals. Starch is a homopolysaccharide and has two forms: amylopectin and α-amylose. In nature, starch is approximately 10 to 30 percent α-amylose. Alpha-amylose is a linear chain polymer composed of **glucose** residues in α (1→4) linkages. Its molecular weight varies from several thousand to more than one million grams (2,205 pounds) per mole. In contrast to amylopectin, which comprises 70 to 90 percent of natural starch, α-amylose is a branching polysaccharide. Although amylopectin, like α-amylose, is composed entirely of α-glucose, its α-glucose residues are joined not only in α (1→4) linkages but also at α (1→6) branch points. Branches occur at every twelve to thirty residues along a chain of α (1→4) linked glucoses. As a result, amylopectin has one reducing end and many nonreducing ends. Amylopectin and α-amylose are broken down by the enzyme amylase. In animals, salivary α-amylase begins the digestion process in the mouth. Pancreatic α-amylase continues the process in the intestine.

glucose: common hexose monosaccharide; monomer of starch and cellulose; also called grape sugar, blood sugar, or dextrose

Glycogen is the energy storage carbohydrate in animals. Glycogen is found mainly in the liver (where it is responsible for up to 10 percent of liver mass) and skeletal muscle (1 to 2 percent of skeletal muscle mass). Like amylopectin, it consists of α-glucose residues in α (1→4) linkage, with α (1→6) branch points. However, glycogen branches more abundantly than amylopectin, with branches at every eight to twelve residues. As a result, it has many more nonreducing ends. Glycogen is broken down at these nonreducing ends by the enzyme glycogen phosphorylase to release glucose for energy. Having many reducing ends, glycogen is more readily broken down in cases in which an animal needs a sudden burst of energy.

The primary structural homopolysaccharides are cellulose and chitin. Cellulose, a major component of plant cell walls, is the most abundant natural polymer on Earth. It is responsible for much of the mass of wood. Cotton is almost pure cellulose. Like α-amylose, cellulose is a linear polysaccharide composed entirely of glucose. However, in cellulose the glucose residues occur in β(1→4) linkage rather than α (1→4) (see Figure 1). This change in linkage has profound effects on the chemical and structural properties of cellulose. The glucose molecules in cellulose are alternately inverted (every other one inverted) such that each chain has a highly extended and rigid conformation. In addition, individual cellulose strands can form **hydrogen bonds** with one another to provide additional strength. Most animals, including humans, lack the enzymes necessary to dissolve β(1→4) linkages and so cannot digest cellulose. The animals that can (such as ruminants) do so via a symbiosis with bacteria that secrete cellulose-degrading enzymes.

hydrogen bond: interaction between H atoms on one molecule and lone pair electrons on another molecule that constitutes hydrogen bonding

The second most abundant polymer on Earth is chitin. Chitin comprises much of the exoskeletons of crustaceans, insects, and spiders, as well as the cell walls of fungi. Structurally, chitin is very similar to cellulose, except that its basic monosaccharide is N-acetylglucosamine. Chitin, like cellulose, has its repeating units joined in β(1→4) linkages. SEE ALSO CARBOHYDRATES; DISACCHARIDES.

Stephanie E. Dew

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International Union of Pure and Applied Chemistry. Information available from <http://www.chem.qmw.ac.uk/iupac/>.

Postactinides ***See Transactinides.***

Potassium

MELTING POINT: 63.38°C
BOILING POINT: 759°C
DENSITY: 0.862 g/cm^3
MOST COMMON IONS: K^+

19
K
POTASSIUM
39.0983

metal: element or other substance, the solid phase of which is characterized by high thermal and electrical conductivities

fractional distillation: separation of liquid mixtures by collecting separately the distillates at certain temperatures

Potassium is a soft, silvery alkali **metal** that reacts strongly with water to produce hydrogen gas. The word "potassium" is derived from "potash" or "pot ashes," as Humphry Davy isolated the element in 1807 via the electrolysis of caustic potash, KOH. The element's symbol is derived from *kalium* (Latin), which originated from *qali* (Arabic for "alkali"). Currently, potassium metal is generated by the reduction of molten potassium chloride, KCl, with sodium and the use of **fractional distillation** to separate the resulting mixture. In nature it is never found in its elemental form. Compounds of potassium are found primarily in the minerals sylvite, carnallite, langbeinite, and polyhalite, as well as in the brines of the Dead Sea in Jordan and the Great Salt Lake in Utah. Potassium is the second most abundant alkali metal and the eighth most abundant element in Earth's crust (18,400 ppm). Potassium burns violet in the flame test.

alloy: mixture of two or more elements, at least one of which is a metal

nuclear: having to do with the nucleus of an atom;

The industrial demand for potassium metal is much smaller than that for sodium. Potassium-sodium **alloys** (which are liquid at room temperature) serve as heat-exchange liquids in the cooling systems of **nuclear** reactors. Strong bases such as potassium amides and alkoxides are formed from the reaction of potassium with amines and alcohols, respectively.

Compounds of potassium are economically more important than the metal. KCl is used extensively in fertilizers. KOH is used to make liquid soaps and detergents. Potassium nitrate, KNO_3, serves primarily as an oxidizing agent in gunpowder and pyrotechnics. Potassium superoxide, KO_2, is used in backup ventilation equipment as it generates oxygen gas in the presence of CO_2. Potassium ions are essential to plants and animals as many metabolic reactions and pathways depend on their presence. SEE ALSO Alkali Metals.

Nathan J. Barrows

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Praseodymium

MELTING POINT: 935°C
BOILING POINT: 3,017°C
DENSITY: 6.475 g/cm^3
MOST COMMON IONS: Pr^{3+}, Pr^{4+}

59
Pr
PRASEODYMIUM
140.908

In 1885 C. A. von Welsbach isolated two elements as oxides, praseodymium (the word meaning "green twin") and neodymium (meaning "new twin"), from a mixture of **lanthanide** oxides called didymia. The oxides can be transformed to fluorides by reaction with HF at 700°C (1,292°F), or with NH_4HF_2 at 300°C (572°F). The hydrated fluorides are then dehydrated in vacuo in a current of HF gas. The **metals** praseodymium and neodymium are obtained via metallothermic reduction with calcium at approximately 1,450°C (2,642°F), or via electrolytic reduction of the melts. The metals can also be obtained from anhydrous chlorides, obtained via reaction of the oxides with ammonium chloride at 350°C (662°F), which are then reduced with lithium-magnesium at approximately 100°C (212°F).

lanthanides: a family of elements (atomic number 57 through 70) from lanthanum to lutetium having from 1 to 14 4f electrons

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Praseodymium halides (except the fluoride), nitrate, and acetate are soluble. The hydroxide, carbonate, oxalate phosphate, and oxide compounds are insoluble. Praseodymium's solutions and most of its solids are green.

When oxo-compounds of Pr(III) are ignited in the atmosphere, a black oxide of composition Pr_6O_{11} (approximately) is obtained. Fluorocomplexes of Pr(IV) that have the compositions Na_2PrF_6, $Na_7Pr_6F_{31}$, and PrF_4 have been obtained.

Pr(III) salts and complexes are weakly luminescent. The salts are used to color some special glasses and as pigments in ceramics. The compound $Zr_{1-x}Pr_xSiO_4$ is used often as a yellow pigment in the ceramic industry; it is very stable in color and resistant to high temperatures. Pr(III), in Pr_2S_3, is an excellent pigment for plastics and paints. Other uses of praseodymium include tires (Pr-doped $ZrSiO_4$), photographic filters (Pr_2O_3), and welding masks (Pr-Nd). SEE ALSO Lanthanides.

Lea B. Zinner
Geraldo Vicentini

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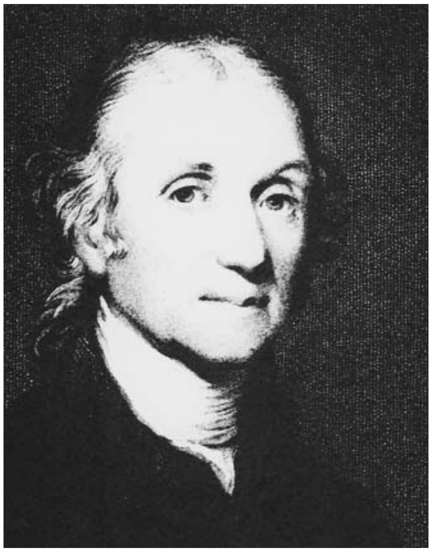
Precious Metals ***See Gold; Palladium; Platinum; Silver.***

Priestley, Joseph

ENGLISH THEOLOGIAN AND CHEMIST
1733–1804

Joseph Priestley was a dissenting Unitarian minister in England at a time when adherence to the established Church of England was of great importance. Preaching was a difficult career for Priestley—because his Unitarian views were unpopular and because he spoke with a stammer. Priestley pub-



English chemist Joseph Priestley, the first person to isolate a number of gases, including oxygen.

lished widely in a variety of subjects, including theology, education, history, politics, and science. Most often, Priestley is remembered as one of the discoverers of oxygen, but his impact on other lives went much further than this.

Royal Society: The U.K. National Academy of Science, founded in 1660

Newtonian: based on the physics of Isaac Newton

His first major science publication was *The History and Present State of Electricity* (1767), which gained him admission to the **Royal Society**; it was followed by *The History and Present State of Discoveries Relating to Vision, Light and Colours* (1772). Both light and electricity were regarded as aspects of the **Newtonian** "imponderable fluid" or "ether." They were called "imponderable fluids" (or subtle fluids) because they had no detectable weight (no "poundage"), but still had some fluidlike characteristics. Another form of this "ether" was "phlogiston." Phlogiston was the postulated substance of fire, the active principle of acids, and the driving force behind chemical reactions.

nitric oxide: compound, NO, which is involved in many biological processes; the drug Viagra enhances NO-stimulation of pathways to counteract impotence; may be involved in killing tumors

As Priestley expanded his studies in chemistry he became active in the field of pneumatic chemistry, the study of air and gases. Priestley was the first to isolate and characterize a number of gases, including oxygen, nitrogen, hydrogen chloride, ammonia, sulfur dioxide, carbon monoxide, **nitric oxide**, and nitrous oxide. Priestley's names for these compounds were different from the modern names, in part because he never adopted the oxygen theory of chemistry. The names he used were in terms of the older "phlogiston theory." Priestley did this work using very simple apparatuses, such as saucers, glasses, tubes, cylinders, and tubs of water or mercury.

Among the chemical phenomena he investigated was the behavior of a gas or other substance in contact with fire. If fire was the visible escape of phlogiston from a burning substance, then some gases had a greater affinity for phlogiston than ordinary air and encouraged the flame. Other gases had a lesser affinity for phlogiston than ordinary air (or no affinity at all) and would extinguish the flame.

calx: substance produced by roasting or burning a mineral, taken as the essence of the mineral

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

One gas was found to be especially able to support a flame. Priestley called this gas "eminently respirable air." He later called this same substance "dephlogisticated air," reasoning that because it had a large affinity for phlogiston, it must be particularly devoid of it, or dephlogisticated. Priestley found that the heating of a sample of "red precipitate" (a **calx** of mercury) to produce pure mercury generated very pure dephlogisticated air. Priestley's discovery of the large amount of "air" generated during the heating of red precipitate was similar to Joseph Black's discovery of "fixed air." The production of dephlogisticated air also fit Priestley's belief that a **metal** is phlogiston compounded with a calc. The dephlogisticated air liberated from red precipitate also fit well with the observation that when a candle burned out in a closed vessel, the volume of the air was diminished. It was thought that the presence of phlogiston decreased the "springiness" of air. Thus, adding phlogiston to air would cause it to contract, and removing phlogiston from air would cause it to expand. Priestley also found that air saturated with phlogiston could be "revivified" (or dephlogisticated) by green plants in the presence of sunlight. Dephlogisticated air would be renamed "oxygen" by Antoine Lavoisier, who made it the cornerstone of his theory of chemistry.

Priestley resisted the oxygen theory of chemistry to the end of his life. For Priestley, phlogiston was more than just the active principle of fire—it

PHLOGISTON

There never was a widespread coherent theory of phlogiston. German chemist Johann J. Becher (1635–1682) brought the term "phlogiston" into use among European chemists in the middle 1600s. The word is based upon a Greek word used by Aristotle in his writings on matter. German chemist Georg Stahl (1660–1734) further articulated the phlogiston theory in the early 1700s.

According to the phlogiston theory, a flame was thought to be the visible escape of matter called phlogiston from a burning substance. Another key feature of the theory was that a metal was thought to be composed of phlogiston and earth. Luster, high heat conductivity, malleability, and ductility are all unusual characteristics for metals, but according to the theory, metals share these features because of their postulated phlogiston content. If the phlogiston was removed from a metal, the result was an earth called calc (plural, calx), often the metal's naturally occurring ore. Under certain conditions, phlogiston might even exhibit a negative weight! This anomaly became problematic after Sir Isaac Newton's 1687 Law of Universal Gravitation.

—David A. Bassett

was the active principle of life. Here Priestley's scientific theory merged with some of his religious beliefs. If phlogiston were the active principle of fire, heat, light, electricity, acids, chemical reactivity, and life, then it might also be the active principle of spirit. This accorded well with his Unitarian belief in one omnipresent active principle in the universe. In his book *Disquisition on Matter and Spirit* (1777), he asserted that there was only matter and void in the universe—there were no immaterial spiritual influences. Thus, the material existence of phlogiston corresponded well with his religious beliefs.

Priestley also had strong convictions in favor of broad-based democratic reforms and freedom of thought. He advocated wider religious toleration in England. He supported the American colonists in their revolution against the British Crown and supported the French Revolution, even in the face of atrocities such as the Reign of Terror. Priestley made enemies as a result of his political beliefs, and in 1791 his house and laboratory in Birmingham were attacked and burned by a mob. Priestley fled to London and was able to emigrate from there to the United States in 1794. In the United States he was a renowned international figure. When he landed in New York, both the mayor and the governor greeted him. When he arrived in Philadelphia, he was received by President Washington.

In 1794 Priestley declined an offer to be a professor of chemistry at the University of Pennsylvania. He retired from public life in Northumberland, Pennsylvania, and died there in 1804. His home in Northumberland is now preserved as a historical landmark. According to Peter Miller (1993), "A work entitled 'Joseph Priestley in Context' would . . . far surpass the competence of any single chronicler." SEE ALSO GASES; LAVOISIER, ANTOINE; NITROGEN; OXYGEN.

David A. Bassett

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Primary Structure

There are four recognized levels of protein structure: primary, secondary, tertiary, and quaternary. The primary structure refers to the **amino acid sequence** of a protein. The primary structure is important to the protein's unique three-dimensional structure, its mechanism of action, and its relationship to other proteins with similar physiological roles. The amino acids in a protein✷ are linked together by a specific type of **covalent bond**, called a peptide bond, that exists between adjacent amino acids in the **polypeptide** chain. Another important aspect of the primary structure is the sequence or order of amino acids in the polypeptide chain. The sequence of amino acids in a protein is specified by the nucleotide sequence of the segment of **DNA** containing the gene that codes for that protein. Each protein has a characteristic number and sequence of amino acid residues. The primary structure of a protein determines how the protein folds into a unique three-dimensional structure (further described by the secondary, tertiary, and quaternary structures), which in turn determines the biological function of the protein. SEE ALSO Peptide Bond; Proteins; Quaternary Structure; Secondary Structure; Tertiary Structure.

Elizabeth S. Roberts-Kirchhoff

amino acid sequence: twenty of the more than five hundred amino acids that are known to occur in nature are incorporated into a variety of proteins that are required for life processes; the sequence or order of the amino acids present determines the nature of the protein

✷See the Amino Acids article for a table of the amino acids.

covalent bond: bond formed between two atoms that mutually share a pair of electrons

polypeptide: compound containing two or more amino aryl—C(O)NH—units; produced by the condensation of two or more amino acids

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

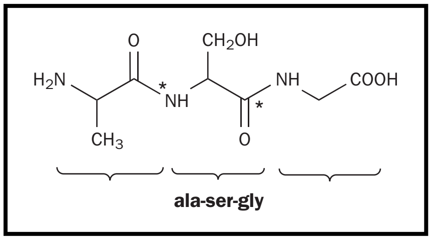

Figure 1. Structure of a tripeptide with the peptide bonds marked with an asterisk. The primary sequence is the order of amino acids, and in this example the primary sequence is ala-ser-gly.

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Promethium

61
Pm
PROMETHIUM
145

MELTING POINT: 1,100°C
BOILING POINT: 3,000°C
DENSITY: 7.22 g/cm^3
MOST COMMON IONS: Pm^{3+}

The existence of promethium was first theorized in 1902 by Bohuslav Brauner, who predicted that an element between neodymium and samarium was missing from the periodic table. Because only minuscule amounts of promethium are naturally present in Earth's crust, full confirmation of this prediction was not made until 1945. Working at the Oak Ridge National Laboratory in Oak Ridge, Tennessee, Jacob Marinsky, Lawrence Glendenin, and Charles Coryell produced promethium by the **nuclear fission** of uranium and by neutron irradiation of neodymium, chemically identifying the new element using **ion exchange chromatography**.

In compounds, promethium is known to exist in the tripositive **oxidation** state only (Pm^{3+}), which is the most stable oxidation state for all of the **rare earth elements**. Consequently, its chemistry is like that of other rare earth elements and of the tripositive actinide ions, especially Am^{3+}, which is almost the same size as Pm^{3+}. When enough material is present to see, promethium compounds are generally a pale pink color under white light. In the dark, however, the intense radioactivity of all promethium **isotopes** causes macroscopic amounts of promethium compounds to glow pale blue or green. The isotope ^{145}Pm has the longest half-life (17.7 years), but ^{147}Pm (half-life 2.6234 years) is produced in significant quantities from the fission of uranium and plutonium in nuclear reactors, and convenient methods for isolating gram amounts of ^{147}Pm by displacement **chromatography** have been described. The availability, high specific activity (928 Ci/gram), and pure β-particle emission of ^{147}Pm lend it to industrial applications in thickness gauges, nuclear batteries, and emergency lights that operate without an external power source. SEE ALSO CERIUM; DYSPROSIUM; ERBIUM; EUROPIUM; GADOLINIUM; HOLMIUM; LANTHANUM; LUTETIUM; NEODYMIUM; NUCLEAR FISSION; PRASEODYMIUM; SAMARIUM; TERBIUM; YTTERBIUM.

Mark Jensen

nuclear: having to do with the nucleus of an atom

fission: process of splitting an atom into smaller pieces

ion exchange chromatography: form of liquid-solid chromatography based on the reversible formation of bonds between the fixed ions bound to an insoluble matrix of an ion exchanger and mobile counter ions present in the liquid phase passing over the insoluble matrix

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

rare earth elements: older name for the lanthanide series of elements, from Lanthanum to Lutetium

isotope: form of an atom that differs by the number of neutrons in the nucleus

chromatography: the separation of the components of a mixture in one phase (the mobile phase) by passing it through another phase (the stationary phase) making use of the extent to which the components are absorbed by the stationary phase

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Protactinium

91
Pa
PROTACTINIUM
231.036

MELTING POINT: 1,568°C
BOILING POINT: Unknown
DENSITY: 15.37 g/cm^3
MOST COMMON IONS: Pa^{4+}, PaO(OH)2^{+}

An **isotope** of protactinium (having mass number 234 and a half-life of 1.1 minutes) was first identified by Kasimir Fajans and O. Gohring in 1913 as a short-lived member of the naturally occurring ^{238}U decay series and was given the name *brevium*, meaning brief. The existence of protactinium was confirmed in 1918 when another isotope of protactinium (of mass 231 and a half-life of 3.3×10^4 years) was studied independently by Otto Hahn and

isotope: form of an atom that differs by the number of neutrons in the nucleus

Lise Meitner in Germany, and by Frederick Soddy and John Cranston in Great Britain. The current name of the element is a shortened version of the original *protoactinium*, derived in part from the Greek *protos*, meaning parent; protoactinium thus meant parent of actinium (its decay product). There are twenty-four known isotopes of Pa, having mass numbers ranging from 214 to 238, the most stable isotope being ^{231}Pa. Protactinium **metal** is silvery and relatively nonreactive. It occurs at ppm levels in uranium ores and is extracted from these ores. There are about 125 grams (4.4 ounces) of protactinium in the world today. Its ground state electronic configuration is $[\mathrm{Rn}]5f^2 6d^1 7s^2$, placing it in Group IIIB. Its **principal oxidation state** is +5, but there is no stable Pa^{5+} ion because it is hydrolyzed so quickly to species such as $\mathrm{PaO(OH)}^{2+}$, or forms complexes with **anions** such as fluoride. Protactinium in its +4 state may exist in **aqueous solution** or in compounds. The most important solid compound of protactinium is $\mathrm{Pa_2O_5}$. SEE ALSO Actinium; Berkelium; Einsteinium; Fermium; Lawrencium; Mendelevium; Neptunium; Nobelium; Plutonium; Rutherfordium; Thorium; Uranium.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

principal oxidation state: oxidation state that is most important

anion: negatively charged chemical unit, like Cl^-, $\mathrm{CO_3}^{2-}$, or NO^{3-}

aqueous solution: homogenous mixture in which water is the solvent (primary component)

Walter Loveland

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Proteins

Excluding the water present in the human body, about one half of the remaining mass is composed of a class of molecules called proteins. It should therefore be of no surprise that proteins carry out many important biological processes.

Amino Acids

Proteins are essentially natural polymers composed of long chains of subunits. These smaller units are called amino acids. One "end" of an amino acid has acidic character because it has a carboxyl (COOH) **functional group**. The other end has basic character because it has an amino ($\mathrm{NH_2}$) functional group. When two amino acids react, they form what is called a peptide bond. The resulting molecule, called a dipeptide, still has one end that is acidic and another that is basic (Figure 1). With this fundamental reactive pattern, it is possible to string together many amino acids to form a **polypeptide**. For such a chain, the end that has the **carboxyl group** is referred to as the C-terminus; the amino end is referred to as the N-terminus.

functional group: portion of a compound with characteristic atoms acting as a group

polypeptide: compound containing two or more amide units—C(O)NH—produced by the condensation of two or more amino acids

carboxyl group: an organic functional group, –C(O)–, found in aldehydes, ketones, and carboxyl acids

Some proteins, including a number of hormones, have only a relatively small number of amino acid units, while others have literally thousands. Once an amino acid is incorporated into the polypeptide, it is referred to as a residue. When biochemists identify a particular portion of a protein, they usually refer to the residue with its name and a number, referring to how far from the N-terminus that residue is located.

In the human body, there are twenty different amino acids that are found in proteins✷. The body is capable of synthesizing most of the amino acids it needs, but there are eight molecules that cannot be made. These are called

✷See table of amino acids in the Amino Acids article.

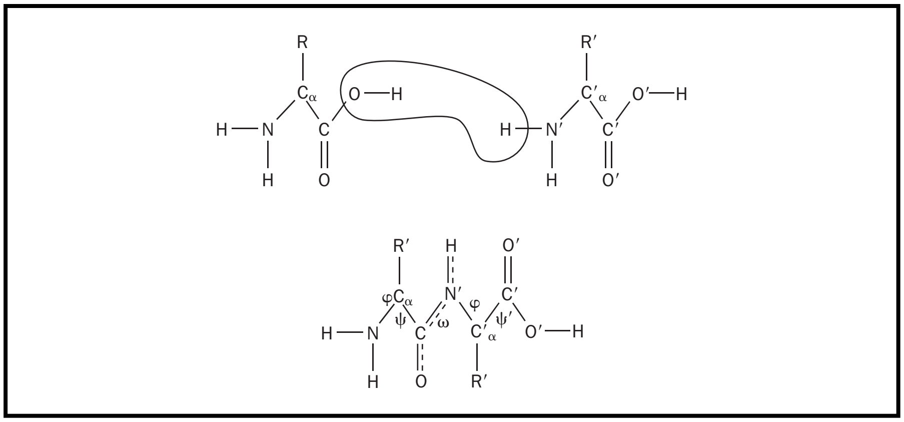

Figure 1. When amino acids react, they form what is called a peptide bond. The resulting molecule, called a dipeptide, has one end that is basic and another that is acidic.

the essential amino acids, and they must be present in the diet or a person will develop malnutrition. Many people gain the amino acids they need by eating a diet that contains complete proteins. Most meats (such as beef, poultry, or fish) have complete proteins. The body metabolizes (breaks down) these ingested proteins and in so doing provides the raw materials needed for making the proteins.

People who do not eat meat must be careful to eat a diet that includes the essential amino acids. This can be accomplished by eating complementary proteins. For example, corn has many essential amino acids but is low in tryptophan. Beans, however, have ample tryptophan; cultures that use cornmeal often complement this food source with beans. Similarly, cultures in Asia often eat rice with soy sauce; this combination provides complementary proteins in the diet.

Protein Structure

The order of the amino acids in a protein dictates the primary structure of the protein. While other levels of structure are important, they all follow from the order of the residues. The primary structure is dictated by genetic information found in a cell; deoxyribonucleic acid (**DNA**) contains the **code** that directs which amino acids are linked together. The processes by which the genetic code is read and proteins are synthesized are called **transcription** and translation.

The next level of protein structure is called the secondary structure. The side chains of the residues have various functional groups that can have different types of forces: some are **hydrophobic** and others are **hydrophilic**; some participate in **hydrogen bonding** interactions while others do not. These forces lead to conformations (geometric arrangements of the residues) that result in lower energies. Two specific arrangements that are found regularly are shown in Figure 2: a **helix** (which looks like a corkscrew) and a pleated sheet (which looks like a paper that has been folded and opened).

The secondary structure of the protein is the result of interactions of side chains that are located within a few residues of each other. Proteins are sufficiently long that they can eventually fold back on themselves, allowing residues that are farther apart in the primary structure to interact with each other. These interactions give rise to the tertiary structure of the protein

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

code: mechanism to convey information on genes and genetic sequence

transcription: enzyme-catalyzed assembly of an RNA molecule complementary to a strand of DNA

hydrophobic: a part of a molecule that repels water; if an entire molecule is hydrophobic, it will not dissolve in water

hydrophilic: a part of a molecule having an affinity for water

hydrogen bonding: intermolecular force between the H of an N–H, O–H, or F–H bond and a lone pair on O, N, or F

helix: form of a spiral or coil such as a corkscrew

Figure 2. The secondary structure of protein. Darker grey portion is the helix and lighter grey portion is the pleated sheet.

(Figure 2). Some proteins can form structures with multiple units (dimers, trimers, or tetramers). These collections of units provide yet another level of structure called the quaternary structure.

Solubility is one property that can be used to classify the proteins that result from the various levels of structure. For example, fibrous proteins are not soluble in water. Many familiar components of tissues are composed of fibrous proteins, including keratin (the protein present in hair), collagen (a structural protein found in tendons and cartilage), myosin (a protein found in most muscle tissue), and fibrin (the protein that allows blood to clot and form scabs). Conversely, globular proteins are soluble in water. For example, albumins are water-soluble proteins that provide a familiar example of what happens when a protein loses its secondary and tertiary structure, a process called denaturation. When an egg is cooked, the egg white changes from translucent to white; this color change is indicative of the change in structure that has taken place in the albumin proteins.

In many cases, the structure of a protein defines a key location called the active site, the region that is associated with the primary activity of a protein, even though it is often made up of only a small number of residues.

Biological Functions

The variety of structures associated with proteins suggests the large number of biological tasks that they carry out. It is possible to classify proteins based on their biological functions.

Enzymes are proteins that catalyze chemical reactions that take place in living systems. A **catalyst** is a molecule that speeds up a reaction but is not consumed by that reaction. Enzymes are particularly interesting because they often are quite specific, capable of catalyzing only one type of biochemical reaction. Learning about the structure of the active site is often a

catalyst: substance that aids in a reaction while retaining its own chemical identity

crucial component of studies that look at the **catalytic** properties of an enzyme.

Many hormones are proteins, often containing only a relatively small number of residues. Insulin is perhaps the most well known peptide hormone; because of its role in the **metabolism** of carbohydrates, it plays an important role in the control of diabetes. Growth hormone is another example of a protein.

Some neurotransmitters are closely related to proteins, differing from them only because they have relatively few residues. There are many known neurotransmitters; endorphins and enkephalins are examples of peptides that carry out this role.

Many **antibodies** and other components of the immune response system are proteins. One important component of a body's defenses is the ability to form clots to stop bleeding from cuts. A protein called fibrinogen plays a key role in this.

Proteins comprise a majority of muscle tissue. Two classes of protein, actin (which makes moving filaments) and myosin (which remains stationary), are primary components of the muscles in the body.

Proteins are often involved in the storage of nutrients in the body. For example, iron is stored (mostly in the spleen) in a protein called ferritin. In plants, nutrients needed for the growth of a new plant are a major component of seeds, and storage proteins carry out this task.

In addition to storing nutrients, proteins can transport them. Perhaps the most critical transport protein is hemoglobin, which transports oxygen and carbon dioxide in the bloodstream. In the lungs the percentage of oxygen is high, so it binds to the protein in an **equilibrium** process. When hemoglobin reaches tissue that has produced carbon dioxide, the oxygen is released and used by cells in metabolism. The hemoglobin can then bind carbon dioxide and carry it to the lungs to be released.

There are several ways that proteins contribute to the structure of living things. Glycoproteins play a major role in the structures of cell membranes. While **lipids** are more numerous in the membrane, many of the key functions that occur at the membrane level, such as transport of materials, are carried out by transmembrane proteins. **Receptors**, including those in nerve cells, are proteins that help cells interact with their external environment. Some tissues like cartilage have proteins that help provide structure on a larger scale.

Proteins can also be dangerous or unhealthy. For many who suffer from allergies to agents like pollen, it is proteins on the surface of the pollen that cause an immune response that triggers the allergic reaction. More seriously, many natural **toxins** are proteins. Snake venom is one example of a naturally occurring protein-based toxin. SEE ALSO ACTIVE SITE; AMINO ACID; DENATURATION; ENZYMES; FIBROUS PROTEINS; GLOBULAR PROTEINS; NEUROTRANSMITTERS; PEPTIDE BOND; PROTEIN SOLUBILITY; PROTEIN SYNTHESIS; PROTEIN TRANSLATION; RNA SYNTHESIS; SECONDARY STRUCTURE; TERTIARY STRUCTURE; TRANSMEMBRANE PROTEINS; VENOM.

Thomas A. Holme

catalysis: the action or effect of a substance in increasing the rate of a reaction without itself being converted

metabolism: the complete range of biochemical processes that take place within living organisms; comprises processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those that break down complex food molecules, thus liberating energy (catabolism)

antibody: protein molecule that recognizes external agents in the body and binds to them as part of the immune response of the body

equilibrium: condition in which two opposite reactions are occurring at the same speed, so that concentrations of products and reactants do not change

lipid: a nonpolar organic molecule; fatlike; one of a large variety of nonpolar hydrophobic (water-hating) molecules that are insoluble in water

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

toxin: poisonous substance produced during bacterial growth

CARBON MONOXIDE POISONING

Carbon monoxide, CO, poisons the body by combining with hemoglobin some 250 times more tightly than O_2, thus hindering the transport of O_2 to the body's tissues. In an environment of 0.1 percent CO (within the lung), more than half the binding sites of hemoglobin become occupied with CO, and the victim dies within an hour.

—N. M. Senozan

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Protein Solubility

hydrophilic: a portion of a molecule that attracts water

At the surfaces of proteins are amino acid residues that interact with water. The amino acids are referred to as **hydrophilic** amino acids and include arginine, lysine, aspartic acid, and glutamic acid. At pH 7 the side chains of these amino acids carry charges—positive for arginine and lysine, negative

A scientist adjusts equipment used in fast protein liquid chromatography, which is used to isolate specific proteins from sample mixtures. Soluble proteins have a charge on their surfaces.

for aspartic acid and glutamic acid. As the pH increases, lysine and arginine begin to lose their positive charge, and at pHs greater than about 12 they are mainly neutral. In contrast, as pH decreases, aspartic acid and glutamic acid begin to lose their negative charges, and at pHs less than 4 they are mainly neutral.

The surface of a protein has a **net charge** that depends on the number and identities of the charged amino acids, and on pH. At a specific pH the positive and negative charges will balance and the net charge will be zero. This pH is called the isoelectric point, and for most proteins it occurs in the pH range of 5.5 to 8. A protein has its lowest solubility at its isoelectric point. If there is a charge at the protein surface, the protein prefers to interact with water, rather than with other protein molecules. This charge makes it more soluble. Without a net charge, protein-protein interactions and precipitation are more likely.

net charge: total overall charge

The solubility of proteins in blood requires a pH in the range of 7.35 to 7.45. The bicarbonate–carbonic acid buffer system of blood ($HCO_3^- + H^+ \longleftrightarrow H_2CO_3$), in which the bicarbonate is in excess of the carbonic acid, helps to maintain the correct pH. Exhalation of carbon dioxide from the lungs causes some of the bicarbonate ions in blood to combine with protons, and this would raise the pH. However, because there is an excess of bicarbonate ions and protons, the loss of a small number of protons does not influence the pH significantly.

The proteins of protein mixtures can be separated using a technique known as isoelectric focusing. A mixture is placed in a polyacrylamide gel that has a pH gradient. An anode (positive electrode) and a cathode (negative electrode) are positioned at the low and high ends of the pH gradient, respectively. If a protein is located in the high pH region, it will be negatively charged and will move toward the anode. As the protein moves to a lower pH region, its surface charge will become less negative, and a pH region will be reached at which the protein net charge is zero (the isoelectric point). The protein will stop moving and, because different proteins have different isoelectric points, separation can be achieved. SEE ALSO PROTEINS.

Ian S. Haworth

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Protein Synthesis

There is no task more important to the function of living cells than the **synthesis** of proteins. Because proteins carry out so many different tasks, the mechanism to synthesize them is intricate. There are several stages involved in the synthesis process, including transcription and translation.

synthesis: combination of starting materials to form a desired product

Transcription

The primary role of deoxyribonucleic acid (**DNA**) is to direct the synthesis of proteins. DNA, however, is located in the nucleus of the cell, and

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

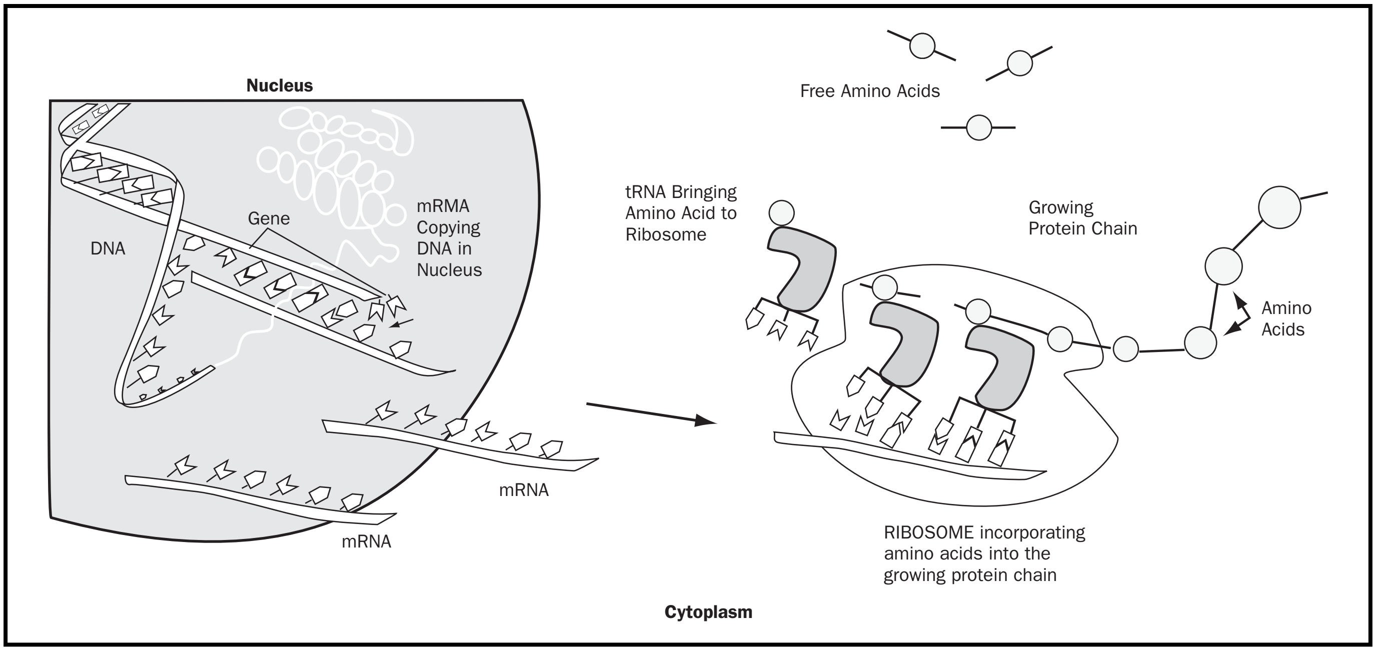

Figure 1. Protein synthesis requires transcription (shown on the left side of the figure) and translation (shown on the right side of the figure).

ribosome: large complex of proteins used to convert amino acids into proteins

protein synthesis occurs in cellular structures called **ribosomes**, found outside the nucleus. The process by which genetic information is transferred from the nucleus to the ribosomes is called transcription. During transcription, a strand of ribonucleic acid (RNA) is synthesized. This messenger RNA (mRNA) is complementary to the portion of DNA that directed it—it has a complementary nucleotide at each point in the chain.

RNA polymerase: enzyme used to make RNA using DNA as a template

eukaryotic cell: cell characterized by membrane-bound organelles, most notably the nucleus, and that possesses chromosomes whose DNA is associated with proteins

A specialized protein called an enzyme controls when transcription occurs. The enzyme called **RNA polymerase** is present in all cells; **eukaryotic cells** have three types of this enzyme. DNA has a section called the promoter region that identifies the sites where transcription starts and must be recognized by one subunit of the RNA polymerase called the sigma (σ) factor. Recognition between the promoter and the σ-factor helps to regulate how often a particular gene is transcribed. Once bound, the polymerase initiates the construction of mRNA (or other RNA molecules).

Initiation of the synthesis of a new RNA molecule does not always lead to a complete synthesis. After roughly ten nucleotides have been strung together, the continued addition of complementary base pairs takes place more readily in a process called elongation. The speed of addition of new nucleotides is remarkable—between twenty and fifty nucleotides per second can be added at body temperature.

Eventually the elongation process must stop. There are certain sequences of nucleotides that stop elongation, a process called termination. Often, termination occurs when the newly formed section of RNA loops back on itself in a tight formation called a hairpin. Once the hairpin structure has formed, the last component is then a string of **uracil** residues.

uracil: heterocyclic, pyrimidine, amine base found in RNA

After transcription has taken place, the mRNA produced is not necessarily ready to direct the subsequent protein synthesis. Depending on the type of cell, segments of nucleotides may be removed or appended before the actual synthesis process takes place. This type of post-transcriptional processing often occurs in human cells.

Translation

Once the mRNA has been synthesized, and perhaps modified, the next step of protein synthesis, translation, takes place. For this stage, additional forms of RNA are needed.

Transfer RNA (tRNA) plays the role of carrying an amino acid to the synthesis site at the ribosome. tRNA molecules are relatively small, with around seventy-five nucleotides in a single strand. They form several loops, one of which is an anti-codon, a three-residue series that is complementary to the codon present in the mRNA (Figure 2). The opposite end of the tRNA is where an amino acid is bound. The correct binding of an amino acid to a specific tRNA is every bit as important as the anti-codon in ensuring that the correct amino acid is incorporated in the **polypeptide** that is synthesized. There are different tRNA molecules for each of the twenty amino acids that are present in living systems; some amino acids have more than one tRNA that carry them to the synthesis site.

polypeptide: compound containing two or more amide units—C(O)NH—produced by the condensation of two or more amino acids

When translation begins, mRNA forms a complex with a ribosome to form an assembly site. This complex requires the assistance of proteins called initiation factors, so the existence of an mRNA does not mean that a protein will always be synthesized. The first tRNA that takes part in the initiation always carries the same amino acid, methionine. When the protein is completely synthesized, this initial methionine is often removed.

With the initial methionine in place, another tRNA with its amino acid joins the assembly site as dictated by the codon on the mRNA. With two amino acids present, a peptide bond can be formed and the polypeptide can begin forming. The new amino acid is added to the carbon end of the polypeptide (the C-terminus) with the peptide bond forming between the C-O of the polypeptide and the amine of the new amino acid. This structural specificity is enforced by the nature of the binding between the amino acid and the tRNA. The portion of the amino acid that is unbound in the tRNA complex is the amine.

Elongation ultimately requires the repetition of several steps: (1) The tRNA–amino acid complexes must be made. (2) This complex must bind to the mRNA-ribosome assembly site. The correct amino acid is assured by the matching of the anti-codon on the tRNA to the codon on the mRNA. (3) A peptide bond is formed between the new amino acid and the growing polypeptide chain. (4) The amino acid is **cleaved** from the tRNA, which can be cycled back to form another complex with an amino acid for a later synthesis. (5) The growing polypeptide forms a fiber-like tendril. (6) The ribosome essentially moves along the mRNA, reopening the initiation site for additional protein synthesis. In this way, proteins are synthesized by several ribosomes acting on the same mRNA molecule.

cleave: split

The structure of the ribosome plays an important role in this elongation process. There must be two sites available for synthesis to occur. One site, called the P site (for peptide), is where the growing (or nascent) polypeptide is located. Adjacent to this location is another site where the tRNA with

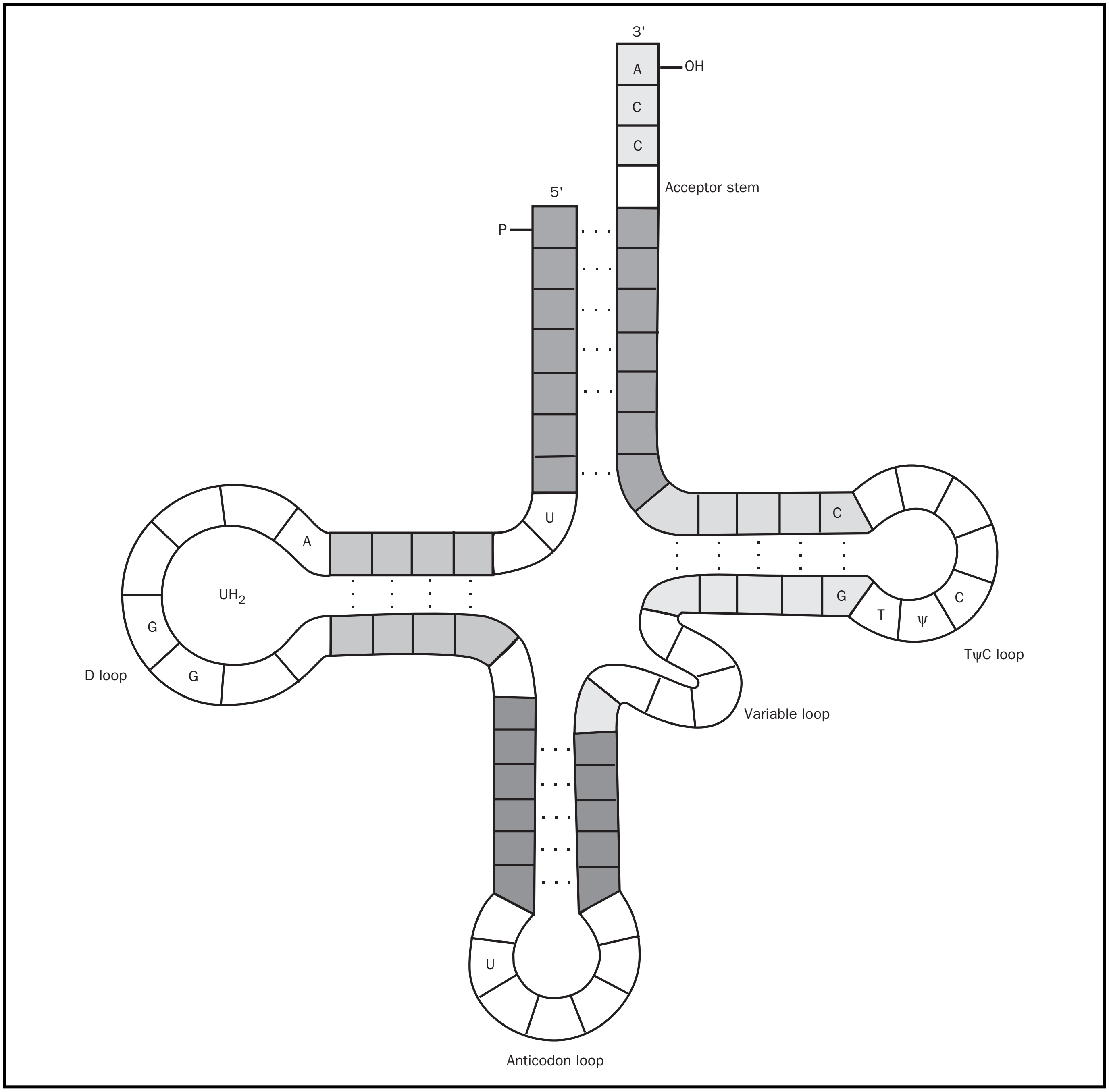

Figure 2. A tRNA molecule. tRNA carries amino acid to the synthesis site at the ribosome.

its new amino acid can bind. This site is called the A site (for the amino acid that is delivered there along with the tRNA).

As was the case in the elongation of mRNA noted earlier, somehow the emerging polypeptide must stop adding amino acids. The termination is actually part of the coding present in the codons. Three specific codons are known as stop codes, and when they are present in mRNA, the elongation is stopped.

Despite the overall complexity of this process, it occurs with remarkable accuracy. The rate of error is roughly one in every 10,000 amino acids.

Using the processes of transcription and translation, the body makes an amazing number and variety of proteins.

The transcription and translation processes provide the correct primary structure of the protein. The protein must fold to obtain the correct secondary and tertiary structures. Protein folding remains an active research area.

Medical Applications

Protein synthesis is critical to the growth of cells; medicines that work by killing cells often target this process. A majority of antibiotics work by disrupting the translation process. Tetracycline is an antibiotic that inhibits the binding of tRNA to the assembly site. **Streptomycin** works by causing the translation process to make more mistakes than usual—as high as one mistake for every 100 amino acids. Proteins with this many errors are not capable of performing their tasks, and the cells (in this case, bacteria) die. Streptomycin also inhibits the initiation of the synthesis process. SEE ALSO PEPTIDE BOND, PROTEINS.

streptomycin: antibiotic produced by soil bacteria of genus *Streptomyces*

Thomas A. Holme

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Protein Transcription *See RNA Synthesis.*

Protein Translation

Protein translation is the process of synthesizing proteins from amino acids. This series of reactions translates the **code** provided to messenger ribonucleic acid or RNA (mRNA) by deoxyribonucleic acid or **DNA** into a sequence of amino acids that makes up the active protein molecule. Protein **synthesis** begins with a strand of mRNA synthesized in response to the genetic code located in a gene on a strand of DNA. The process of translation is slightly different in **eukaryotic cells** from that in **prokaryotic** cells; for the sake of simplicity, translation in prokaryotes will be discussed here.

code: mechanism to convey information on genes and genetic sequence

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

synthesis: combination of starting materials to form a desired product

eukaryotic cell: cell characterized by membrane-bound organelles, most notably the nucleus, and that possesses chromosomes whose DNA is associated with proteins

prokaryotic: relating to very simple cells of the type found in bacteria

Proteins are made up of combinations of the twenty common amino acids. Placement of each amino acid is specified by a three-nucleotide codon. Four different nucleotides are available to code; taken three at a time, they can form sixty-four combinations. Some amino acids have more than one codon (a phenomenon known as redundancy). Translation also requires a start codon and stop codon.

Four general actions comprise protein translation: The mRNA binds to a **ribosome**; amino acids are carried to the ribosome by transfer RNA (tRNA); the amino acids are joined, forming peptide bonds; and the completed protein molecule is released from the ribosome. The synthetic processes are called initiation, elongation, and termination and are assisted by protein factors essential for each step.

ribosome: large complex of proteins used to convert amino acids into proteins

adenosine triphosphate (ATP): molecule formed by the condensation of adenine, ribose, and triphosphoric acid, HOP(O)OH–O–(O)OH–OP(O)OH–OH; it is a key compound in the mediation of energy in both plants and animals

Adenosine triphosphate (ATP) provides energy for the attachment of amino acids by specific enzymes to tRNA. For reference, the ends of DNA and RNA strands are designated 5′ and 3′. Translation begins with attachment of the 5′-end of mRNA to the small unit of a ribosome. A tRNA molecule carrying formylmethionine attaches to the ribosome at a location matching the initiation codon (AUG) on mRNA. The large subunit of the ribosome then attaches to this complex, forming a complete, active ribosome. During periods of rapid translation, a number of ribosomes may cluster together with mRNA, forming polyribosomes. A second tRNA brings another amino acid to the ribosome, matching the codon on mRNA for the second amino acid. A peptide bond forms between the two amino acids, and the first tRNA is released.

polypeptide: compound containing two or more amide units—C(O)NH—produced by the condensation of two or more amino acids

Guanosine triphosphate (GTP) provides energy to move the growing peptide chain along as mRNA passes through the ribosome. As more amino acids are added, the **polypeptide** chain grows longer until the ribosome reaches the stop codon of mRNA.

carboxylic acid: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the $-CO_2H$ functional group

When the growing peptide chain approaches the **carboxylic acid** end (at the stop codon on mRNA), protein termination factors help to disassemble the ribosome and release the completed protein chain. Protein translation is interrupted by antibiotics such as tetracycline or chloramphenicol that interfere with protein synthesis. SEE ALSO Codon; Proteins; Protein Synthesis; Ribonucleic Acid.

Dan M. Sullivan

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Protons *See Atomic Nucleus; Atomic Structure.*

q

Quantum Chemistry

quantum mechanics: theoretical model to describe atoms and molecules by wave functions

spectroscopy: use of electromagnetic radiation to analyze the chemical compostion of materials

Quantum chemistry is the application of **quantum mechanical** principles and equations to the study of molecules. In order to understand matter at its most fundamental level, we must use quantum mechanical models and methods. There are two aspects of quantum mechanics that make it different from previous models of matter. The first is the concept of wave-particle duality; that is, the notion that we need to think of very small objects (such as electrons) as having characteristics of both particles and waves. Second, quantum mechanical models correctly predict that the energy of atoms and molecules is always quantized, meaning that they may have only specific amounts of energy. Quantum chemical theories allow us to explain the structure of the periodic table, and quantum chemical calculations allow us to accurately predict the structures of molecules and the **spectroscopic** behavior of atoms and molecules.

Background: Wave-Particle Duality for Light

Quantum mechanical ideas began with studies of the physics of light. By the late nineteenth century, virtually all scientists believed that light behaved as a wave. Although some earlier scientists, such as Isaac Newton in the seventeenth century, had thought of light as consisting of particles, the early nineteenth-century experiments of Thomas Young and Augustin Fresnel demonstrated that light has wavelike properties. In these experiments, light was passed through a pair of slits in a screen, and produced alternating light and dark regions (interference patterns) on a second screen. This phenomenon, known as diffraction, cannot be explained using a particle model for light. In the late nineteenth century, James Clerk Maxwell derived a set of equations based on the wave model for light, which beautifully explained most experimental results.

Despite this apparent certainty that light was a wave, Max Planck and Albert Einstein, at the beginning of the twentieth century, showed that some experiments required the use of a particle model for light, rather than a wave model. Since both models were necessary for an accurate description of all of the properties of light, scientists today use mathematical equations appropriate to both waves and particles in describing the properties of light.

Waves and particles are fundamentally different: a particle exists at a particular point in space, whereas a wave continues on for (sometimes) a great distance. It defies intuition to think that both of these models might describe the same thing. Nevertheless, an accurate description of light requires the use of both wave and particle ideas.

The Wave Nature of Matter

The success of wave-particle duality in describing the properties of light paved the way for using that same idea in describing matter. Experiments in the early twentieth century showed that the energy in atoms is quantized✷; that is, a given atom can have only specific amounts of energy. For hydrogen, the simplest of the atoms, an accurate formula for the possible energies had been experimentally determined but was unexplainable using any particle model for the atom. The best picture that the particle model could give, consistent with experiments on atoms, put the electron in a sort of "orbit" around the nucleus. Unfortunately, the particle model predicts that the electron should collide with the nucleus, releasing energy in the process. Obviously there was a need for a different model for the electron.

✷One example of quantization would be to think of your distance from the ground when standing on a ladder—your distance from the ground can only change one rung at a time.

In 1924 Louis de Broglie presented a theory for the hydrogen atom that modeled the electron as a wave. Calculations made for this model give the quantization of energy that is experimentally observed in this atom. De Broglie also postulated a general formula for obtaining the wavelength of a moving object. His formula, which is analogous to that used for light, states that the wavelength of a moving object is inversely proportional to its momentum (mass times velocity). When one uses de Broglie's formula to determine wavelengths of macroscopic objects, one discovers that the wavelengths of even the smallest objects visible to the naked eye are too small for the wavelike characteristics of these objects to be significant in any real situation. For the electron, however, the wavelength is large enough to be measurable. Diffraction experiments have been performed using electrons, demonstrating conclusively that they have wave properties.

It is contrary to our intuition that electrons might behave as waves. The repercussions of this notion are that the electron does not have a definite size, but is spread out over a region in space. We are more comfortable with the thought of the electron being a microscopic particle, moving around in an orbit near the nucleus of an atom. As with light, however, we do not abandon the particle model for electrons; rather, we employ mathematical equations arising from both particle and wave models. For quantum chemical calculations, the wave model turns out to be more useful.

The Heisenberg Uncertainty Principle

One consequence of the wave nature of matter is that the position and momentum of small objects are not well known, as they would be for a particle model. In some circumstances, a wave may be confined to a very narrow region in space; however, there is still some uncertainty as to its position. Additionally, the value of the momentum of a quantum object is often not known precisely. In 1927 Werner Heisenberg showed that the product of the uncertainty in position and the uncertainty in momentum is greater than or equal to a certain constant (Planck's constant divided by 4π). This constant is very small; accordingly, quantum mechanical uncertainty in position and momentum of objects that are large enough to see is not noticed experimentally. For electrons, however, quantum mechanical uncertainties in position and momentum are important considerations in interpreting both theoretical models and experimental results. The relationship between the uncertainties in position and momentum is known as the Heisenberg Uncertainty Principle. It tells us that the more we know about the position of a small object, such as an electron, the less we know about its momentum (and vice versa).

Calculating the Wavefunction

For a scientist, knowing that matter behaves as a wave is useful only if one knows something about that wave. The wavefunction is a mathematical function describing the wave. For example, $y(x) = A \sin(kx)$ might be the wavefunction for a one-dimensional wave, which exists along the x-axis. Matter waves are three-dimensional; the relevant wavefunction depends on the x, y, and z coordinates of the system being studied (and sometimes on time as well). We conventionally label the wavefunction for a three-dimensional object as $\psi(x, y, z)$. In 1926 Erwin Schrödinger introduced a mathematical equation whereby, if one knows the potential energy acting on an object, one can calculate the wavefunction for that object. Heisenberg had already introduced a mathematical formalism for performing quantum mechanics calculations, without explicitly including the concept of waves. It was later shown that, although the approaches of Schrödinger and Heisenberg looked very different, they made exactly the same predictions. In practice, the Schrödinger formalism is more useful for explaining the problem being studied, and the Heisenberg methodology allows for more straightforward computation. Accordingly, a mixture of the two approaches is typically used in modern quantum chemistry. Once we know the wavefunction of the atom or molecule under study, we can calculate the properties of that atom or molecule.

Quantum Mechanics of Atoms

An exact solution for Schrödinger's wave equation can be obtained for the hydrogen atom; however, for larger atoms and molecules (which contain more than one electron), Schrödinger's equation can be solved only approximately. Although this may sound so restrictive as to make the equation useless, there are well-established approaches that allow for practical and accurate calculations on atoms and molecules. This is done by making some assumptions about larger systems based upon the hydrogen atom, as explained below.

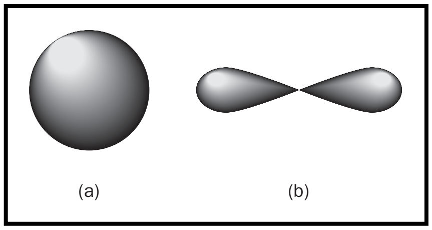

Figure 1.

When the Schrödinger equation is solved for the hydrogen atom, the resulting wavefunctions for the various possible energies that the atom can have are used to determine **atomic orbitals**. An orbital is a region in space where an electron is most likely to be found. For example, the lowest-energy wavefunction for a hydrogen atom is the so-called 1s orbital (see Figure 1), which is a spherical region in space surrounding the nucleus. For some higher-energy states, the orbitals are not necessarily spherical in shape (e.g., the 2p orbital pictured in Figure 1).

atomic orbital: mathematical description of the probability of finding an electron around an atom

For atoms larger than hydrogen, one assumes that the orbitals occupied by the electrons have the same shape as the hydrogen orbitals but are differing in size and energy. The energies corresponding to these orbitals may be found by solving an approximate version of Schrödinger's equation. These atomic orbitals, in turn, may be used as the building blocks to the electronic behavior in molecules, as we shall see below. As it happens, two electrons may share an atomic orbital; we say that these electrons are paired. Chemists have developed a system of rules for determining which orbitals are occupied in which atoms; calculations can then be done to determine the energies of the electrons in the atoms.

Quantum Mechanics of Molecules

Molecules are held together by **covalent bonds**. The simplest definition of a covalent bond is a shared pair of electrons. There are two basic approaches to modeling covalent bonds in molecules: the **valence** bond model and the molecular orbital model. In the valence bond model, we think of atomic orbitals on each of two atoms combining to form a bond orbital, with one electron from each atom occupying this orbital. Both the bond orbital and the electron pair now "belong" to both of the atoms. This sharing of electrons brings about a lowering in the energy, which makes the formation of molecules from atoms an energetically favorable process. The valence bond model gives the simplest quantum mechanical picture of chemical bonding, but it is not the best method for accurate calculations on molecules containing more than two atoms.

covalent bond: bond formed between two atoms that mutually share a pair of electrons

valence: combining capacity

Molecular orbital theory differs from valence bond theory in that it does not require the electrons involved in a bond to be localized between two of the atoms in a molecule. Instead, the electron occupies a molecular orbital, which may be spread out over the entire molecule. As in the valence bond approach, the molecular orbital is formed by adding up contributions from the atomic orbitals on the atoms that make up the molecule. This approach, which does not explicitly model bonds as existing between two atoms, is somewhat less appealing to the intuition than the valence bond approach. However, molecular orbital calculations typically yield better predictions of molecular structure and properties than valence bond methods. Accordingly, most commercially available quantum chemistry software packages rely on molecular orbital methods to perform calculations.

SCHRÖDINGER'S WAVE EQUATION

Schrödinger's Wave equation may be written (in abbreviated form) as:

$$\hat{E}_K\psi\,(x, y, z) + \hat{E}_P\psi\,(x, y, z) = \hat{E}\psi\,(x, y, z)$$

The first term, $\hat{E}_K\psi\,(x, y, z)$, represents the kinetic energy of the system being studied. The second term, $\hat{E}_P\psi\,(x, y, z)$, represents the potential energy of the system. E and $\psi(x, y, z)$ are the total energy of the system and wavefunction describing the system, respectively. Once the wavefunction is determined, virtually any property of the molecule may be calculated.

A lot of the modern research in quantum chemistry is focused on improving the valence bond and molecular orbital methods for calculating molecular properties. Different underlying approximations and different orbital functions are tried, and the results are compared with previous calculations and with experimental data to determine which methods give the best results. It is often the case that the best choice of quantum chemical method depends on the particular molecule or molecular property being studied. SEE ALSO ATOMIC STRUCTURE; COMPUTATIONAL CHEMISTRY; MOLECULAR STRUCTURE; THEORETICAL CHEMISTRY.

Wayne B. Bosma

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Quaternary Structure

polypeptide: compound containing two or more amide units—C(O)NH—produced by the condensation of two or more amino acids

hydrophobic: water repelling

nonpolar: molecule, or portion of a molecule, that does not have a permanent, electric dipole

electrostatic interaction: force that arises between electrically charged particles or regions of particles

Many proteins are made up of a single, continuous **polypeptide** chain and are thus called monomeric. Other proteins are composed of two or more polypeptide chains called subunits. The quaternary structure describes the arrangement and position of each of the subunits in a multiunit protein. The stabilizing forces that hold the polypeptide subunits together are the same forces that are responsible for tertiary structure stabilization. A major force stabilizing the quaternary structure is the **hydrophobic** interaction among **nonpolar** side chains at the contact regions of the subunits. Additional stabilizing forces include interactions between side chains of the subunits, including **electrostatic interactions** between ionic groups of opposite charge:

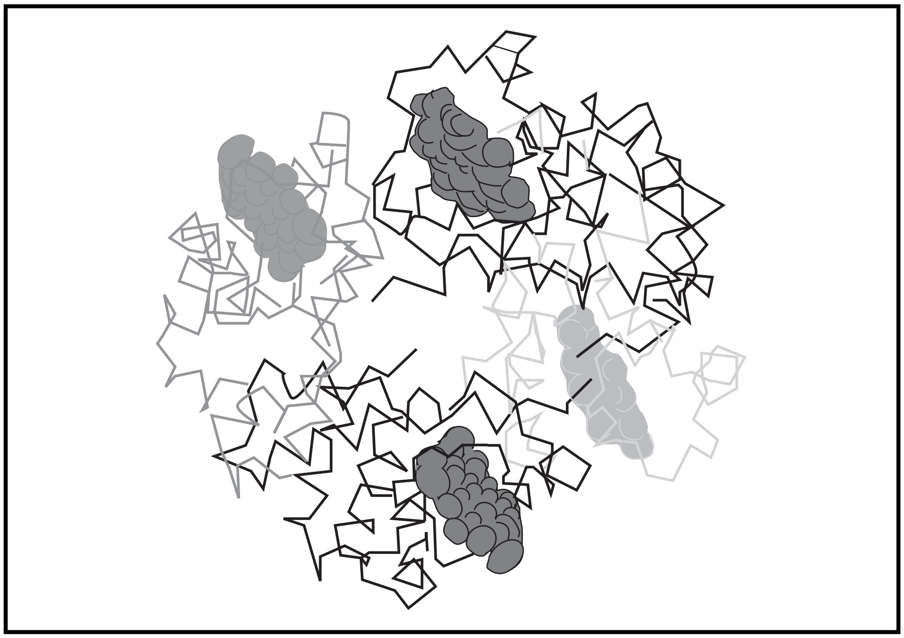

Figure 1. Hemoglobin.

hydrogen bonds between polar groups; and **disulfide bonds**. An example of a protein with quaternary structure is hemoglobin. Hemoglobin, an oxygen transport protein, is a tetrameric (four unit) protein consisting of two α and two **β subunits**. SEE ALSO Primary Structure; Proteins; Secondary Structure; Tertiary Structure.

Elizabeth S. Roberts-Kirchhoff

hydrogen bond: interaction between H atoms on one molecule and lone pair electrons on another molecule that constitutes hydrogen bonding

disulfide bond: bond that involves two bonding sulfur atoms, –S–S–

β subunit: subunit that exists when two or more polypeptide chains associate to form a complex functional protein, the chains are referred to as "subunits"; these subunits are often identified as a, b, etc.

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Radiation

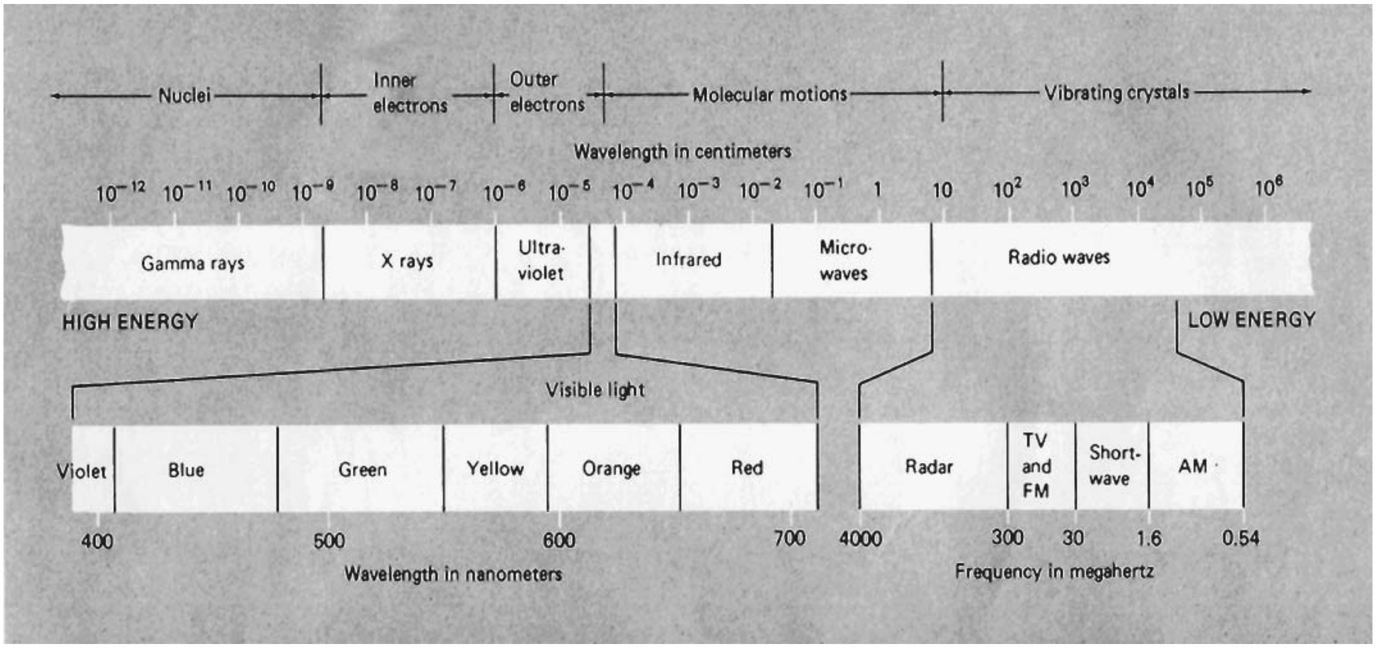
Radiation takes many forms, including both electromagnetic waves and subnuclear particles. The electromagnetic spectrum consists of light waves ranging in length from very short (10^{-16} meters, or 3.937×10^{-15} inches) to very long (10^8 meters, or 621,400 miles). The product of the velocity of electromagnetic waves and their wavelength is a constant equal to the velocity of light, 3×10^8 meters per second (m/s); therefore, as the length of waves increases, the frequency decreases. Thus, if the waves were 1 meter (3.3 feet) long, the frequency would be 3×10^8 hertz (Hz) or 300,000,000/s (meaning 300,000,000 light waves would pass by each second). The electromagnetic spectrum consists of light waves ranging in length from very short γ (gamma) rays through x rays, ultraviolet (UV) rays, the spectrum of visible light, infrared (IR) rays, and microwaves, to very long radio and television waves.

Forms of Radiation

The shortest electromagnetic waves are classified as γ rays. One of the forms of energy emanating from natural sources of radioactivity here on Earth and also from energy sources in space, γ rays can be thought of as very short x rays. Discovered by the German physicist Wilhelm Conrad Röntgen in 1895, the remarkable penetrating effect of γ rays and x rays results from their very short wavelength (from about 10^{-12} to 10^{-8} meters, or 3.28×10^{-11} to 3.28×10^{-7} feet). The waves are so small that they can pass through many substances with little interaction. X rays pass through skin and organs with little effect but are diffracted somewhat when they pass through denser materials such as bone; the resulting pattern enables technicians to make x-ray images of bones and of the contents of packages in airport scanners.

The energy of electromagnetic radiation is directly proportional to the frequency. Since both x rays and γ rays have very high frequencies, they carry large amounts of energy, and high intensities of x rays and γ rays can damage many materials (including living tissue). The rays may be focused by special lenses and used to kill cancer cells or organisms that might cause disease or hasten spoilage in food.

Bonds between atoms in chemical compounds vibrate at characteristic frequencies. Some molecules possess bonds capable of absorbing electromagnetic



The electromagnetic spectrum, showing wavelengths and kinds of light.

energy, causing the bonds to bend, stretch, or vibrate and sometimes break. Certain bonds in particular (e.g., that between carbon and oxygen atoms) capture energy at specific frequencies of IR radiation, allowing technicians to use instruments called spectrophotometers to detect the presence of these bonds in chemical compounds. UV, visible, and IR **spectroscopy** are tools that permit chemists to readily identify and characterize small amounts of chemical substances.

spectroscopy: use of electromagnetic radiation to analyze the chemical composition of materials

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

Most animals, including humans, have visual **receptors** that detect light in the visible spectrum ranging from 400 nanometers (15.75×10^{-6} inches) for blue light to 700 (27.56×10^{-6} inches) for red light. (A nanometer equals 10^{-9} meters.) Just below the visible spectrum lies UV light, ranging in wavelength from about 10 to 400 nanometers (3.937×10^{-7} to 157.5×10^{-7} inches). UV light is more energetic than visible light; UV radiation in the sunlight can damage molecules in the skin and is the cause of sunburn. Green plants carry out **photosynthesis** by using **chlorophyll** molecules that readily capture light energy in the visible spectrum.

photosynthesis: process by which plants convert carbon dioxide and water to glucose

chlorophyll: active molecules in plants undergoing photosynthesis

Microwave radiation consists of electromagnetic waves somewhat longer than infrared waves (from about 10^{-3} meters, or 0.3937 inches, to 1 meter, or 39.37 inches, long) and having a lower frequency, ranging from about 1,000 to 300,000 megahertz (MHz). Waves in this range are readily absorbed by bonds in water molecules. Microwave ovens take advantage of the fact that foods usually contain large amounts of water, and dishes do not. The waves of IR or microwave radiation are usually too long to pass through the small holes in the doors of microwave ovens; thus, one can use a microwave oven to heat food without heating the dish or being harmed by the radiation. Magnetron tubes generate radiation that can be used for radar or for the microwave transmission of electronic signals.

An immense amount of radiation passes undetected through the environment. Our surroundings contain large amounts of radio waves, generally from one to thousands of meters long. X rays and γ rays also pass through us and the space around us with little effect. From time to time, fears have been raised concerning the electromagnetic radiation emanating from power lines, cathode ray terminals such as television sets and computer monitors, and the earphones of personal transistor radios or CD players, but there is little actual evidence of injury or illness from low intensity radiation. However, workers have been injured or killed by high intensity microwave radiation, and technicians working with radioactive materials must take special precautions.

Much radiation arrives on Earth from the Sun, and some of the energy of this radiation exists in the form of UV light. UV light waves can damage skin and would be much more hazardous were it not for the layer of ozone that exists in Earth's upper atmosphere. In a process known as the Chapman cycle, UV radiation splits oxygen molecules (O_2) in the **stratosphere** to form free oxygen atoms (O). Some of these atoms combine with oxygen molecules to form ozone molecules (O_3). The O_3 molecules are especially sensitive to UV radiation; the absorption of UV photons converts the ozone back into oxygen atoms and oxygen molecules:

stratosphere: layer of the atmosphere where ozone is found; starts about 6.2 mi (10 km) above ground

$$O_2 \xrightarrow{UV} 2\ O \qquad (1)$$

$$O + O_2 \longrightarrow O_3$$

$$O_3 \xrightarrow{UV} O_2 + O$$

In recent years the amount of O_3 in the stratosphere over the South Pole has decreased periodically, resulting in an ozone "hole" in the atmosphere. The decrease is most pronounced during the summer months of the Southern Hemisphere. If the amount of ozone continues to decrease, more UV light will reach the surface of Earth, probably causing some skin damage and increasing the incidence of cancer. Chlorine atoms react with and destroy ozone:

$$Cl + O_3 \longrightarrow ClO + O_2 \qquad (2)$$

Increasing atmospheric amounts of chlorine atoms or free radicals probably result in the destruction of ozone; the source of the chlorine atoms is thought to be synthetic substances known as **chlorofluorocarbons (CFCs)**. Some CFCs may be released from air-conditioning equipment or aerosol spray cans, and some may result from the production of plastic foams. Several international agreements, including the Montréal Protocol of 1987 and the Copenhagen amendment of 1992, have been established to limit the production of CFCs.

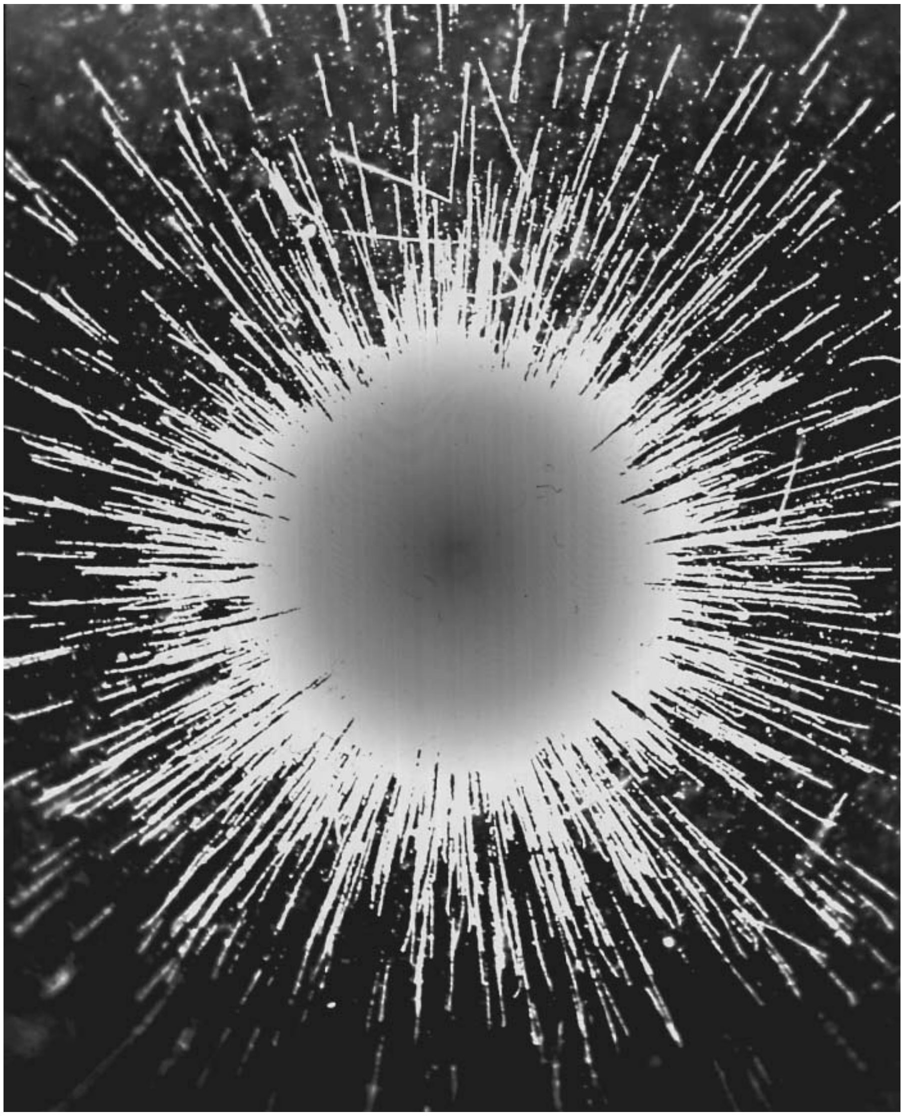
chlorofluorocarbon (CFC): compound that contains carbon, chlorine, and fluorine atoms, which remove ozone in the upper atmosphere

Radioactivity

Although many forms of electromagnetic radiation exist, special consideration is often given to radiation from unstable (radioactive) atomic nuclei. This radiation is usually one of three types, α- and β-particles or γ rays, but some nuclear reactions may also result in the emission of neutrons. **α-particles** are relatively large and highly charged particles identical with the nuclei of helium atoms. Each has a mass of four **atomic mass units** (AMU) and a charge of +2. Radioactive ores containing sources of α-particles often produce helium gas as a result of the capture of electrons by the

α-particle: subatomic particle with 2+ charge and mass of 4; a He nucleus

atomic mass units: a unit of mass used to indicate the relative mass of an atom; abbreviated as AMU, and equal to 1.674 × 10^{-24}g



The radioactive emission of alpha particles from radium, captured on photographic film.

α-particles. β-particles are high-speed electrons, having a mass of about 1/1,800 amu and a charge of -1. γ rays are similar to x rays.

X rays, γ rays, and neutron beams are considered ionizing radiation. Ionizing radiation may break molecules into pieces, creating ionic free radicals that can be very damaging to tissue. Contaminated food or dust containing radionuclides that emit α- and β-particles may be very dangerous if the sources of radiation are ingested. Strontium-90 (^{90}Sr) present in fallout from nuclear weapons testing may be absorbed from soil, incorporated in plant tissues, eaten by cows, and eventually find its way into milk. Strontium is chemically similar to calcium. The ^{90}Sr may then be absorbed from the digestive tract and deposited in bone, where α-particles released by radionuclide decay damage the blood-producing reactions in bone marrow.

Several methods are used to detect radiation; the earliest of these, also discovered by Röntgen, is exposure of photographic film. Since x rays can pass through solid materials, they expose photographic film sealed in lightproof envelopes. Workers in industrial settings today often wear film badges that contain a sheet of photographic film inside a plastic container fitted with aluminum and lead shields. In order to determine the amount and type of radiation exposure, the badges are collected periodically and the film developed. Darkening of the film indicates exposure. Workers may also wear dosimeters, pencil-like tubes that are examined daily for exposure. For large-scale operations or as survey monitors at factory gates, Geiger-Mueller counters are utilized. These devices detect radiation by using a tube consisting of a metal can containing a charged wire. The tube is sealed with a thin plastic or mica window. Radiation penetrating the can or window ionizes molecules of gas inside the tube, and the ions allow an electrical discharge, which can be detected and registered by an electrical circuit. Civil defense and military personnel often carry Geiger counters to survey large areas for contamination by radioactivity.

Uses of Radiation

Radiation is a versatile tool for the diagnosis and treatment of disease, as well as a means of industrial testing and treating foods to avoid spoilage. Many common metabolic substances can be labeled by replacing atoms such as carbon or hydrogen with radioactive atoms such as ^{14}C or ^{3}H. The resulting molecules are absorbed by the body and react in the same way as nonradioactive molecules, but the decay of the radioisotope releases tiny amounts of radioactivity that can be detected with sensitive instruments. Some compounds are absorbed more rapidly by diseased tissue (a cancerous organ, for example, might rapidly absorb **glucose** from blood), and the use of substances such as radioactive iodine can help diagnose tumors of the thyroid gland without invasive surgery. Some diseases such as cancer can be treated by administering a preparation containing radionuclides within molecules that are taken up by an organ and release their radioactivity within the diseased tissue.

glucose: common hexose monosaccharide; monomer of starch and cellulose; also called grape sugar, blood sugar, or dextrose

Cells that are growing and dividing rapidly are the most sensitive to radiation. In the human body, these include gonadal tissue, hair follicles, the immune system, bone marrow, **intestinal epithelium**, and cancer cells. Cancer may be treated by external beam radiation, using γ-type radiation to deliver energy to abnormal cells, in the hope of killing them. Normal tissues are protected by lead shielding, and also by rotating the radiation source, passing the beam of γ rays through a larger range of tissue, and avoiding the intense irradiation of nontumorous tissues. In some cases, malignant cells can be treated with brachytherapy, the implantation of tiny metallic seeds containing radioisotopes that emit small amounts of radiation, killing the cancer from the inside. Radioisotopes decay at a known rate; often a nuclide that decays rapidly may be chosen, allowing the patient to be radiation-free upon discharge.

intestinal epithelium: layer of cells in the intestines that allows the passage of water and solutes

Gamma radiation is widely used in manufacturing to make images of welds in pipes. A recent application of radiation in the food industry involves the use of radiation (usually either γ rays or high-energy beams of electrons) to irradiate food, killing organisms that cause spoilage. The irradiation of food presents several advantages: foodstuffs may last weeks longer with little refrigeration; the use of dangerous chemical preservatives can be avoided; and foods may be prepared, wrapped, and preserved with less contact by human workers, lessening the chances of spreading disease-producing organisms.

In recent years, especially virulent and damaging strains of *Escherichia coli* have caused outbreaks of illness among persons who consumed contaminated hamburger, and some cases of salmonella poisoning have been associated with the consumption of poultry products. Food irradiation may help to make such foods much safer.

Our environment contains many sources of radiation, such as cosmic rays that constantly bombard Earth. The atmosphere filters out some cosmic rays, so exposure is greater at higher altitudes than at sea level. Radiation sources also include smoke detectors, luminous watch dials, television and computer monitors, and medical x rays. We are exposed daily to electromagnetic radiation in the form of radio waves as well as α- and β-particles and γ rays emanating from radioactive carbon, hydrogen, and potassium, which are part of all living things. A small amount of radiation is probably harmless and may, in fact, be helpful. Radon in our homes is a potential cause of cancer. Although radon is a colorless, odorless gas, it decays to more chemically reactive and radioactive products that may bind in lung tissue. Like many dangerous gases, radon is much more hazardous in the presence of particulate matter such as the tiny particles present in cigarette smoke. SEE ALSO PHOTOSYNTHESIS; RADIOACTIVITY; RÖNTGEN, WILHELM.

Dan M. Sullivan

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Radition Exposure

All matter is potentially damaged when exposed to radiation. This article examines radiation exposure to living systems. Radiation exposure occurs when the energy associated with radiation is deposited in a living organism, which is said to "receive a radiation dose." In the United States, radiation doses are measured in "rems" or "millirems" (mrems); "rem" stands for *r*adiation *e*quivalent *m*an. The international unit of radiation is the Grey, and 100 rem = 1 Grey.

Natural Radioactivity

Radioactivity is a natural and spontaneous process that occurs when unstable atoms of an element emit or radiate excess energy in the form of particles or waves. Such emissions are called ionizing radiation. Ionization, the process by which molecules lose electrons, is a particular characteristic of the radiation produced when radioactive elements decay. The capacity of radioactive emissions to cause ionization of molecules is the basis for health hazards and provides the means by which radiation can be detected.

Low levels of radioactivity are commonly found in the air, the rocks, and the soil, in the water and oceans, and even in our building materials. Several important radioactive nuclides occur naturally, such as carbon-14 (C-14) and potassium-40 (K-40). These **isotopes** are generated by cosmic ray interactions and make their way into the food chain. Once ingested, they can decay and deposit an internal dose of radioactivity, however mild. Carbon-14 is a particularly useful isotope. All living organic material has a constant natural ratio of carbon-14 to nonradioactive carbon-12. Once an organism dies, the remaining organic material is no longer involved in the cycle of absorbing carbon and moving the carbon along the living metabolic chain. For example, plants absorb CO_2 and during their life processes produce a variety of carbohydrates $(C_6H_{12}O_6)_x$. As long as the plant lives, all of the carbon in the plant is in the naturally occurring ratio and is in equilibrium with the natural ratio of carbon-14 to carbon-12 in the atmosphere. When the plant dies, that ratio in the dead plant starts changing because the carbon-14 decays, whereas the carbon-12 does not. By measuring that ratio of C-14 to C-12 in the dead plant, the approximate date of death can be determined. This process of establishing the date of the death of a living organism is called "carbon dating." Potassium-40 is naturally found in the soil and taken up by plants such as bananas. This fruit with the incorporated K-40 then becomes part of a food chain cycle.

isotope: form of an atom that differs by the number of neutrons in the nucleus

Radiation in small doses, usually below 10 rem, generally does not have demonstrable biological effects. And there are suggestions that small doses may provide a health benefit in the form of radiation hormesis. Hormesis is a modification of the word hormone that describes stimulation induced at low doses of agents that are harmful or even lethal at high doses. Generally, hormesis is any stimulatory or beneficial effect, induced by low doses of an agent that cannot be predicted by the extrapolation of detrimental or lethal effects induced by high doses of the same agent.

Large doses of radiation, at the level of several hundred rems, may cause serious injury if received in a short time period (days or hours). This condition is called "acute radiation syndrome." Much larger doses can cause death. Doses between the large doses and small doses increase the risk of cancer.

Types of Radiation

Common types of ionizing radiation are alpha (α), beta (β), neutron, x-ray, and gamma (γ) radiation. Radioactive elements are often called radioactive isotopes or "radionuclides." An alpha particle consists of 2 protons and 2 neutrons; since there are no electrons in the alpha particle, it carries a charge of $+2$. Beta particles are electrons and carry a -1 charge. Both are referred to as "charged particles." Neutrons carry no charge. Gamma and x rays have neither mass nor charge. They are electromagnetic waves and are sometimes referred to as "photons." Cosmic radiation is divided into two types: primary and secondary. Primary cosmic radiation consists of high-energy particles, such as protons, that come from the Sun or other sources outside our solar system. The Sun-derived cosmic radiation is produced during solar flares. Only a small fraction of the primary cosmic radiation penetrates to Earth's surface; most interacts with the atmosphere, producing the secondary cosmic radiation, which produces other lower-energy radiation in the form of photons, electrons, neutrons, and muons that eventually reach the surface.

Earth's atmosphere and magnetic field act as shields against cosmic radiation, reducing the amount that reaches Earth's surface. The average radiation dose from cosmic radiation in the United States is 27 mrem per year. This dose roughly doubles with every increase of 6,000 feet of elevation. Traveling at high altitudes in an airplane increases exposure to cosmic radiation. A typical exposure obtained from flying in a commercial jet across the United States (coast to coast) provides a radiation dose of approximately 0.5 rem for each hour traveled.

Cosmic radiation can cause genetic changes. Some scientists believe that this radiation has been important in driving the development of life on our planet. While cosmic radiation can cause some damage to individuals, it also may have played an important role in the development of humans.

Earth's atmosphere is a natural shield against the harmful effects of primary cosmic radiation. If humans were to leave Earth and travel to some distant planet, exposure to high levels of primary radiation is a serious potential risk. Future space travelers will have to be shielded from exposure to cosmic rays. SEE ALSO Radiation; Radioactivity.

John Pickering

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Radioactivity

In 1896 Henri Bequerel, a French physicist, was studying the fluorescence of uranium compounds. He placed crystals of potassium uranyl sulfate on top of photographic film wrapped in dark paper and exposed the crystals to sunlight. Bequerel interpreted darkening of the film to be the result of penetration of the paper by the fluorescence of the uranium. A second experiment on this uranyl fluorescence was delayed for some days due to cloudy, wintry weather in Paris, leading Bequerel to decide to repeat the experiment, using new film. However, he developed the earlier film, expecting to see little, if any, darkening. To his surprise the film was as dark as if sunlight had been striking the uranium throughout the whole cloudy period. He concluded that uranium was spontaneously emitting high-energy rays that caused the observed darkening of the photographic plate and asked Madame Marie Curie, a research assistant in his laboratory, to join him in further studies of this new phenomenon. Curie named the spontaneous, high-energy radiation "radioactivity."

By 1898 Madame Curie and her husband Pierre, in collaboration with Bequerel, had isolated two new elements from the **radioactive decay** of uranium in pitchblende ore. Both were more radioactive than uranium itself. They named the first element polonium (Po) after Madame Curie's native land (Poland), and the second was named radium (Ra). Isolation of these two elements required chemical separation of very small amounts of Po and Ra from tons of pitchblende. Radium was found to be over 300,000 times more radioactive than uranium.

radioactive decay: process involving emission of subatomic particle from nucleus, typically accompanied by emission of very short wavelength electromagnetic radiation

The French experiments attracted the attention of Ernest Rutherford, a physicist at the University of Manchester in England. Using an electrical field, Rutherford demonstrated that the radiation emitted from a radioactive sample could be separated into three types of rays, which he named alpha, beta, and gamma rays. The α rays (alpha rays) were positively charged, as they were deflected strongly to the negative side, whereas the negative β rays (beta rays) were deflected to the positive side. The γ rays (gamma rays) were not deflected and are uncharged high-energy electromagnetic radiation, similar to x rays and light rays. Gamma rays are the result of rearrangements of neutrons and protons in nuclei that yield lower-energy states and usually accompany other forms of radioactive decay.

Emission of an **α-particle** produces a new nucleus with a reduction in **atomic number** by two and in mass number by four. When a nucleus emits a β-particle, the atomic number of the new nucleus increases by one (over that of the decaying nucleus), but the mass numbers are unchanged. Some radioactive nuclei do not increase in atomic number in decay, but decrease by one unit of mass number due to the emission of a positron (a positively charged β ray). For example, in β decay with electron emission, ${}^{14}_{6}\text{C}$ is converted to ${}^{14}_{7}\text{N}$, whereas in positron β decay, ${}^{22}_{11}\text{Na}$ is converted to ${}^{22}_{10}\text{Na}$. An alternative process to β decay involves the absorption of an orbital electron by the nucleus in a process known as electron capture, which results in a decrease in the atomic number of the product nucleus, for example, ${}^{195}\text{Au}$ decaying to ${}^{195}\text{Pt}$. Gamma-ray decay results in no change in either mass number or atomic number.

α-particle: subatomic particle with 2+ charge and mass of 4; a He nucleus

atomic number: the number assigned to an atom of an element that indicates the number of protons in the nucleus of that atom

fission: process of splitting an atom into smaller pieces

Another type of radioactive decay that is observed in the heaviest elements is spontaneous **fission**. In this process, a nucleus splits into two roughly equal parts, simultaneously releasing a large amount of energy. For example, for the nuclide ${}^{252}_{98}\text{Cf}$, of every 100 nuclei that decay, approximately 97 do so by α decay and 3 undergo spontaneous fission.

The rate of radioactive decay is directly proportional to the amount of radioactive species present. A radioactive nucleus is characterized by its half-life, which is the amount of time it takes for 50 percent of the atoms present initially to decay. The half-life of ${}^{131}\text{I}$ is eight days: an original sample of 1 gram (0.035 ounces) of ${}^{131}\text{I}$ after eight days has only 0.5 grams (0.018 ounces) remaining; after sixteen days, only 0.25 grams (0.0088 ounces), and so on. The half-life is unaffected by differences in temperature, pressure, or chemical state. This constancy has made study of the half-lives of radioactive nuclei very useful to scientists engaged in dating archaeological and geological materials.

Since the discovery of radioactivity, radioactive nuclei serving as "tracers" have been of immense value to science, agriculture, medicine, and industry.

HANS GEIGER (1882–1945)

Hans Geiger worked in Ernest Rutherford's laboratory manually and meticulously counting **α-particle** scintillations for the famous experiments that led to the discovery of the nucleus. Because of this work, he developed an α-particle detector. After World War I, Geiger developed the modern Geiger–Mueller counter and worked until his death to increase its speed and sensitivity.

—Valerie Borek

These radiologists are measuring radioactivity levels in the soil near the Chernobyl nuclear plant, Ukraine.

In the use of radioactive tracers it is assumed that the radioactive **isotopes** studied are identical in chemical behavior to the nonradioactive isotopes. The first experiments that used radioactive tracers were carried out in 1913 in Germany and were designed to measure the solubility of lead salts via the use of a radioactive isotope of lead. In industry, radionuclides have been used for analytical purposes, for measurements of flow in pipes, and as part of many other applications. Another example of an important tracer study has been the investigation of **photosynthesis** of carbohydrates from atmospheric CO_2 in the presence of light and **chlorophyll**. Scientists used $^{14}_{6}C$, $^{32}_{15}P$, and $^{3}_{1}H$ to identify the intermediate steps involved in the photosynthesis of carbohydrates in plants that had been placed in an atmosphere composed of $^{14}_{6}C$-labeled CO_2 and had been irradiated with light. The presence of the radioactive carbon in the synthesized carbohydrate was evidence that O_2 was involved in the **synthesis**.

isotope: form of an atom that differs by the number of neutrons in the nucleus

photosynthesis: process by which plants convert carbon dioxide and water to glucose

chlorophyll: active molecules in plants undergoing photosynthesis

synthesis: combination of starting materials to form a desired product

The process of **neutron activation analysis**, in which radioactivity is induced in stable nuclei by their bombardment with neutrons, has allowed measurement of impurities on the level of less than one part per billion. Neutron activation analysis has been used in determining the authenticity of paintings, in criminology, in analyzing lunar soil, and in many other areas.

neutron activation analysis: method for detecting traces of elements by bombardment with high-flux neutrons and then measuring the decay rate of the radioactive products

The largest single use of radionuclides has been in medical science. If a radioactive compound, such as a radioactively labeled amino acid, **vitamin**, or drug, is administered to a patient, the substance is incorporated in

vitamins: organic molecules needed in small amounts for the normal function of the body; often used as part of an enzyme-catalyzed reaction different organs to varying degrees. The substance undergoes chemical change within the body, and the movement of the radioactive atoms in the body can be followed with radiation detectors. Such information is of great diagnostic value toward identifying the presence of tumors and other diseases in different organs in the body. Radioactivity has also been used in medicine for therapeutic purposes (radiotherapy); for example, it attacks cancerous cells more efficiently than normal cells. SEE ALSO Nuclear Fission; Nuclear Medicine; Transactinides; Transmutation.

Gregory R. Choppin

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Radium

MELTING POINT: **700°C**
BOILING POINT: **1,140°C**
DENSITY: **5.00 g/cm^3**
MOST COMMON IONS: **Ra^{2+}**

88
Ra
RADIUM
226.03

Radium is the last of the alkaline earth **metals** comprising the second column of the Periodic Table. While there are twenty-five known **isotopes** of radium (only four of which are found naturally), all of them are radioactive. Of these isotopes, radium-226 is the most common, with a half-life of about 1,600 years.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

isotope: form of an atom that differs by the number of neutrons in the nucleus

Radium was first isolated in 1898 by Marie Sklodowska Curie and her husband, Pierre Curie. They were studying the radioactivity of pitchblende, a uranium-rich ore, and noticed that the ore was still radioactive with all the uranium removed. After years of painstaking work, the Curies eventually isolated radium and named it for the Latin word *radius*, meaning "ray." For this work, Madame Curie was awarded the Nobel Prize in Chemistry in 1911, her second such honor (the first one, in physics, shared with her husband and Henri Becquerel in 1903 for their initial studies of radioactivity).

Radium is rare in nature, being only the eighty-fifth most abundant element in Earth's crust. When the Curies and their assistant, Gustave Bemont, first isolated radium, they had to reduce many tons of pitchblende ore to obtain only a few grams of the element. As a metal, radium has a silvery white color and is luminous due to its inherent radioactivity. In the past, radium salts were mixed with phosphorescent zinc sulfide into a paint that was placed on the faces of some clocks and watches so that they could be seen at night. However, the workers who painted the clocks suffered and often died of radiation poisoning and cancer, and so the practice was ended. These days, the uses for radium are as rare as the element itself, with annual world production totaling less than 1 kilogram (2.2 pounds). SEE ALSO Curie, Marie Sklodowska.

David A. Dobberpuhl

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86
Rn
RADON
222

Radon

MELTING POINT: −71°C
BOILING POINT: −61.8°C
DENSITY: 9.73 g/cm^3
MOST COMMON IONS: None

Radon is a member of the **noble gas** family and was the first radioactive gas to be discovered. It is colorless, odorless, and chemically **inert** (like the other noble gases), but it is a highly radioactive ***α*-particle** emitter.

Radon was discovered in 1899 by the McGill University professors Ernest Rutherford and Robert Owens, who found that radioactive thorium produced radioactive gas. They named this gaseous substance thorium emanation, later to become thoron. It was found that radium gave off a similar emanation (radon), as did actinium (actinon), in 1900 and 1904, respectively. Once the structure of the atom and the elemental transmutation process became better understood, it was determined that thoron, radon, and actinon were different **isotopes** of the same element (radon)—^{220}Rn, ^{222}Rn, and ^{219}Rn, respectively.

Radon has a tiny natural abundance as the product of uranium and thorium decay; it has a background concentration of 6×10^{-14} parts per million by volume in air. Because radon is a short-lived α-emitter, the **synthesis** of compounds that contain radon has been limited to just fluorides and oxides. Radon saw considerable therapeutic use between 1920 and 1950 in the irradiation of tumors, but its modern usages stem from its being an easily detected radioactive gas. It is used to trace gas flow and air movement, and

noble gas: element characterized by inert nature; located in the rightmost column in the Periodic Table

inert: incapable of reacting with another substance

***α*-particle:** subatomic particle with 2+ charge and mass of 4; a He nucleus

isotope: form of an atom that differs by the number of neutrons in the nucleus

synthesis: combination of starting materials to form a desired product

Radon is radioactive and is responsible for 10 percent of all lung cancer deaths. Many homes are equipped with radon detectors, such as the one at the far left in this photograph.

its presence below Earth's surface can yield information about tectonic movement, earthquake potential, and mineral deposits.

During the 1980s it became recognized that there was widespread contamination of households by radon, which is now estimated to cause 10 percent of all lung-cancer deaths. The primary source of household radon is surrounding bedrock rich in uranium and also present in a permeable matrix that permits diffusive and convective transport of the radon isotopes derived from the uranium. The U.S. Environmental Protection Agency encourages corrective action when household radon levels surpass 4 picoCuries per liter, yet in some parts of the country more than 40 percent of the residences exceed this value. SEE ALSO Noble Gases.

Laurence E. Welch

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Raman, Chandrasekhara

INDIAN PHYSICIST
1888–1970

Chandrasekhara Venkata Raman described himself as a "child of nature"; he was indeed a profound student of nature all his life, a keen and resourceful observer of the world around him. In addition to discovering the physical effect that bears his name, he can also be considered the father of modern Indian experimental science.

Raman was born near Trichinopoly (now Tiruchipalli) in southern India on November 7, 1888. His father, whose family had been farmers in the area for many generations, turned to teaching and became a lecturer in physics and mathematics at a small college in Vizagapatam when Raman was four years old. During Chandrasekhara's childhood, his father conveyed to him not only an interest in science but also a love of music. He attended Presidency College at the University of Madras, where he excelled in science and graduated in 1904 at the age of sixteen. Although his teachers urged him to go to England for graduate study, he was prevented from doing so for health reasons and remained at Presidency College to work on his master's, which he obtained in 1907. During this time Raman began his longtime interest in optical phenomena, publishing a paper in the *Philosophical Magazine* on the diffraction patterns of reflected light. At that time, modern scientific research was practically unknown in India, especially from someone who had not attended school outside the country.

Since there was scarce opportunity for Raman to pursue a scientific career when he graduated, he entered the civil service, becoming an accountant in the Indian Finance Department. During his ten years of service in this capacity, spent mostly in Calcutta, he continued to conduct scientific research under the auspices of the Indian Association for the Cultivation of Science, a small, privately endowed organization. Using simple and inexpensive equipment, and working outside his regular office hours, Raman published thirty papers in ten years, mostly in the area of sound. His work attracted the attention of the officers of the University of Calcutta, and in 1917 he was offered a professorship in physics, becoming the first Indian-educated scientist to hold such a post. He was then able to pursue his research more actively and to supervise graduate students.

While traveling to England in 1921 to attend a scientific congress, Raman was struck by the blue color of the Mediterranean Sea, caused by the scattering of sunlight in the clear water. This observation prompted the studies that culminated in his discovery of the characteristic changes in wavelength of scattered light caused by certain materials—the so-called Raman effect. Although previously predicted by others as a consequence of the interaction of light **quanta** with molecules, the actual effect was very weak and required long and careful measurements to establish. It represented a significant advance in chemical analysis, since at that time, other **spectroscopic** methods such as infrared spectroscopy were difficult and inexact without expensive instrumentation. On the contrary, only relatively simple equipment was necessary to observe the shifts in wavelength (the "Raman shifts") exhibited by a wide variety of chemical substances. Raman was knighted for this work in 1929 and received the Nobel Prize in physics in 1930, becoming the first Asian to receive the award.

quantum: smallest amount of a physical quantity that can exist independently, especially a discrete amount of electromagnetic energy

spectroscopy: use of electromagnetic radiation to analyze the chemical composition of materials

Raman left Calcutta in 1933 to become the director of the Indian Institute of Science, in Bangalore, where he remained until 1948. He continued his research on optical and electromechanical phenomena but also worked on a wide range of problems that reflected his fascination with the natural world—diamonds, seashells, and the coloration of flowers and feathers. In 1948 he established the Raman Research Institute in Bangalore, where he continued to carry out research until almost the end of his life. He died on November 21, 1970. SEE ALSO SPECTROSCOPY.

Bartow Culp

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Ramsay, William

SCOTTISH CHEMIST
1852–1916

William Ramsay, the only child of civil engineer and businessman William Ramsay and his wife Catherine, was born on October 2, 1852, in Glasgow, Scotland. Despite the scientific background of his family, he was expected to study for the ministry. He completed his secondary education at the Glasgow Academy and in 1866 entered the University of Glasgow, where he pursued a standard course of study in the classics. He became interested in chemistry when he read about gunpowder manufacture in a textbook, and he began attending lectures on chemistry and physics as a result. Starting in 1869, he also worked as a chemical apprentice to Glasgow City Analyst Robert Tatlock.

Scottish chemist Sir William Ramsay, recipient of the 1904 Nobel Prize in chemistry, "in recognition of his services in the discovery of the inert gaseous elements in air, and his determination of their place in the periodic system."

From April 1871 to August 1872, Ramsay worked on toluic and **nitrotoluic acids** under Rudolf Fittig at the University of Tübingen; these research efforts earned him a Ph.D. at the age of nineteen. In 1872 he became an assistant in chemistry at the Anderson College (now the Royal Technical College) in Glasgow and in 1874 a tutorial assistant at the University of Glasgow. He was appointed a professor of chemistry at University College, Bristol, in 1880. In 1887 he became a professor of inorganic chemistry at University College, London, where he remained until his retirement in 1913.

nitrotoluic acid: benzoic acid molecule with methyl and nitro groups attached

Ramsay was a scientist of exceptionally wide interests and talents. His earliest works centered on organic chemistry. Beginning in the 1880s, he pursued topics related to physical chemistry, such as stoichiometry, thermodynamics, surface tension, density, molecular weights, and the critical states of liquids and vapors. However, his most important achievements involved inorganic chemistry.

In 1785 English chemist Henry Cavendish suggested that, in addition to nitrogen, oxygen, carbon dioxide, and water vapor, air might contain another gas. In 1892 Lord Rayleigh (John William Strutt) found that nitrogen prepared from ammonia (NH_3) was less dense than nitrogen prepared from air. He reported his results in the journal *Nature* and asked readers to suggest an explanation for the discrepancy, which was beyond experimental error. At an 1894 meeting of the **Royal Society**, Lord Rayleigh posited that chemically prepared nitrogen might be contaminated with a less dense gas.

Royal Society: The U.K. National Academy of Science, founded in 1660

Ramsay believed that, on the contrary, atmospheric nitrogen might contain a denser gas. In large-scale experiments he passed atmospheric nitrogen over hot magnesium, which reacted to form solid magnesium nitride (Mg_3N_2) and left behind a small amount of unreactive gas. When he analyzed the gas spectroscopically, he observed, in addition to the lines of nitrogen, lines of a gas at that point still unknown. Simultaneously, Rayleigh repeated Cavendish's experiments and confirmed the presence of an unknown gas (1/107 of the original volume).

On August 13, 1894, Rayleigh and Ramsay announced their discovery of a new element in the atmosphere to the British Association at Oxford. Because of its unreactivity, they later called the gas argon, from the Greek word meaning "lazy." Ramsay suggested that argon be placed within a new group of zero-valent elements in the Periodic Table, between chlorine and potassium. In 1895 Ramsay and, independently, Per Theodor Cleve and Nils Abraham Langlet in Sweden, discovered helium, previously known from its solar spectrum, in a radioactive mineral. Also in 1895, Ramsay and the English chemist Morris W. Travers discovered the **inert** gases krypton (from the Greek, meaning "hidden"), neon (from the Greek, meaning "new"), and xenon (from the Greek, meaning "stranger"). From 1962, when English-born American chemist Neil Bartlett prepared xenon hexafluoroplatinate(V), $XePtF_6$, inert gases became known as **"noble gases."**

inert: incapable of reacting with another substance

noble gas: element characterized by inert nature; located in the rightmost column in the Periodic Table

In 1904 Ramsay received the Nobel Prize in chemistry "in recognition of his services in the discovery of the inert gaseous elements in air, and his determination of their place in the periodic system," becoming the first British recipient of this award. SEE ALSO ARGON; CLEVE, PER THEODOR; STRUTT, JOHN (LORD RAYLEIGH).

George B. Kauffman

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Rayleigh, Lord ***See Strutt, John.***

Reaction Rates

In chemistry, there is much interest in how quickly reactant molecules are transformed into product molecules and in the reaction steps or "mechanism" by which the chemical transformation occurs. We focus here on the speed with which chemical transformations occur, hence the title "reaction rates."

To calculate the impact of changing reactant concentrations, temperature, or pressure on a chemical reaction rate, a reliable quantitative measure of the change in the concentration of a reactant or product chemical species versus the change in time is needed. The first quantitative reaction rate study, carried out by Ludwig Wilhelmy in 1850, illustrates this. He followed the course of the "inversion of sucrose" in **aqueous solution**

aqueous solution: homogenous mixture in which water is the solvent (primary component)

$$sucrose + H_2O \xrightarrow{\text{dilute acid}} glucose + fructose$$

by observing a gradual rotation of the plane of polarized light passed through the solution over time. Sucrose rotates the plane of polarized light clockwise, whereas fructose rotates the plane of polarized light more strongly counterclockwise. Wilhelmy thus found that the concentration c of sucrose decreases with time t according to the following equation

$$-dc/dt = k_1c$$

where k_1 is the rate constant, a factor that has a temperature and pressure dependence but does not have a concentration dependence. This is called a first-order rate expression and k_1 is called a first-order rate constant, because the concentration c is raised to the first power in this rate equation. The half-line of this reaction, the time required for half of the sucrose

Half-lives of Some Radioactive Isotopes.

Radionuclide	Half-life (Days)	Radionuclide	Half-life (Days)
3H	4.50×10^3	90Sr	1.00×10^4
14C	2.09×10^6	99Mo	2.79
32P	14.3	99mTc	0.250
35S	87.1	99Tc	7.70×10^6
42K	0.52	109Pd	0.570
45Ca	16.4	111In	2.81
47Ca	4.90	129I	6.30×10^9
59Fe	45.1	131I	8.00
57Co	270	135I	0.280
72Ga	0.59	207T1	3.33×10^{-3}
58mCo	0.38	207Bi	1.53×10^{-3}
58Co	72.0	226Ra	5.84×10^5
60Co	1.9×10^3	235U	2.60×10^{11}
64Cu	0.538	236U	8.72×10^{-5}
67Cu	2.58		

initially present in solution to react, is given for a first-order reaction by the expression

$$t_{1/2} = \ln 2/k_1$$

where the first-order rate constant k_1 has the units of reciprocal time. This is a general expression for all first-order reactions.

Overall Reaction Order

When the sucrose inversion reaction was later run in nonaqueous solvents it was recognized that a better description of the rate of disappearance of sucrose S is given by the following equations:

$$S + H^+ \rightleftharpoons SH^+$$

$$Kc = [SH^+]/[S][H^+]$$

$$SH^+ + H_2O \xrightarrow{\text{slow}} glucose + fructose + H^+$$

$$-d[S]/dt = k[SH^+][H_2O] = kK_c[S][H^+][H_2O]$$

Thus, the reaction rate is first-order in sucrose, first-order in the **catalyst** H^+, and first-order in H_2O. The reaction is said to be "third-order overall," third because of the sum of the powers on the three concentration factors.

catalyst: substance that aids in a reaction while retaining its own chemical identity

The "initial rate method" is usually used to deduce reaction order from experimental rate data. This means that the reaction rate is determined over a short range of times after mixing reactants to avoid the complicating effects of reaction products undergoing further reactions. The initial reaction rate $R = k[A]^a[B]^b[C]^c$ . . . is measured several times, with the concentrations of the reactants A, B, C, and so on systematically varied. Then, taking the logarithm of both sides of each rate equation $\log R = \log k + a \log[A] + b \log[B] + c \log[C]$ . . . the several resulting simultaneous linear equations for the values of a, b, c, and so on can be solved. Often, all but one of the reactant concentrations are kept constant, and the concentration dependence of the variable reactant is then most easily determined.

Temperature Dependence of Rates

In 1889 Svante Arrhenius noted that an increase in Kelvin temperature T caused the rate constant k of many reactions to increase according to the relation

$$k = Ae^{-Ea/RT}$$

or

$$\ln/k = \ln A - Ea/RT$$

where the activation energy E_a is related to the minimum amount of energy that a reactant molecule must acquire from collisions or some other form of excitation to go on to form reaction products. R is the perfect gas (ideal gas) constant.

If the rate constant k for a reaction is determined at several different temperatures, all that one needs to do to obtain a numerical value of E_a is to construct a plot of ln k on the vertical axis versus $1/T$ on the horizontal axis. If the chemical reaction obeys the Arrhenius equation, a straight line plot of the experimental data having a negative slope is obtained. The slope of this line is equal to $-E_a/R$. Readers living in temperate climates will recall that the rate at which crickets chirp gradually declines in autumn as outside temperatures become cooler. If the natural logarithm of the frequency of the chirping of crickets is plotted versus the reciprocal of the Kelvin temperature, the observer deduces from the slope of the resulting straight line that the activation energy for chirping is about $E_a = 5 \times 10^4$ joules/mole.

If k_1 is the rate constant for a given reaction at a Kelvin temperature T_1, we may estimate the magnitude k_2 of the rate constant of that reaction at some other temperature T_2 from the following alternative form of the Arrhenius equation:

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} + \frac{1}{T_2}\right)$$

A familiar rule in chemistry states that "the rate of a chemical reaction doubles for each increase in temperature of ten degrees." From this second form of the Arrhenius equation it becomes clear that the moderate success of this rule of thumb proceeds from the fact that for many chemical reactions the activation energy E_a has a magnitude in the general ballpark area of 5×10^4 joules/mole.

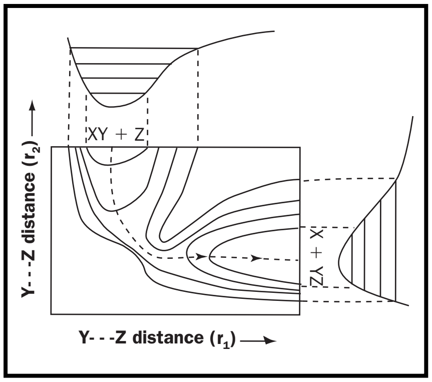

Figure 1. Typical potential energy surface for the reaction XY + X → x + YZ.

The Activated Complex

A chemical reaction in which a diatomic molecule A–B collides end-on with an atom C, to form a diatomic molecule B–C and an atom A, can be depicted as occurring on a surface within a theoretical three-dimensional space in which the vertical axis is potential energy and the other two axes are the A–B and the B–C bond distances. In 1931 Henry Eyring and Michael Polanyi took reaction rate studies to the individual molecule level by calculating a potential energy surface for the colinear gas **phase** reaction

$$D + H_2 \rightarrow DH + H$$

phase: homogeneous state of matter

where D denotes the deuterium **isotope** of hydrogen. They visualized the passage of the system from reactants to products as occurring via a linear configuration of the three atoms corresponding to the top of a potential energy barrier that they called the "activated complex." This entity had a presumed lifetime of only 10^{-13} seconds or less, and no one in the 1930s foresaw that activated complexes would finally be observed experimentally (in 1987) by Ahmed Zewail using femtosecond duration (10^{-15} seconds) laser pulses.

isotope: form of an atom that differs by the number of neutrons in the nucleus

In 1935 Eyring and Polanyi independently formulated a "transition state theory" expression for the A-term in the Arrhenius equation pertaining to the rate constant of a gas phase reaction. Their work was based on the idea that a chemical **equilibrium** exists between the reactant species and the activated complex, even though some of the activated complex species must be "leaking" over the top of the potential energy barrier and forming products. Powerful concepts that still have wide application in explaining reaction rates emerged from transition state theory. For instance, gas phase reactions between two large molecules are typically slower than one would predict using a billiard ball collision model of reaction rates. This is because much of the collision energy can be stored unreactively in the internal vibrations of a collisionally excited molecule.

equilibrium: condition in which two opposite reactions are occurring at the same speed, so that concentrations of products and reactants do not change

Pressure Dependence of Rates

Another application of transition state theory is its explanation of the effect of pressure on reaction rates. Increasing pressure by a factor of 10^3 decreases the rate constant for a ring-closure reaction

$$Mo(\mathrm{CO})_5L \xrightarrow{k} \mathrm{Mo}(CO)_4L + CO$$

by a factor of 1.3 (where L is the bidentate **ligand** 1,10-phenanthroline and the solvent is liquid toluene at 25°C). The change in volume in going from reactants to activated complex is $\Delta V^{\neq} = +6.1\ \mathrm{cm^3 mol^{-1}}$. Applying le Chatelier's principle to the quasi-equilibrium between reactants and activated complex molecules, the transition state theory point of view maintains that the increase in pressure favors formation of reactants over formation of activated complexes, because the reactants are more compact. With fewer activated complexes present, the reaction-yielding product from activated complexes slows down.

ligand: molecule or ion capable of donating one or more electron pairs to a Lewis acid

Reaction Time Scales

Many important reactions, such as the conversion of atmospheric nitrogen and hydrogen into ammonia, are very slow and remain that way until a catalyst (in this case iron oxide) is identified. In our bodies, enzymes can function as catalysts to speed up essential reactions. In order to understand reaction mechanisms, chemists focus on discrete reaction steps and often need very short-term experimental methods to follow rates of individual reaction steps. For instance, Manfred Eigen and Leo De Maeyer (1955) used an electrical conductance "relaxation method" to measure the rate of the reaction

$$H^+(\mathrm{aq}) + OH^-(\mathrm{aq}) \xrightarrow{k} H_2O(\mathrm{l})$$

in liquid water. They found a rate constant $k = 1.4 \times 10^{11}$ liters $mol^{-1}s^{-1}$ at 25°C (77°F) by measuring relaxation times (roughly reaction half-lives) on a time scale of tens of microseconds. In recent years femtosecond laser pulses have proved to be the most powerful experimental tool for elucidating the details of chemical reaction steps and their rates. Zewail has speculated that attosecond (10^{-18} second) laser pulses will be achieved that will enable scientists to track the paths of electrons within molecules as the molecules undergo chemical reactions. SEE ALSO CATALYSIS AND CATALYSTS.

Edward M. Eyring

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Reaction Speed ***See Kinetics.***

Recombinant DNA

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

Recombinant **DNA** (rDNA) is made of segments of DNA (polymers of deoxyribonucleotides) from two or more sources. Nature has been recombining DNA in living cells for eons, but humans have only recently discovered the means to carry out this operation in the test tube. DNA is the molecule of heredity, and the procedure used for preparing rDNA is referred to as genetic engineering. The biotechnology industry and much of modern medicine, basic research, and agriculture depend on the use of rDNA.

How the Technology Developed

cleave: split

hydrolyze: to react with water

hydrogen bond: interaction between H atoms on one molecule and lone pair electrons on another molecule that constitutes hydrogen bonding

The discovery of restriction endonucleases, enzymes that reproducibly **cleave** double-stranded DNA molecules at specific sequences, paved the way for the development of rDNA technology. Restriction endonucleases are produced in bacteria as a defense mechanism of that bacterium to restrict the growth of invading bacterial viruses; they act by destroying viral DNA. The enzymes **hydrolyze** or "cut" specific sites within a DNA molecule. In 1978, the Nobel Prize in medicine was awarded to Werner Arber, Daniel Nathans, and Hamilton O. Smith for the discovery and investigation of restriction endonucleases. The cuts made by these enzymes often leave single DNA strands with sticky ends due to the asymmetry of the cut (made to a double-stranded molecule) and the tendency of the bases in DNA to form **hydrogen bonds** with complementary bases on another strand. Scientists realized that these enzymes could serve as a powerful tool for manipulating DNA in a controlled way. The 1980 Nobel Prize in chemistry was awarded to Paul Berg for constructing the first recombinant DNA molecules.

When scientists became concerned about whether this new technology posed risks to humans and the environment, there was an unprecedented (and temporary) suspension of experiments using rDNA. In 1975, a conference was held in Asilomar, California, to assess such risks, and it was determined that most rDNA work should continue as long as appropriate safeguards were in place. A Recombinant DNA Advisory Committee was established through the auspices of the National Institutes of Health to set up guidelines and assess risks and benefits of proposed projects using rDNA. That committee, composed of scientists, physicians, ethicists, and legal experts, has met regularly since that time.

Preparing rDNA

When a DNA carrier, called a vector, and a targeted DNA sample are treated with the same restriction enzyme, the resulting fragments are left with matching, or complementary, sticky ends. When mixed, the two samples of treated DNA will "stick" together, and another enzyme, DNA ligase, will seal pieces of DNA together with the formation of **covalent bonds** (see Figure 1). Vectors are often plasmids, small extrachromosomal and circular DNA that are incorporated into bacterial DNA such as that of *E. coli*, so that the inserted or cloned genes can be reproduced manyfold and products of the inserted genes (protein molecules) can be manufactured, sometimes in large quantities. Some vectors are designed to induce protein **synthesis** from the information in the inserted genes. Other vectors are designed to deliver large segments of DNA to specific cells.

covalent bond: bond formed between two atoms that mutually share a pair of electrons

synthesis: combination of starting materials to form a desired product

Uses of rDNA Technology

Essentially every area of biological research has been affected by the use of rDNA technology. Protein structure/function relationship studies and gene expression and regulation research have been enormously enhanced by this powerful tool. Transgenic animals (into which DNA from another species has been inserted) have been bred to expand the study of human biochemical processes and diseases. Transgenic mice that are highly susceptible to breast cancer or Alzheimer's disease have furthered the understanding of those diseases.

Modern medicine is inextricably linked with rDNA technology. Gene therapy replaces defective genes with functional ones, delivered to the patient by way of a suitable vector, usually a disabled virus. The first moderately successful gene therapy was instituted to treat an inborn immune deficiency disease (ADA deficiency) caused by a defective enzyme, **adenine** deaminase. Cancer research and treatments as well as some vaccine development make use of rDNA technology. Attempts to modify animals genetically in such a way that organs suitable for transplant into humans may be harvested are now being made.

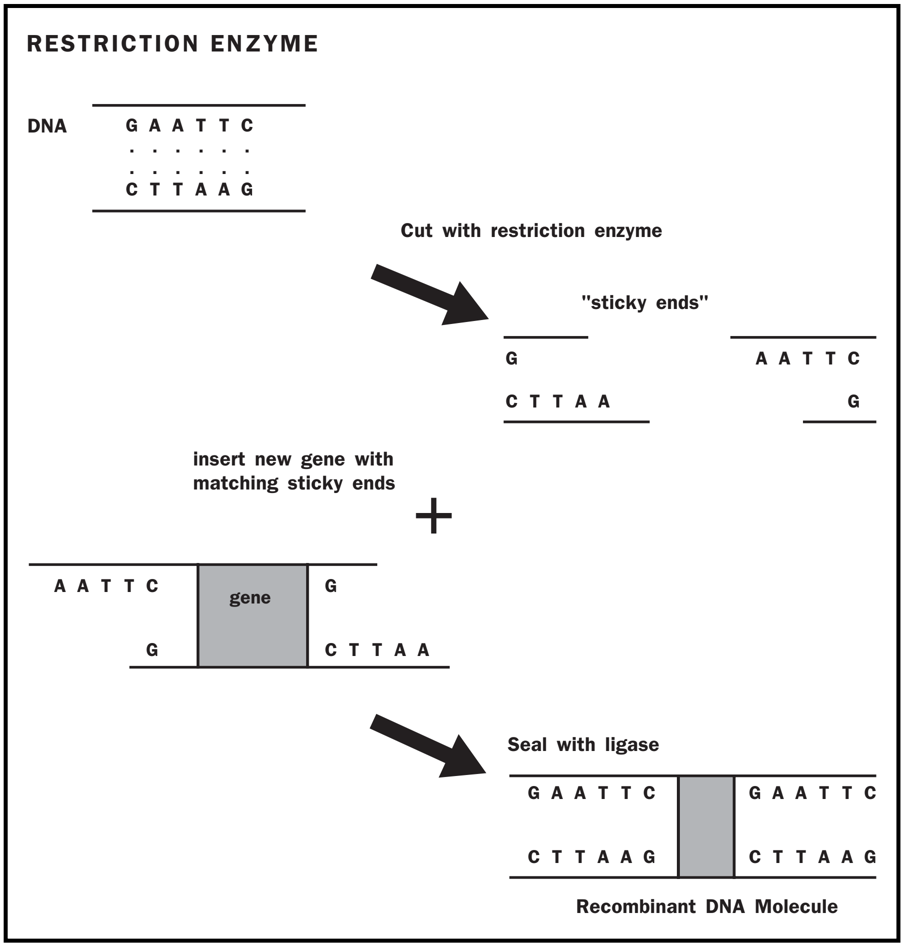
adenine: one of the purine bases found in nucleic acids, $C_5H_5N_5$

Agricultural uses of recombinant DNA technology are expanding. Genetically engineered bacteria sprayed onto strawberries protect the strawberries from freezing. Genes that promote herbicide resistance are incorporated into plants so that herbicides can be used for no-till farming. Some plant species have been transformed by rDNA containing genes that promote resistance to insects and pathogens.

The industrial use of rDNA technology includes the production of bleach-resistant enzymes that are used in laundry detergents to **degrade**

degrade: to decompose or reduce the complexity of a chemical

Figure 1. Scheme for producing an rDNA structure made from a plasmid and DNA to be cloned.



proteins. Transgenic cows that produce human milk for use in baby food have been bred. In 1980 the verdict of a landmark case heard before the U.S. Supreme Court stated that a genetically engineered bacterium, designed to digest oil in oil spills by researchers at Exxon, could be patented.

Recombinant DNA technology was used as an artist's tool in a macabre incident in which a jellyfish gene for a green fluorescent protein, often used in research as a marker for gene transfer, was inserted into a rabbit, making the rabbit fluoresce under green light. This and other dubious uses of rDNA technology have engendered a number of ethical, economic, safety, and legal debates. SEE ALSO Clones; DNA Replication; Hydrogen; Restriction Enzymes.

Sharron W. Smith

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Recycling

Remains of human settlements through the ages are characterized by garbage. Early human encampments are surrounded by discarded bones, shells, and broken tools and weapons. While such material is a boon to archaeologists, the mountains of discarded materials produced by today's society threaten to consume available land near large cities, and they pollute the water supplies of both rural and urban environments. Nearly every object and material discarded by humans can be recycled, reducing the cost and danger of disposal and providing valuable resources for industry and the home. Recycling also restricts many dangerous substances to facilities designed to handle them.

The Emergence of Recycling

Many Americans remember when garbage disposal was as simple as placing the material in a can in the alley or, in the case of rural residents, feeding the pig, or tossing everything into a nearby ditch in the name, at least, of erosion control. Our ancestors lived lives much simpler and were much less encumbered by material possessions. Bottles, buttons, nails, and wood all passed through a progression of steps and were smelted, rewoven, reshaped, or burned. Few people anywhere lived in societies where many materials were simply thrown away. The largest furniture store now operating in the United States was founded by two immigrants who began their careers as rag and bottle pickers during the early 1900s.

Every bottle or jar in early America was recycled, and pieces were used for purposes as varied as arrowheads and grit for chickens. Birds, lacking teeth, must collect small rocks, or grit, in order to grind their food in the craw. Old-time farmers sometimes ground glass when oyster shell or other sources of grit were unavailable. Ground glass was also mixed with glue to make abrasives. The vast numbers of buffalo killed by Native American or European hunters left huge quantities of bones on the prairie, but early scavengers collected them and shipped them to plants where they were ground for fertilizer. Early-day cloth was collected and treated to reclaim fiber, which could be woven into string or rope. Most cities contain parks, and below many of these parks are landfills dating back as far as the 1800s. A lack of landfill space, increasing transportation costs, and tougher government regulations now diminish the use of landfills, and many smaller communities sport signboards denouncing the importation of waste from other cities or states.

Recycling falls into two categories: direct and indirect. Direct recycling is the reuse of components of manufactured materials before sale, often in the case of damaged or unsold products. Indirect recycling is the practice of recycling products or materials that consumers have used and discarded.

Shortages during World War I and World War II prompted scrap iron, fiber, and rubber drives, reclaiming many essential materials. The first items to be recycled through organized programs other than in wartime were milk and other beverage bottles. In days when milkmen placed bottles on doorsteps, the heavy bottles were returned, washed, and refilled dozens of times. During the 1940s and 1950s, families scavenged for soda and beer bottles and cans along highways, and many children supplemented or earned allowances by collecting bottles for the two-cent deposit. Plastic bottles and aluminum cans have largely replaced the reusable bottles of the twentieth century. Many states now mandate five- to ten-cent deposits on the plastic replacements. The scrap material drives of the World Wars brought the public's attention to the fact that many more fabrics, metals, and rubber items could be recycled.

Water

The most commonly recycled material is water. Seldom destroyed in use, water serves as a medium for chemical reactions and as a heat transfer mechanism in steam or hot water systems, car engines, and various industrial processes. Moderately dirty water may be dumped directly into streams, injected into wells, or, in the case of cooling water from power plants, allowed to pass through wetlands to cool.

Water containing sewage is given primary treatment consisting of settling and filtration and secondary aeration treatment to allow oxidative bacteria to reduce the bacterial oxidative demand (BOD). Tertiary treatment with chlorine, chloramines, or ozone is used if the water is needed for consumption. In rural areas, sewage may pass through a cesspool for sedimentation and anaerobic bacterial action, and the effluent may be distributed through a series of pipes into a disposal field. Water that has low BOD is usually purified by bacterial action in soil so that after passing some distance through the ground, biodegradable substances are removed. It is particularly important that detergents be biodegradable and contain minimal amounts of phosphates and nitrates, as these substances, along with high BOD water, contribute to eutrophication, a rapid growth of bacteria. Eutrophication may consume so much available oxygen that fish and other organisms die.

Farms, ranches, and feedlots provide food but often are major sources of pollution. Modern feedlots store sewage in lagoons where solids can be collected. Effluent water from lagoons often contains microorganisms that serve as food in fish farms, and solids from the lagoons can be processed into fertilizer. The effectiveness of these operations is often determined by the size of the operation and the need for cleanup. Larger operations can afford more complex remediation equipment and tend to be more cost-effective than small ones. Most large feedlots are located away from population centers whose residents often complain of the odors.

heavy metal: by convention, a metal with a density greater than 5 g/cm^3; 70 elements are thus classified as heavy metals

synthesis: combination of starting materials to form a desired product

Federal, state, and municipal laws mandate that industries reclaim most pollutants, such as **heavy metals** or organic chemicals, from wastewater. Prior to this legislation, toxic chemicals often made their way into the water table. Reclaiming toxic substances protects the environment and, in many cases, provides a valuable source of materials needed for **synthesis**. In many cases, industries are located near other manufacturing plants that pass their waste to another plant, which uses it as a raw material.

Paper, Steel, and Aluminum

Paper, in the form of used newspapers, packing materials, and telephone books, may be burned for energy, but it still makes up 30 percent to 45 percent of the average landfill. Landfilled paper requires decades to decay and may release methane, a greenhouse gas that is twenty times as deleterious as carbon dioxide. Most paper could be reused or converted to materials used for blown insulation. Nearly 40 percent of office paper and newspapers is now recycled. Two problems occur in recycling paper. Each time paper is reprocessed, the fibers break and become shorter. Office copiers work best with long-fiber paper that has higher tensile strength and produces less dust. Fiber from used paper is often blended with new fibers to produce the desired qualities. A second problem in recycling office paper is the demand for white paper. Used paper pulp often contains ink or other colored materials that must be removed. Some inks and adhesives can be removed by flotation, and bleaching then whitens the pulp. Older methods of chlorine bleaching produced toxic dioxin. Oxygen and hydrogen peroxide are now used to whiten paper and are considered less damaging to the environment. Use of colored papers for printing and copying greatly decreases the need for bleaching.

Steel is widely recycled. Soon after steel was first produced, damaged steel items were recycled into new products. Today, 68 percent of used steel is recycled. The basic oxygen process of steel manufacture uses 25 percent scrap as starting material, and nearly 100 percent of the starting material for steel production by the electric arc process is scrap. Many states have "clunker" laws that require that the purchase of a new car be accompanied by turning in a junked car, and most municipalities have programs for collecting and recycling used auto parts and furniture.

Aluminum is one of the most commonly recycled metals. Although many aluminum products are still discarded, 65 percent of aluminum materials are recycled; 95 percent less energy is needed to produce aluminum from recycled cans than from aluminum ore.

Plastics and Oil

Plastics make up only about 8 percent of the volume in the average landfill but represent a huge investment of energy and raw materials. Most plastics produced from petroleum materials by polymerization of monomers such as ethylene or vinyl chloride are thermoplastic materials and can be cleaned, melted, and re-formed. Thermosetting plastics can also be cut into pieces that are mixed with other plastics or used as fillers. High-density polyethylene (HDPE) and polyethylene terephthalate (PETE) are the most widely reused plastic materials, but polyvinyl chloride (PVC), polypropylene, and polystyrene account for 5 percent of the recycled plastics. In 2001 80 million pounds (36 million kilograms) of plastics were recycled in the United States. Recycled plastic materials are used in the production of bottles, fabrics, flowerpots, furniture, plastic lumber, injection molded crates, and automobile parts.

According to the Environmental Protection Agency, Americans discard 120 million gallons (454 million liters) of oil each year as a result of automobile oil changes. Virtually all this oil can be recycled, and most states require recycling. Used motor oil contains particulate matter and some chemical substances that must be removed during re-refining. As much as 80 percent of used motor oil is used with little change as a fuel for ships or industrial heating equipment, but this practice probably poses a greater danger to the environment than burning refined oil.

Batteries, Rubber, and Paint

Used lead-acid automobile batteries represent a major hazard to the environment. Most landfills accept batteries but place them aside for recycling, which includes collecting and neutralizing the acid, removing the cases, and resmelting the lead plates. Fragments of cases can be recycled into new battery cases, and resmelted lead is used to cast new battery plates. In New Zealand alone, 500,000 lead-acid storage batteries are recycled each year.

Rechargeable batteries from power tools, telephones, and most other devices can be recycled. Nonrecyclable batteries often contain mercury or other toxic metals that are harmful to the environment, but in the early twenty-first century, most were still discarded in landfills.

Rubber products pose a special problem in the environment, and their dumping in landfills usually requires a special fee. Discarded in piles or buried, they occasionally catch fire and produce noxious gases. In developing countries, many used or damaged automobile tires are repaired or disassembled to make other products. Granulated rubber produced from

Freon is being removed from a refrigerator. The Sacramento Municipal Utility District sells the freon to DuPont, drains the oil from the refrigerators, and sells the scrap metal.

discarded tires can be used to make floor mats and rubber wheels, and it can be used as a component of asphalt-paving materials. Used rubber can be heated to reclaim petroleum products, treated chemically to obtain components used as filler in manufacturing rubber products, or incinerated as a source of energy.

Many recyclable materials consist of mixed materials that pose special problems. Discarded automobile oil filters contain steel, fiber, and contaminated petroleum. Oil filters are crushed and heated to remove oil, and the metal reclaimed. Discarded household appliances contain large amounts of steel but must often be dismantled, with other materials removed. A special fee is charged at recycling centers to discard most appliances. Fluorescent lamps contain small amounts of mercury that can be reclaimed. Used computers and television sets contain usable materials and, often, some toxic materials that can be collected for safe disposal.

The small amounts of paint generated by the average household cannot be recycled economically, but most municipalities sponsor paint exchange programs and collect oil-based paints. Spent fuel rods from nuclear power plants can be recycled to reclaim unused uranium, and some spent uranium is used to produce armor-piercing bullets. Yard waste from households is often recycled and made into mulch for farming and gardening. Discarded Christmas trees are used to form mulch or are immersed in lakes as a habitat for fish. SEE ALSO Environmental Pollution; Water; Water Pollution; Water Quality.

Dan M. Sullivan

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Remsen, Ira

AMERICAN CHEMIST AND EDUCATOR
1846–1927

Most great chemists are remembered for their research. Ira Remsen, although he contributed significantly to the research of his time, is one of the few chemists remembered mainly for his teaching and mentorship. It was under his leadership that American chemical research came of age in the late nineteenth and early twentieth centuries.

Remsen was born in New York City on February 10, 1846, into a family that traced its lineage back to seventeenth-century Dutch colonial settlers. In his early schooling, he excelled in the classics and had almost no exposure to science. He attended the New York Free Academy (later the City College of New York), but in accordance with his father's wishes, he left before graduation to become an apprentice to a homeopathic physician.

He received an M.D. in 1867 from the Columbia College of Physicians and Surgeons. His prize-winning thesis, "The Fatty Degeneration of the Liver," was written on the basis of information Remsen gleaned from books without ever seeing a liver. His interest in chemistry had been awakened during medical school, and Remsen resolved upon graduation to further pursue his studies in that field of science.

At that time, there were no American schools that engaged in serious chemical research; the epicenter of the chemical world was Germany, and Remsen embarked for Munich to study under Justus Liebig, the most renowned scholar of the time. Unfortunately, Remsen learned upon his arrival in Munich that Liebig had stopped supervising students. There was, however, no shortage of excellent teachers there. Remsen remained in the German university system for five years, studying under Jacob Volhard, Friedrich Wöhler, and Rudolph Fittig. He received his Ph.D. from Göttingen in 1870 in the newly organized field of organic chemistry.

Upon returning to the United States, Remsen accepted an appointment as a professor of chemistry and physics at Williams College in Massachusetts. There, despite a lack of facilities or administrative encouragement, he managed to continue the research that he had started in Germany. Recognizing the lack of chemistry textbooks in English, he translated Wöhler's *Outlines of Organic Chemistry* and wrote the first of his eight textbooks, *Principles of Theoretical Chemistry.* The excellent quality of these books led to Remsen's appointment to the newly founded Johns Hopkins University in Baltimore, Maryland, the first institution in the United States devoted primarily to research. Remsen remained there for thirty-six years, first as professor of chemistry and later as its president (1901–1912). During his tenure, he established the distinctly German tradition of chemistry research that he had learned in his studies in that country.

The research carried out in Remsen's laboratories, although of less lasting import than his teaching, was significant in its time. These studies derived mostly from his earlier work and centered on the reactions of derivatives of substituted benzenes. The artificial sweetener saccharin was discovered, partially by accident, by one of his students. He was also noted for his clear and straightforward teaching style and for his devotion to his students. Under his tutelage, the first great generation of American academic chemists was established across the country.

In 1879 Remsen founded the *American Chemical Journal* in order both to promote the research being done at Johns Hopkins and elsewhere in the United States and to make this work widely available to American readers. It was the first American journal devoted to chemistry and quickly became recognized for its excellence both at home and abroad. It later merged with the *Journal of the American Chemical Society*.

Remsen retired in 1912 but remained active as a consultant to the chemical industry. He died on March 4, 1927, in Carmel, California. The next year his ashes were returned to Johns Hopkins and interred behind a bronze memorial tablet in the newly renamed Remsen Hall. SEE ALSO LIEBIG, JUSTUS VON; WOHLER, FRIEDRICH.

Bartow Culp

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Residue

A residue is a single molecular unit within a polymer. *Residue* is thus another term for monomer. Although the term *residue* is most often used to refer to a specific amino acid within a **polypeptide**, it is also used to refer to sugars within a carbohydrate molecule and nucleotides within deoxyribonucleic acid (**DNA**) or ribonucleic acid (RNA).

polypeptide: compound containing two or more amide units—C(O)NH—produced by the condensation of two or more amino acids

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

A protein or a polypeptide is composed of amino acids linked together by peptide bonds, with amino acids as the monomeric units of the polypeptide. The order of amino acids in a protein is known as the primary structure of that protein. The specific sequence of amino acids in the protein determines its three-dimensional structure and ultimately its function. The amino acids are numbered sequentially, beginning at the amino terminus of the polypeptide. For example, the 45th amino acid in the sequence would be identified as residue 45. Most often, scientists refer to an individual residue using both the name of the amino acid and its position. Therefore, if residue 45 in a particular polypeptide sequence is serine, that residue would be referred to as serine-45. SEE ALSO PEPTIDE BOND; PRIMARY STRUCTURE; PROTEINS.

Robert Noiva

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Restriction Enzymes

Restriction enzymes (also known as restriction endonucleases) are enzymes that cut double-stranded DNA at very specific recognition sites. They were originally discovered in bacteria that use them to restrict the growth of viruses but are now among the workhorse enzymes of biotechnology and recombinant DNA research.

It has long been known that bacteria are susceptible to attack by viruses known as *bacteriophages* ("eaters of bacteria"). The presence of restriction enzymes in bacteria is part of the defense system against bacteriophages that has evolved in these bacteria. These highly specific enzymes will scan DNA until a certain sequence of nucleotide bases is identified. The specificity is such that the sequence is apt to occur at only one or two sites in the viral DNA, with no such occurrence in the host bacterial DNA. Restriction enzymes recognize a sequence such as:

5′ G A A T T C 3′
3′ C T T A A G 5′

Interestingly, the enzyme can recognize the paired sequences from either strand because they are a palindrome (reading the same in either direction). The restriction enzyme can cut this palindromic sequence in one of two manners: across both strands at the same spot, or in a staggered manner that yields free single-stranded ends called "sticky ends." These sticky ends have proved most useful in recombinant DNA work.

The names of restriction enzymes are derived from their bacterial sources. One of the enzymes most widely used in recombinant DNA work is *Eco*R1, which is isolated from *Escherichia coli* RY13. Other examples include HindII (isolated from *Haemophilus influenza* Rd), and Xba I (isolated from *Xanthomonas badrii*). The specificity of each enzyme allows researchers to cut DNA in a predictable and reproducible manner. Using *Eco*R1 on the above sequence, one would always obtain the ends:

--------- 5′ G   A A T T C 3′ ---------
--------- 3′ C T T A A   G 5′ ---------

A small circular piece of DNA (such as a bacterial plasmid) with one *Eco*R1 site would yield a linear piece of DNA with the CTTAA sticky ends. Now suppose one could obtain the DNA (the gene) coding for a foreign protein such as human insulin. At each end of the insulin gene, one could attach complementary single-stranded sticky ends that would exactly "match" the ends of the cut plasmid. As if made of Velcro, the complementary ends would stick together, and if one were to use an enzyme called DNA ligase to form a stronger covalent bond between parts joined together, one would have incorporated a human (or other species) gene into bacterial DNA. This technique is known as recombinant DNA. The bacteria can now be grown in large batches and made to synthesize the foreign protein (insulin). SEE ALSO Deoxyribonucleic Acid; Enzyme; Recombinant DNA.

C. Larry Bering

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Retinoic Acid ***See Retinol.***

Retinol

vitamins: organic molecules needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

Retinol, or **vitamin** A, is a necessary nutrient in all higher animals. It plays an important role in vision, in the maintenance of epithelial cell layers, in spermatogenesis, and in fetal development. Retinol must be obtained from

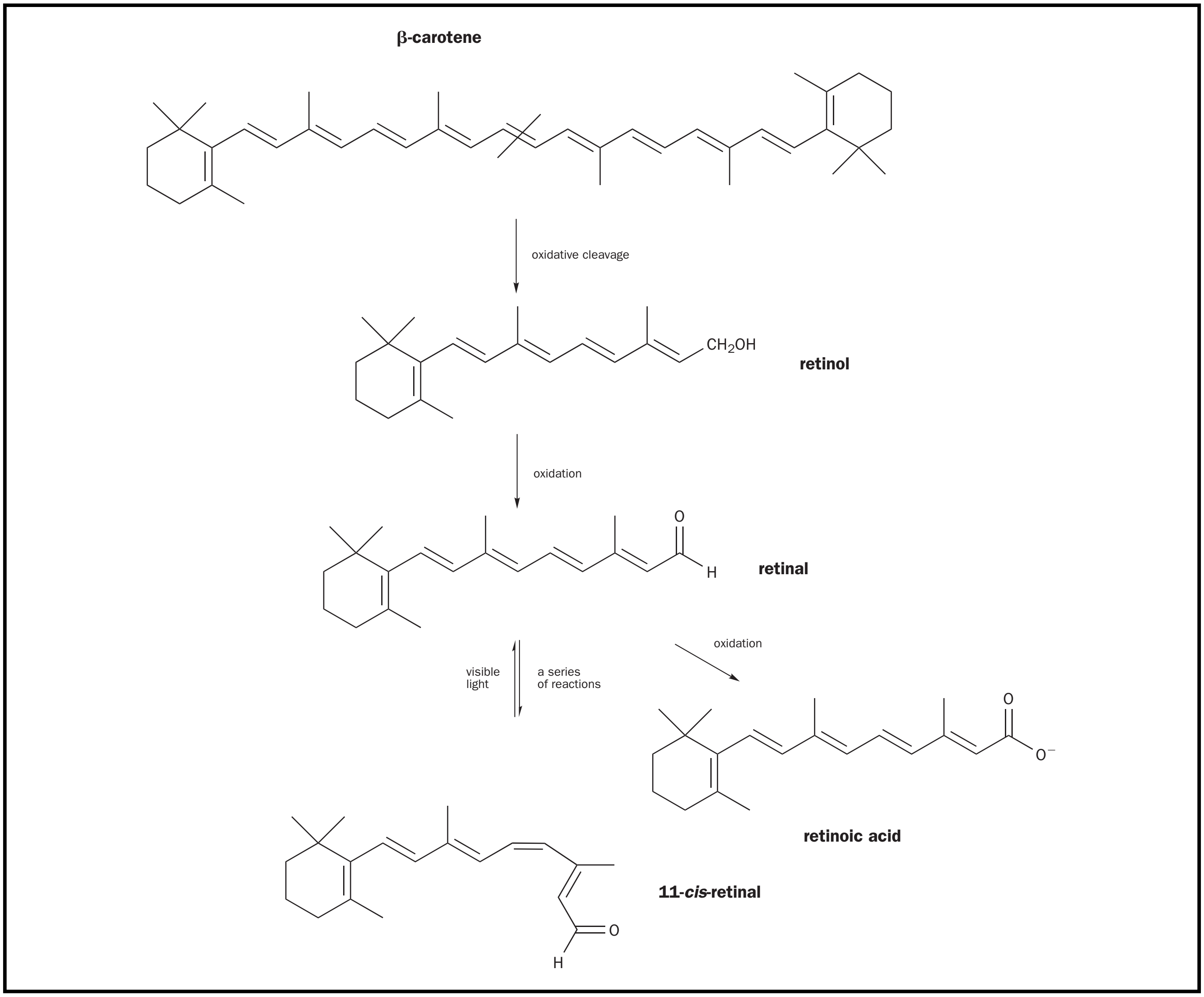

Figure 1. Vitamin A (retinol) and its derivatives.

the diet, either from organic compounds that are in animal products, such as retinyl **esters**, or from compounds in plants, most notably β-carotene (see Figure 1). Retinol and its derivatives are collectively called retinoids.

Chemically, retinol is an isoprenoid; isoprenoids are a group of compounds that includes vitamins E and K and cholesterol, which are synthesized from **isoprene** units. As shown in Figure 1, retinol is a hydrocarbon molecule with a single hydroxyl group at one end. This hydroxyl group can be oxidized to form an **aldehyde** group (yielding retinal), or to a **carboxylic acid** group (yielding retinoic acid). Retinal and retinoic acid are the biologically active forms of retinol. In addition to these different **oxidation** states, retinol occurs as a number of different **isomers**. The retinol structure shown in Figure 1 is all-*trans*-retinol, as all of the double bonds are in the *trans* configuration. Many *cis* isomers also occur. Two important examples are 11-*cis*-retinal, which is required for vision (see Figure 1), and 13-*cis*-retinoic acid (or isotretinoin), which is used as an anti-acne drug.

ester: organic species containing a carbon atom attached to three moieties: an O via a double bond, an O attached to another carbon atom or chain, and an H atom or C chain; the R(C=O)OR functional group

isoprene: common name for 2-methyl-1,3butadiene, the monomer of the natural rubber polymer

aldehyde: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the RC(O)H functional group

carboxylic acid: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the $-CO_2H$ functional group

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

isomer: molecules with identical compositions but different structural formulas

One of the symptoms of vitamin A deficiency is night blindness. If the deficiency persists over time, the eyes will eventually deteriorate, and permanent blindness will result. In specialized cells of the eye, 11-*cis*-retinal is linked covalently to the enzyme opsin. Opsin is also a membrane protein; it comprises approximately 95 percent of the membrane protein of disks in the outer segments of the eye's rod cells. The disks in a rod cell are circular layers of membrane stacked on top of each other. Each cell contains hundreds to thousands of these disks. This greatly increases the membrane surface area, and thus the amount of opsin, in these light-detecting cells. The combination of 11-*cis*-retinal and opsin is called rhodopsin. Visible light is absorbed by the 11-*cis*-retinal, causing it to isomerize to all-*trans*-retinal (see Figure 1). The resulting shape change in the rhodopsin initiates a series of reactions that ultimately sends signals to the brain.

nuclear: having to do with the nucleus of a cell

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

transcription: enzyme-catalyzed assembly of an RNA molecule complementary to a strand of DNA

The other active form of vitamin A is retinoic acid. Retinoic acid exerts its physiological functions via its interactions with a family of **nuclear receptors** called the retinoic acid receptors (RARs). RARs are members of a superfamily of nuclear receptors that include steroid hormone and thyroid hormone receptors. RARs are involved in regulating the **transcription** of many genes, including genes involved in the cell growth and cell differentiation of developing organisms. Because of this link between retinoic acid and development, female patients taking isotretinoin (13-*cis*-retinoic acid) must not become pregnant due to the considerable risk to offspring of severe birth defects. SEE ALSO Acne Medication.

Stephanie E. Dew

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75
Re
RHENIUM
186.207

Rhenium

MELTING POINT: 3,180°C
BOILING POINT: 5,627°C
DENSITY: 21.02 g/cm^3
MOST COMMON IONS: $[ReO_4]^-$, $[Re(Cl)_6]^{2-}$

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

catalyst: substance that aids in a reaction while retaining its own chemical identity

Rhenium was discovered in a sample of gadolinite in 1925 by Walter Noddack, Ida Tacke, and Otto Berg, and was named after the Rhine River. The concentration of rhenium in Earth's crust is on the order of 7×10^{-8} percent. Rhenium crystallizes in the hexagonal close-packed arrangement and resembles platinum in appearance. It is usually obtained as a gray powder. It has the second highest melting point (3,180°C, or 5,756°F) of any **metal**. Rhenium is used in conjunction with platinum in thermocouples (thermoelectric thermometers) and as a Pt/Re reforming **catalyst** in the petroleum industry. It is used as filaments in mass spectrometry and as furnace heater windings.

IDA TACKE (1896–1979)

Working with her husband and using x rays, Ida Tacke discovered element number 75, rhenium. Her birthplace, next to the Rhine River, inspired its name. Tacke is also known for predicting nuclear fission prior to its realization, although she principally studied the chemistry of light in the human eye.

—Valerie Borek

Rhenium can be prepared by the thermal decomposition of NH_4ReO_4 or $(NH_4)_2ReCl_6$ in the presence of H_2, and by electrodeposition of $HReO_4$ from H_2SO_4 solutions. The metal is soluble in H_2O_2, concentrated HNO_3, hot H_2SO_4, and warm Br_2 water, but is not soluble in concentrated HF and

Heating elements in electric ovens are made from rhenium alloys.

HCl. It reacts in air above 400°C (752°F) to give Re_2O_7. It has the widest range of valences of any element. Dissolution of Re_2O_7 in H_2O yields Re_2O_3, ReO_2, Re_2O_5, ReO_3, and the strong acid $HReO_4$. With sulfur it forms Re_2S_7, which decomposes into ReS_2 and pure sulfur upon heating. It forms halides of stoichiometry ReX_n, where $n = 2$ to 7 for F, 3 to 6 for Cl, 3 to 5 for Br, and 2 to 4 for I. Rhenium forms coordination compounds with alkyl, aryl, carbonyl, dinitrogen, hydrido, isocyanide, nitrido, and nitrosyl **ligands**, and with other ligands containing nitrogen, phosphorus, oxygen, and sulfur donors. **Octahedral** complexes with mixed ligands are numerous; for example, $[Re(bpy)(CO)_3(py)]^{=}$, where bpy is 2,2′-bipyridine and py is pyridine.

ligand: molecule or ion capable of donating one or more electron pairs to a Lewis acid

octahedral: relating to a geometric arrangement of six ligands equally distributed around a Lewis acid; literally, eight faces

D. Paul Rillema

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Rhodium

45
Rh
RHODIUM
102.9

MELTING POINT: 1,960°C
BOILING POINT: 3,700°C
DENSITY: 12.41 g/cm³
MOST COMMON IONS: +, +2, +3

Rhodium was discovered in 1804 by the English chemist William Wollaston. Its name derives from the Greek word *rhodos*, meaning rose—the color of solutions containing rhodium salts. The abundance of rhodium in Earth's crust is approximately 0.0004 ppm. Its purification requires its separation from other platinum **metals**. Treatment of a crude platinum with metal concentrate with aqua regia leaves an insoluble portion that is then fused with bisulfate; this dissolves only the rhodium component, which is eventually converted to a solution of chloro complexes, whose treatment with H_2 precipitates the metal.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

The extremely unreactive, silvery-white element is used in jewelry plating and is part of anodic and thermocouple materials. However, compounds containing Rh in **oxidation** states from (VI) to (−I) can be produced, the most common being those of Rh(III). Developments in Rh chemistry since the late 1960s have focused on various **catalytic** processes that use Rh(I) complexes, particularly those containing phosphines such as PR_3 (R is an aryl or alkyl group) and/or CO, because such **ligands** stabilize this oxidation state.

The catalytic processes, which operate via mechanisms that cycle between Rh(I) and Rh(III) **intermediates**, include: (1) hydrogenation (the activation of H_2 for the reduction of unsaturated organic compounds), (2) hydroformylation (the activation of H_2 and CO for their addition to olefins to generate aldehydes or alcohols); and (3) carbonylation (the activation of CO for its addition to organics). Some of the processes have been developed commercially.

1. An Rh(I) complex containing a chiral (**optically active**) phosphine ligand (i.e., one with three different substituents on the **pyramidal**

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

catalysis: the action or effect of a substance in increasing the rate of a reaction without itself being converted

ligand: molecule or ion capable of donating one or more electron pairs to a Lewis acid

intermediate: molecule, often short-lived, that occurs while a chemical reaction progresses but is not present when the reaction is complete

optically active: capable of rotating the plane of plane-polarized light

pyramidal: relating to a geometric arrangement of four electron-donating groups at the four vertices of a pyramid

P-atom) can catalyze a reaction such as R(R′)C=CHR′ + H_2 → R(R′)C*HCH_2R′ (where *R*, *R*′, and *R*′ are different substituents); the C* atom of the product has four different substituents and is therefore chiral, and thus the use of a small amount of a chiral Rh **catalyst** generates large amounts of chiral product. Such a catalytic asymmetric hydrogenation has been used for the production of L-dopa, a drug used to treat Parkinson's disease.

catalyst: substance that aids in a reaction while retaining its own chemical identity

2. An Rh(I) complex containing CO and P*R*$_3$ ligands can catalyze the formation of butan-1-al from propene (CH_2=$CHCH_3$ + H_2 + CO → $CH_3CH_2CH_2CHO$), a commercially operated process.
3. An Rh(I) complex containing CO is used industrially to synthesize acetic acid from methanol (CH_3OH + CO → CH_3COOH). SEE ALSO PLATINUM.

Brian R. James

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Riboflavin

Riboflavin, also known as **vitamin** B_2, gets its name from its sugar alcohol (ribitol), and from its yellow color and its fluorescence under UV light (*flavin* comes from the Latin word for yellow). Its systematic names are 7,8-dimethyl-10-(D-ribo-2,3,4,5-tetrahydroxypentyl)isoalloxazine and 7,8-dimethyl-10-ribitylisoalloxazine; its formula is $C_{17}H_{20}N_4O_6$. Riboflavin has a molar mass of 376.37 grams (13.3 ounces). It is heat-stabile but easily degraded by light. Riboflavin was referred to as vitamin G in the early part of the twentieth century because it was recognized as a dietary factor needed for growth. Riboflavin was first isolated in 1879, and its chemical structure was determined in 1933.

vitamins: organic molecule needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

excrete: to eliminate or discharge from a living entity

As determined by the National Research Council of the National Academy of Sciences, the recommended daily allowance (RDA) of riboflavin for adults is about 1.5 milligrams (5.3×10^{-5} ounces). The amount required by an individual varies with factors such as age, gender, and amount of physical activity. Riboflavin is found in many foods, such as eggs, nuts, grains, dairy products, organ meats, and dark green vegetables. Overall, riboflavin content in the body can be estimated by measuring the activity of glutathione reductase (a riboflavin-containing enzyme) in red blood cells. No one has been known to ever die of riboflavin deficiency, but it can occur as a consequence of malnourishment, intake of certain medication, chronic diarrhea, or alcoholism. The first symptoms of riboflavin deficiency are often light sensitivity, blurred vision, and bloodshot eyes. Other symptoms are skin and mucous membranes lesions. Because riboflavin is water-soluble and easily **excreted**, toxicity resulting from excess intake is not considered a health problem.

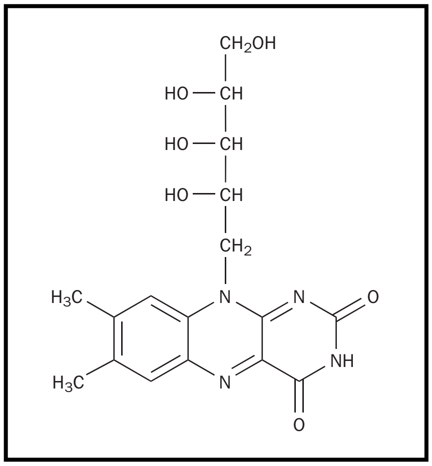

Figure 1.

Riboflavin is important biochemically because it is vital for proper utilization of carbohydrates, fats, and proteins as energy sources. It is a component

adenine: one of the purine bases found in nucleic acids, $C_5H_5N_5$

polypeptide: compound containing two or more amide units—C(O)NH—produced by the condensation of two or more amino acids

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

of two coenzymes, flavin **adenine** dinucleotide (FAD) and flavin mononucleotide (FMN). (Coenzymes are molecules that must be added to certain **polypeptides** to make them functional enzymes.) In general, FAD and FMN, when tightly bound to specific enzymes, easily lose or gain one or two electrons, or hydrogen atoms, and so drive **oxidation**/reduction reactions. In the 1930s, Warburg and Christian studied "the old yellow enzyme," a riboflavin-requiring enzyme, and laid the groundwork for our current understanding of cyclic oxidation-reduction reactions in electron transport systems vital to cell respiration. In addition to their role in electron transport chains, FAD- and FMN-requiring enzymes catalyze reactions that are part of a wide array of metabolic pathways. SEE ALSO COENZYME.

Sharron W. Smith

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Ribonucleic Acid

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

guanine: heterocyclic, purine, amine base found in DNA

cytosine: heterocyclic, pyrimidine, amine base found in DNA

uracil: heterocyclic, pyrimidine, amine base found in RNA

adenine: one of the purine bases found in nucleic acids, $C_5H_5N_5$

thymine: one of the four bases that make up a DNA molecule

Ribonucleic acid (RNA) is a nucleic acid, like **DNA**, and is also made up of sugars, phosphates, and nitrogenous bases (or just a base). It contains a ribose sugar, whereas DNA contains a deoxyribose sugar. The four main bases found in RNA are **guanine** (G), **cytosine** (C), **uracil** (U), and **adenine** (A). DNA contains **thymine** (T) instead of uracil.

The ribose sugar of RNA gives it very different structural properties from those of DNA. RNA forms complex structures by folding a single strand upon itself. Ribose sugar makes RNA less stable than DNA, and it has to be produced often in a cell.

In most organisms RNA is made from their DNA. Some viruses, called retroviruses, contain RNA as their primary genetic material, for example, the AIDS virus and poliovirus.

ribosome: large complex of proteins used to convert amino acids into proteins

There are many different kinds of RNA manufactured in a cell. Messenger RNA (mRNA) is produced to take the information contained in a specific segment of DNA and then use it to make proteins. Ribosomal RNA (rRNA) is part of a large RNA protein complex called the **ribosome** that binds mRNA and joins amino acids to make a protein. Transfer RNA (tRNA) brings amino acids to the ribosome and ensures that the amino acid used is in the order specified by mRNA. Many other kinds of RNA are also present in a cell. RNA plays an important role in the proper functioning of a cell. SEE ALSO DNA REPLICATION; NUCLEIC ACIDS; PROTEINS.

Neena Grover

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Ritalin *See Methylphenidate.*

RNA *See Ribonucleic Acid.*

RNA Synthesis

Biochemists refer to RNA synthesis as **transcription**. Transcription is the process of synthesizing ribonucleic acid (RNA). Synthesis takes place within the nucleus of **eukaryotic cells** or in the cytoplasm of prokaryotes and converts the genetic **code** from a gene in deoxyribonucleic acid (**DNA**) to a strand of RNA that then directs protein synthesis.

Three types of RNA are found in cells. Transfer RNA (tRNA) carries amino acids to the site of protein synthesis. Ribosomal RNA (rRNA) along with protein makes up **ribosomes** (the mechanism that synthesizes protein). Messenger RNA (mRNA) is the code or template for protein synthesis. Special enzymes synthesize the different forms of RNA.

DNA consists of a series of regions called operons, each containing one or more genes capable of coding for an mRNA strand. An operon consists of a number of segments, principal among which are a promoter region to which **RNA polymerase**, the enzyme that synthesizes RNA, readily attaches, an operator region that acts as an on/off switch for the operon, and one or more genes that code for mRNA production. For convenience, biochemists describe locations on chains of nucleotides by speaking of the ends of the sugar-phosphate chains as having 3′ (three-prime) and 5′ ends. Both DNA and RNA are synthesized by enzymes that start at the **5′ end** of the strand being synthesized.

Transcription begins when RNA polymerase approaches the promoter gene, which often contains extended nucleotide sequences that help to match and bind the polymerase. After the polymerase binds, it is thought to move along the strand of DNA to the operator region. Protein repressor molecules that block transcription bind to operators; inducing agents may attach to the repressor molecules and pull them away from the operator, allowing the synthesis of mRNA. An example of this is the induction or turning on of the lac operon in *Escherichia coli* by the presence of lactose, producing mRNA that codes for enzymes that **metabolize** lactose.

RNA polymerase moves along the DNA molecule from the **3′ end** of the operon to the 5′ end, copying only one strand. (Copying the complementary strand would result in useless or harmful nonsense mRNA.) DNA and RNA are similar in composition, but DNA contains deoxyribose instead of ribose and the **pyrimidine base thymine** instead of **uracil**. The newly formed RNA is complementary to the DNA code; **adenine** bases on one strand pair with thymine or uracil on the other strand, and **guanine** bases

transcription: enzyme-catalyzed assembly of an RNA molecule complementary to a strand of DNA

eukaryotic cell: cell characterized by membrane-bound organelles, most notably the nucleus, and that possesses chromosomes whose DNA is associated with proteins

code: mechanism to convey information on genes and genetic sequence

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

ribosome: large complex of proteins used to convert amino acids into proteins

RNA polymerase: enzyme used to make RNA using DNA as a template

5′ end: situation in nucleic acids in which the phosphate group is attached at the fifth carbon atom from where the base is attached

metabolize: performing metabolism—the processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those that break down complex food molecules, thus liberating energy (catabolism)

3′ end: situation in nucleic acids in which the phosphate group is attached at the third carbon atom from where the base is attached

pyrimidine base: one of two types of nitrogen bases found in nucleic acids

thymine: one of the four bases that make up a DNA molecule

uracil: heterocyclic, pyrimidine, amine base found in RNA

adenine: one of the purine bases found in nucleic acids, $C_5H_5N_5$

guanine: heterocyclic, purine, amine base found in DNA on one strand pair with **cytosine** on the complementary strand. The strands are said to be antiparallel; that is, the 3′ end of the DNA strand matches the 5′ end of the new mRNA strand. Since protein synthesis (translation) begins at the 5′ end of mRNA, protein synthesis in **prokaryotic** cells can begin while transcription is still under way, increasing the speed with which the organism responds to changes in its environment. SEE ALSO DEOXYRIBONUCLEIC ACID; PROTEIN SYNTHESIS; RIBONUCLEIC ACID.

cytosine: heterocyclic, pyrimidine, amine base found in DNA

prokaryotic: relating to very simple cells of the type found in bacteria

Dan M. Sullivan

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Robinson, Robert

ENGLISH ORGANIC CHEMIST
1886–1975

English chemist Sir Robert Robinson, recipient of the 1947 Nobel Prize in chemistry, "for his investigations on plant products of biological importance, especially the alkaloids."

An acknowledged giant of twentieth-century organic chemistry, Robert Robinson authored 700 research papers that continue to influence the way organic chemists think about **synthesis**, natural products, and reaction mechanisms. He received many awards during his sixty-year career, including the 1947 Nobel Prize in chemistry "for his investigations on plant products of biological importance, especially the alkaloids."

synthesis: combination of starting materials to form a desired product

Robinson was born on September 13, 1886, near Chesterfield, England. His father owned a surgical dressing factory and invented many of the machines used to produce and package such dressings. In high school Robinson excelled in mathematics and physics and hoped to become a mathematician. However, his father encouraged him to study chemistry instead, so Robinson accepted the inevitable and entered the chemistry program at the University of Manchester.

Robinson received his D.Sc. from Manchester in 1910 and lectured there for two additional years. He then accepted successive academic appointments at Sydney, Liverpool, Manchester, London, and finally Oxford University.

Today chemists use computer-driven instruments to determine the structures of unknown organic compounds. In Robinson's era, however, chemists relied less on instruments and more on degrading the compound into smaller, less complex fragments and then piecing them back together again. Using these techniques, Robinson determined the structures of complex alkaloids and worked on the antibiotic penicillin during World War II. His work on the structure of strychnine (see Figure 1) is still regarded as an outstanding example of molecular puzzle solving.

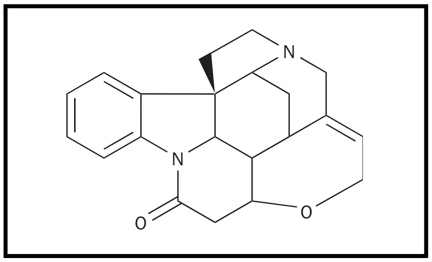

Figure 1. Strychnine.

After structure comes synthesis, and modern chemists synthesize complex medicines and other important compounds using ideas originated by Robinson. But organic synthesis was in its infancy when Robinson started out, and in his stunning synthesis of tropinone (a compound related to cocaine) in 1917, he introduced a novel strategy for preparing complex organic compounds. On paper, Robinson disconnected, or broke, certain bonds in tropinone and arrived at three simpler building blocks. He then went to the laboratory, where he combined the three building blocks using

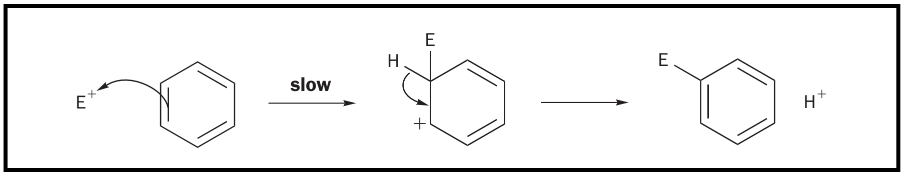

Figure 2. Curly arrows. E+ = an electrophile (a chemical compound or group that is attracted to electrons and tends to accept them).

standard procedures and produced tropinone. This process is now called retrograde synthesis.

Because Robinson wanted to take a systematic approach to organic synthesis, he developed a set of theoretical tools to predict the outcomes of organic reactions. Many important drugs and natural products contain substituted benzene rings, so Robinson began his research by trying to predict the outcomes of substitution reactions in benzene derivatives. He and his wife, Gertrude, successfully explained one class of substitution reactions in a 1917 paper but were unable to provide a general theory.

Using ideas developed in Arthur Lapworth's 1922 paper, Robinson devised a new theory in 1924 that explained the chemistry of unsaturated systems such as benzene and 1,4-butadiene (a four-carbon chain with alternating double bonds). Using his new theory, Robinson successfully predicted the outcomes of chemical reactions in these unsaturated systems. And for the first time ever, he used curly arrows to show the distribution of electrons in conjugated systems and to predict substitution reactions in benzene analogs. Hardly a day goes by when a modern organic chemist does not use curly arrows to explain a reaction mechanism or to plan a synthetic route.

Although Robinson considered the curly arrow concept his most important contribution to knowledge, few chemists know he invented it. Most chemists attribute the discovery to Christopher Ingold. Ingold embraced Robinson's ideas and over time published so many of his own related papers that chemists tended to overlook Robinson's groundbreaking work. Robinson never forgave Ingold for taking credit for his ideas.

Robinson retired from Oxford in 1955 but remained active in the field of chemistry. In his younger days he climbed the Alps, Pyrenees, and major mountains in New Zealand and Norway. Chess was another of his passions: Robinson spent three years as president of the British Chess Federation. He died on February 8, 1975. SEE ALSO ORGANIC CHEMISTRY.

Thomas M. Zydowsky

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Rocketry

The Chinese, in the second century B.C.E., were the first to make simple rockets that used gunpowder for fuel. These simple rockets were fireworks that were used for religious ceremonies. The idea of fireworks soon took on a military usage. Rocket motors were attached to arrows, to greatly extend their range. The same principles that made the rocket arrows fly has allowed people to go to the moon, launch satellites, fly the space shuttle, and even launch rockets that have bowling balls as nose cones. Rocket launches can be seen at Tripoli Rocketry Association and National Association of Rocketry launches throughout the United States. One can see small rockets as well as rockets taller than 14 feet (4.3 meters) being launched.

Rockets fly because of Newton's Third Law of Motion: for every action there is an equal and opposite reaction. Hot gases are produced from the burning of fuel in the rocket motor. The gases push against the inside of the rocket motor as they expand. The hot gas is forced out of the rocket, creating an action force. This creates a reaction force that moves the rocket in the opposite direction. The same thing happens when the end of an inflated balloon is released: the gas escapes in one direction, and the balloon moves in the opposite one.

Until the twentieth century, rockets were small. They were used for firework displays, weapons, to send life lines to ships at sea, and to send signals. Scientists such as Robert Goddard, Konstantin Eduardovich Tsiolkovsky, Hermann Oberth, and Wernher von Braun developed the science and technology that allowed large rockets to fly. In doing so, they developed the science that allowed human space travel.

Goddard realized the potential of rockets and space flight. His analysis of liquid-fuel rocket motors and rocket motors with adjustable thrust, as well as his analysis that rockets could work in space, allowed for the development of today's large rockets. Goddard holds close to seventy patents in rocketry.

In 1903 Konstantin Eduardovich Tsiolkovsky proposed using liquid propellants in rockets, and in 1929 he proposed using multistage rockets as a means of space travel. Hermann Oberth showed that liquid fuels provide a better source of energy for space flight than solid fuels. He worked with young German engineer von Braun to test liquid-fuel motors. Motors were tested in the early 1930s by tossing lit gasoline-soaked rags under a rocket motor, running for cover, and then opening the valve.

Von Braun started to develop rockets for the German army in 1932. He worked in the secret rocket laboratory in Peenemünde, in northeast Germany. He developed the V2 rocket, which served as a guide to start the space programs in the United States and the Soviet Union. This rocket was about 46 feet (14 meters) long and could carry a 2,200-pound (998-kilogram) payload of explosives at speeds of up to 3,500 miles (5,633 kilometers) per hour. Germany first launched the V2 rocket as a weapon of war at Paris on September 6, 1944, and rocket attacks on Britain followed. At the war's end, in 1945, the United States shipped home 100 V2 rockets along with many of the best rocket scientists from Peenemünde. Most of these rockets were launched for scientific research in White Sands, New Mexico. Von Braun spent fifteen years developing missiles for the United States military. He was transferred to NASA in 1960 with a mandate to develop the Saturn rocket, the rocket that went to the moon with the *Apollo* program.

The world of rocketry changed dramatically on October 4, 1957. The Soviet Union launched *Sputnik* to an orbit 340 miles (547 kilometers) high.

A captured German V2 rocket, fired from the USS *Midway,* September 6, 1947. The V2 was used in the first military attacks on a city by a ballistic missile.

The satellite circled Earth, sending back a beeping sound that amazed the world. In 1958 the United States successfully launched the 31-pound (14-kilogram) *Explorer* satellite into space for the first time.

In 1961 humans first reached outer space, when Soviet cosmonaut Yury Gagarin flew for 60 minutes in *Vostok 1*. On May 5, 1961, Alan Shepard Jr. became the first U.S. astronaut to fly in space. Shepard's Project *Mercury* flight lasted 15 minutes. John Glenn became the first American astronaut to circle Earth, on February 20, 1962.

Project *Gemini* launched a capsule for two astronauts. *Gemini's* ten flights provided experiences with space walks, docking, weightless conditions, and spacecraft recovery that made the *Apollo* missions to the moon possible.

On July 20, 1969, Neil Armstrong and Buzz Aldrin landed on the moon, where they collected soil and rock samples, took pictures, and performed experiments.

In 1973 astronauts first spent long missions in space on *Skylab*. This space station enabled experimentation and long stays in space. In 1981 *Columbia*, the first reusable spacecraft, was launched.

Fuels used in the solid-fuel rockets are a mixture of aluminum **metal** and ammonium perchlorate. This fuel is used to power the space shuttle boosters. It also powers amateur rockets flown at Tripoli Rocketry Association and National Association of Rocketry launches.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Engines on the space shuttle also burn a mixture of hydrogen and oxygen. The hydrogen and oxygen are compressed and cooled to a liquid in the main fuel tank. When they burn to form water, the **combustion** is so complete that it often does not look like the motor is burning. Liquid-fuel motors may also burn combinations of kerosene and liquid oxygen. Hybrid motors, using a liquid and solid fuel, are used in amateur rocketry. The fuel

combustion: burning, the reaction with oxygen

A full-scale operational model of the Mars *Viking* Lander, with its mechanical soil-collecting arm extended.

is solid cellulose, and the liquid oxidizer is nitrous oxide (N_2O). The hybrid motors are advantageous, as they have a lower cost per flight than does a solid fuel motor.

voltage: potential difference expressed in volts

NASA's Lewis Research Center is applying new battery technology with space flights. Lithium-ion batteries are flat batteries that are connected in series to obtain the required **voltage**. They are more efficient and weigh much less than the rechargeable NiCd batteries. They do not use lithium metal and do not require liquid; instead, they use a solid polymer electrode. Even when subjected to high pressure or shorts, the batteries do not explode. Possible spin-off uses include powering cell phones, laptop computers, and electric vehicles. SEE ALSO New Battery Technology.

Bill Bertoldi

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Röntgen, Wilhelm

GERMAN PHYSICIST
1845–1923

In 1901 Wilhelm Conrad Röntgen (or Roentgen) was the recipient of the first Nobel Prize in physics, awarded to him "in recognition of the extraordinary services he has rendered by the discovery of the remarkable rays subsequently named after him." The "remarkable rays" Röntgen called x rays (for want of a better name), but in Germany they very quickly came to be called Röntgen rays. A very shy man, Röntgen declined to give the customary acceptance speech at the awards ceremony.

Röntgen's critical discovery was made in 1895 when he happened to observe that, as a cathode-ray tube was being operated in a darkened room, paper covered with barium platinocyanide lying some distance from the tube "lit up with brilliant fluorescence." The fluorescence of barium platinocyanide was used at that time to establish the presence of invisible rays of the solar spectrum (such as ultraviolet). However, on this occasion, the tube had been surrounded by a close-fitting shield of black cardboard, quite opaque to ultraviolet light or sunlight.

With further experimentation Röntgen learned that the fluorescent screen lit up when it was placed "behind a book of a thousand pages" or "behind two packs of cards." Similarly, tinfoil, blocks of wood, and glass (as long as it contained no lead) offered little resistance to the enigmatic radiation. Moreover, "if a hand be held before the fluorescent screen, the shadow shows the bones darkly, with only faint outlines of the surrounding tissues." Röntgen soon found that his x rays darkened a photographic plate. One of his first x-ray photographs revealed the bone structure of his wife's hand.

When Röntgen first published his results, the macabre revelation of living bone structures created a sensation, and within a month articles on the value of x rays within medicine appeared in major medical journals. x rays have been an invaluable tool in medicine, dentistry, and industry ever since. A roentgen, abbreviated as R, is the international unit of quantity or dose for both x rays and gamma rays. It is equal to the amount of x or gamma radiation that produces as a result of **ionization** one electrostatic unit of charge in one cubic centimeter (0.034 ounces) of dry air.

ionization: dissociation of a molecule into ions carrying + or − charges

Röntgen was born in Lennap, Germany, in 1845, but his family shortly thereafter moved to Holland. At age sixteen, he entered the Utrecht Technical School, where he remained for three years. He then moved to the Polytechnic Institute in Zurich, where he earned a diploma as a mechanical engineer in 1868 and a Ph.D. degree a year later. He became an assistant to the physicist August Kundt, whom he accompanied to the University of Würzburg in 1871, and then to the University of Strasbourg. The volume of his research output at this time resulted in his being offered the chair of physics at the University of Giessen in Hesse, where he resided from 1879 until 1888. In 1888 he returned to the University of Würzburg as professor of physics and director of its Physical Institute. It was here that he made his momentous discovery of x rays. In 1900 he moved to the University of Munich, from which he retired in 1920. He died in 1923, aged seventy-seven. SEE ALSO RADIATION.

Keith L. Manchester

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Rubber

Rubber is an elastomer—that is, a polymer that has the ability to regain its original shape after being deformed. Rubber is also tough and resistant to weathering and chemical attack. Elastomers can be naturally occurring polymers, such as natural rubber, or they can be synthetically produced substances, such as butyl rubber, Thiokol, or neoprene. For a substance to be a useful elastomer it must possess a high molecular weight and a flexible polymer chain.

Natural Rubber

Natural rubber is one of nature's unique materials. The Native Americans of tropical South America's Amazon basin knew of rubber and its uses long before Christopher Columbus's explorations brought it to the attention of Europeans. The Indians made balls of rubber by smoking the milky, white latex of trees of the genus *Hevea* that had been placed on a wooden paddle, to promote water evaporation and to cure the substance.

Spanish navigator and historian Gonzalo Fernández de Oviedo y Valdes (1478–1557) was the first European to describe these balls to a European audience. In 1615 a Spanish writer enumerated the practical uses of rubber. He reported that the Indians waterproofed their cloaks by brushing them with this latex and made waterproof shoes by coating earthen molds with it and allowing these coatings to dry.

In 1735 interest was revived in this unusual substance when French mathematical geographer and explorer Charles-Marie de La Condamine (1701–1774) sent several rolls of crude rubber to France with an accompanying description of products made from it by the South American natives. Although it met with some use in waterproofing boots, shoes, and garments, it largely remained a museum curiosity. Crude rubber possessed the valuable properties of elasticity, plasticity, strength, durability, electrical nonconductivity, and resistance to water; however, products made from it hardened in winter, softened and became sticky in summer, were attacked by solvents, and smelled bad.

Early Uses

Rubber, sometimes called "gum-elastic," was known to the Indians by the name of *caoutchouc* (from *caa*, "wood," and *o-chu*, "to flow or to weep"). In 1770 English chemist and Unitarian clergyman Joseph Priestley (1733–1804), the discoverer of oxygen, proposed the name "rubber" for the substance because it could be used to erase pencil marks by its rubbing on paper in lieu of previously used bread crumbs.

In 1791 rubber was first used commercially when English manufacturer Samuel Peal patented a method for waterproofing cloth by treating it with a solution of rubber in turpentine. In 1820 the modern rubber industry began when English coachmaker and inventor Thomas Hancock (1786–1865) established the first rubber factory. He was the first to compound rubber with other materials to be shaped into molds, a common modern industrial practice.

In 1823 Scottish chemist and inventor Charles Macintosh (1766–1843) began to manufacture double-textured rainproof garments known as "mackintoshes." He made these by introducing a coal tar naphtha solution of rubber between two pieces of fabric, thus circumventing the sticky (when warm) and brittle (when cold) surfaces associated with single-textured rubber-containing garments.

Composition and Structure

Crude rubber is primarily hydrocarbon in nature. In 1826 English chemist Michael Faraday (1791–1867) analyzed natural rubber and found it to have the empirical (simplest) formula C5H8, along with 2 to 4 percent protein and 1 to 4 percent acetone-soluble materials (resins, fatty acids, and sterols). In 1860 English chemist Charles Hanson Greville Williams (1829–1910) confirmed Faraday's analysis and in 1862 distilled natural rubber to obtain the pure monomer, which he named **isoprene**. He determined isoprene's vapor density and molecular formula, and he showed that it polymerizes to a rubbery product—an observation that led to the notion that rubber is a linear polymer of isoprene, proposed in 1910 by English chemist Samuel Shrowder Pickles (1878–1962).

isoprene: common name for 2-methyl-1,3butadiene, the monomer of the natural rubber polymer

The molecular weights of rubber molecules range from 50,000 to 3,000,000. Sixty percent of the molecules have molecular weights of greater than 1,300,000. The repeating unit in natural rubber has the *cis* configuration (with chain extensions on the same side of the ethylene double bond), which is essential for elasticity. If the configuration is *trans* (with chain extensions on opposite sides of the ethylene double bond), the polymer is either a hard plastic (naturally occurring gutta-percha, obtained from the leaves of *Palaquium*, a species of sapotaceous Malaysian and East Indies trees) that was used for wire and cable coating during the nineteenth century; or a substance like gutta-percha (balata, obtained from *Mimusops globosa*, trees native to Panama and South America), used for modern golf ball covers.

Vulcanization

Because there are few (if any) cross-links in the chains of rubber molecules, natural rubber is thermoplastic; that is, it becomes soft and sticky in summer and hard and brittle in winter. It is also malodorous and softened or dissolved by various solvents, as noted. These undesirable properties of natural rubber were not overcome until 1839, when American inventor Charles Goodyear (1800–1860), at the end of five years of constant experimentation, accidentally placed a sample of rubber mixed with sulfur and litharge (lead oxide, PbO) on a hot stove in Woburn, Massachusetts. The operation converted rubber into a heavily cross-linked, and therefore insoluble and infusible, thermosetting polymer or "thermoset." William Brockedon, a friend of Hancock's, named Goodyear's curing process "vulcanization" (after Vulcan, the ancient Roman god of fire and metalworking). Goodyear later used the term, but only reluctantly.

In practice, vulcanization was so simple that many persons used it without paying royalties, and Goodyear spent much of his time contesting approximately sixty infringements of his patent. He died a pauper and left behind debts estimated at between $200,000 and $600,000. His name lives on in Goodyear tires and Goodyear blimps.

Paradoxically, neither Goodyear nor any of his family members or descendents were involved with the Goodyear Tire and Rubber Company, whose founder, Frank A. Seiberling, named it to honor one of America's most famous inventors and the founder of an industry that is indispensable to modern life. In 1851 Goodyear's brother Nelson used sulfur to convert natural rubber into ebonite, the first thermosetting plastic.

The Modern Rubber Industry

Vulcanization marked the birth of the modern rubber industry, and although later discoveries have somewhat modified Goodyear's original procedure, today it remains essentially the same as his process of 1839. Vulcanization is still an imperfectly understood chemical reaction between rubber and sulfur. It results in cross-linking between linear chains of rubber molecules and prevents slippage of the chains as the material retains the desired elasticity.

covalent bond: bond formed between two atoms that mutually share a pair of electrons

Temperatures of 140–180°C (184–356°F) are used for modern vulcanization, and additives other than sulfur are often used. Accelerators permit the reaction to occur at lower temperatures and in less time, and antioxidants prolong the life of rubber products by reducing the deterioration that is caused by atmospheric oxygen (or ozone), which breaks **covalent bonds** and lowers the molecular weight. Reinforcing agents (e.g., carbon black) increase stiffness, tensile strength, and resistance to abrasion. Coloring agents and fillers are sometimes added.

The Search for Substitutes

The earliest synthetic polymers were synthetic rubbers. Before 1920 natural rubber was the only available elastomer, but constant attempts, with varying degrees of success, to develop commercial rubber substitutes had been made previously, especially by English and German chemists, who competed with each other in the search.

As mentioned, natural rubber is a polymer consisting of repeating units of isoprene, its "mother substance." Scientists at first sought an exact chemical equivalent. But they attained their first success in preparing a suitable substitute only when they abandoned their attempts to synthesize rubber from isoprene, butadiene, or other dienes (hydrocarbons with two double bonds) and tried to synthesize an original polymer that possessed the physical properties of natural rubber.

The development of a synthetic rubber was a slow process, because it was almost impossible for the early synthetic products to compete economically with cheap natural rubber and because they were not as good as natural rubber for most uses. The driving force in the search for synthetic rubber was the shortages created by wartime needs.

CARL "SPEED" MARVEL (1894–1988)

During World War II, the United States was almost entirely blockaded from its rubber suppliers. Carl Marvel became a part of the successful effort to meet the demand for synthetics. Along with others, he worked to increase the efficiency and production of existing rubber syntheses.

—Valerie Borek

During World War I German chemists, whose country was cut off from its sources of natural rubber by the British blockade, polymerized 3-methylisoprene (2,3-dimethyl-1,3-butadiene) units, ($CH_2=C(CH_3)C(CH_3)=CH_2$), obtained from acetone, to form an inferior substitute called methyl rubber. By the end of the war Germany was producing 15 tons (13.6 metric tons) of this rubber per month. The USSR (Union of Soviet Socialist Republics), which built a **pilot plant** at Leningrad (now St. Petersburg) in 1930 and three factories in 1932 and 1933, was the first country to institute a full-scale synthetic rubber industry.

pilot plant: intermediate stage of testing for chemical process, between bench-top and production scale

Two Serendipitous Discoveries

During World War II the United States, cut off from India, Ceylon (now Sri Lanka), Malaysia, and the Dutch East Indies (areas which, since the late nineteenth century, had replaced South America as the main suppliers of natural rubber), developed several superior synthetic rubbers. The U.S. synthetic rubber industry originated from two discoveries that were serendipitous; that is, they occurred while the researchers were searching for something else.

In 1922 independent inventor and physician Joseph C. Patrick (1892–1965) was trying to make ethylene glycol ($HOCH_2CH_2OH$) to be used as antifreeze. Instead he discovered Thiokol (a trade name that has become generic), a rubbery polysulfide condensation product of ethylene dichloride and sodium tetrasulfide. This early product is still used for gaskets, sealants, sealer adhesives, and hoses because it is resistant to oil and organic solvents.

In 1931 Arnold Collins, a chemist in the Du Pont research group of Wallace Hume Carothers (1896–1937), the discoverer of nylon, discovered neoprene accidentally while studying the by-products of divinylacetylene ($H_2C=CH\text{-}C\equiv CH$). There are several types of neoprenes. They have high tensile strength, high resilience, and excellent resistance to oxygen, ozone, other chemicals, and oil. They also resist heat, flame, and tearing. They are good general-purpose rubbers, but they are limited to uses requiring rubbers with special properties because of their high cost.

Other Synthetic Rubbers

In 1937 Robert McKee Thomas (1908–1986) and William Joseph Sparks (1904–1976) at the Standard Oil Development Company (now Exxon) synthesized butyl rubber via the copolymerization (polymerization of a mixture of monomers) of isobutylene (2-methylpropene ($(CH_3)_2C=CH_2$) with a small amount of isoprene.

By 1929 the German firm I. G. Farben developed a series of synthetic rubbers similar to those produced in the USSR. They were called Buna rubbers ("Bu" for butadiene, one of the copolymers, and "na" for sodium, the polymerization **catalyst**). They included the oil-resistant Buna S (S for styrene) and Buna N (N for nitrate). Buna S, styrene butadiene rubber, is currently called SBR, and it is produced at about twice the volume of natural rubber, making it the most common synthetic rubber. Buna N, acrylonitrile-butadiene rubber, is now called NBR. During World War II the United States produced these rubbers for the American war effort.

catalyst: substance that aids in a reaction while retaining its own chemical identity

stereospecific: yielding one product when reacted with a given compound but the opposite product with its stereoisomer

While earlier attempts to produce satisfactory synthetic rubber from isoprene were unsuccessful, in 1955 American chemist Samuel Emmett Horne Jr. (b. 1924) prepared 98 percent *cis*-1,4-polyisoprene via the **stereospecific** polymerization of isoprene. Horne's product differs from natural rubber only in that it contains a small amount of *cis*-1,2-polyisoprene, but it is indistinguishable from natural rubber in physical properties. First produced in 1961, BR (for butadiene rubber), a rubberlike polymer that is almost exclusively *cis*-1,4-polybutadiene, when blended with natural or SBR rubber, has been used for tire treads.

Polyurethane (PU) was first synthesized in the 1930s by German chemist Otto Bayer (1902–1982), who was trying to prepare a nylonlike fiber. PU is a versatile polymer that is used for rigid and flexible foams, bristles, coatings, fibers, and automobile parts, such as bumpers. Other synthetics are used in products such as stretchable fabrics and binders for paints.

After the end of World War II the American synthetic rubber industry declined sharply. However, by the early 1950s, as better and more uniform synthetic rubbers became available, it underwent a renaissance. By the early 1960s the amount of synthetic rubber produced worldwide equaled that of natural rubber, and it has increased steadily ever since. Although natural rubber performs well for most uses, some of the newer synthetics are superior to it for specialized purposes. Today rubber is indispensable for a variety of products and industries, and our modern world, with its many necessities and luxuries, would be unthinkable without it. SEE ALSO POLYMERS, NATURAL; POLYMERS, SYNTHETIC.

George B. Kauffman

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metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

37
Rb
RUBIDIUM
85.4678

Rubidium

MELTING POINT: 39.5°C
BOILING POINT: 688°C
DENSITY: 1.532 g/cm^3
MOST COMMON IONS: Rb$^+$

Rubidium is a soft, silvery alkali **metal** that reacts explosively with water. The word *rubidium* is derived from "rubidus" (Latin for "deepest red"), due

Rubidium is the sixteenth most abundant element in the earth's crust. Among its compounds' uses are as batteries.

to the deep red lines observed by Robert Bunsen and Gustav Kirchoff during their analysis of lepidolite ore using a spectroscope in 1861. Currently, rubidium metal is obtained via the electrolysis of molten RbCl or by treating molten RbCl with calcium and distilling the mixture. Rubidium is usually obtained as a by-product of lithium processing because it is found in low concentrations in the minerals lepidolite, carnallite, and pollucite, as well as in the brines at Searles Lake, California. It is the sixteenth most abundant element in Earth's crust (about 78 ppm). Rubidium is never found in its elemental state in nature. It is the second most electropositive element and will ignite in air (unlike Na and K). Rubidium burns yellow-violet in the flame test.

The demand for rubidium metal and its compounds is quite small. The metal is used as a getter to remove oxygen in vacuum tubes. The crystalline compound $RbAg_4I_5$ has a conductivity similar to dilute sulfuric acid, which may make it useful in batteries and other electrochemical applications. Rubidium carbonate, Rb_2CO_3, is used in the manufacture of specialized glasses. SEE ALSO Alkali Metals.

Nathan J. Barrows

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Rust ***See Corrosion.***

44

Ru

RUTHENIUM

101.07

Ruthenium

MELTING POINT: 2,310°C

BOILING POINT: 3,900°C

DENSITY: 12.2 g/cm^3

MOST COMMON IONS: Ru^{2+}, Ru^{3+}, RuO_4^{2-}, RuO_4^{-}

Ruthenium was discovered in 1844 in ores extracted from the Ural Mountains in Russia by Karl Klaus, who named it after *Ruthenia*, the Latin name for Russia. Its abundance in Earth's crust is about 0.0001 ppm. Ruthenium crystallizes in the hexagonal close-packed arrangement, is lustrous, and is silvery in color. It is used primarily to harden platinum and palladium in **alloys**. It is extracted from platinum **metal** ore concentrates and isolated as a gray powder or a sponge using chemical techniques. Ruthenium will dissolve in fused KOH to give $K_2[RuO_4]$. It will react with F_2 to give RuF_5, and with Cl_2, Br_2, or I_2 to yield RuX_3, where X = Cl, Br, or I. It also combines with the elements As, P, Si, and B at high temperatures to form binary compounds of various stoichiometries, and with air upon heating to yield RuO_2. RuO_4 (mp 25.5°C, or 77.9°F), a powerful oxidizing agent, is obtained by reaction of ruthenium in acidic solution with oxidizing agents such as MnO_{4-} and has found use as a **catalyst** in the **oxidation** of various substrates. In the +2 and +3 oxidation states, ruthenium forms numerous coordination complexes with **ligands** containing carbon, nitrogen, phosphorus, oxygen, and sulfur donors. It also forms oxo- and ligand-bridged binuclear and trinuclear metal complexes, such as $[(NH_3)_5Ru\text{–}N\text{–}N\text{–}Ru(NH_3)_5]^{4+}$ and $[(NH_3)_5Ru\text{–}O\text{–}Ru(NH_3)_4\text{–}O\text{–}Ru(NH_3)_5]^{6+}$, and dioxo-compounds such as *cis-* or *trans-* $[Ru(bpy)_2(O)_2]$, where bpy is 2,2′-bipyridine. In the lower oxidation states, ruthenium together with carbonyl, phosphine, and/or hydrido ligands form alkene, diene, alkyne, and allyl complexes. SEE ALSO PALLADIUM; PLATINUM.

D. Paul Rillema

alloy: mixture of two or more elements, at least one of which is a metal

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

catalyst: substance that aids in a reaction while retaining its own chemical identity

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

ligand: molecule or ion capable of donating one or more electron pairs to a Lewis acid

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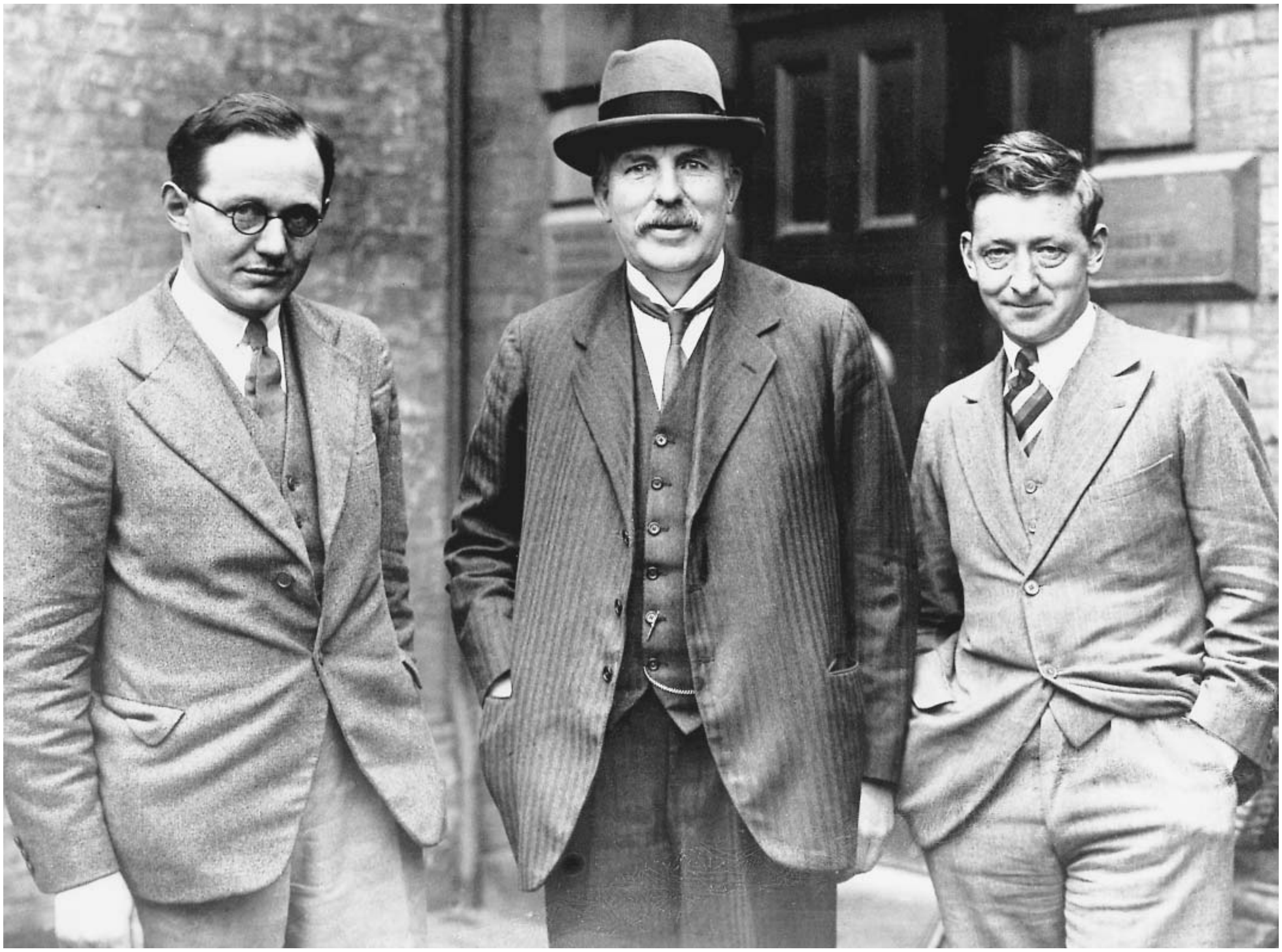
BRITISH PHYSICIST
1871–1937

Ernest Rutherford was born on August 30, 1871, near Nelson, New Zealand. He was a very good student, excelling at science and mathematics. In 1889 Rutherford won a scholarship to study at Canterbury College, Christchurch, New Zealand, and it was at college that he began his work as a scientist. He conducted experiments on the speed of induction in iron placed in rapidly alternating magnetic fields. In 1894, in part because of his original work, he was awarded a scholarship to study at Trinity College, Cambridge, with famed physicist J. J. Thomson. At first he continued his research on magnetism, but by 1896 Rutherford and Thomson were working together on the conductivity of electricity in gases using x rays.

Rutherford's skill and experience in conceiving and building delicate experimental apparatus were crucial to another project that would prove to be



his most important contribution to science. Following his research on x rays, Rutherford began to study the effect of radiation from uranium on the conductivity of gases. During this work, he determined that there were two kinds of radiation, which he called α and β rays. These could be distinguished by their ability to penetrate materials: α rays would not pass through a thin piece of paper; β radiation was more powerful and could penetrate thin sheets of **metal** foil.

British physicist Ernest Rutherford (middle), recipient of the 1908 Nobel Prize in chemistry, "for his investigations into the disintegration of the elements, and the chemistry of radioactive substances."

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

In 1903, with the scientist Frederick Soddy, Rutherford concluded that radiation was caused by atoms of radioactive material breaking apart. The tiny bits that broke off were the α and β rays. This was a revolutionary idea, since it had been a basic principle of physics and chemistry that atoms were the smallest possible particles of matter and therefore indivisible. Rutherford went on to demonstrate that **α-particles** were, in fact, a form of the helium atom. He did this by placing a delicate glass bulb containing radon gas, which emitted α-particles, in an evacuated tube. The particles would penetrate the glass of the bulb but not escape the tube, and could then be analyzed.

α-particle: subatomic particle with 2+ charge and mass of 4; a He nucleus

As part of these studies, Rutherford and his assistant Hans Geiger created an α-particle detector (known today as the Geiger counter) in 1908. In 1909 Rutherford gave his student Ernest Marsden the task of studying whether metal would deflect the path of an α-particle. This was the well-known gold foil experiment, in which it was observed that one particle in about 8,000 bounced off a thin foil of gold rather than passing through it. This surprised everyone, and as Rutherford stated, “It was about as credible as if you had fired a 15-inch shell at a piece of tissue paper and it came back and hit you” (Glasstone, p. 93). Rutherford showed that the collision had to occur with something that was small and very massive (compared to the α-particle) and that carried an electrical charge.

These experiments led to Rutherford’s 1911 hypothesis that the atom consisted of a hard core (named the *nucleus* in 1912) that contained almost all the mass of the atom and had a positive charge, and that the electrons, which had little mass and a negative charge, orbited the core at a distance. Rutherford’s work transformed the concept of the atom from that of a solid body into one of mostly empty space. Although the new model explained the experimental results, it was not compatible with classical physics. If the electrons orbited the nucleus like planets orbit the Sun, they would slow down and collapse into the center. In 1912 the Danish physicist Niels Bohr arrived in England to work with Rutherford, and he applied the quantum theory of the German physicist Max Planck to the model. According to this theory, electrons could only gain or lose energy in fixed amounts called **quanta**. So long as an electron did not change its orbit, it would never collapse into the nucleus. Although there have been further refinements to the Bohr-Rutherford model of the atom—for example, electrons do not actually orbit—it is an important model of atomic structure.

quantum: smallest amount of a physical quantity that can exist independently, especially a discrete amount of electromagnetic energy

Rutherford won many awards for his work as a scientist and teacher. He won the Nobel Prize for chemistry in 1908 and was knighted in 1914. In 1919 he became the Cavendish Professor of Physics at Cambridge. He was made Lord Rutherford of Nelson in 1931. Rutherford died at Cambridge on October 19, 1937. SEE ALSO Bohr, Niels; Marsden, Ernest; Soddy, Frederick; Thomson, Joseph John.

Andrew Ede

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104
Rf
RUTHERFORDIUM
261

Rutherfordium

MELTING POINT: **Unknown**
BOILING POINT: **Unknown**
DENSITY: **Unknown**
MOST COMMON IONS: **Unknown**

Rutherfordium is the first transactinide element. It was discovered in 1969 by Albert Ghiorso and his coworkers, who carried out the reactions ^{249}Cf

$(^{12}\mathrm{C}, 4\mathrm{n}) \rightarrow {}^{257}\mathrm{Rf}$ (half-life of approximately 3.8 seconds) and ${}^{249}\mathrm{Cf}$ $(^{13}\mathrm{C}, 3\mathrm{n})$ [→] ${}^{259}\mathrm{Rf}$ (half-life of approximately 3.4 seconds). There are ten known **isotopes** of rutherfordium, having mass numbers that range from 253 to 262, the isotope with the longest measured half-life being ${}^{261}\mathrm{Rf}$ (half-life of approximately 1.1 minutes). After its discovery, it was postulated that rutherfordium, as the first transactinide element, should be a member of a new, fourth transition series, extending from Z=104 to Z=112, and an atom in which the *6d* electronic shell is filled. The outer orbital electronic configuration of Rf should be $[\mathrm{Rn}]5f^{14}6d^{2}7s^{2}$. As such, it should behave similarly to its analogs titanium and hafnium and should form **volatile** tetrachlorides that are *less* volatile than $\mathrm{HfCl_4}$. The first gas **chromatographic** studies showed that rutherfordium forms *more* volatile chlorides than hafnium—a deviation from Periodic Table trends that was predicted from **relativistic calculations**. The first aqueous chemistry studies showed the neutral and anionic complexes of Rf to behave like the corresponding complexes of the Group IVB elements, rather than of the trivalent actinides, demonstrating that Rf is indeed a transactinide. Detailed studies of the extraction chromatography of Rf complexes have shown chemical behavior similar to that observed of Rf complexes in gas chromatographic experiments—that is, Rf does not behave as expected according to a simple extrapolation of Periodic Table trends, but in a more complicated manner. For example, in the extraction of substances with tributylphosphate, the extraction sequence Zr > Rf > Hf is observed. These and other experiments show that the aqueous chemistry of rutherfordium is a challenge to current relativistic molecular theories. SEE ALSO Actinium; Berkelium; Einsteinium; Fermium; Lawrencium; Mendelevium; Neptunium; Nobelium; Plutonium; Protactinium; Thorium; Uranium.

isotope: form of an atom that differs by the number of neutrons in the nucleus

volatile: low boiling, readily vaporized

chromatography: the separation of the components of a mixture in one phase (the mobile phase) by passing it through another phase (the stationary phase) making use of the extent to which the components are absorbed by the stationary phase

relativistic calculation: quantum mechanical model that includes the effects of relativity, particularly for core electrons

Walter Loveland

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Rydberg, Johannes

SWEDISH MATHEMATICIAN AND PHYSICIST
1854–1919

Johannes Robert Rydberg was born in Halmstad, Sweden, on November 8, 1854. His father, Sven, was a local merchant and minor shipowner who died when Rydberg was young. Rydberg attended the local gymnasium (or high school) in Halmstad and studied languages, religion and philosophy, history and geography, and natural history, along with mathematics and physics. Although a good all-around student, Rydberg chose to pursue mathematics at the university.

He entered the University of Lund in the autumn of 1873, and it is fair to say that he never left. He received his doctorate in mathematics from that institute in 1879 and was appointed a teacher of mathematics there in 1881. But in 1876 Rydberg was also appointed as a teaching assistant at Lund's physics institute. His experimental study on friction electricity led to a position as a teacher of physics in 1882.

As a physicist and mathematician, Rydberg was driven by a desire to understand the basic physical laws behind the Periodic Table. He set out to

spectroscopy: use of electromagnetic radiation to analyze the chemical composition of materials

find order in the mass of **spectroscopic** data that was then available. Atomic spectra had been used to characterize minerals and to ascertain the chemical composition of distant stars, but the underlying order was not apparent. While various spectroscopists had noted that line spectra could be discriminated into "sharp," "principal," and "diffuse" patterns, a guiding relationship between the lines had not yet emerged.

hyperbolic relationship: a geometric system in which two or more lines can be drawn through any point in a plane and not intersect a given line in that plane

Rydberg decided to use the wave number as a measure of frequency in his calculations. A wave number is the reciprocal of the wavelength, and, although Rydberg did not know this at the time, it is directly related to energy, unlike the more common wavelength that bears an inverse relationship. Having made this change, patterns began to emerge in the data with a particular series of lines for any atom leading to a **hyperbolic relationship**. Indeed, the same relationship was observed for all the different spectroscopic series and for different elements.

Rydberg devised the formula

$$n = n_0 - N_0/(m + m')^2$$

and was testing it against the data when the Swiss mathematician and physicist Johann Balmer published his result for hydrogen atoms, wavelength = $hm^2/(m^2 - 4)$. Rydberg quickly realized that this was just a special case of his formula with $m' = 0$ and $N_0 = 4n_0$ and that N_0 must be a universal constant. Using this information, Rydberg was able to show that his equation was more general and published it in 1890, well before the spectroscopic series discovered by Balmer, the American Theodore Lyman, or the German Friedrich Paschen provided experimental confirmation.

The formula is now written as

$$1/\lambda = \mathrm{R_H}(1/\mathrm{n_1}^2 - 1/\mathrm{n_2}^2)$$

nuclear: having to do with the nucleus of an atom

where both values of n are integers, but n_2 n_1. The term N_0 has been replaced by R_H, the so-called Rydberg constant. It is a fundamental constant of nature and a measure of the strength of the **nuclear**-electron interaction in atoms. SEE ALSO BALMER, JOHANN JAKOB; SPECTROSCOPY.

Todd W. Whitcombe

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S

Saccharides *See Carbohydrates.*

Saccharine *See Artificial Sweeteners.*

Salt

The word "salt" is a general chemical term that refers to ionic compounds formed when an acid reacts with a base. They may be simple salts such as

A large pile of salt at an Uppington, South Africa, salt mine.

NaCl, KCl, and Na_2SO_4; acid salts like $NaHCO_3$ and NaH_2PO_4; or double salts like $KAl(SO_4)_2$. Table salt is sodium chloride, a chemical compound with the formula NaCl. Sodium chloride has been used to flavor and preserve food for thousands of years. As a result, salt became an essential part of commercial transactions and was often used as money or barter. Exchange of salt for slaves in ancient Greece gave rise to the expression "not worth his salt." The Romans gave a *salarium* (salary) to those who were "worth their salt," and Roman soldiers were given salt rations known as *salaria argenta*. Today, salt continues to be of major economic importance, with thousands of uses in addition to flavoring and preserving food.

Sodium chloride forms colorless, cubic crystals that are made up of large numbers of NaCl formula units, to give a three-dimensional crystalline **lattice** in which each sodium ion is surrounded by six chloride ions and each chloride ion is surrounded by six sodium ions. The strong electrostatic attractions between the positive and negative ions, known as ionic bonds, hold the solid sodium chloride together.

lattice: systematic geometrical arrangement of atomic-sized units that describe the structure of a solid

Sodium chloride occurs naturally as the mineral halite, commonly called rock salt, in large underground deposits on every continent. Seawater contains about 3.5 percent dissolved minerals, of which 2.8 percent is sodium chloride and the other 0.7 percent is primarily calcium, magnesium, and sulfate ions. Natural brines, or salty waters other than seawater, are found in wells and lakes, such as the Great Salt Lake of Utah and the Dead Sea. Salt is also found in surface deposits in regions subject to arid climates.

The manufacture and use of salt is one of the oldest chemical industries. The three main methods for recovering salt are: (1) underground salt mining, which uses techniques similar to those for mining coal; (2) solar evaporation of seawater or natural **brine** in lakes or large lagoons; and (3) evaporation of brines obtained by pumping water into a rock salt deposit, dissolving the salt, and bringing the brine to the surface. If the salt is going to be used for food flavoring or preservation, additional purification is required, usually by methods that use multi-stage evaporation of brine solutions. The annual world salt production is about 200 million tons (181,436,948 metric

brine: water containing a large amount of salts, especially sodium chloride (NaCl) tons). The top producers are the United States and China with 45 million and 30 million tons (40,823,313 and 27,215,542 metric tons), respectively.

Uses

Table salt is pure salt that has been ground into fine particles. Because salt tends to cake in humid climates, an anti-caking agent such as magnesium carbonate or calcium silicate is often added. Table salt is also available as iodized salt with 0.1 percent potassium iodide by weight. Because iodide ion is essential to thyroid gland function, the routine use of iodized salt ensures adequate iodine in the diet.

Salt is used to cure meat and fish by soaking them in brine, rubbing salt onto them, or injecting them with a salt solution. Bacon and cured ham are examples of meats preserved by the use of salt. Salt is also used to make pickles by soaking cucumbers in brine.

Rock salt is sprinkled on highways to melt ice. The lowest temperature at which salt can melt ice is −21°C (−6°F), at a concentration of 23 percent salt, and it works best when temperatures are at or slightly below freezing, 0°C (32°F).

Nearly half of the 45 million tons (40,823,313 metric tons) of salt produced each year in the United States is used in the chemical manufacture of chlorine and sodium hydroxide (caustic soda) by electrolysis of brine solution

$$2\ \mathrm{NaCl}\ (aq) + 2\ \mathrm{H_2O}\ (l) \rightarrow 2\ \mathrm{NaOH}\ (aq) + \mathrm{H_2}\ (g) + \mathrm{Cl_2}\ (g)$$

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Electrolysis of molten sodium chloride produces sodium **metal** and chlorine gas

$$2\ \mathrm{NaCl}\ (l) \rightarrow 2\mathrm{Na}\ (l) + \mathrm{Cl_2}\ (g)$$

Salt is also one of the raw materials used in the Solvay process for manufacturing sodium carbonate (soda ash).

Both sodium chloride and potassium chloride are essential to the electrolyte balance in body fluids. Good health depends on the proper ratio of potassium ions to sodium ions. Typical values are greater than one. Natural, unprocessed foods have high K^+/Na^+ weight ratios. Fresh, leafy vegetables average a K^+/Na^+ ratio of 35, and fresh, non-leafy vegetables and fruits average a ratio of 360, with extreme values of 3 for beets and 840 for bananas. After such foods are eaten, the body achieves K^+/Na^+ ratios of greater than 12. However, during processing (and cooking, if foods are boiled), both potassium and sodium compounds are dissolved by the water used, which is then discarded. The sodium ions are replenished by the salting of the food, which gives it a lower K^+/Na^+ weight ratio. One solution is to eat unprocessed, natural foods and to salt foods with a commercial product that contains both potassium and sodium chlorides called "Lite Salt." SEE ALSO ALKALI METALS; CHLORINE; HALOGENS; SODIUM.

Melvin D. Joesten

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Samarium

MELTING POINT: 1,072°C
BOILING POINT: 1,900°C
DENSITY: 7.536 g/cm^3
MOST COMMON IONS: Sm^{2+}, Sm^{3+}

62
Sm
SAMARIUM
150.36

In 1886, French chemist P. E. Lecoq de Boisbaudran, working with the mixture of oxides known as didymia, isolated the element gadolinium and, three years later, a mixture known as samaria. Working with this mixture, Eugene-Anatole Demarçay (1901) discovered the elements europium and samarium (getting its name from the mineral samarskite). The element comprises 6.47 $\times 10^{-4}$ percent of the igneous rocks of Earth's crust. The important minerals are bastnasite (in which are found fluorocarbonates of the cerium group), and monazite and xenotime (in which are found phosphates of the cerium and yttrium group, respectively). Two crystal structures exist: α-Sm (at room temperature to 917°C) and β-Sm (at $>$917°C, body-centered cubic).

The chemistry of samarium(III) is essentially that of all the **lanthanide** (III) ions. Sm(III) can be reduced to Sm(II) under special conditions, but in solution it is rapidly oxidized to the +3 state. With respect to the solid state, the halides (SmX_2) and some chalogenides(II) (oxide, sulfide, selenide, and telluride compounds) have been obtained. SmF_3, together with the oxide, hydroxide, carbonate, oxalate, and phosphate compounds are insoluble in **aqueous solution**. The halide, perchlorate, nitrate, and acetate compounds are water-soluble.

lanthanides: a family of elements (atomic number 57 through 70) from lanthanum to lutetium having from 1 to 14 4f electrons

aqueous solution: homogenous mixture in which water is the solvent (primary component)

The commercially important samarium-containing minerals are treated with concentrated sulfuric acid or, in the case of monazite, with a solution of sodium hydroxide (73%) at approximately 40°C (104°F) and under pressure. The element is separated from the solutions via solvent extraction or ion exchange. Sm^{3+} salts are weakly yellow and may exhibit ion emission. Sm^{2+} ions show luminescence and are sometimes used to generate lasers. Samarium is used in the manufacture of headphones and tape drivers. SEE ALSO Cerium; Dysprosium; Erbium; Europium; Gadolinium; Holmium; Lanthanum; Lutetium; Neodymium; Praseodymium; Promethium; Terbium; Ytterbium.

Lea B. Zinner

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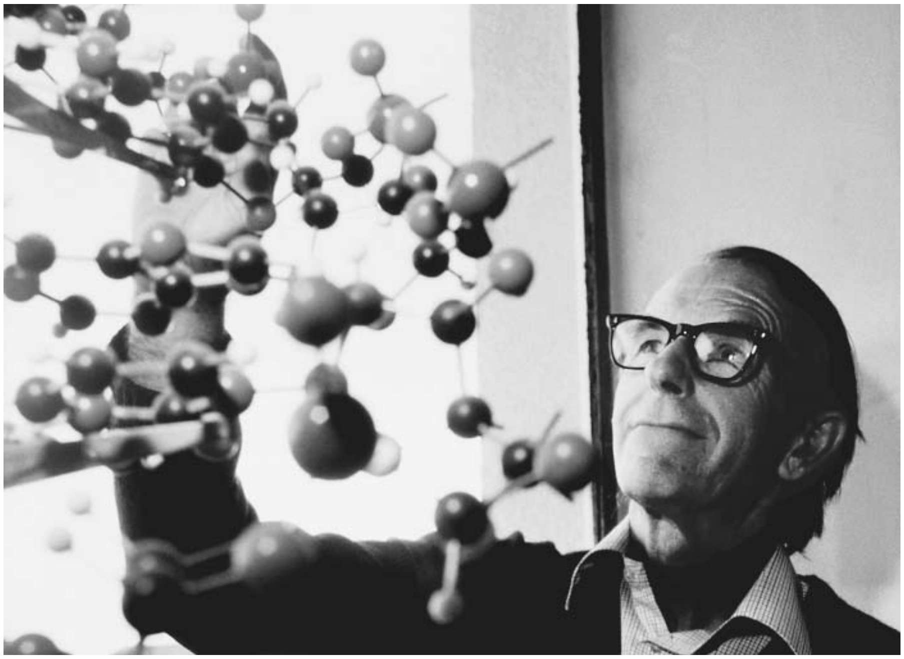
Sanger, Frederick

BRITISH CHEMIST
1918–

Frederick Sanger is surely one of the most outstanding biochemists of modern times. His methods for determining the exact sequence of amino acids in proteins and of nucleotides in deoxyribonucleic acid (**DNA**) have won him numerous awards, including two Nobel Prizes in chemistry.

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

Sanger was born on August 13, 1918, in the village of Rendcombe in Gloucestershire, England. He attended St. John's College, Cambridge Uni-



British biochemist Frederick Sanger, recipient of the 1958 Nobel Prize in chemistry, "for his work on the structure of proteins, especially that of insulin," and co-recipient, with Walter Gilbert and Paul Berg, of the 1980 Nobel Prize in chemistry, "for their contributions concerning the determination of base sequences in nucleic acids."

versity, from which he received a B.A. in biochemistry in 1939. He remained at Cambridge as a conscientious objector during World War II and earned his Ph.D. in biochemistry for work on amino acid **metabolism** and the nitrogen of potatoes with Albert Neuberger in 1943. Later that year he joined Antony C. Chibnall's group at Cambridge and began research on proteins and, in particular, insulin.

The basic principles of protein chemistry were firmly established when Sanger started his work on insulin. It was known that proteins were composed of amino acids linked through amide bonds to form long **polypeptide** chains. Although the relative number of each of the twenty amino acids could be obtained for a given protein, the particular order, or sequence, of those amino acids in the protein had never been determined. Sanger saw sequence as the key to understanding living matter and set out to determine the exact sequence of amino acids in insulin.

Sanger first needed to characterize the free amino groups in insulin. For this he developed a **reagent**, dinitrofluorobenzene (FDNB), that reacted with amino groups present in proteins to form an acid-stable dinitrophrenyl (DNP) derivative. The DNP protein was treated with acid to break the polypeptide backbone, and the free DNP amino acid derivatives were isolated and compared to standards prepared from known amino acids. In this way, Sanger determined that insulin was made up of two peptide chains: one (chain A) with an amino-terminal glycine residue and another (chain B) with an amino-terminal phenylalanine. Subsequent work revealed that chain A was composed of twenty amino acids and chain B thirty-one.

The individual chains were then broken down into smaller components: Acid was used to **cleave** the polypeptide backbone, performic acid was used to break the cysteine **disulfide bonds**, and proteolytic enzymes were used to **hydrolyze** the polypeptide at specific sites on the chain. The reaction products were separated from each other and their sequence determined.

metabolism: all of the biochemical processes that take place within living organisms; comprises processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those that break down complex food molecules, thus liberating energy (catabolism)

polypeptide: compound containing two or more amide units—C(O)NH—produced by the condensation of two or more amino acids

reagent: chemical used to cause a specific chemical reaction

cleave: split

disulfide bond: bond that involves two bonding sulfur atoms, –S–S–

hydrolyze: to react with water

Sanger was able to deduce the complete sequence of insulin after twelve years of painstaking research and molecular puzzle solving. The Nobel committee was quick to recognize Sanger's accomplishment and awarded him the 1958 Nobel Prize in chemistry for "his work on the structure of proteins, especially that of insulin."

In 1962 Sanger moved to the Medical Research Council Laboratory of Molecular Biology in Cambridge, where he became interested in nucleic acid sequencing. He and his colleagues developed a cleave-and-sequence method for small ribonucleic acid (RNA) molecules, but they soon realized that a different method was needed to sequence the much larger DNA molecules. For DNA sequencing, he chose to investigate copying procedures.

Sanger eventually settled on a procedure that uses DNA polymerase to copy short fragments (200 nucleotides) of single-stranded DNA obtained from enzyme-catalyzed cleavage of the parent DNA. In addition to the usual radiolabeled deoxyribonucleotide triphosphates, the DNA **synthesis** cocktail contains a 2′, 3′-dideoxy analog that is incorporated into the growing DNA strand and blocks further DNA synthesis. After repeating the reaction using each of the remaining dideoxy nucleotides, the various chain-terminated fragments are separated by gel **electrophoresis** and the DNA sequence read directly from the gel. Sanger used this method to sequence a DNA containing more than 5,000 nucleotides and shared the 1980 Nobel Prize in chemistry for "contributions concerning the determination of base sequences in nucleic acids."

synthesis: combination of starting materials to form a desired product

electrophoresis: migration of charged particles under the influence of an electric field, usually in solution; cations, positively charged species, will move toward the negative pole, and anions, the negatively charged species, will move toward the positive pole

Sanger retired in 1983 after forty years of service at the Medical Research Council and after helping to usher in a new era in biology and medicine. SEE ALSO DNA Replication; Insulin; Proteins.

Thomas M. Zydowsky

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Scandium

MELTING POINT: 1,539°C
BOILING POINT: 2,832°C
DENSITY: 2.989 g/cm^3
MOST COMMON IONS: Sc^{3+}

21
Sc
SCANDIUM
44.9559

Drawing on his periodic law and his categorization of the elements, Russian chemist Dimitri Mendeleev predicted the existence of element 21 in 1871. However, it was not until 1879 that Swedish chemist Lars Frederick Nilson identified the element scandium as part of a novel compound he had isolated. Working with 10 kilograms (22 pounds) of euxenite, a mineral found only in Scandinavia at that time, Nilson eventually succeeded in purifying 2 grams (0.07 ounces) of what later became known as scandium oxide.

Since its discovery, scandium has been found only in several rare minerals. It is found in highest concentration in the Norwegian mineral thortveitite (35–40% scandium). Its abundance in Earth's crust is a point of conjecture; it is generally agreed that scandium occurs in greater abundance in the Sun and certain stars.

In addition to forming an oxide (scandium oxide, Sc_2O_3), scandium is capable of forming a number of colorless salts. For instance, scandium reacts with **halogens** to form halides that have the formula ScX_3 (where X = F, Cl, Br, or I). Additionally it occurs as an aqua ion, $[Sc(H_2O)_6]^{3+}$, which undergoes hydrolysis to form hydroxide-bridged **metal** clusters. A wide range of organic compounds may also react with scandium.

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Because of its scarce distribution and difficulties associated with its extraction, scandium is very expensive. As a result and despite more than 100 years of research, it still has only a limited number of applications. It is added to aluminum **alloys** to increase the strength, thermal resistance, and durability of the materials (without adding much weight). Such alloys have been used to make everything from missiles to premium bicycle frames. Scandium is as light as aluminum but has a much higher melting point, thus its appeal to space missile designers. SEE ALSO Aluminum; Halogens; Hydrolysis.

alloy: mixture of two or more elements, at least one of which is a metal

Helen R. Webb

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Scheele, Carl

SWEDISH CHEMIST
1742–1786

Carl Wilhelm Scheele was born in Pomerania (on the Baltic coast of northeastern Europe, then under Swedish control). As a young man Scheele worked as an apothecary and studied chemistry under the famous chemist Torbern Bergman. Bergman once called Scheele one of his greatest discoveries. Scheele's laboratory techniques in chemistry were so exacting that his work fostered advances in several areas of chemistry. Scheele's achievements in organic chemistry included the isolation of glycerin and twelve organic acids—among them tartaric, citric, oxalic, mucic, malic, lactic, uric, gallic, and tannic acids. Among the **metals** Scheele was the first to identify were barium, molybdenum, and tungsten. He was the first to isolate elemental phosphorus from bone. Scheele was the first to characterize plumbago (graphite) as a form of carbon. He was one of the discoverers of the adsorption of gases by "activated charcoal." In 1777 Scheele was the first to describe the reduction of silver salts to metallic silver via the action of sunlight (the basis of photography).

Swedish chemist Carl Wilhelm Scheele, who discovered oxygen with Joseph Priestley and Antoine-Laurent Lavoisier.

Scheele developed a general method for investigating organic acid. His first step was to precipitate the acid as a crystalline calcium salt. He would purify the salt and then decompose it using sulfuric acid. (Calcium sulfate precipitates out, leaving the free organic acid for characterization.) Another of Scheele's separation techniques was the precipitation of the lead salts of acids, which were generally less soluble than the calcium salts. The lead salts were also decomposed with sulfuric acid to produce the free organic acids.

His investigations of reactive gases and corrosive liquids included such compounds as ammonia, hydrogen chloride (the gaseous form of hydrochloric acid), hydrogen fluoride (which can dissolve glass), silicon fluoride (highly corrosive), hydrogen sulfide (the active ingredient of a stink bomb), hydrocyanic acid, and **arsenic** acid. He was the first to isolate chlorine gas, which became the basis of the bleaching industry.

arsenic: toxic element of the phosphorus group

Scheele is most often remembered as one of the discoverers of oxygen, along with Joseph Priestley and Antoine Lavoisier. Scheele's work on the gas he called "fire-air" was completed between 1770 and 1773. This predated the work of Lavoisier or Priestley. Scheele's *Chemical Observations and Experiments on Air and Fire* was not published until 1777, after the comparable findings of Lavoisier and Priestley had been reported. Like Priestley, Scheele retained use of the phlogiston theory in most of his chemical work. Unlike Priestley, Scheele died at a young age. He died at forty-three, at a time when Lavoisier was consolidating the chemical revolution. SEE ALSO Chlorine.

David A. Bassett

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AUSTRIAN THEORETICAL PHYSICIST
1887–1961

Erwin Schrödinger was born in Vienna, Austria, in 1887. In 1906 he entered the University of Vienna with the intention of studying statistical thermodynamics with the mathematician and physicist Ludwig Boltzmann. Unfortunately it was the year Boltzmann committed suicide, and Schrödinger studied under Boltzmann's successor, Fritz Hasenöhrl. Schrödinger received his doctorate in 1910 for a dissertation on electrical conduction. The next four years were spent as an assistant instructor in experimental physics at the University of Vienna. In 1914 he was drafted to serve in the Austro-Hungarian army and fought on the side of Germany during World War I. In 1917 he returned to his former position in Vienna. In the aftermath of several research successes, Schrödinger found himself to be in great demand, and he accepted, one right after the other, faculty positions at the Universities of Jena, Stuttgart, and Breslau. Finally, in late 1921 he accepted the chair in **theoretical physics** at the University of Zurich (in Switzerland). Although his stay there was relatively short (six years), it was there that he published his most significant work—in quantum statistics, the dynamics of crystal lattices, the theory of color vision, and quantum theory.

theoretical physics: branch of physics dealing with the theories and concepts of matter, especially at the atomic and subatomic levels

Schrödinger's work in quantum theory resulted in the creation of a new scientific discipline—wave mechanics, which has as its centerpiece the Schrödinger wave equation, explained in a series of four papers published in 1926. This equation and the later relativistic versions are considered by many scientists to have the same central importance to molecular quantum mechanics as Newton's laws of motion have to large-scale classical mechanics.

Austrian physicist Erwin Schrödinger, co-recipient, with Paul Adrien Maurice Dirac, of the 1933 Nobel Prize in physics, "for the discovery of new productive forms of atomic theory."

Schrödinger began to search for a wave equation in 1925 after reading a paper by Albert Einstein about Louis de Broglie's ideas that matter could possess both wave and particle properties simultaneously, as expressed in the de Broglie equation relating the wavelength of a matter wave to its momentum. Schrödinger demonstrated that the de Broglie equation could be generalized so as to apply to particles such as electrons in atoms. The Schrödinger equation is a wave equation that explains the properties and behavior of all types of submicroscopic particles with small masses and that are in the presence of electric and magnetic fields. Schrödinger's work was immediately accepted worldwide, and he received a call to accept the challenge of succeeding Max Planck in the department of theoretical physics at the University of Berlin. He stayed until 1933, but by that time he had become so outraged by the German government's treatment of Jewish scientists that he accepted a position at Oxford University in England, just before he was informed that he had been awarded the 1933 Nobel Prize in physics for his development of wave mechanics. For the next seven years (during which time a return to Vienna would have been most difficult), he accepted several temporary appointments. In 1941 he became director of the School of Theoretical Physics at the Dublin Institute for Advanced Studies (in Ireland). There he worked mainly on unified field theory.

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

He also published a number of books. Of these, *What Is Life? The Physical Aspect of the Living Cell* is credited with having persuaded physicists to take an interest in the problems of biology. It is also credited with having attracted many young people to the new field of molecular biology. For instance, James Watson, one of the discoverers of the structure and function of **DNA**, stated that, from the moment he read the book, he "became polarized toward finding out the secret of the gene."

In 1955 Austria became free of Soviet occupation, and Schrödinger returned to the University of Vienna, where he received many honors as Austria's greatest living scientist. Schrödinger retired in 1958 and died in 1961. SEE ALSO DE BROGLIE, LOUIS; QUANTUM CHEMISTRY; WATSON, JAMES DEWEY.

John E. Bloor

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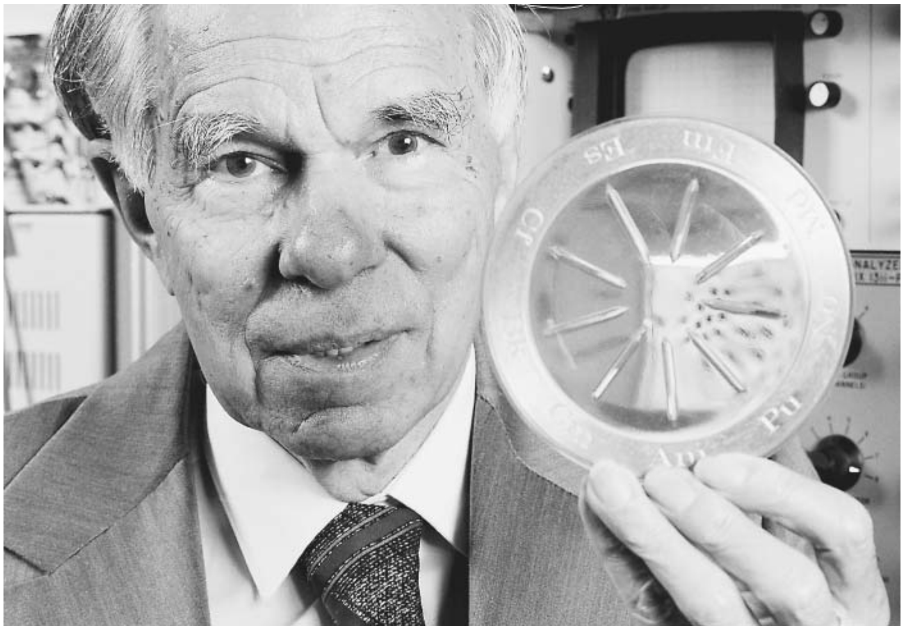
Scurvy ***See Ascorbic Acid.***

Seaborg, Glenn Theodore

AMERICAN NUCLEAR CHEMIST
1912–1999

Elder statesman, chemist, and codiscoverer of more elements than any other scientist, Glenn Theodore Seaborg started life in Ishpeming, Michigan, in



American chemist Glenn Theodore Seaborg, corecipient with Edwin Mattison McMillan of the 1951 Nobel Prize in chemistry, "for their discoveries in the chemistry of the transuranium elements." Here, Seaborg holds a container of samples of the radioactive elements 94 through 102.

1912. In an autobiographical account Seaborg divided his life into eight periods—a notion that perhaps sprang from his consideration of the eight periods of the present Periodic Table. In that account the first two periods correspond to his childhood and youth and conclude with his graduation from UCLA in 1934.

Seaborg went on to the University of California at Berkeley for graduate work, obtaining his Ph.D. in 1937. It was around this time that his interest in transuranium elements (elements of higher **atomic number** than uranium) took shape. His research interest was in **nuclear** physics but, as he once said, "one could get a chemistry Ph.D. in those days doing nuclear physics."

atomic number: the number assigned to an atom of an element that indicates the number of protons in the nucleus of that atom

nuclear: having to do with the nucleus of an atom

Upon finishing his doctoral dissertation, Seaborg went to work as personal research assistant to the chemist Gilbert Newton Lewis. His work with Lewis dealt with the concepts of primary and secondary acids (part of traditional chemistry). However, during his tenure as instructor (1939–1941) and assistant professor (1941) at Berkeley, his research in transuranic elements and **isotope** production reemerged. During the period 1934 to 1942, Seaborg participated in the discovery of plutonium and its **fissionable** isotopes (which were essential to the construction of a nuclear bomb). During this period he was also deeply involved in the **synthesis** of radioactive isotopes from nonradioactive elements ^{131}I, ^{60}Co, and ^{99m}Tc, which have found important applications in the diagnosis and treatment of diseases.

isotope: form of an atom that differs by the number of neutrons in the nucleus

fissionable: of or pertaining to unstable nuclei that decay to produce smaller nuclei

synthesis: combination of starting materials to form a desired product

From 1942 to 1946, Seaborg, on leave from Berkeley, was employed by the Metallurgical Laboratory, at the University of Chicago. It was during this period that he devised chemical processes for the separation and purification of plutonium. Plutonium, critical to the success of the **Manhattan Project**, was given the code name "copper." When actual copper was required in the project, the resulting confusion was eliminated by the use

Manhattan Project: government project dedicated to creation of an atomic weapon; directed by General Leslie Groves of "honest-to-God copper." Also at this time, Seaborg maintained his research on transuranium elements; he took part in the discoveries of both americium (element 95) and curium (element 96). But it was upon his return to Berkeley in 1946 that his transuranium research program gained momentum, whereupon it generated a string of discoveries: berkelium (element 97), californium (98), einsteinium (99), fermium (100), mendelevium (101), and nobelium (102). In 1951 Seaborg and Edwin Mattison McMillan received the Nobel Prize in chemistry "for their discoveries in the chemistry of the transuranium elements."

Between 1953 and 1958 Seaborg served as the faculty athletic representative at the University of California at Berkeley and helped to redesign the Intercollegiate Athletic Union, giving it new rules and regulations that would govern athletic scholarships. From 1958 to 1961, Seaborg served as chancellor at the University of California at Berkeley, during which time he oversaw notable successes in athletics, new building construction, and the establishment of research centers.

From 1961 to 1971, Seaborg was chairman of the United States Atomic Energy Commission. Solicited for the job by President Kennedy, Seaborg at first had doubts about taking on the position. (Seaborg disliked the idea of quitting research.) Kennedy gave him one day to decide. (Seaborg accepted.) His ten years as chairman, during which he served under three presidents and through some of the most turbulent times in U.S. history, established his credentials as an elder statesman.

Seaborg returned to the University of California at Berkeley in 1971. There, in 1974, he discovered with his colleagues one more element. Although it was a controversial discovery due to competing claims, the element was eventually named "seaborgium" (with the result that prior to his death in 1999, Glenn Seaborg was the only living person after whom an element had been named).

In his career he was president of both the American Chemical Society and the American Association for the Advancement of Science. Because of his belief in the importance of education, he undertook to reform the chemistry and science curricula of high schools. CHEM Study, a project designed to improve the teaching of chemistry at the high school level, became an internationally recognized educational resource under his direction. He was a founder of GEMS (Great Explorations in Math and Science) and many other science education projects.

Seaborg worked hard to ensure that science education was not slighted and that science would be seen as a tremendous boon to humanity. Along these lines, it was his leadership that helped to bring into existence the Lawrence Hall of Science at Berkeley as a tribute to Ernest Orlando Lawrence. SEE ALSO Americium; Curium; Lawrence, Ernest; Plutonium.

Todd W. Whitcombe

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Secondary Structure

The secondary structure refers to the conformation present at a local region of a **polypeptide**. A few types of secondary structure are particularly stable and occur widely in proteins. These include the α-helix and β-sheet conformations, which are both stabilized by **hydrogen bonds**. The α-helix is a rigid, rod-like structure that forms when a polypeptide chain twists into a helical conformation. Hydrogen bonds form between the amino (N–H) group of one amino acid and the carbonyl (C=O) group of the amino acid four residues away. The amino acid side chains extend outward from the helix. In the β-sheet, two or more polypeptide chains (or two or more portions of the same chain) are arranged side by side to form a sheet. Hydrogen bonds form between the backbone amino groups and the carbonyl groups of adjacent chains. The sheets are pleated, not flat, and the amino acid side chains of adjacent amino acids extend from the pleat structure in opposite directions. In a protein, loops or bends can connect the secondary structures. SEE ALSO Primary Structure; Tertiary Structure.

Elizabeth S. Roberts-Kirchhoff

polypeptide: compound containing two or more amide unit—C(O)NH—produced by the condensation of two or more amino acids

hydrogen bond: interaction between H atoms on one molecule and lone pair electrons on another molecule that constitutes hydrogen bonding

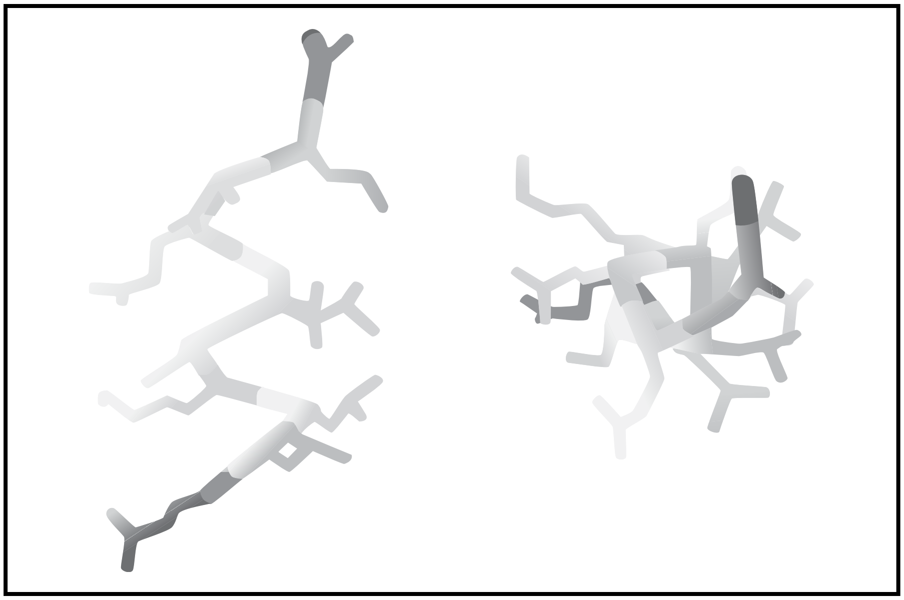

Figure 1. Alpha helix.

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Seibert, Florence

AMERICAN BIOCHEMIST
1897–1991

Florence Seibert made several important contributions to medicine during her long career. Most notably, she purified a protein from tuberculosis bacteria that became the international standard for tuberculosis testing. She also greatly improved the safety of intravenous injections by inventing a method to make distilled water free of contaminants that had caused serious problems in many patients.

Seibert was born in Easton, Pennsylvania. As a girl she contracted polio; although the disease left her with a lifelong limp, it did not affect her academic skills. She graduated as high school valedictorian, earning a scholarship to Goucher College in Maryland. After graduating in 1918, Seibert briefly worked as a chemist at a paper mill. She then attended Yale University to earn a doctoral degree in biochemistry, graduating in 1923. During her graduate work at Yale, Seibert devised an improved method for making distilled water that eliminated bacterial contaminants that had caused fevers in some patients receiving injections with substances dissolved in distilled water.

In 1924, following additional studies at the University of Chicago, Seibert became an instructor, then an assistant professor, at the Sprague Memorial Institute in Chicago. In 1932 she moved to the University of Pennsylvania, where she remained until retiring in 1958 as a full professor.

It was at the University of Pennsylvania that Seibert began her important work in tuberculosis research. Robert Koch had reported as early as 1891 that animals previously infected with tuberculosis had a unique reaction when tuberculosis bacteria fragments or dead bacteria were injected under the skin. The culture extract used by Koch and others was called tuberculin, and the appearance of welts in response to the injection was called the tuberculin reaction. The reaction is due to an immune response known as delayed hypersensitivity and appears in humans who have either active tuberculosis infections or who have had active infections in the past. It is thus valuable to public health officials for identifying potential tuberculosis carriers. The preparations of tuberculin prepared by Koch and others, however, were complex mixtures of many substances, including the presumed active protein component, and the contents were not consistent from batch to batch. Thus the ability to induce the tuberculin reaction varied enormously from preparation to preparation.

Seibert devised a way to purify a protein causing the tuberculin reaction, which allowed standardization of strength from one preparation to another. She published her first work on purification of tuberculin in 1934. The

American biochemist Florence Seibert, who developed the procedure that isolated the crystalline tuberculin derivative, which is used in the standard TB test.

protein she isolated was much improved over old tuberculin and was called Purified Protein Derivative (PPD). By 1940 Seibert had improved her protein purification procedure sufficiently for it to become the international standard for use in tuberculin tests, contributing enormously to public health campaigns. For this work she was awarded the Trudeau Medal by the National Tuberculosis Association in 1938 and the Garvan Medal by the American Chemical Society in 1941.

Over the years Seibert's research interests evolved from tuberculosis to cancer research. Following her retirement from the University of Pennsylvania she became director of the cancer research laboratory at a hospital in St. Petersburg, Florida. In 1968 she published an autobiography entitled *Pebbles on the Hill of a Scientist*. Seibert continued publishing scientific research papers until 1977, when declining health forced her to give up research. She was inducted into the National Women's Hall of Fame in 1990, one year before her death.

Robert K. Griffith

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Selenium

34
Se
SELENIUM
78.96

MELTING POINT: **217°C**
BOILING POINT: **685°C**
DENSITY: **4,819 kg/m^3**
MOST COMMON IONS: **SeO_3^{2-}, SeO_4^{2-}, Se^{2-}**

Selenium (from the Greek word *selēnē*—the Moon), discovered by Swedish chemist Jöns Jakob Berzelius in 1817, ranks thirty-fourth among elements in Earth's crust. It has six naturally occurring **isotopes**, a large number of allotropes (elemental forms), and in compounds has **oxidation** states −2, +4, and +6. The gray elemental form has the unique photoelectric property of exhibiting lowered electrical resistance when struck by light, and it is used in photovoltaic cells and photocells (e.g., light meters) and in xerography. It conducts electricity in a "unipolar" manner, hence it is commonly used in electrical rectifiers. It is also used to tint glass red and to decolorize green glass.

isotope: form of an atom that differs by the number of neutrons in the nucleus

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

Selenium substitutes for sulfur in amino acids to form seleno-cysteine, cystine, and methionine. The selenium-containing antioxidant glutathione peroxidase is biologically important, and selenium is a necessary trace nutrient in warm-blooded animals. Grazing animals develop a form of **muscular dystrophy** and other disorders when grazing in areas in which the selenium has been depleted; with selenium-depleted diets, people develop

muscular dystrophy: medical condition in which there is gradual atrophy of skeletal muscles

The element selenium contains important antioxidants and nutrients but is also harmful to some life-forms.

Keshan disease, a form of cardiomyopathy. When its intake is too high, selenium disrupts enzyme function, causing poor health in mammals and birth defects and reproductive failure in birds and fish. Good sources of selenium in human diets include wheat, garlic, Brazil nuts, and walnuts. SEE ALSO Chalcogens.

John Harwood

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Semiconductors

The development of semiconductors is clearly among the most significant technological achievements to evolve from the study of solid-state chemistry and physics. Aside from their well-known applications in computers and electronics, semiconductors are also used in a wide variety of optical devices such as lasers, light-emitting diodes, and solar panels. The diversity of applications can be readily understood with only a basic understanding of the theory behind these materials.

Theory

The operation of semiconductors is best understood using band theory. At its most fundamental level, band theory can be extremely complex, requiring relatively advanced mathematics and physics. When a large number of atoms combine to form a solid, the electrons e^- in the solid are distributed into energy bands among all the atoms in the solid. Each band has a different energy, and the electrons fill these bands from the lowest energy to the highest, similar to the way electrons occupy the orbitals in a single atom. The variation in properties between electrical insulators, conductors (**metals**), and semiconductors stems from differences in the band structures of these materials (see Figure 1). For this discussion, three terms must be defined. The highest energy band that contains electrons is called the **valence** band, whereas the lowest energy empty band is called the conduction band. The band gap is the difference in energy between the valence and conduction bands. The laws of quantum mechanics forbid electrons from being in the band gap; thus, an electron must always be in one of the bands.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

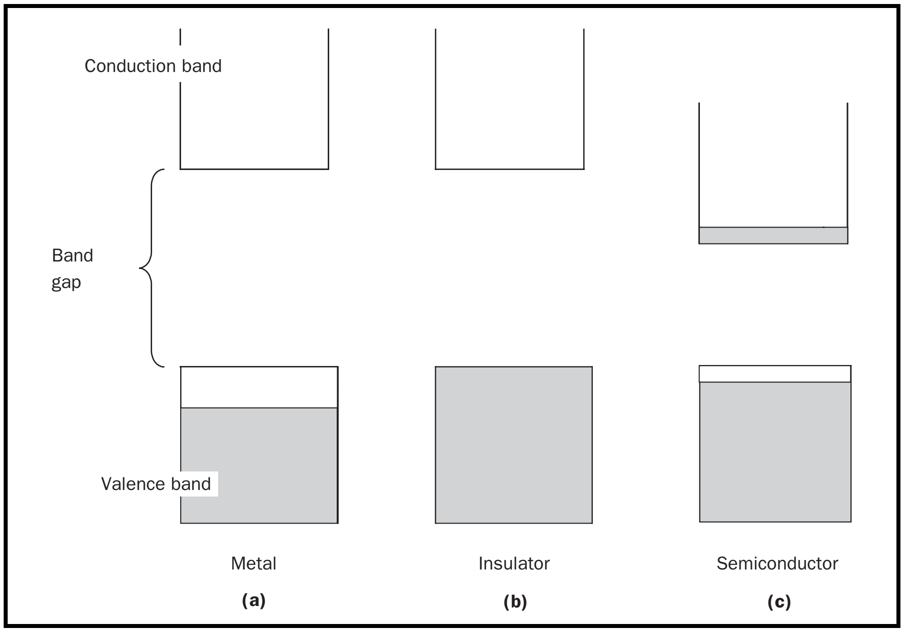
valence: combining capacity

voltage: potential difference expressed in volts

In a metal (e.g., copper or silver), the valence band is only partially filled with electrons (Figure 1a). This means that the electrons can access empty areas within the valence band, and move freely across all atoms that make up the solid. A current can therefore be generated when a **voltage** is applied. In general, for electrons to flow in a solid, they must be in a partially filled band or have access to a nearby empty band. In an electrical insulator, there is no possibility for electron flow (Figure 1b), because the valence band is completely filled with electrons, and the conduction band is too far away in energy to be accessed by these electrons (the band gap is too large). A semiconductor (Figure 1c) is a special case in which the band gap is small enough that electrons in the valence band can jump into the conduction band using thermal energy. That is, heat in the material

A conventional tube amplifier, at left, and a solid-state memory cell, at right. The size of such semiconductors allows for the manufacturing of smaller devices.

Figure 1. Schematic of the electronic band structures of different types of solids. Electrons are represented by shaded areas.



(even at room temperature) gives some of the electrons enough energy to travel across the band gap. Thus, an important property of semiconductors is that their conductivity increases as they are heated up and more electrons fill the conduction band. The most well-known semiconductor is silicon (Si), although germanium (Ge) and gallium arsenide (GaAs) are also common.

dope: to add a controlled amount of an impurity to a very pure sample of a substance, which can radically change the properties of the substance

To complete the development of semiconductor theory, the concept of **doping** must be described (see Figure 2). In principle, the idea is to introduce a different kind of atom into a semiconductor in order to modify its electronic structure. Consider, for example, adding a small amount of phosphorus, P, into a silicon host. Phosphorus is one column to the right of silicon in the Periodic Table, so it contains one additional electron. This means that doping P into Si has the effect of introducing additional electrons to the material, such that some e^- must go into the conduction band. Because extra negatively charged electrons are added to the system, phosphorus-doped Si is called an *n*-type semiconductor, and phosphorus is described as a donor (of electrons). Similarly, a *p*-type semiconductor can be fabricated by adding an element to the left of Si in the Periodic Table. Boron, B, is a common dopant for a *p*-type. In this case, the valence band will be missing electrons. These empty locations in a *p*-type semiconductor are also referred to as holes. Since holes represent the absence of an electron, they carry a positive charge. In *p*-type semiconductors, boron is referred to as an acceptor (of electrons). From Figure 2, it can be seen that both *n*- and *p*-type materials create partially filled bands, allowing for electrical conduction. Dopant concentrations are fairly small, around 10^{16} atoms/cm^3, constituting only about ten-billionths of the total mass of the material.

If *p*- and *n*-type materials are layered together, a *p-n* junction results (Figure 2c). Right at the interface, some of the excess electrons from the *n*-type combine with holes from the *p*-type. The resulting charge separation creates an energy barrier that impedes any further movement of electrons. In most technological applications, the important properties of semiconductors are the result of the band structure of the *p-n* junction. A single

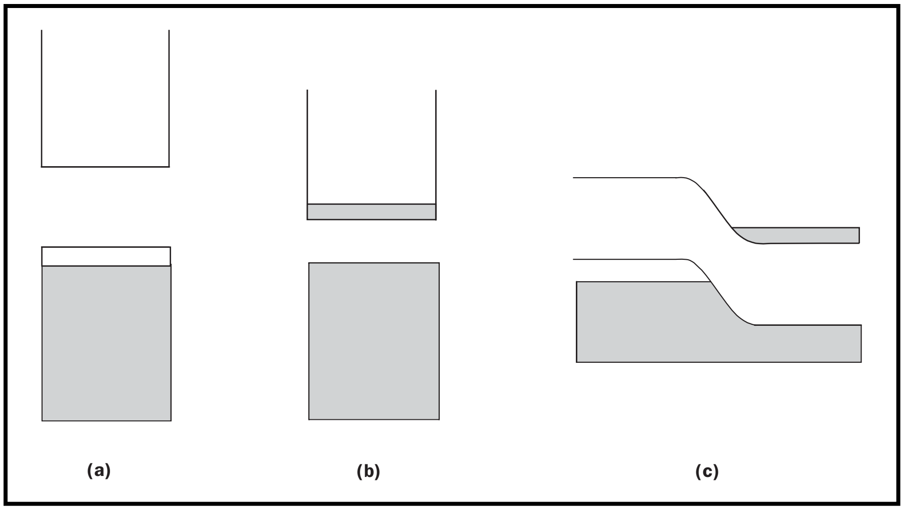


Figure 2. Schematic diagrams of the band structures of (a) *p*-type semiconductors, (b) *n*-type semiconductors, and (c) a *p*-*n* junction.

junction based on the same host material (e.g., one interface of *p*- and *n*-doped silicon) is called a homojunction. The homojunction model is used here to describe the properties of many devices that are based on semiconductors. However, it should be noted that real systems are typically composed of multiple *p*-*p*, *n*-*n*, and *p*-*n* junctions, called heterojunctions. Such configurations greatly improve the performance of these materials; in fact, the development of heterojunction devices was critical to the widespread practical application of this technology.

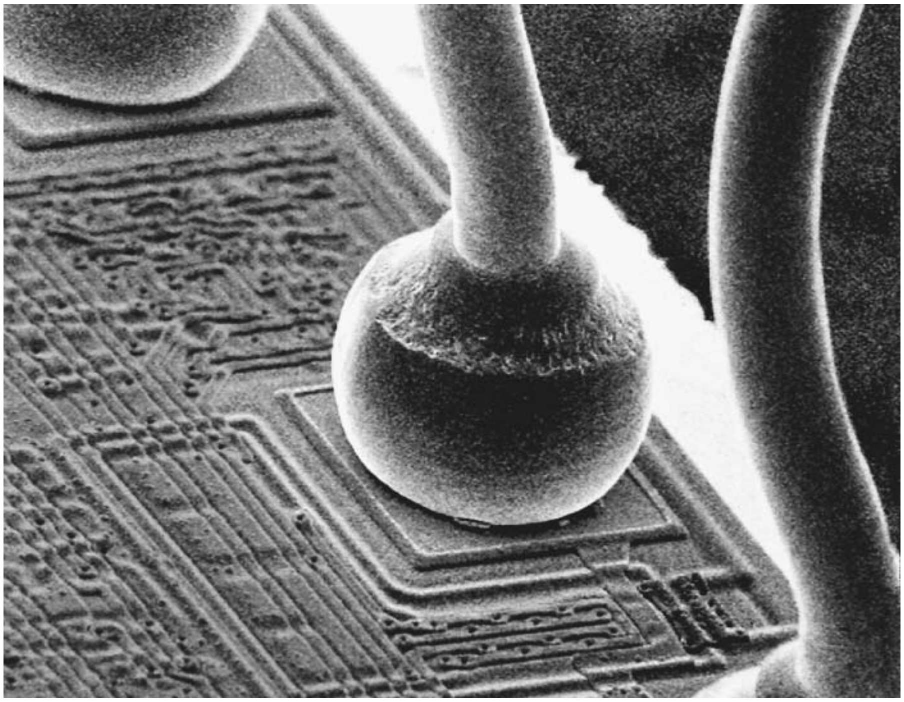
Semiconductors in Electronics

Semiconductors are used extensively in solid-state electronic devices and computers. The majority of materials for these applications are based on doped silicon. An important property of *p*-*n* junctions is that they allow electron flow only from the *n* side to the *p* side. Such one-way devices are called diodes. Consider Figure 2c again. If a positive voltage (also called a forward bias) is applied that lowers the energy barrier between *n* and *p*, then the electrons in the conduction band on the *n* side can flow across the junction (and holes can flow from *p* to *n*). A reverse bias, however, raises the height of the barrier and increases the charge separation at the junction, impeding any flow of electrons from *p* to *n*.

Diodes have several important applications in electronics. The power supplied by most electrical utilities is typically alternating current (AC); that is, the direction of current flow switches back and forth with a frequency of sixty cycles per second. However, many electronic devices require a steady flow of current in one direction (direct current or DC). Since a diode only allows current to flow through it in one direction, it can be combined with a capacitor to convert AC input to DC output. For half the AC cycle, the diode passes current and the capacitor is charged up. During the other half of the cycle, the diode blocks any current from the line, but current is provided to the circuit by the capacitor. Diodes applied in this way are referred to as rectifiers.

The by far most important application of semiconductors is as logic gates and transistors in computers. Logic gates, such as OR and AND gates, take advantage of the one-way nature of diodes to compare the presence or

Micro-wires bonded on a silicon chip.



absence of current at different locations in a circuit. More complex solid-state transistors are composed of *npn* or *pnp* junctions. The device geometry is slightly more complicated than that observed in a diode, but the result is materials that allow for the generation of the zeros and ones required for the binary logic used by computers.

Optoelectronic Devices

Optoelectronic materials are a special class of semiconductors that can either convert electrical energy into light or absorb light and convert it into electrical energy. Light-emitting diodes (LEDs), for example, are commonly used for information display and in automotive interior lighting applications. In an LED, a forward bias applied across the junction moves electrons in the conduction band over holes in the valence band. The electron and hole combine at the junction, and the energy created by this process is conserved via the emission of light (Figure 3a). The wavelength of emitted light will depend on the band gap of the material; larger band gaps lead to shorter wavelengths of light. Only certain kinds of semiconductors, called direct gap semiconductors, exhibit this behavior. GaAs is an example of a direct gap semiconductor used in these applications. Silicon is an indirect gap material, and electrons and holes combine with the generation of heat instead of light.

A diode laser operates in essentially the same fashion as an LED. Two additional requirements must be met for a direct gap semiconductor to be an efficient laser. The first is that larger forward bias currents are needed for a laser than for an LED, because lasers require a higher degree of population inversion—a large number of electrons in the conduction band above empty levels in the valence band. Lasers also require an optical cavity; light bounces back and forth within the cavity, building up intensity. In a diode

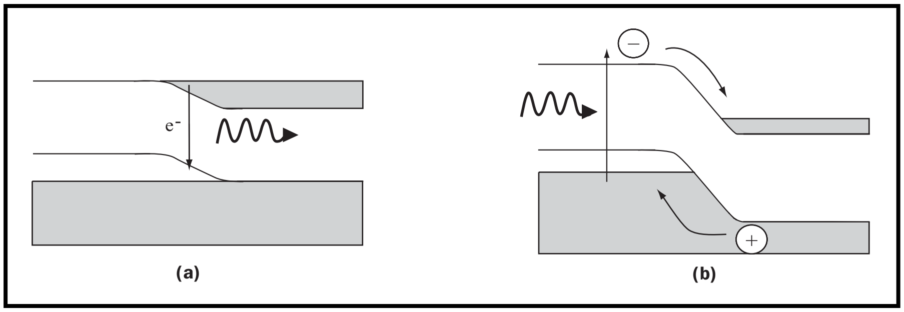


Figure 3. Principle of operation of (a) a light-emitting diode or diode laser and (b) a photodetector or solar cell.

laser, this can be achieved by cleaving and polishing opposite faces of the diode. The smooth faces act like partially reflecting mirrors. This kind of laser is used to read information on compact disks and is also used in laser pointers.

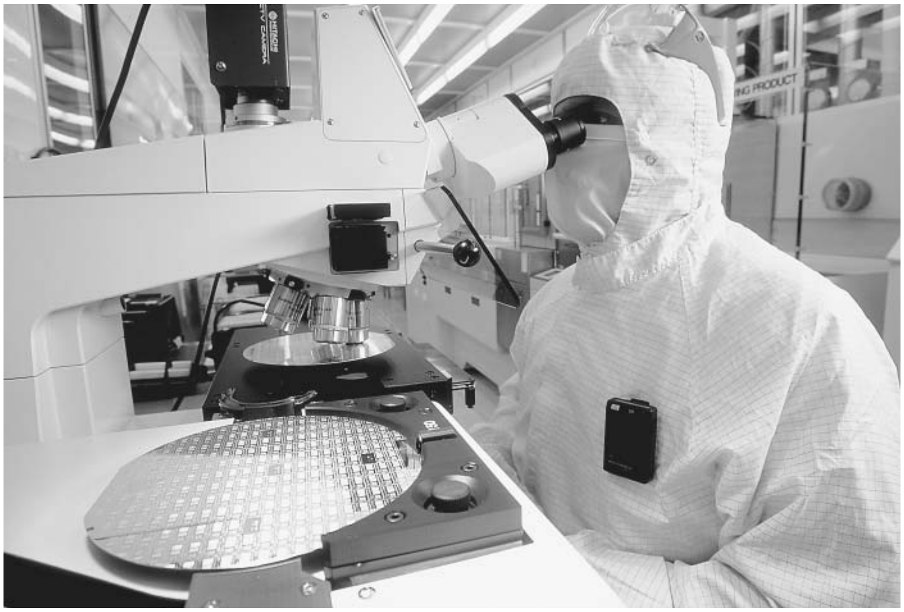
The most common materials for lasers and LEDs are heterojunctions based on GaAs. More complex systems containing Ga, As, P, Al, and N are also used. The band gap of these materials can be tailored to create emission from infrared to yellow. In optical data storage systems, such as compact disks, the amount of information that can be stored is dependent in part on the wavelength of light being used to read the disk—shorter wavelengths allow for denser information storage. Thus, there has been considerable interest in developing larger band gap LEDs and lasers that emit in the blue. This has been achieved in semiconductors based on GaN (gallium nitride). Further refinement of these materials will no doubt lead to significant advances in optoelectronic technology in the coming years.

A final important class of optoelectronic devices based on semiconductors is photovoltaics, such as photodetectors and solar cells. In some respects, these can be regarded as LEDs operating in reverse. Light energy incident on the *p*-*n* junction is absorbed by an electron, which then jumps to the conduction band (Figure 3b). Once in the conduction band, the electron travels downhill (energetically) to the *n* side of the junction, with a hole migrating to the *p* side. This creates a flow of current that is the reverse of what is seen in a forward biased diode. The result is the conversion of light energy to electrical energy. These devices can therefore be used to detect light, as in digital imaging systems or miniature cameras; or the electrical energy can be stored, as in solar cells. Commercial photovoltaics are based on a variety of host materials, including Si, AlGaAs, and InAlAs.

Fabrication

The industrial fabrication of semiconductors can be extremely complex, involving high-purity materials, sophisticated equipment, and hundreds of steps. Most processes begin with the growth of a large single crystal of *n*-type Si, called a wafer. A dopant (e.g., phosphorus) is added to high-purity molten silicon, and a crystal is then slowly extracted from this melt. The polished wafer is 20 to 30 centimeters (7.9–11.8 inches) in diameter.

The rest of the processing will depend on the nature of the device being produced. A simple *p*-*n* junction is usually fabricated via photolithography and etching processes. In this method, a layer of silicon dioxide, SiO_2, is created on the surface of the wafer by heating it in the presence of



A worker is testing silicon wafers at the Matsushita Semiconductor plant in Puyallup, Washington. Semiconductors are used in many different electronic products, such as computers, lasers, and solar panels.

oxygen. Some of the SiO_2 is then chemically stripped away, or etched, exposing only a portion of the Si wafer. This exposed part of the wafer is made into *p*-type material by bombarding it with boron ions. As these ions diffuse into the Si wafer, *p*-type Si is formed. Since the original wafer was *n*-type, a *p-n* junction forms where the diffusion of boron stops. Metal contacts can then be added to each side of the junction to create a simple homojunction device.

Fabrication of more complicated devices is achieved via combinations of etching, deposition, and ion implantation steps. In the production of integrated circuits for computers, about 400 chips can be synthesized on a single 30-centimeter (11.8-inch) wafer. Each chip may contain as many as 50 million transistors in a space barely more than 1 centimeter (0.39 inches) on a side—a truly remarkable technological achievement. As faster and faster systems are developed, the demand for smaller and smaller features increases. Such miniaturization is the most significant challenge facing the semiconductor industry today.

Semiconductors are used in a wide variety of electronic and optoelectronic applications. The useful properties of semiconductors arise from the unique behavior of doped materials, the special control of electron flow provided by *p-n* junctions, and the interaction of light energy with electrons at these junctions. The industry continues to grow, and research in this and related areas (i.e., organic semiconductors and molecular transistors) is occurring at academic institutions around the world. SEE ALSO GERMANIUM; SILICON.

Anthony Diaz

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Silicon

14
Si
SILICON
28.086

MELTING POINT: 1,410°C
BOILING POINT: 2,355°C
DENSITY: 2.329 g/cm^3
MOST COMMON IONS: Si^{4+}, $H_3SiO_4^-$, $H_2SiO_4^{2-}$, $HSiO_4^{3-}$, SiO_4^{4-}

Silicon is the second most abundant element in Earth's crust and mantle, after oxygen. It is the seventh most abundant element in the universe. It was first obtained in elemental form by Jöns Jakob Berzelius in 1823, from reduction of a complex fluoride, K_2SiF_6, by potassium. It has a strong chemical affinity for **electronegative** elements such as oxygen and fluorine. It is always found in nature in bound form, as the oxide, SiO_2, or in silicate minerals such as olivine, $(Mg,Fe)_2SiO_4$. The principal hydride is silane (SiH_4), a pyrophoric gas, and the halides (e.g., SiF_4, $SiCl_4$) are gases or liquids. Silicate minerals form in a wide variety of crystallographic structures, i.e., a mineral's internal (repeating) structure; many of these minerals are important ceramics (e.g., heated mica produces clays used in pottery; calcium silicates are the primary components of cement). Amorphous (noncrystalline) silicates form glasses used in windows and containers. Silicon nitride, Si_3N_4, is an important ceramic used in turbine engines. Silicon carbide, SiC, is an ultrahard solid used in abrasives.

electronegative: capable of attracting electrons

Silicon is extracted from quartz (SiO_2) sand by high temperature reduction with carbon. The crystalline element is a shiny gray semiconducting solid with the tetrahedral diamond structure. Usually **doped** with boron, **arsenic**, or phosphorus, it conducts electricity via the diffusion of electrons or positive "holes" (electron vacancies). Polymorphs of silicon formed under high pressure conditions are metallic and contain **octahedral** silicon; the liquid is metallic also. Amorphous silicon formed by vapor **phase** decomposition of silane is used to transform light into electricity in solar cells. Silicones (organic silicon compounds containing Si-O-Si linkages) are prepared from silane, silicon halides, or **metal**-Si **alloys** by hydrolysis of the silicone material to give oils, greases, synthetic rubbers, and adhesives. SEE ALSO SEMICONDUCTORS; SOLAR CELLS.

Paul F. McMillan

dope: to add a controlled amount of an impurity to a very pure sample of a substance, which can radically change the properties of the substance

arsenic: toxic element of the phosphorus group

octahedral: relating to a geometric arrangement of six ligands equally distributed around a Lewis acid; literally, eight faces

phase: homogeneous state of matter

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

alloy: mixture of two or more elements, at least one of which is a metal

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Silicone

The term "silica" denotes the compound silicon dioxide, SiO_2. It is a ubiquitous chemical substance with rich chemical, geological, and commercial importance. Commercially, it has many uses, and it is the only source of elemental silicon.

The Evolution of Silicones

Silicon is a member of the Group IV elements in the Periodic Table. However, little of the chemistry of silicon can be inferred from carbon, one of its closest neighbors. Although silicon is the second most abundant element in Earth's crust (approximately 26%), it does not exist in nature as a free element. Silicon must be freed from its oxides through a chemical process known as carbothermic reduction. In this reaction, silica and a carbon source (generally wood) are heated together at extremely high temperatures to yield silicon in its elemental form. The Swedish chemist Jöns Jakob Berzelius (1824) was the first to isolate silicon from its natural matrix. Silicon is widely used in the electronics and chemical industries.

Silanes, siloxanes, and silicones are commercially produced from silicon and methyl chloride in a process known as the "direct reaction" or the "Rochow-Muller direct process."

$$\mathrm{Si} + (\text{excess})\ \mathrm{CH_3Cl} \rightarrow (\mathrm{CH_3})_x\mathrm{SiCl}_{(4-x)}$$

This reaction yields methylchlorosilanes (silicon compounds containing both methyl groups and chlorine). They are distilled (purified), and the isolated dimethyldichlorosilane is hydrolyzed to give siloxanes and silicones. This product can be formulated or finished into thousands of different products, which are sold to every major industrial segment. Although the direct reaction is used to commercially produce silicon-based materials today, the first example of an organosilicon compound (a material containing a silicon-carbon bond) was described in 1863 (as the U.S. Civil War raged and author Mark Twain was just beginning his literary career). French chemist Charles Friedel and U.S. chemist James Mason Crafts are credited for not only making the first compound that contained a silicon-carbon bond, but also determining the molecular weight of silicon during their years of research in this area of chemistry. By the turn of the twentieth century English chemist Frederic Stanley Kipping began to investigate this new area of science, publishing fifty-four papers on the subject between 1899 and 1937, but he failed to foresee the potential commercial value of his work. In one publication, he actually referred to the products from his work as "uninviting oils and glues."

In 1930 chemist J. Franklin Hyde, called the "father of silicone chemistry," met with Eugene Sullivan, vice president and director of research at Corning Glass Works. Sullivan was worried about the emerging plastics industry and its potential for competitive advantage over glass. Sullivan believed that it might be possible to combine the advantages of glass with some of the superior properties of organic plastics to produce a hybrid material. The idea was radical, but Hyde took Sullivan's idea for an inorganic-organic hybrid and used it as the foundation for what is now an $8 billion global industry, organosiloxanes. Hyde recognized the commercial importance of some of Kipping's observations and applied them to forge his

PUTTY WARS

Bouncing Putty, later sold as Silly Putty®, is an example of a silicon-based material with very unusual properties. It is a liquid that behaves as a solid or a solid that acts like a liquid. The material is a mixture of silicone polymers and boric acid. The polymers are terminated (end group) at both ends with an alcohol group (-OH) in contrast to the typical methyl group (-CH_3). The polymer ends (-OH) and the boric acid react with each other in a reversible fashion. This reversible reaction allows Silly Putty® to be a very thick viscous liquid because bonds between the polymers and the boric acid are constantly being formed and broken. Stress (pulling the material sharply or striking it against the table) interferes with the reverse reaction, and the material behaves as a solid until the stress has been removed. The identity of the person who really invented bouncing putty is still debated today. R. R. McGregor and E. L. Warrick hold the U.S. Patent (2,431,878) that was issued in 1947 to Dow Corning Corporation. However, James Wright, an engineer for General Electric, has claimed that he conducted the initial experiments in 1943 that led to Silly Putty®'s discovery. The truth is that neither company could find a good use for the interesting material. Silly Putty® was brought to commercial success by Ruth Fallgatter (owner of the Block Shop toy store in New Haven, Connecticut) and her marketing consultant (Peter Hodgson of Marketing, Inc.) around 1950, with General Electric being the sole supplier of the material until 1959. Silly Putty® remains a wonderful curiosity to all who handle the "liquid solid." It has been to the Moon (aboard *Apollo 8*) and was commemorated in a Smithsonian exhibit devoted to significant objects from the 1950s that shaped American culture.

hybrid technology. The Dow Corning Corporation was thus formed; at Dow the first commercial "silicones" were produced.

Silicones

Silicones (or silicon-based materials) are an integral part of daily life. These materials make our denim clothing feel softer; they help our hair to shine and our skin to feel silky. Silicon-based materials are used in our food and drink to control foam. They lubricate and protect critical surfaces. They can be found in automobiles, buildings, and homes. These materials allow for the construction of skyscrapers as well as seal our aquariums and bathtubs. Have you ever wondered why you can peel a name tag from its paper backing and it still remains sticky enough to adhere to your clothing? The answer is silicones. Each day, we unknowingly come into contact with scores of products that contain silicones for the very special properties that they possess.

The German chemist Friedrich Wöhler first coined the term "silicone" in 1857. However, his strategy to name silicon-containing materials based on a nomenclature system derived from organic chemistry was lost when the silicon analog to a **ketone** could not be isolated. Today the term is often used as a generic for nearly all substances that contain a silicon atom. However, it is more properly described as an entirely synthetic polymer containing a Si-O backbone. To this backbone, organic groups are attached.

ketone: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the RC(O)R functional group

This general description defines the broad class of polymers known as silicones or silicon-based materials. The most common example is poly(dimethylsiloxane) or PDMS. This polymer has a repeating $(CH_3)_2SiO$ unit.

These materials are the basic building blocks of the silicone industry. Depending on the number of repeat units in the polymer chain and the degree of cross-linking (how the polymer chains are tied together), at least six classes of commercially important families of products can be produced: fluids, emulsions, compounds, lubricants, resins, and elastomers or rubbers.

How Are Silicones Used?

Silicones are highly valued materials because they have a combination of physical properties not found in other polymers. They have outstanding heat stability and can be used in applications where organic materials would melt or decompose. Many silicones seem to be impervious to the effects of aging, weather, sunlight, moisture, heat, cold, and some chemical assaults. Numerous silicones are used to stick, bond, or couple things together.

Unique surface properties further distinguish silicones from other materials. The low surface tension of silicone fluids makes them ideal for applications such as paper release agents, fiber lubricants, textile hand modifiers, mold release agents, antifouling materials, and water repellents. In fact, silicones have been used in foam control and as anticaking aids, corrosion inhibitors, emulsifiers, lubricants, conditioners, and gloss enhancers—all because of their special surface properties. SEE ALSO Polymers, Synthetic.

Thomas H. Lane

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47
Ag
SILVER
107.868

Silver

MELTING POINT: 961°C
BOILING POINT: 2,212°C
DENSITY: 10.53 g/cm^3
MOST COMMON IONS: Ag^+, Ag^{2+}

Silver is a precious **metal** and (like gold and copper) is classified as a coinage metal. The date of its discovery is not known, but it has been identified in jewelry, coins, and religious ornaments dating to more than 2,000 years ago from ancient civilizations in South America, Egypt, Mesopotamia, and China.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

isotope: form of an atom that differs by the number of neutrons in the nucleus

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

Silver exists as two **isotopes**, ^{107}Ag and ^{109}Ag, occurring in similar proportions. It exhibits three valance/**oxidation** states: Ag(I), Ag(II), and Ag(III). The chemistry of silver was not well-known before 1980, although silver nitrate was used medicinally in the 1800s. Recent research has recognized the highly reactive nature of the silver ion and its ability to form numerous inorganic and organic complexes (halide, sulfide, nitrate, oxide, and acetylide compounds, cyano-derivatives, olefin complexes, etc.). Ag(II) complexes are less stable than those of Ag(I) and Ag(III), but unlike many other silver compounds are brightly colored red or blue. Silver ion binds readily to proteins in the human body (including albumins and **metallothioneins**) and interacts with trace metals in metabolic pathways.

Silver is the sixty-third most abundant metal in Earth's crust; the average concentration of silver in water is 0.5 ppb, in soil it is 10 ppb. It is found naturally as native metal or in ores in which it is complexed with lead, copper, tellurium, mercury, **arsenic**, or antimony. Silver is found mainly throughout the Americas, Japan, Australia, and central Europe. Extraction is by **amalgamation** and displacement (using mercury), solution, or **smelting** methods.

Silver is used in the manufacture of photographic film chemicals such as silver nitrate, as an analytic **reagent** in organic chemistry, as a **catalyst** in photo-oxidation reactions, in electrochemical reactions, in **nuclear** magnetic resonance and analyses, and in silver plating.

Medically, silver is used in the manufacture of bone prostheses, cardiac implants and replacement valves, needles used in ocular surgery, peritoneal catheters, and wound sutures. It is an antiseptic ingredient used in wound management (silver nitrate, siler sulfadiazine, and cerium nitrate). A new generation of sustained silver release products is showing promise in the treatment of skin wounds, skin ulcers, and burns; silver ion is released from the dressings (Acticoat™, Actisorb™, etc.) in the presence of wound fluids, exudates, and is "activated." Activated silver ion is toxic to bacteria and yeasts. Silver is used in the making of dental amalgam fillings. Silver exhibits wide-spectrum antibacterial activity; it is toxic to bacteria at low concentrations (10^{-5} to 10^{-7} Ag ions per cell), the so-called oligodynamic effect.

Silver is toxic. Silver nitrate used in antiseptic mouthwashes leads to deposits of silver sulfide in the skin and a slate-gray skin discoloration (known as argyria); argyria is also caused by the colloidal silver used in antiseptics and mouthwashes. Silver absorbed through the skin is deposited in the liver and kidney and complexes with albumin and cellular proteins. Another silver hazard is allergy to silver, occurring as a result of the silver that is used in jewelry, medicinal products, coins, and antiseptics.

Alan B. G. Lansdown

metallothionein: class of low molecular weight proteins and polypeptides with very high metal and sulfur content; thought to play a role in concentration and flow of essential elements (e.g., Cu and Zn) and in ameliorating the influence of toxic elements (e.g., Hg and Cd) in the body

arsenic: toxic element of the phosphorus group

amalgam: metallic alloy of mercury and one or more metals

smelting: process by which ores are reduced in the production of metals

reagent: chemical used to cause a specific chemical reaction

catalyst: substance that aids in a reaction while retaining its own chemical identity

nuclear: having to do with the nucleus of an atom

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Soap

Soaps are cleaning agents that are usually made by reacting alkali (e.g., sodium hydroxide) with naturally occurring fat or fatty acids. The reaction produces sodium salts of these fatty acids, which improve the cleaning process by making water better able to lift away greasy stains from skin, hair, clothes, and just about anything else. As a substance that has helped clean bodies as well as possessions, soap has been remarkably useful.

History of Soap

The discovery of soap predates recorded history, going back perhaps as far as six thousand years. Excavations of ancient Babylon uncovered cylinders with inscriptions for making soap around 2800 B.C.E. Later records from ancient Egypt (c. 1500 B.C.E.) describe how animal and vegetable oils were combined with alkaline salts to make soap.

According to Roman legend, soap got its name from Mount Sapo, where animals were sacrificed. Rain would wash the fat from the sacrificed animals along with alkaline wooden ashes from the sacrificial fires into the Tiber River, where people found the mixture helped clean clothes. This recipe for making soap was relatively unchanged for centuries, with American colonists collecting and cooking down animal tallow (rendered fat) and then mixing it with an alkali **potash** solution obtained from the accumulated hardwood ashes of their winter fires. Similarly, Europeans made something known as castile soap using olive oil. Only since the mid-nineteenth century has the process become commercialized and soap become widely available at the local market.

potash: the compound potassium oxide, K_2O

Chemistry of Soap

The basic structure of all soaps is essentially the same, consisting of a long hydrophobic (water-fearing) hydrocarbon "tail" and a hydrophilic (water-loving) anionic "head":

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2COO^-$$
$$\text{or } CH_3(CH_2)_nCOO^-$$

The length of the hydrocarbon chain ("n") varies with the type of fat or oil but is usually quite long. The anionic charge on the **carboxylate** head is usually balanced by either a positively charged potassium (K^+) or sodium (Na^+) cation. In making soap, triglycerides in fat or oils are heated in the presence of a strong alkali base such as sodium hydroxide, producing three molecules of soap for every molecule of glycerol. This process is called saponification and is illustrated in Figure 1.

carboxylate: structure incorporating the –COO– group

Like synthetic detergents, soaps are "surface active" substances (**surfactants**) and as such make water better at cleaning surfaces. Water, although a good general solvent, is unfortunately also a substance with a very high surface tension. Because of this, water molecules generally prefer to stay together rather than to wet other surfaces. Surfactants work by reducing the surface tension of water, allowing the water molecules to better wet the surface and thus increase water's ability to dissolve dirty, oily stains.

surfactants: surface-active agents that lower the surface tension of water; e.g., detergents, wetting agents

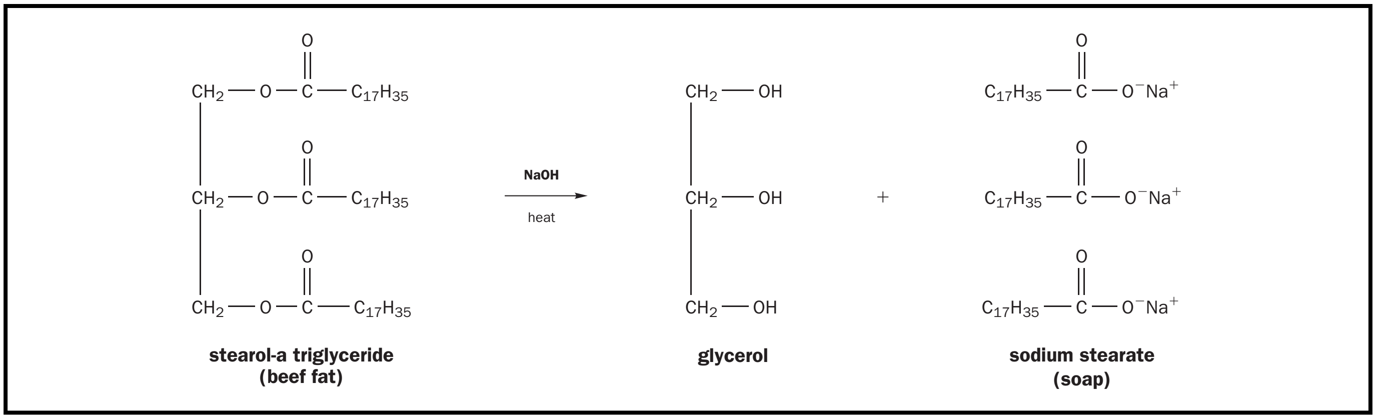

Figure 1.

In studying how soap works, it is useful to consider a general rule of nature: "like dissolves like." The **nonpolar** hydrophobic tails of soap are **lipophilic** ("oil-loving") and so will embed into the grease and oils that help dirt and stains adhere to surfaces. The hydrophilic heads, however, remain surrounded by the water molecules to which they are attracted. As more and more soap molecules embed into a greasy stain, they eventually surround and isolate little particles of the grease and form structures called micelles that are lifted into solution. In a micelle, the tails of the soap molecules are oriented toward and into the grease, while the heads face outward into the water, resulting in an **emulsion** of soapy grease particles suspended in the water.

nonpolar: molecule, or portion of a molecule, that does not have a permanent, electric dipole

lipophilic: a molecule that tends to congregate in solution with lipids—it will be a nonpolar molecule or the nonpolar portion of a molecule

emulsion: immiscible two-phase mixture in which one phase is dispersed (as small droplets) in the other phase

With agitation, the micelles are dispersed into the water and removed from the previously dirty surface. In essence, soap molecules partially dissolve the greasy stain to form the emulsion that is kept suspended in water until it can be rinsed away (see Figure 2).

As good as soaps are, they are not perfect. For example, they do not work well in hard water containing calcium and magnesium ions, because the calcium and magnesium salts of soap are insoluble; they tend to bind to the calcium and magnesium ions, eventually precipitating and falling out of solution. In doing so, soaps actually dirty the surfaces they were designed to clean. Thus soaps have been largely replaced in modern cleaning solutions by synthetic detergents that have a sulfonate ($R\text{-}SO_3^-$) group instead of the carboxylate head ($R\text{-}COO^-$). Sulfonate detergents tend not to precipitate with calcium or magnesium ions and are generally more soluble in water.

Uses of Soap

Although the popularity of soap has declined due to superior detergents, one of the major uses of animal tallow is still for making soap, just as it was in years past. Beyond its cleaning ability, soap has been used in other applications. For example, certain soaps can be mixed with gasoline to produce gelatinous napalm, a substance that combusts more slowly than pure gasoline when ignited or exploded in warfare. Soaps are also used in "canned heat," a commercialized mixture of soap and alcohol that can be ignited and used to cook foods or provide warmth. Overall, soap is a remarkably useful substance, just as it has been for thousands of years.

David A. Dobberpuhl

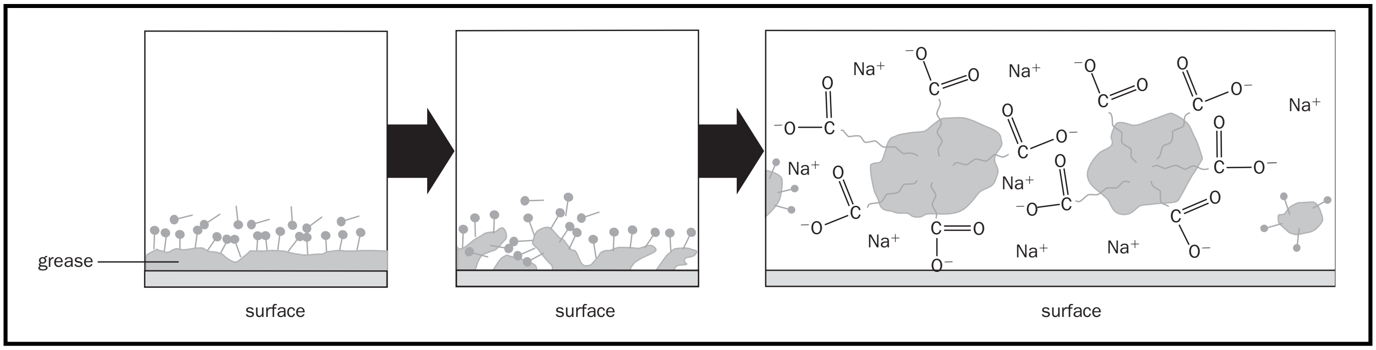

Figure 2. How soap works: The hydrophobic tails of soap molecules embed in grease and oil, breaking it up into particles called micelles that lift off the surface and disperse into water.

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Soddy, Frederick

ENGLISH RADIOCHEMIST
1877–1956

Frederick Soddy, the youngest of seven sons of a London corn merchant, was born on September 2, 1877, in Eastbourne, England. Raised by his half-sister, this precocious scientist attended Eastbourne College (1892–1894) and the University College of Wales, Aberystwyth (1895). In 1895 he won a scholarship to Merton College, Oxford University, from which he graduated with the highest honors in chemistry (1898).

After two years of research at Oxford, Soddy served as a demonstrator (laboratory instructor) at McGill University in Montreal, Canada (1900–1902), where he worked with Ernest Rutherford, studying the gaseous emanation of radium and showing that radioactivity involved the disintegration of radioactive atoms to form new elements. He called the process "transmutation," a term that he borrowed from **alchemy**.

alchemy: medieval chemical philosophy having among its asserted aims the transmutation of base metals into gold

radioactive decay: process involving emission of subatomic particle from nucleus, typically accompanied by emission of very short wavelength electromagnetic radiation

The two proved the existence of two **radioactive decay** series: one starting with uranium and the other with thorium. The final product of both series was lead. They predicted that helium should be the decay product of radium, and they were the first to calculate the tremendous amount of energy that could be evolved during radioactive reactions.

spectroscopy: use of electromagnetic radiation to analyze the chemical composition of materials

Soddy then worked with William Ramsay at University College, London (1903–1904), where they used **spectroscopy** to show that helium was formed during the radioactive decay of radium and that it was also evolved in the decay of radium emanation. From 1904 to 1914 he served as a lecturer in physical chemistry and radioactivity at the University of Glasgow.

α-particle: subatomic particle with 2+ charge and mass of 4; a He nucleus

At Glasgow, Soddy posited his "group displacement law," which stated that the emission of an **α-particle** (a doubly charged particle consisting of two protons and two neutrons, identical to the helium nucleus, He^{2+}) from a radioactive element causes that element to move back two places in the

Periodic Table. In a short letter to the editor of *Nature*, published on December 4, 1913, he first proposed the term ***isotope*** to designate chemically identical elements with different atomic weights (in modern terms, elements with the same atomic numbers but different mass numbers). Isotopes occupy the same place in the Periodic Table.

Soddy wrote and spoke about the practical applications of radioactivity and envisioned **nuclear** energy as the basis for an advanced civilization and as a solution to the increasing depletion of natural resources. His book *The Interpretation of Radium* (1914) inspired H. G. Wells to write his science fiction novel *The World Set Free* (published the same year).

After he left Glasgow, Soddy abandoned his work on radioactivity and no longer followed recent advancements in the field. He developed an interest in financial, economic, social, and political theories, which found no general acceptance, as well as unusual mechanical and mathematical problems.

In 1914 Soddy assumed the chair of chemistry at Aberdeen University, Scotland, but his teaching and research were largely interrupted by World War I. In 1919 he was appointed to the Lee Chair of Chemistry at Oxford University, a post he held until his retirement in 1937. In 1921 Soddy received the Nobel Prize in chemistry "for his contributions to our knowledge of the chemistry of radioactive substances, and his investigations into the origin and nature of isotopes." He died in Brighton, England, on September 22, 1956. SEE ALSO Ramsay, William; Rutherford, Ernest.

George B. Kauffman

English chemist Frederick Soddy, recipient of the 1921 Nobel Prize in chemistry, "for his contributions to our knowledge of the chemistry of radioactive substances, and his investigations into the origin and nature of isotopes."

isotope: form of an atom that differs by the number of neutrons in the nucleus

nuclear: having to do with the nucleus of an atom

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Sodium

MELTING POINT: **97.8°C**

BOILING POINT: **883°C**

DENSITY: **0.971 g/cm^3**

MOST COMMON IONS: **Na^+**

11

Na

SODIUM

22.989770

Sodium is a soft, silvery alkali **metal** and reacts vigorously with water to generate hydrogen gas. The word *sodium* is derived from "sodanum" (a Medieval Latin name for a headache remedy), and "natrium" (Latin for "soda") is the origin of the element's symbol. Humphry Davy isolated the element in 1807 via the electrolysis of caustic soda, NaOH. Currently, sodium metal is obtained from the electrolysis of a molten mixture of sodium chloride and

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Water and sodium acetate mixing causes a hot pack to release heat. Hot packs are used to relieve stiffness and pain.

calcium chloride (in an electrochemical cell called the Downs cell). In nature it is never found in its elemental form, but sodium compounds are quite common. Sodium is the most abundant alkali metal and the seventh most abundant element in Earth's crust (22,700 ppm). Sodium burns yellow-orange in the flame test.

The demand for metallic sodium is declining. Its primary use had been as a substance used in the production of tetraethyl lead, an antiknocking gasoline additive; however, because of its damaging effects on the environment, tetraethyl lead is being phased out. Sodium is used to produce sodamide from reaction with ammonia and to reduce $TiCl_4$, $ZrCl_4$, and KCl to Ti, Zr, and K, respectively. An **alloy** of Na and K is used in **nuclear** reactors as a heat transfer agent.

alloy: metallic mixture of two or more elements, at least one of which is a metal

nuclear: having to do with the nucleus of an atom

Several sodium compounds are economically important. NaCl (ordinary salt) is a de-icing compound, a condiment, and a food preservative. NaOH finds use in the manufacture of soaps, detergents, and cleansers. Na_2CO_3 (washing soda) is used to make glass, soaps, fire extinguishers, and "scrubbers" that remove SO_2 from gases generated in power plants before it escapes into the atmosphere. The paper industry uses Na_2SO_4 (salt cake) to make brown wrapping paper and corrugated boxes.

Appropriate sodium ion levels (along with potassium levels) are essential for proper cell function in biological systems. SEE ALSO ALKALI METALS.

Nathan J. Barrows

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Solar Cells

A solar cell is, in principle, a simple semiconductor✷ device that converts light into electric energy. The conversion is accomplished by absorbing light and ionizing crystal atoms, thereby creating free, negatively charged electrons and positively charged ions. If these ions are created from the basic crystal atoms, then their ionized state can be exchanged readily to a neighbor from which it can be exchanged to another neighbor and so forth; that is, this ionized state is mobile; it behaves like an electron, and it is called a hole. It has properties similar to a free electron except that it has the opposite charge.

✷Solar cells can be made from single crystals, crystalline and amorphous semiconductors. For simplicity this article begins with a description of crystalline material.

Each photon of the light that has a high enough energy to be absorbed by the crystal's atoms will set free an electron hole pair. The electron and hole are free to move through the **lattice** in a **Brownian motion**; however, on average they will never move too far from each other. When the electron comes too close to a hole during their Brownian motion, they will recombine. On the other hand, when they experience an electric field, this will tend to separate the electrons from the holes; the electrons will drift toward the positive pole (the anode), and the positively charged holes will drift toward the cathode. Recombination will then take place in the external circuit (within the electric wires). Consequently a current will flow. Since it is generated by photons, one speaks of a photo current. And the semiconductor that performs this effect is called a photo conductor. Photo conductors are passive devices. They react to light by changing their electric conductivity. In order to activate them an external electric power source, such as a battery, needs to be supplied to draw a current that increases with increasing light intensity. There are many photo conductor devices in our surroundings; as for example, in cameras, in streetlight controls to switch the lights off at dawn and on at dusk, or for light barriers in garage door safety controls.

lattice: systematic geometrical arrangement of atomic-sized units that describe the structure of a solid

Brownian motion: random motion of small particles, such as dust or smoke particles, suspended in a gas or liquid; it is caused by collisions of the particle with gas or solvent molecules, which transfer momentum to the particle and cause it to move

However, if an electric field is incorporated into the semiconductor, it will separate the electrons and holes. The part of the crystal that accumulates the electrons will be negatively charged; the part that accumulates the holes will be positively charged. The resulting potential difference, referred to as an open circuit, can be picked up by an electrometer. When electrodes are provided at both sides, a current can flow between them. The crystal, when exposed to sunlight, acts as a battery and becomes a solar cell (see Figure 1).

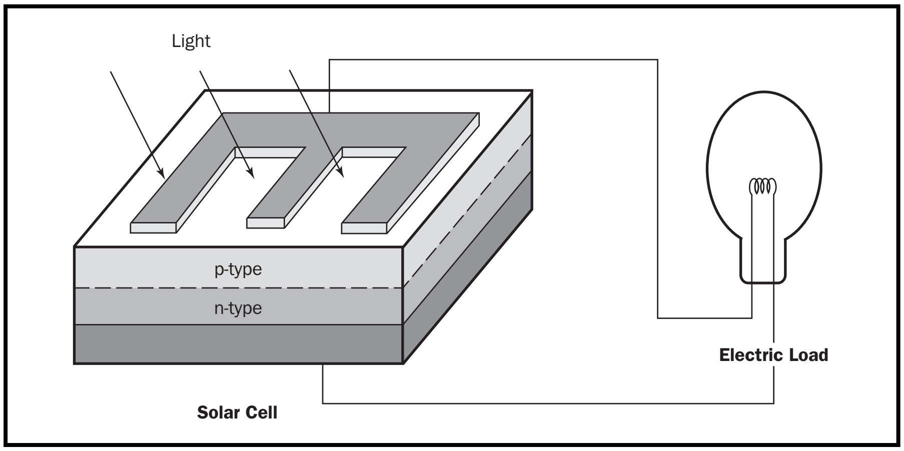


Figure 1. Schematics of a typical solar cell with light falling through an electrode grid onto a semiconductor sheet containing a *pn* junction that separates electrons and holes that flow to the respective electrodes and create a current through an external circuit.

Such a built-in field is easily created in certain semiconductors that can dissolve a *small quantity* of different impurities; can donate a free electron, called a donor; and can also accept an additional electron, called an acceptor. When dissolving these impurities (called doping) separately in different parts of the crystal, the region that contains donors is called the *n*-type region, the region with acceptors is called the *p*-type region. Between these two regions lies an *np* junction. This region represents the built-in field, since the *n*-type region is negatively charged compared to the *p*-type region. Here electrons that are created by light can be separated from the accompanying holes, with the electrons moving into the attracting *p*-type region and the holes moving preferably into the *n*-type region.

This, in principle, describes the essentials of a solar cell. The following portions of the article deal with each part of the solar cell in more detail, present a quantitative description of its performance, indicate performance limitations (called the "efficiency" of the solar cell), and give a variety of solar cell materials with comparative performance.

The *pn* Junction

The *pn*-junction can be easily understood in the band model with the conduction band populated by free electrons and the valence band populated by free holes. Without light, these carriers are created in thermodynamic equilibrium by donors and acceptors respectively. Mathematically their concentration is given by the Fermi-function (Eq.1)

$$n \approx N_C \exp -\left(\frac{E_C - E_F}{kT}\right) \tag{1}$$

with the determining Fermi level E_F , in the *n*-type region lying essentially in the middle between the donor level and the lower edge of the conduction band, E_c. N_c is the effective density of states at the lower edge of the conduction band and is on the order of 10^{19} cm^{-3}. A similar equation holds for the density of holes; here the Fermi level lies between the acceptor level and the upper edge of the valence band (see Figure 2a).

In thermodynamic equilibrium the Fermi level is horizontal throughout the crystal, thereby forcing both conduction and valence bands to bend, creating the *pn*-junction (see Figure 2b). Electrons from the *p*-type region will thereby "roll down" the hill and holes from the *n*-type region will "bubble up" the slope; hence both will be separated until their charge will force a reduction potential barrier so that the thermal motion across the junction will become equal from the left and from the right.

With light, additional carriers are created, hence equation 1 needs to be modified, replacing E_F with E_{Fn} or E_{Fp}, the two quasi-Fermi levels in the *n*-type or *p*-type region respectively. These quasi-Fermi levels are now split; the higher the light intensity the more they split. Close to the electrode both quasi-Fermi levels collapse toward the majority quasi-Fermi level, where they are connected to the metal Fermi level (Figure 3). This shift of the Fermi levels in the electrodes represents the open circuit voltage that can be approximated by the shift of the minority quasi-Fermi levels (Figure 3):

$$V_{oc} \approx E_{Fn}(p) - E_{Fp}(n) \tag{2}$$

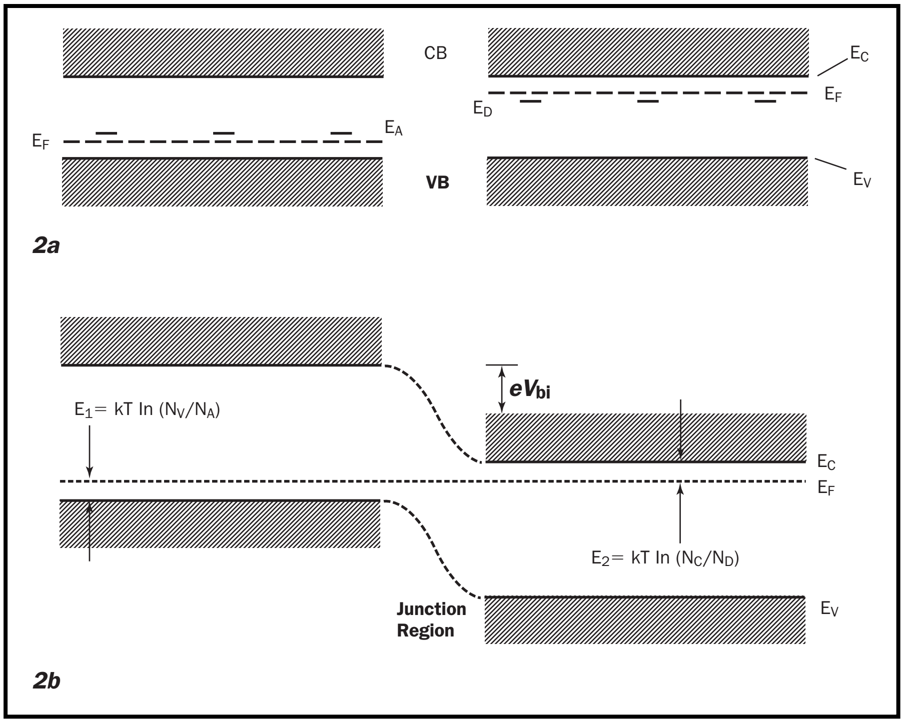


Figure 2a. Band picture with conduction band (CB) and valence band (VB) in an *n*- and a *p*-type region with the Fermi level E_F identified, which usually lies close to the donor-(E_D) or acceptor level (E_A) respectively. Figure 2b. A *pn* junction when both regions are joined resulting in the junction region with a barrier height of eV_b; of the built-in electric field.

Current-Voltage Characteristics

Materials with a *pn*-junction show a nonlinear, rectifying characteristic, since it is much easier to move electrons from the electrode through the *p*-type region and through the junction than from the *n*-type region over the junction barrier into the *p*-type region. The current-voltage characteristic through a *pn*-junction is given by the typical diode equation:

$$j = j_o\,[\exp\left(\frac{eV}{kT}\right)-1] \tag{3}$$

as shown as the dark current curve in Figure 4.

When the device is exposed to light, the additional carriers cause an increased current, recognized by an essentially parallel shift of the characteristic downward by j_L, shown in Figure 4. (For a more precise discussion see Böer, 2002.)

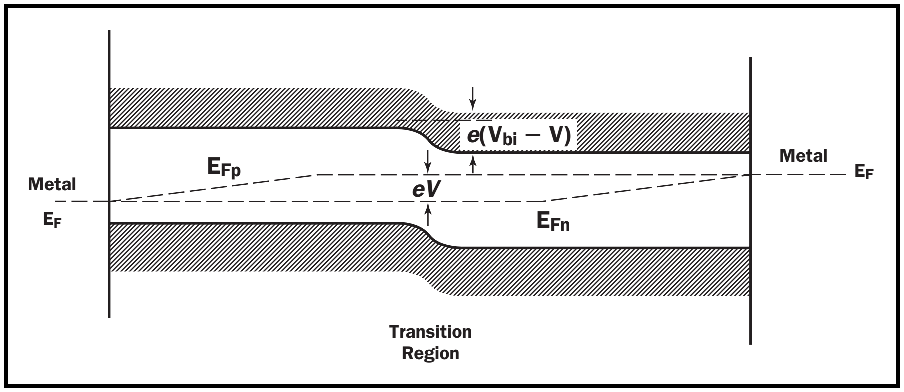


Figure 3. A *pn* junction with light, showing the quasi-Fermi levels and their connection to the electrodes, with V the applied voltage and V_{bi} the built-in voltage. Close to the metal surface enhanced surface recombination will cause both quasi-Fermi levels to collapse.

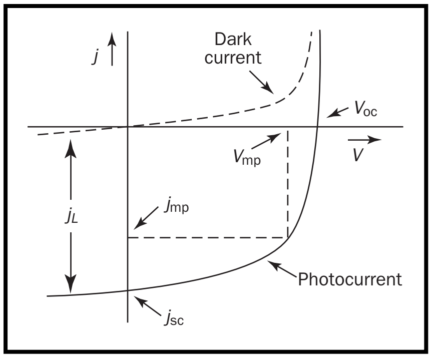


Figure 4. Current-voltage characteristics. Dark current (dashed) and photo current (solid); (the shift from the dark current is shown j_L) indicating open circuit voltage and short circuit current. The inscribed maximum rectangle represents the maximum power point voltage and current.

The photovoltaic characteristic is consequently given by (see, e.g., Fahrenbruch and Bube 1983):

$$j = j_o\,[\exp\left(\frac{eV}{kT}\right) - 1] - j_L \tag{4}$$

j_L is the maximum current obtained in short-circuiting the device. With $j_0 << j_L \sim j_{SC}$ one obtains for the open circuit voltage (when $j = 0$) from Eq. 4:

$$V_{oc} \approx \frac{kT}{e}\ \ln\left(\frac{j_L}{j_o}\right) \tag{5}$$

Whenever the current-voltage characteristic extends into the fourth quadrant, electric power can be extracted. Its maximum value is given by the largest rectangle that can be inscribed in the characteristic (Figure 4). This identifies the maximum power current, j_{mp} and the maximum power voltage $V_{mp.}$ The ratio of the products of these maximum power points to the products of the short circuit current and open circuit voltage is called the fill factor, which can be approximated for ideal solar cells by (see, e.g., Green 2001):

$$FF = \frac{V_{mp}\,j_{mp}}{V_{oc}\,j_{sc}} \approx \frac{\nu_{oc} - 1\mathrm{n}(\nu_{oc} + 0.72)}{\nu_{oc} + 1} \tag{6}$$

with $v_{oc} = V_{oc}/(kT/e)$. The actual fill factor is usually somewhat smaller and is a measure of the quality of the solar cell. It is a function of the diode doping and of solar cell materials.

The net carrier transport in a solar cell can be pictured as shown in figure 5, with light (*hv*) coming from the left and generating (g_0) electron hole pairs in the *p*-type front layer (of thickness *d*). The electrons move towards and through the junction, the holes in opposite direction. When both are shown as electron current (the arrow head is inverted for holes) one visualizes the continuity of the carrier flow and its building up with increasing depth of the front layer.

Solar Cell Materials

A wide variety of materials have the potential of yielding solar cells; several are considered attractive candidates for reasons of high conversion efficiency and ease of fabrication.

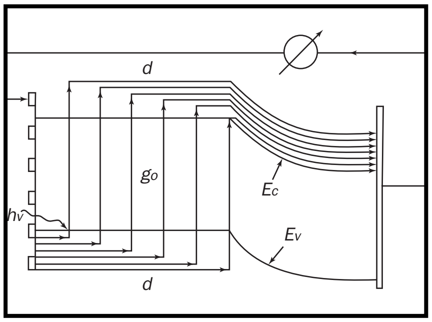


Figure 5. Generation of electron hole pairs and their motion to the respective electrodes.

For a solar cell one can select a single semiconductor having a junction, usually referred to as homojunction, or a combination of two materials, with the junction at the interface referred to as heterojunction. The selected material needs to match the solar spectrum; i.e., it has to absorb most of the spectrum for maximizing the short circuit output, therefore it has to have a low band gap. However, this is counteracted by the desire to also have a large open circuit voltage, requiring a larger band gap and forcing a compromise. Consequently, for homojunction materials a band gap between 1 and 1.5 eV is preferred.

Typical representatives of this class of homojunction semiconductors are Si; several III-V compounds, most prominently GaAs; and from the class of II-VI compounds CdTe, since it can be doped *p*- and *n*-type, while others cannot. Several ternary compounds are also used, most prominently $CuInSe_2$ and similar ternaries. An example for a heterojunction cell is the CdS/CdTe combination (Meyers and Birkmire, 1995). For more details see Green (2001).

These materials can be employed as single crystals (Si and GaAs), as polycrystals (Si), other thin-film materials (CdTe and all ternaries), and as amorphous material (a-Si:H). Single crystals have the advantage of having high crystal quality and a minimum density of recombination centers; therefore they have a high carrier lifetime that is essential for the carriers to reach the junction after generation, in order to be separated and to contribute to the current.

Other factors that influence the output of solar cells are degradation of surfaces and of electrodes; the first causes a reduction of carrier lifetime, the second causes a reduction in solar cell life expectancies. An example of the first is the beneficial effect of a natural oxide layer that reduces surface recombination of Si solar cells, while special efforts need to be made for GaAs cells to passivate the surface. An example for the second effect is the CdTe solar cell, which has difficulties maintaining stable electrodes on the *p*-type side.

Optimization of Photon Absorption

In order to make maximum use of the impinging photons and obtain maximum solar cell output, one has to maximize surface penetration, minimize reflection, and reduce obstacles, such as electrodes.

A typical example for such optimization is the structure (shown in Figure 6) developed by Martin Green and his group in order to produce highly-efficient Si solar cells. In addition to an anti-reflecting coating, it contains an etched pyramidical surface that permits light capture (velvet effect) by multiple reflections downward. It also reduces the surface cover of electrodes that are of sufficient thickness to carry the current by depositing it vertically into narrow grooves. It also minimizes the probability of both types of carriers reaching the same electrode by providing a repulsive field through strong doping of a thin surface layer.

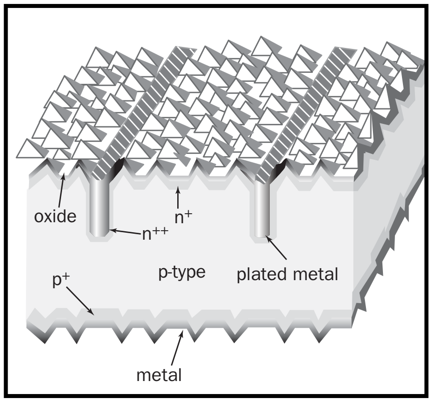
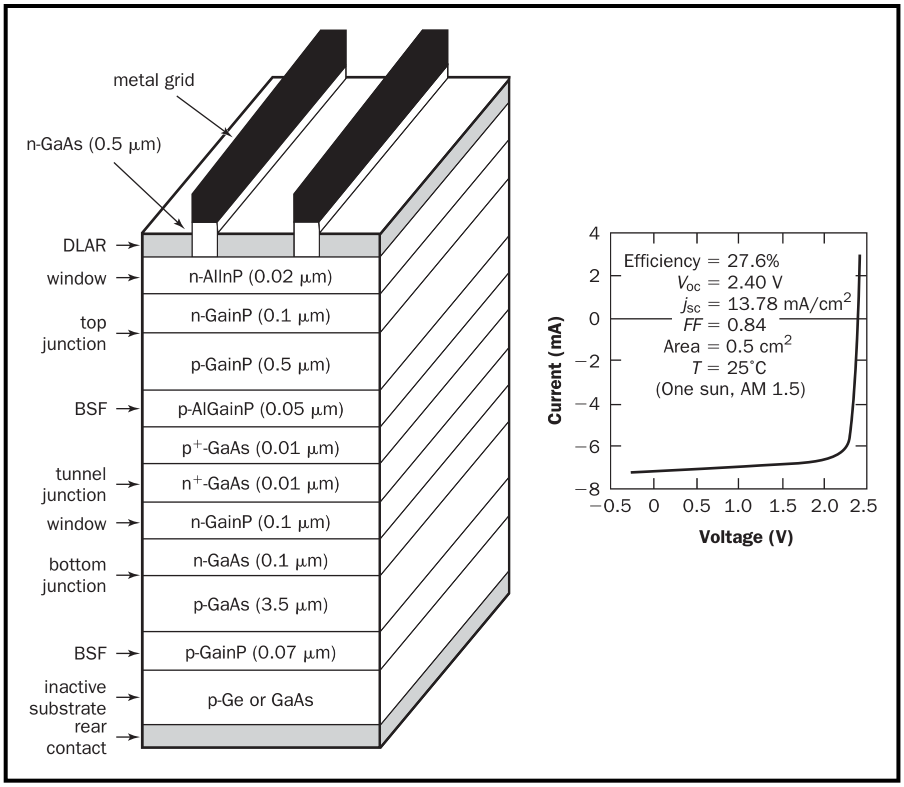


Figure 6. Solar cell that optimizes light penetrations through the surface by anti-reflecting coating and pyramidal surface shaping, as well as using buried contacts that minimize surface obstruction while still providing sufficient electrode cross section to carry the current. (See Green, 2001.)

Solar Cell Efficiency

Solar cell efficiency is a most valuable measure of its performance. With sunlight impinging from the zenith on a sunny day, a surface perpendicular to the light receives about 1 kW/m^2. When converted by a solar cell of 10 percent efficiency (presently reached or exceeded by most commercially available solar panels), this means that 100 W/m^2 in electrical energy can be harvested. This is sufficient if surface areas are ample and the panels are relatively inexpensive. However, where surface areas are at a premium—e.g., on top of a solar car or in some satellites—it is essential to use more efficient solar cells. These are available from carefully engineered Si cells or from GaAs, reaching efficiencies close to 25 percent.

Figure 7. Monolytic GaInP/GaAs solar space cell (panel a) and a similar AlGaAs/GaAs solar cell have reached 27.6% efficiency at AM 1.5 insolation (after Chung et al., 1990). [AM refers to the airmass, and AM 1.5 indicates a solar angle at which the light penetrates through 1.5 times the vertical thickness of the air, that is at a zenith angle of 48.19°.]



When still higher efficiencies are desired, one can resort to tandem solar cells made by adding a semiconductor of a lower band gap on the bottom, so that photons of lower energy that were not absorbed in the top cell have a second chance to be absorbed and produce additional electric power. Adding a third layer to such a tandem can be beneficial. An example is shown in Figure 7 for a monolytic cell (with matched current and only two electrodes). AlGaAs/GaAs tandem cells reach 27.8 percent efficiency. Mechanically stacked cells (with four electrodes) between GaAs and Si have reached 31 percent (Gee and Virshup, 1988). For more on a large variety of solar cell materials and their best efficiencies, see Green (2001) or Bube (1998). Comprehensive solar cell efficiency tables are provided in Green et al. (2000). SEE ALSO SOLID-STATE DEVICES.

Karl W. Böer

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Solid State

Matter is commonly encountered in one of three states—solid, liquid, or gas. Air is an example of a gas and water an example of a liquid. Objects such as rocks, concrete buildings, or pages in a book can be classified as solids. But what exactly is a solid?

Defining the solid state is difficult because while many things are described as solids, they may be heterogeneous (i.e., they may contain molecules of liquids or gases). Consider, for example, the pages of a book, which are made from paper and are primarily cellulose. Even though there is no question that they are solid, they do contain a quantity of water within the cellulose structure—typically about 5 percent. Paper is not described as a liquid, however, because it would not be a useful way to describe its properties.

The defining characteristics of a solid are a question of molecular motion. Atoms and molecules in a gaseous state move rapidly and independently, with little interaction. A gas therefore occupies the shape of the container that holds it as the gas molecules bounce off the walls. Particles in the liquid state do not move as rapidly or as independently as molecules in a gas, but they do move past one another, forming only loose and temporary associations. Liquids also lack definable shape, adopting the shape of the container that holds them. Conversely, particles in a solid do not change position and can interact strongly with their neighbors. They may vibrate in place and oscillate about their average position, but they do not shift from one location to another. It is incorrect to say that particles in a solid do not move, as they do “jiggle” in place, but they do not move from their fixed position. In the case of paper, the molecules of cellulose and water are, in the absence of an external force, fixed in place. An external force is required to allow the atoms of a solid to shift, such as when a piece of paper is ripped or a strip of metal is bent.

An analogy for the three states of matter is students in a classroom. Sitting at their desks, they represent a solid. Moving around the classroom, they are like a liquid. Once the bell rings, they are like a gas that is spread throughout the neighborhood. The arrangement of the components of a solid—in this analogy, how the students’ desks would be arranged—allows for solids to be classified in one of two broad categories: amorphous or crystalline.

Glass is a classic example of an amorphous material and diamond of a crystal material. Both are transparent solids with molecules and atoms that are held together with strong covalent bonds. Yet it would be hard to mistake one for the other, as diamonds are the hardest known natural substance while glass breaks fairly easily. To use the classroom analogy, the difference between glass and diamonds is that in glass, the desks are arranged completely at random, whereas in diamonds, the desks are lined up in neat and orderly rows.

Amorphous Solids

Glass is a heterogeneous material formed from silicon, oxygen, sodium, and a variety of other elements, depending upon the type of glass. It lacks long-range structure: Short units of silicon dioxide are bound together, but there is no overall order. At an atomic level, glass looks like a frozen liquid. Individual clusters exist, but they are not connected to each other and are held together only by van der Waals interactions. This is why when glass breaks it forms curved or jagged edges and why it shatters if struck with a hard blow.

Glass is only one example of an amorphous material. Another is paper, composed of randomly oriented cellulose molecules. Many familiar objects are made up of amorphous solid materials, all lacking long-range structure or order. They are aperiodic substances—substances that do not display periodicity. Consequently, it is hard to analyze the structure of amorphous materials as each sample is unique.

Crystalline Solids

Crystalline solids make up a much smaller percentage of everyday objects, but they are easier to understand. A subdiscipline of chemistry called crystallography is devoted to analyzing crystalline material. The defining characteristic of a crystalline material is that it is periodic with an underlying structure that is regular and repeating. A crystal displays long-range structure made up of the same building block used over and over.

Consider a crystal of gold, composed of endless planes of gold atoms. Within each plane, gold atoms adopt a regular pattern, with each atom occupying the center of a hexagon and surrounded by its closest neighbors. Each gold atom looks just like the one next to it—the pattern is repeated countless times. Also consider the diamond, which is like glass in appearance but is a covalent network solid with a three-dimensional lattice of tetrahedrally bound carbon atoms. Each carbon is attached to four neighbors in endless repetition. The three-dimensional structure and covalent bonds ensure that diamonds are incredibly hard.

The critical feature of crystalline material is that it is periodic. Although it may not be intuitively obvious, there are only seven shapes in nature that can be packed in a long-range periodic three-dimensional pattern. Packing a collection of spheres leaves a hollow shape between one sphere and the next, so a sphere is not one of the basic shapes for packing crystals. A cube, on the other hand, gives a three-dimensional, repeating structure with no voids. Considering the difference between a stack of boxes and a stack of bowling balls, it is easy to see that the boxes make a much more solid structure.

This is not to say that atoms and molecules are little boxes but rather that particles are arranged in a solid as if they were contained in molecular-size boxes. Each of these boxes is called a unit cell, and the overall arrangement of the unit cells is called a lattice. There are seven unit cell types possible for crystal growth, and all crystals belong to one of these seven crystal systems (see Table 1).

The spatial arrangement of atoms and molecules in any crystalline solid can be assigned to one of these seven geometric systems, even though the atoms themselves are spherical in shape. For example, the lattice of tetrahedrally bonded carbon atoms in a diamond can be described using a repeating cube. Another example is the cube that is described by sodium chloride (NaCl), or common table salt. In this instance, a sodium atom can be found at the center of the cube, surrounded by six chloride ions, each

System	Edges	Angles
cubic	$a=b=c$	$\alpha=\beta=\gamma=90°$
tetragonal	$a=b\neq c$	$\alpha=\beta=\gamma=90°$
orthorhombic	$a\neq b\neq c$	$\alpha=\beta=\gamma=90°$
hexagonal	$a=b\neq c$	$\alpha=\beta=90°$; $\gamma=120°$
monoclinic	$a=b\neq c$	$\alpha=\gamma=90°$; $\beta=90°$
trigonal	$a=b=c$	$\alpha=\beta=\gamma\neq 90°$
triclinic	$a\neq b\neq c$	$\alpha\neq\beta\neq\gamma\neq 90°$

Table 1. Crystals belong to one of these seven crystal systems.

occupying one of the faces. Twelve more sodium atoms occupy the edges and eight more chlorides occupy the corners. Considering that each chloride at each corner resides in eight different cubes, that each sodium along an edge resides in four different cubes, and that each chloride on a face resides in two different cubes, only one ion—the central sodium—is contained entirely within the unit cell. However, one-eighth of the eight chlorides at the corners and two of the six chlorides on the faces result in a total of four chlorides in the unit cell. Similarly, one-fourth of the twelve sodium atoms along the edges and the one in the middle results in a total of four sodium ions. The net result is that each repeating unit—each cube of sodium and chloride—has four of each atom and, overall, the formula for table salt can be written as NaCl.

This idea of repetition—of using unit cells to build up a crystalline solid—allows crystallographers to use x-ray diffraction and neutron diffraction to map out electron density within a unit cell. Using mathematics and a knowledge of where the electrons are located, it is possible to determine the exact position of each and every atom within the cell. From this, it is possible to determine which atoms are in close contact. Physically, two atoms are said to be bonded together by a covalent interaction when the distance between them is less than the sum of their respective van der Waals radii. Chemists and physicists have been able to use the concept of bonding and the techniques of crystallography to determine the structure of a great many substances. Indeed, approximately 100,000 crystal structures have been determined and registered in the Cambridge Crystallographic Database.

Diamonds represent a class of compounds called network crystals because they extend the full length of the crystal. Every carbon in a diamond is connected, via covalent bonding, with every other carbon atom. Sodium chloride, or table salt, represents a class of compounds called ionic crystals because it is composed of oppositely charged ions held in place by electrostatic attraction. These interactions can be incredibly strong and give rise to minerals and gemstones, such as magnetite and rubies. Ionic interactions are the binding force in all salts, regardless of whether they are crystalline. In the crystalline state, however, they give rise to almost all minerals and gems.

Two other classes of crystalline solids are molecular crystals and metallic crystals. Molecular crystals are assembled through the interaction of molecules to form a regular and repeating lattice. The most familiar example would be solid water (ice). Each water molecule in a crystal of ice is independent and internally bonded through covalent interactions. In the gaseous state, water molecules move independently and do not interact. In the solid state, the amount of energy present is insufficient to overcome hydrogen bonding interactions, and the molecules link one to the other to form an extended hexagonal lattice. Each molecule is held tightly in place by its neighbors. The interactions between molecules tend to be weaker than in either a network or ionic crystal, with the result that these crystals are easily broken—think of trying to crush an ice cube versus a diamond.

In a metallic crystal, the latticework of the atoms is bound together by a sea of electrons. Each atom—or, more accurately, each nucleus—occupies a position within a crystalline lattice. The electrons, on the other hand, move among all of the available atoms in a series of conduction bands. The net result is that even in an amorphous state metals readily conduct electricity and heat, they are ductile and malleable, and they exhibit the luster seen on metallic surfaces. In the crystalline form, metals can do all of the above and exhibit other properties such as magnetism (which requires ordered crystalline domains). SEE ALSO GLASS; SALT.

Todd W. Whitcombe

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Solid-State Devices

Solid-state devices are the controlling components of both high-tech and very ordinary devices. Their widespread usage is related to the fact that they can be utilized to interface with all human senses. Light emitting diodes (LEDs) and solid-state lasers produce light used in all kinds of displays that interface with sight. The first applications of solid-state devices were the use of transistors in radios and amplifiers that interface with our sense of hearing. Thermoelectrics are solid-state devices that can be used for heating or cooling—an interface with the sense of touch. While solid-state devices do not emit odor or flavor, they can be utilized as sensors to monitor odiferous or toxic substances, interfacing with the senses of smell and taste. To a degree, the modern sense of time, driven by the information revolution, points back to solid-state devices.

At the beginning of the twenty-first century, there were more solid-state devices produced than any other manufactured thing. More than ten billion components are fabricated onto a single eight-inch silicon wafer. During the 1940s the jobs of simple solid-state devices were performed with vacuum tubes and mechanical relays. (If a vacuum tube covered one square inch of area, the same ten billion devices that fit on an eight-inch wafer would cover 6.5 square kilometers [2.5 square miles].) The invention of the transistor in 1947 at Bell Laboratories ushered in an electronic age, beginning with telephones and radios and eventually providing ever smaller and faster computers, more efficient lighting, a means to harvest electrical energy from the Sun, and much more.

The Materials of Solid-State Devices

Solid-state devices consist of intricate organizations of crystalline materials that exhibit insulating, semiconducting, or conducting properties. Insulators, typically composed of SiO_2, block the flow of current from one part of the device to another. Semiconductors, typically silicon or materials related to silicon, are the principal materials of solid-state devices, controlling the number and rate of flow of charged carriers (electrons or holes). Holes are formed when an electron is removed and thus carry a positive charge. Conductors, typically **metals** such as aluminum or copper, are used for electrical connections to the devices. The design, operation, and fabrication of solid-state devices are generally the subject of physics and engineering. The properties of the materials used to make the devices, however, are determined by chemistry.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

The difference between conductors, semiconductors, and insulators is determined by how easily electrons (or holes) can move through the crystalline material. The movement (delocalization) of electrons, or their localization on or between particular atoms, is determined by the chemical bonding. In a crystal, it is necessary to consider the repeating bonding interactions between the many atoms rather than just the bonding interactions between two atoms in an isolated molecule.

Consider the bonding analogy between the dihydrogen molecule, H_2, and a hypothetical one-dimensional hydrogen crystal, H_n, symbolically represented in Figure 1. Each hydrogen atom has one electron in one **atomic orbital**. When two such atoms are brought together, the electrons are shared between them in a bonding molecular orbital, σ, where the orbitals are in **phase** with each other. An antibonding orbital, σ^*, is also created at higher energy with the two orbitals out of phase with respect to each other. A stable bonding situation is created when the electron configuration fills bonding molecular orbitals and leaves antibonding molecular orbitals empty.

atomic orbital: mathematical description of the probability of finding an electron around an atom

phase: homogeneous state of matter

When an approximately infinite number of atoms are brought together to form a crystal, they bring along an infinite number of orbitals and corresponding electrons. When all these orbitals are in phase, the lowest energy crystal orbital is obtained. When they are all out of phase, the highest energy crystal orbital is obtained. But with the near infinite number of atoms, and thus a near infinite number of atomic orbitals, there must be a near infinite number of crystal orbitals formed with energies intermediate between the most bonding and most anti-bonding levels. This collection of crystal orbitals is referred to as an energy band.

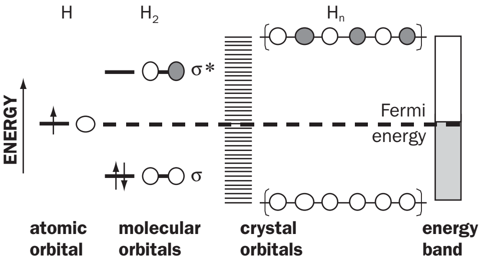

Figure 1. Evolution of an energy band.

Each band can be filled with electrons in a similar fashion to filling a plastic bottle with sand. If that bottle of sand is completely full, it is possible to tilt it or even turn it upside down and the grains of sand will not move. If the plastic bottle is not completely full (i.e., a partially filled band), then the grains of sand can easily move when the bottle is tilted. They are not localized in one position but **delocalized** across the top surface. In a similar way, electrons of a partially filled band are delocalized across the crystal and can conduct electricity. The energy of the highest filled levels is called the Fermi energy.

delocalized: of a type of electron that can be shared by more than one orbital or atom

Understanding Conductivity

A metallic conductor is a substance that has a partially filled band. It takes very little energy to move electrons from a filled level to an empty level in a band; this results in high conductivity because there is no energy gap at the Fermi level. When the temperature of a metallic conductor is lowered, the conductivity increases because the thermal motion of the atoms in the crystal is slowed, allowing the electrons to move more easily.

In contrast, both semiconductors and insulators have band structures in which all of their electronic bands are either completely full or completely empty. Because real crystals have more than one orbital, unlike the hydrogen example, there will be several bands giving rise to the electronic band structure. Bands filled with electrons occur below the Fermi energy and bands at higher energy are empty. The difference in energy between the highest part of the filled band and the lowest part of the empty band is the band gap. The difference between an insulator and a semiconductor is the size of the band gap. A material with a band gap of less than about 3.5 eV is considered a semiconductor, whereas materials with larger band gaps are insulators. In a semiconductor, the filled band below the Fermi level is called the **valence** band and the empty band above the Fermi level is called the conduction band.

valence: combining capacity

If sufficient energy is supplied to a semiconductor, an electron can be promoted from the valence band to the conduction band; this also creates a hole in the valence band. The electron promoted to the conduction band and/or the hole left in the valence band can be delocalized across the crystal, resulting in electronic conductivity. The magnitude of the conductivity is strongly determined by the energy supplied to the semiconductor. For this reason, the conductivity of a semiconductor will increase with increasing temperature.

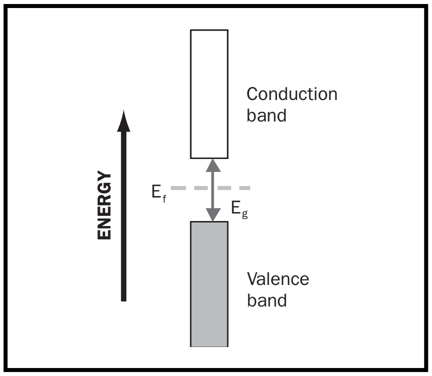

Figure 2. Band structure of a semiconductor. E_f is the Fermi energy and E_g is the band gap.

The Chemistry of Semiconductors

The properties of a semiconductor are determined by the elemental composition of the material, its structure, and the presence of any impurities. Impurities, commonly referred to as dopants, add extrinsic properties to the semiconductor, compared with the properties intrinsic to the pure material itself.

Intrinsic semiconductors. The group fourteen elements carbon, silicon, germanium, and tin can be found to adopt the diamond-type crystal structure shown in Figure 3a. Other crystalline structures are also found; for example, graphite and diamond are different crystal structures of the same element, carbon. Because of its size and orbital energies, carbon forms very strong bonds, so there is large energy separation between the bonding and antibonding bands in diamond. This results in a large band gap of 6.0 eV, making diamond an insulator. In contrast, bonding between the heavier elements (silicon, germanium, and tin) is not as strong, so the band gap decreases going down the column of the Periodic Table: silicon, 1.1 eV; germanium, 0.7 eV; and grey tin, 0.1 eV. In addition, at temperatures below 13°C (55°F), tin undergoes a crystal rearrangement to the structure of white tin that has no band gap because it is metallic.

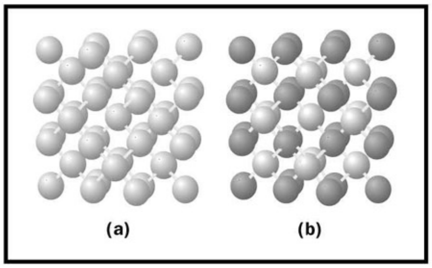

Figure 3. Crystal structure of (a) diamond and (b) a diamond-type compound semiconductor.

Compound semiconductors are made up of more than one element and give the ability to chemically tune the size of the band gap. Typical compound semiconductors will combine elements from group thirteen and group fifteen on the Periodic Table. These compound semiconductors also adopt a diamond-type crystal structure but with alternation of the atom types in the crystal network (Figure 3b). By combining elements with three and five valence electrons (such as aluminum and phosphorus, respectively)—an average of four electrons per atom—a material with properties similar to silicon with four valence electrons is obtained. However, because the orbitals of phosphorus are lower in energy and the orbitals of aluminum are higher in energy than silicon, a larger band gap is observed for the compound semiconductor AlP (3.0 eV). Combination of the heavier elements gallium and arsenic will form gallium arsenide (GaAs), with a band gap of 1.4 eV. A similar chemistry is possible by combining elements of groups twelve and sixteen, which, for example, yield the semiconductors zinc sulfide (ZnS) and cadmium selenide (CdSe), with band gaps of 3.8 eV and 1.8 eV, respectively.

Dopants in semiconductors. Purity for an electronic grade semiconductor must be greater than 99.999 percent. Controlling the amount and type of impurity, however, can fine-tune the properties of the semiconductor. For example, adding a phosphorus impurity (with five valence electrons) to silicon (with four valence electrons) effectively adds one extra electron for each phosphorus atom added to the crystal. Thus the phosphorus is a donor to silicon. The dopant phosphorus atoms will displace silicon atoms in the crystal, but the overall crystal structure does not change, nor does the band structure. The extra electron must go into the conduction band, however, since the valence band was already full. This yields an *n*-type semiconductor. Conversely, **doping** silicon with aluminum provides one too few electrons, leaving one hole in the valence band for each aluminum atom added. Thus aluminum is an acceptor from silicon. Having lost electrons, the holes bear a positive charge, forming a *p*-type semiconductor. Because the gap in energy between the donor levels and the conduction band (E_n) or between the acceptor levels and the valence band (E_p) is very small, these doped semiconductors will exhibit a greater conductivity and much less temperature dependence than is observed for an intrinsic semiconductor.

dope: to add a controlled amount of an impurity to a very pure sample of a substance, which can radically change the properties of a substance

The *P–N* junction. The Fermi level of a *p*-type semiconductor is lower in energy than that of an *n*-type semiconductor. When *p*- and *n*-type semiconductors are joined, a common Fermi level is created by the combination of holes and electrons at the interface. No carriers are present in this depletion zone at the junction. When a positive **voltage** is applied to the *p*-type side of the *p-n* junction and a negative voltage to the *n*-type side, current can flow since the positive voltage pushes the holes toward the

voltage: potential difference expressed in volts

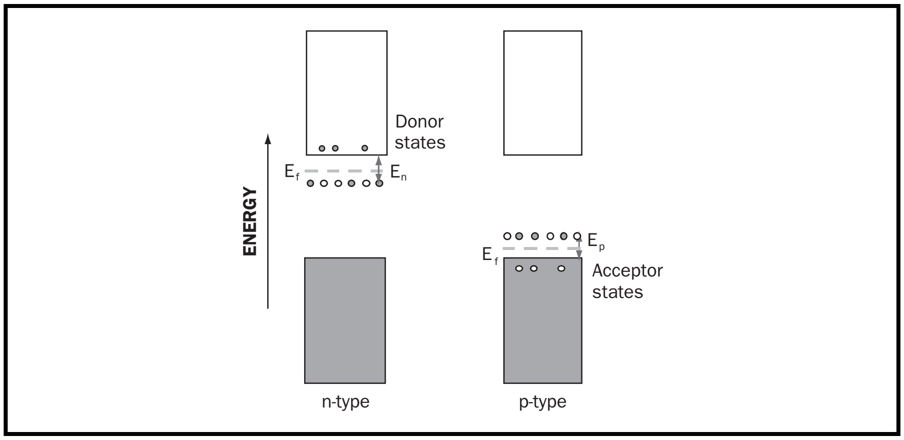

Figure 4. *N*- and *p*-type doping of a semiconductor.

negative cathode and the negative voltage pushes the free electrons toward the positive anode. By contrast, hooking the battery up in reverse will increase the size of the depletion zone, because the negative voltage attached to the *p*-side of the junction will pull more holes toward that electrode and the positive voltage attached to the *n*-type semiconductor will pull electrons toward the electrode and away from the junction, leaving a larger depletion zone. As a result there are no free carriers and no current can flow. Thus this *p-n* junction forms the simplest solid-state device, known as a diode.

Diodes. Diodes are essentially one-way valves for electronic conductivity. Such a device is very important in a power supply that converts AC to DC current, necessary for many electronic devices. Connecting a single diode to an AC electrical circuit will block either the positive or negative voltage swings, described as half rectification. The connection of four diodes (as shown in Figure 6) will give full wave rectification, converting AC to DC current. The addition of capacitors to this circuit will smooth the voltage oscillations for actual device operation.

When electrical current is passed through any *p-n* junction, electrons traveling through the conduction band or holes traveling through the valence band can recombine with holes or electrons, respectively, across the band gap. This recombination primarily occurs to electrons that have been pushed into the *p*-type region of the diode and to holes that have been pushed into the *n*-type region of the diode by the external voltage. As electrons and holes are recombined across the band gap, energy is released, often as a **photon** with an energy equal to that of the band gap. Semiconductors with band gaps between 1.8 eV and 3.1 eV will emit photons of visible light (red [700 nanometers; 2.76×10^{-5} inches] to violet [400 nanometers; 1.58×10^{-5} inches]). These are known as LEDs. In fact, all diodes emit light, but most have a band gap that is smaller than the energy of a visible pho-

photon: particle of light as defined by Max Planck

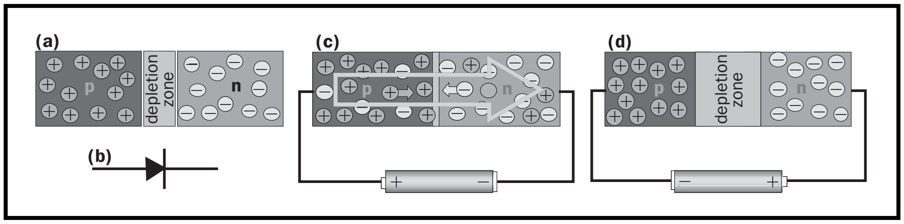

Figure 5 a) Schematic of a *p-n* junction, b) symbol for a diode with arrowhead indicating the direction of current flow, c) a forward biased *p-n* junction indicating the direction of current flow from + to - with the arrow (center), and d) a reverse biased *p-n* junction, which does not allow current to flow.

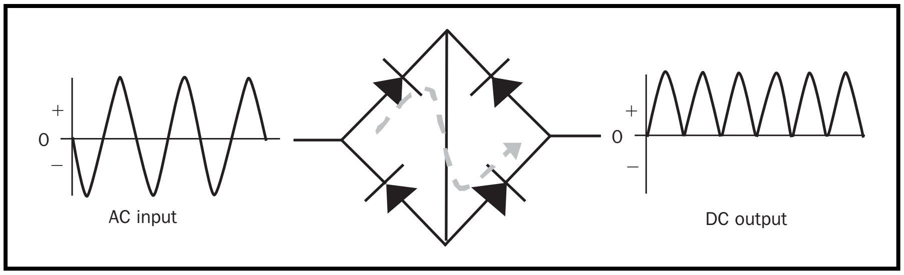

Figure 6. Four diodes linked to form a full wave rectifier. The dotted-line arrow indicates the direction of current flow under the positive AC oscillations.

ton. As a result, most diodes emit infrared photons. Such infrared emission is used for signaling in many remote control devices.

Transistors. Transistors are solid-state switching and amplifying devices, and it was their invention in 1947 that truly began the electronics revolution of the late twentieth century. An *n-p-n* bipolar transistor is formed by connecting *n*-type semiconductors on either side of a thin *p*-type semiconductor. As shown in Figure 7, the transistor acts as a switch for the circuit connected to the 10 V power supply. If a small negative voltage is applied to the base (contact B), the holes are removed from the *p*-type semiconductor, creating an insulating barrier. This is the same process as trying to force current the wrong way through two *p-n* junctions. As a result, no current will flow between any of the contacts. If a small positive voltage is applied to the base contact, however, some current will flow through the control loop (electrons going from the emitter to the base). Because the voltage supplied between the emitter (contact E) and the collector (contact C) is much larger than the base voltage, a much greater fraction of the electrons will cross the thin *p*-type layer, giving the much larger collector current.

As described above, the transistor functions as a simple on/off device, depending on the sign of the voltage applied to across the base and emitter. Because the base current is small and the collector current is large, this same solid-state device can also be used as a signal amplifier. The ratio of the collector current to the base current is essentially constant for a given device. Since the base current is proportional to the base-emitter voltage (voltage between B and E) and the collector current is proportional to the emitter-collector voltage (voltage between E and C), a small oscillation in the voltage input from a microphone, for example, into the BE loop will be

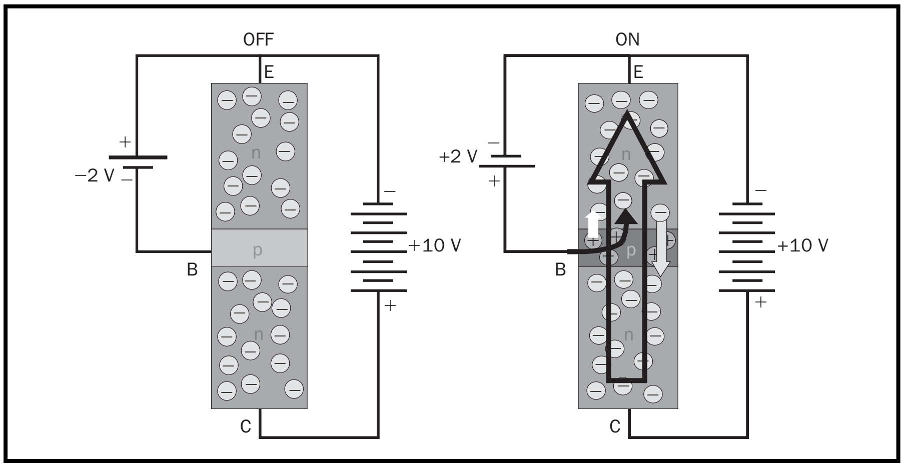

Figure 7. An *n-p-n* bipolar transistor. B, base; E, emitter; and C, collector. The direction of flow for the electrons and holes in the on state is described with grey and white arrows, respectively. The primary current, defined as flow from + to -, is shown in the large black block arrow, and the current through the control loop is represented by the smaller black arrow.

amplified to a large oscillation in the voltage in the EC loop, which then can be connected to a loudspeaker.

Though varying combinations of semiconductors can be fabricated into many different solid-state devices, the operation of the device is strongly dependent on the chemistry of the elements making up the semiconductors. The bonding between elements making up semiconductors determines the electronic band structure and the size of the band gap. The number of valence electrons determines the filling of those bands and thus the electronic properties. Ongoing research efforts continue to discover new semiconductors with new possible applications. In addition, extensive effort is being invested to design smaller and smaller devices with the goal of moving from solid-state devices (based on crystalline materials) to single molecule devices.

James D. Martin

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Solution Chemistry

The majority of chemical processes are reactions that occur in solution. Important industrial processes often utilize solution chemistry. "Life" is the sum of a series of complex processes occurring in solution. Air, tap water, tincture of iodine, beverages, and household ammonia are common examples of solutions.

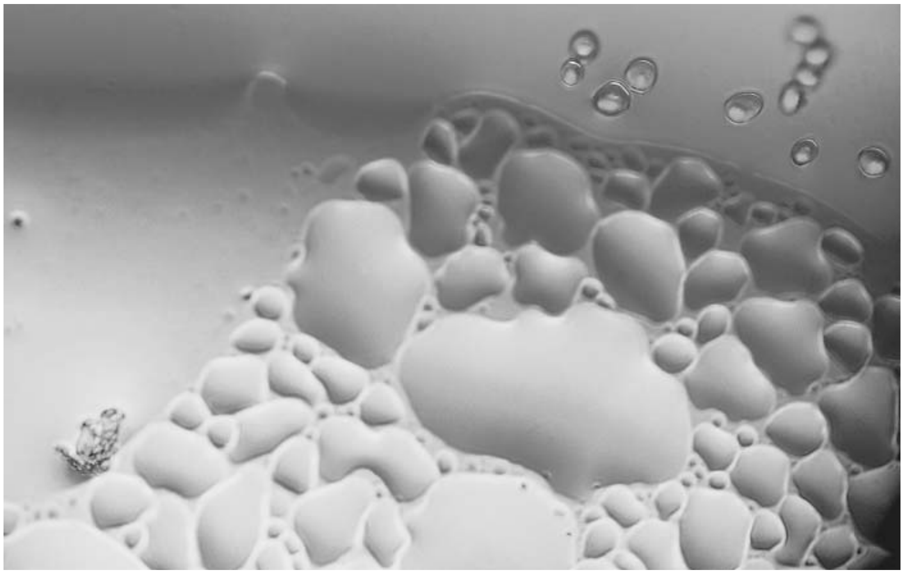
A solution is a homogenous mixture of substances with variable composition. The substance present in the major proportion is called the solvent, whereas the substance present in the minor proportion is called the solute. It is possible to have solutions composed of several solutes. The process of a solute dissolving in a solute is called dissolution.

heterogenous: composed of dissimilar parts

homogenous: composed of similar parts

Many common mixtures (like concrete) are **heterogeneous**—the components and properties of such mixtures are not distributed uniformly throughout their structures. Conversely, solutions are said to be **homogeneous** because they have uniform composition and properties. Solutions are intimate and random homogeneous mixtures of atomic-size chemical species, ions, or molecules.

In addition to their observed homogeneity, true solutions also have certain other characteristics. For example, components of a solution never separate spontaneously, even when a significant density difference exists between the components. Solutions also pass through the finest filters unchanged.



Droplets of a solution of water and oil, exposed to polarized light and magnified.

The components of a solution distribute themselves in a completely random manner, given sufficient time. For example, a lump of sugar dropped into a glass of water dissolves, and eventually molecules of sugar can be found randomly distributed throughout the water, even though no mechanical stirring has been employed. This phenomenon, called diffusion, is similar to the process of diffusion that occurs with gases. The molecules of sugar (as well as those of water) must be in constant motion in the solution. In the case of liquid solutions, the sugar molecules do not move very far before they encounter other molecules; diffusion in a liquid is therefore less rapid than diffusion in a gas.

Kinds of Solutions

Many commonly encountered solutions are those involving a solid that has been dissolved in a liquid, but there are as many types of solutions as there are different combinations of solids, liquids, and gases. Solutions in which the solvent is a liquid and the solute is a gas, liquid, or solid are very common. The atmosphere is a good example of a solution in which a gaseous solvent (nitrogen) dissolves other gases (such as oxygen, carbon dioxide, water vapor, and neon). Solutions of solids in solids are another example, and these are encountered most often among the various metal alloys.

Of all the liquid solvents used in the laboratory, in industry, and in the home, water is the most commonly employed and is the best of the inorganic solvents. The alcohols and numerous other types of compounds are classified as organic solvents; many of these are used in dry cleaning chemicals, nail polish removers, paint thinners, and many other similar purposes.

Concentration

solute: dissolved substance

The concentration of a solution is defined as the amount of **solute** present in a given quantity of solvent. Very often scientists speak of concentrated solutions, dilute solutions, or very dilute solutions, but these designations give only a rough relative qualitative idea of concentration. For example, a "concentrated solution" contains a considerable quantity of solute as compared with a "dilute solution." Although such designations are only qualitatively useful, they are nevertheless widely used.

The most common way to express concentration is on the basis of the weight of solute per unit weight of solvent. For example, a salt solution may be prepared by dissolving 1.64 grams of sodium chloride in 100 grams of water. The concentration of this solution could also be expressed as 0.0164 grams of NaCl per 1 gram of water, or as 16.4 grams of NaCl per 1,000 grams of water. Thus, a statement of the concentration of a solution does not imply anything concerning the amount of solute or the amount of solvent present, but rather gives the ratio of solute to solvent in terms of some convenient (and arbitrary) units. Because the weight of a sample of a liquid is usually more difficult to determine experimentally than its volume, a practical unit of concentration is the weight of solute in a given volume of the solution; for example, a sugar solution may contain 50 grams of sugar per 100 milliliters of solvent.

Solubility

Solubility is a measure of the maximum amount of solute that can be dissolved in a given amount of solvent to form a stable solution. The composition of many solutions cannot be varied continuously because there are certain fixed limits imposed by the nature of the substances involved. Solid salt and sugar can be mixed in any desired proportions, but unlimited quantities of sugar (or salt) cannot be dissolved in a given amount of water; however, up to the solubility limit, solutions can be produced in any desired proportion.

When the solvent contains a maximum quantity of solute, the resulting solution is said to be saturated. The saturation point varies according to the solute. For example, 100 grams of pure water at 25°C (77°F) can dissolve no more than 35.92 grams of NaCl to form a stable saturated solution, but this same amount of water at 25°C dissolves only 0.0013 grams of calcium carbonate. The solubility in these examples is expressed in grams of solute per 100 grams of water, but any suitable units could be used. Water can dissolve any amount of a solute less than that required for a saturated solution. Tables of the solubilities of many substances can be found in various chemistry texts.

In some cases there is no upper limit to the amount of a solute that a given quantity of solvent can dissolve, and these substances are said to be miscible in all proportions. Completely miscible substances give homogeneous mixtures (solutions); for example, a mixture of any two gaseous substances is homogeneous. Often, liquids such as alcohol and water can be mixed in all proportions to give homogeneous mixtures.

When a saturated solution has been achieved, a dynamic equilibrium exists between the solute in solution and any undissolved solute. Molecules of the solute (or atoms or ions, depending upon the nature of the solute) are continuously going into solution, but since the solution is already saturated, an equal number of molecules of the solute leave the solution and redeposit on the excess solid solute. A state of equilibrium exists when these two processes occur at the same rate, the net result being a constant amount of solute in solution. A saturated solution can therefore be defined more precisely as a solution that is in equilibrium with an excess of the solute at a given temperature.

In some instances it is possible to prepare a true solution that contains an excess of the equilibrium amount of solute; this condition is called supersaturation. Supersaturated solutions are unstable. If left undisturbed, they may remain in this state for an indefinite period of time. However, the excess solute can be brought out of solution by a slight agitation or by the addition of any solid particle (dust, a small crystal of solute, etc.) that can act as a center for crystal growth, returning the solution to its normal saturated state.

Conditions That Affect Solubility

In general, three major factors—pressure, temperature, and the nature of the solute and solvent—influence the solubility of a solute in a solvent. Not all these factors are equally important in a specific instance.

Pressure. Changes in pressure have little effect on the solubility of solid or liquid solutes in a liquid solvent, but pressure has a much greater influence on the solubility of a gaseous solute. A commonly observed phenomenon that supports this is the effervescence that occurs when the cap of a bottle of ordinary soda water is removed. Soda water contains carbon dioxide gas dissolved in water under pressure; when the cap is removed, the pressure of the gas on the liquid is decreased to atmospheric pressure. Since carbon dioxide gas leaves the solution at this lower pressure, it follows that the solubility of carbon dioxide in water is dependent upon the pressure of the carbon dioxide above the liquid. The results of this simple observation are summarized in Henry's Law, which states that at any specified temperature, the extent to which a gas dissolves in a liquid is directly dependent upon the pressure of the gas.

Temperature. In general, a change in temperature affects the solubility of gaseous solutes differently than it does the solubility of solid solutes, because the solubility of a gas in a liquid solvent decreases with increasing temperature. With relatively few exceptions, the solubility of solids in liquids increases with an increase in temperature. In some instances, the increase in solubility is very large; for example, the solubility of potassium nitrate in water at 25°C is about 31 grams of KNO_3 per 100 grams of water and about 83 grams of KNO_3 per 100 grams of water at 50°C (122°F). On the other hand, the solubility of some solutes, such as ordinary table salt, shows very little dependence on temperature. Often this difference in solubility can be used as an advantage in the preparation, isolation, or purification of substances by the process of crystallization. In general, it is not possible to arrive at any reliable generalization concerning the influence of temperature upon the solubility of liquids in liquids. In some cases the solubility increases with an increase in temperature, in some cases it decreases, and in others there is very little effect.

The nature of solute and solvent. Crystalline substances consist of a regular arrangement of atoms, molecules, or ions; in the latter case, the forces that hold the crystal together are electrostatic in nature. For an ionic crystal to dissolve in water, the water molecules must be able to shield the charges of the positive and negative ions from each other. The attractive forces between the ions in solution are less than those in the solid state because of the solvent molecules; hence, the ions behave more or less independently in solution. In general, the relative solubilities of ionic substances are a measure of the magnitude of the electrostatic forces that hold the crystals together.

Properties of Solutions

Pure liquids have a set of characteristic physical properties (melting point, vapor pressure at a given temperature, etc.). Solutions in a solvent exhibit these same properties, but the values differ from those of the pure solvent because of the presence of the solute. Moreover, the change observed in these properties in going from the pure solvent to a solution is dependent only upon the number of solute molecules; these properties are called colligative properties. The properties of a solvent that show a predictable change upon the addition of a solute are melting point, boiling point, vapor pressure, and osmotic pressure.

Melting and boiling points. Solutions exhibit higher boiling points and lower melting points than the parent solvent. The increase in boiling point and decrease in melting point is dependent upon the number of solute particles in the solution. The greater the number of solute particles (i.e., the concentration), the greater the boiling point elevation and melting point depression. A common application of this effect in some parts of the world is in the use of antifreeze solutions in the cooling systems of automobiles in cold climates. “Antifreeze” compounds are usually organic liquids that are miscible with water so that large freezing point effects can be attained.

Vapor pressure All liquids exhibit a vapor pressure, the magnitude of which depends on the temperature of the liquid. For example, water boils at 100°C, which means that at 100°C the vapor pressure of water is equal to the atmospheric pressure allowing bubbles of gaseous water (steam) to escape from the liquid state. However, the vapor pressure of a solution (at any temperature) is less than that of the solvent. Thus, boiling water ceases to boil upon the addition of salt because the salt solution has a lower vapor pressure than pure water. The salt solution will eventually boil when the temperature of the solution increases bringing about an increase in vapor pressure sufficient to again form bubbles. Note in this example that the boiling point of water increases with the addition of salt; thus, the boiling point elevation and the vapor pressure depression are related.

Osmosis. This property of solutions is perhaps the least familiar of the colligative properties, but in a sense it is more important than those already mentioned. In 1748 French clergyman and physicist Jean-Antoine Nollet observed that certain animal membranes are selectively permeable to different molecules. Since then, many examples of semipermeable membranes have been discovered, including animal bladder or gut tissues, eggshell lining, and certain vegetable tissues. A semipermeable membrane may be defined as a material that allows molecules of one kind to pass through it but prevents the passage of other kinds of molecules or allows the passage of different kinds of molecules at different rates. Membranes often permit the passage of solvent molecules and prevent the passage of solute molecules.

The phenomenon of osmosis is of far-reaching importance in biology, medicine, and related areas. Many animal and vegetable membranes are semipermeable, and the process of osmosis plays an important role in the transfer of molecules through cell walls in biological processes. Osmosis is responsible in part for the germination of seeds and for the rising of sap into the branches and leaves of trees. The preservative action of sugar solutions (e.g., preserves, jellies) is believed to depend upon osmotic processes; bacteria are literally dehydrated. SEE ALSO WATER.

J. J. Lagowski

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Space Chemistry *See Astrochemistry.*

Space Flight *See Rocketry.*

Spectroscopy

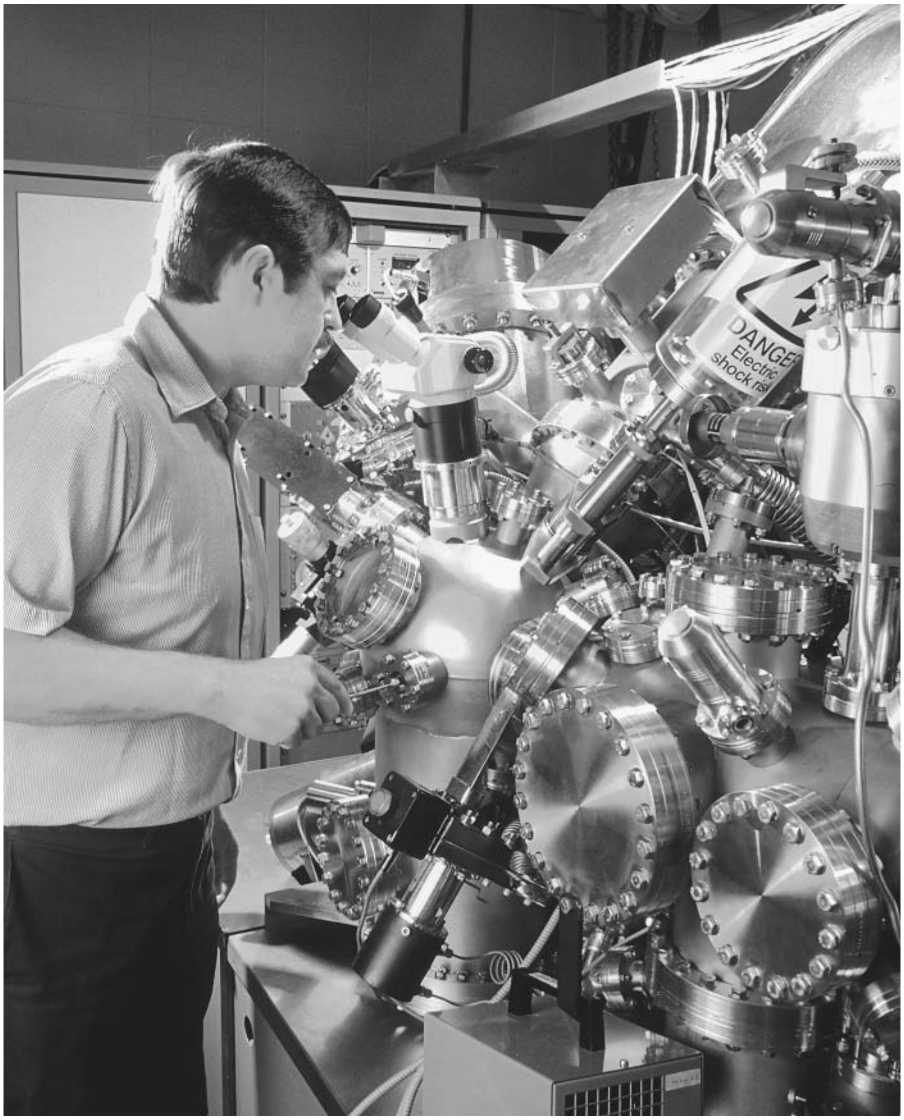
Spectroscopy is the measurement of interactions between electromagnetic radiation and matter. Electromagnetic radiation, which includes light, has characteristics of waves and particles. Each "particle" of light, or "**photon**," has a discrete amount of energy that can be transferred to a molecule. The transverse waves of electromagnetic radiation possess a constantly changing magnitude of electric and magnetic fields in directions that are **perpendicular** to the direction in which the wave is traveling. These changes in the electric and magnetic fields can cause changes in molecules. Electromagnetic radiation can be transmitted, absorbed, or reflected by matter, and each region of the spectrum can be used to investigate different aspects of the structure and properties of molecules, depending on the amount of energy imparted to the molecule. The absorption of radiation by matter is a quantized process, in that a molecule will only absorb radiation of certain discrete frequencies. These frequencies are determined by well-defined spacings of energy levels in the molecule under investigation. The absorption of photons of high energy cause large changes (often irreversible) in the molecules and correlate to moving electrons to higher energies.

photon: a quantum of electromagnetic energy

perpendicular: condition in which two lines (or linear entities like chemical bonds) intersect at a 90-degree angle

Ultraviolet-Visible Radiation

Electromagnetic radiation is often characterized by its wavelength—the distance between successive peaks in the wave. Radiation with wavelengths between 100 and 700 nanometers (3.94×10^{-6} and 2.76×10^{-5} inches) is termed ultraviolet-visible radiation. The transmittance (T) of a sample is the amount of light transmitted (P) by a sample divided by the amount of light transmitted by a blank (P_0)—$T=P/P_0$. The absorbance (A) of a solution is the negative logarithm of the transmittance—$A=-LOG(T)$. The



Electron spectroscopy is used for measuring concentrations, rates of absorption, and molecular structure.

absorbance of a sample is proportional to the length of the sample that is in the path of the probe radiation and the number of the molecules in the beam path. A plot of the absorbance or transmittance versus the wavelength of radiation is called a spectrum.

When molecules absorb photons in the ultraviolet and visible regions of the spectrum—corresponding to waves with wavelengths between 190 and 1,100 nanometers (7.48×10^{-6} and 4.33×10^{-5} inches)—electrons are promoted to higher electronic energy levels. Since molecules absorb photons with energies that match the difference in energy between their electronic energy levels, only a portion of white light is absorbed by a given molecule, giving it color. The color of light absorbed by a molecule is subtracted from white light, and the remaining light will be the complement of the light absorbed. Ultraviolet-visible spectra show the relative spacing of energy levels in molecules. Generally, molecular energy levels are stabilized when a molecule possesses alternating double bonds and the energy of the photons that these molecules absorbed shifts to lower wavelengths. This phenomenon explains the observation that ethylene, possessing one C=C bond, absorbs light of 180 nanometers (7.09×10^{-6} inches) and is colorless, while beta-carotene, possessing eleven alternating C=C bonds, absorbs at 450 nanometers (1.77×10^{-5} inches) and appears orange in color. Light absorbance in the ultraviolet and visible regions is used to determine the concentration of molecules in solution and of atoms in the gas **phase**. Chemists can determine the concentration of lead in drinking water with absorption spectroscopy.

phase: homogeneous state of matter

Nuclear Magnetic Resonance Spectroscopy

Radio waves can be used to probe the electronic environment of the nuclei of atoms. The nuclei of atoms spin in a clockwise or counterclockwise fashion and create a magnetic field. This field can have the same or opposite field as a superconducting magnet surrounding the sample. When radio waves of a particular frequency are applied to the sample, the spin of these nuclei will change. The frequency of radiation absorbed by molecules in a magnetic field is determined by the types of bonds and the way these bonds are connected. Chemists measure the absorption of radio waves by molecules using a technique called nuclear magnetic resonance spectroscopy. This type of spectroscopy can also be used to determine areas of the body that are diseased, through a technique called magnetic resonance imaging.

Microwave Spectroscopy

Microwaves with long wavelengths cause molecules to rotate faster when they are absorbed. Polar bonds in molecules like water and sugar act as handles for the microwave radiation to grab on to, and the rotational energy can be greatly increased by short exposures to microwaves. This fact explains why polar molecules heat up quickly in microwave ovens. By measuring the wavelength of absorption through microwave spectroscopy, researchers can determine the size of the molecule.

Infrared Radiation

The absorption of infrared radiation (1 to 1,000 micrometers, or 0.0000394 to 0.0394 inches) causes bonds in molecules to vibrate. A bond in the molecule must undergo a change in the dipole moment when the infrared radiation is absorbed. The stiffer the bond, the more energy is required to cause the bond to stretch. Therefore the frequency required to cause C–N, C=N, and C≡N bonds to stretch increases from left to right. Often the infrared spectrum is considered to be a fingerprint of the molecule. Matching a sample's spectrum with a standard spectrum can positively identify the sample. This technique is used to measure emissions in automobile exhaust.

Fluorescence

Fluorescence is the process by which molecules emit light. When an electron moves to a level of lower energy, light can be given off with a frequency that matches the spacing between the original and final levels. The electron must initially be placed in a higher energy level by the absorption of light at short wavelengths. In fluorescence, the molecule loses some of this excess energy by emitting light at longer wavelengths instantaneously. This

voltage: potential difference expressed in volts

process is observed in sodium streetlights, where sodium atoms in the gas phase have been excited by an applied **voltage** and the electrons relax to lower energy levels and give off yellow light at 589 nanometers (2.32×10^{-5} inches). Fluorescent dye molecules on clothing are excited by ultraviolet light, and these molecules give off energy of longer wavelengths, as electrons in the molecules relax to lower energy levels. The fluorescence of molecules is very sensitive to the polarity, temperature, and viscosity that the molecule resides in. Unlike absorbance, fluorescence is not measured on a background and can quantitate very low amounts of materials. Richard Mathies and coworkers have detected single molecules in solution by fluorescence spectroscopy.

X Rays and Gamma Rays

X rays and gamma rays have enough energy to remove electrons from atoms and molecules and thereby ionize them. The wavelengths of x rays that are absorbed are determined by the distance that an electron is from the nucleus. Furthermore, the regular spacing of atoms in a molecule can create a diffraction pattern of x rays. By examining the diffraction pattern, researchers can accurately determine the arrangement of atoms in a molecule.

Applications

ultraviolet radiation: portion of the electromagnetic spectrum with wavelengths shorter than visible but longer than x rays

Many scientists use spectroscopy on a daily basis to gain insight into the structure of molecules or the concentration of atoms or molecules in a sample. The chemist uses radio waves and infrared radiation to determine the structure of a new molecule. The geologist uses **ultraviolet radiation** to determine the concentration of a particular element in a rock or mineral. The microbiologist uses fluorescence measurements to determine the concentration of bacteria in solution. SEE ALSO Rydberg, Johannes.

G. Brent Dawson

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Stanley, Wendell

AMERICAN BIOCHEMIST
1904–1971

Wendell Stanley shared the Nobel Prize in chemistry in 1946 with John Northrop, awarded to them "for their preparation of enzymes and virus proteins in a pure form," and with James Sumner "for his discovery that enzymes can be crystallized." In 1926 Sumner had crystallized the enzyme urease; in 1930 Northrop had crystallized pepsin; and in 1935 Stanley had crystallized tobacco mosaic virus. Stanley's result and subsequent findings demonstrated that an infectious agent could possess some of the properties of a chemical molecule. Stanley concluded: "Tobacco mosaic virus is regarded as an autocatalytic self-reproducing protein which, for the present, may be assumed to require the presence of living cells for multiplication."

Large batches of tobacco plants infected with tobacco mosaic virus and ground up while frozen were thawed in buffer solution containing alkaline sodium phosphate, and the solution was filtered. The filtrate at lowered pH was treated with concentrated ammonium sulfate. The precipitate contained virus, which was extracted and reprecipitated (by acidification in the presence of 20 percent saturated ammonium sulfate) as small "needles."

Stanley's achievement was soon reproduced in England by Frederick Bawden and Norman Pirie, who were also able to show that the tobacco mosaic virus and other plant viruses contained **ribonucleic acid** (RNA). Stanley initially considered the RNA to be a contaminant, but later investigations by Seymour Cohen showed RNA to be a very large molecule having a molecular mass of up to 2 million daltons. Surprisingly, the thought that the viral RNA might be the genetic element of the virus was not tested until 1956.

American biochemist Wendell Stanley, corecipient, with John Howard Northrop, of the 1946 Nobel Prize in chemistry, "for their preparation of enzymes and virus proteins in a pure form."

RNA: ribonucleic acid, a natural polymer used to translate genetic information in the nucleus into a template for the construction of proteins

Wendell Meredith Stanley was born in Ridgeville, Indiana, in 1904. On graduation from the University of Illinois in 1926 he aspired to be a football coach. He shortly afterward changed course and embarked on an extremely productive period as a graduate student, with the chemist Roger Adams as his instructor. He received a Ph.D. in chemistry from the University of Illinois in 1929 and stayed there another year, at the end of which he went to work for a year with Heinrich Wieland in Munich. He returned to the United States in 1931, having been given a post at the Rockefeller Institute in New York. In 1932 he moved to the Princeton branch of the institute, where Northrop was also a faculty member. In 1948 he was appointed professor of biochemistry and director of the virus laboratory at the University of California at Berkeley. In 1958 he became a professor of virology. He died suddenly in Spain in 1971, aged sixty-six. SEE ALSO RIBONUCLEIC ACID.

Keith L. Manchester

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Starch

Starch is the chief storage form of carbohydrate in plants and the most important source of carbohydrate in human nutrition. A starch molecule is a polysaccharide assembled from the simple sugar **glucose**; it can contain anywhere from five hundred to several hundred thousand glucose molecules joined by **covalent bonds** into a single structure. In addition to its impor-

glucose: common hexose monosaccharide; monomer of starch and cellulose; also called grape sugar, blood sugar, or dextrose

covalent bond: bond formed between two atoms that mutually share a pair of electrons

tance in human nutrition, starch has many industrial applications: it is used in the manufacture of paper, textiles, pharmaceuticals, and biodegradable polymers, and it is an additive in foods.

Chemically, starch is composed of two different molecules, amylose and amylopectin. In amylose, the glucose molecules are linked in a "linear" fashion; however, the tetrahedral chemistry of carbon (and the bond angles that result from this chemistry) gives amylose an overall spiral shape. Amylopectin, on the other hand, has a linear arrangement of glucose molecules that includes, at regular intervals, a different kind of linkage between two adjacent glucoses. This different linkage results in the formation of a branched structure and an overall treelike shape for this molecule. Plant starch is typically 20 to 30 percent amylose and 70 to 80 percent amylopectin. The classic test for the presence of starch is reaction with iodine. If starch molecules are present in a substance, the addition of iodine yields a deep blue color, which results from I_2 being trapped inside the spiral structures of amylose molecules.

Starch molecules are broken down by enzymes known as amylases. The digestibility of a specific starch is influenced by its physical form. In plants starch is present in microscopic granules, which impair the enzymatic digestion of starch molecules obtained from plants. Cooking starch-containing items results in the hydration of starch molecules and the swelling of starch granules, increasing the rate and enhancing the enzymatic breakdown of starch. Amylases also convert starch to glucose. SEE ALSO CARBOHYDRATES; POLYSACCHARIDES.

Matthew A. Fisher

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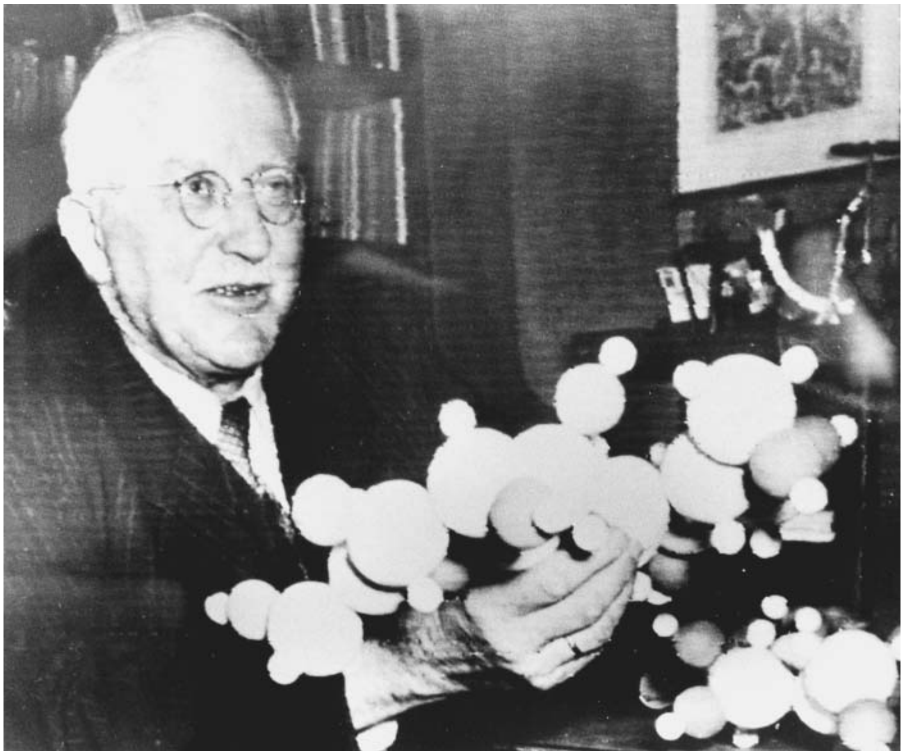
Staudinger, Hermann

GERMAN CHEMIST
1881–1965

Hermann Staudinger was one of the most influential organic chemists of the twentieth century. His wide-ranging research interests included the investigation of many kinds of molecules, ranging from small organic compounds to large polymers. He is generally considered to be the father of macromolecular (polymer) chemistry and won the 1953 Nobel Prize in chemistry for his discoveries in that field.

Staudinger was born in Worms, Germany, on March 23, 1881. He at first planned to study botany at the University of Halle, but he subsequently followed his father's advice and switched to chemistry. After graduating from



German chemist Hermann Staudinger, recipient of the 1953 Nobel Prize in chemistry, "for his discoveries in the field of macromolecular chemistry."

Halle with a degree in chemistry in 1903, Staudinger moved to the University of Strasbourg and became an academic lecturer there in 1907. Subsequent academic appointments took him to Karlsruhe, Zurich, and, finally, Freiburg.

Although Staudinger's work on ketenes, diazo compounds, oxalyl chloride, and pentavalent phosphorus compounds is still relevant, he is more recognized for his seminal contributions to macromolecular chemistry. Staudinger started working on macromolecules in the early 1920s. Following his move to Freiburg in 1926, he discontinued his investigations of small organic compounds and concentrated exclusively on the chemistry of what he believed were high molecular weight compounds.

It was a risky career move for Staudinger, and one that put him at odds with many of the leading organic chemists of the time. He proposed (without much proof to back up his proposal) that macromolecules were long-chain molecules of identical or nearly identical units that were linked by **covalent bonds**. Today it is known that many of Staudinger's ideas were essentially correct, but in the 1920s most chemists disagreed with him. They viewed macromolecules as colloidal aggregates of small molecules and did not believe that covalent bonding was involved.

covalent bond: bond formed between two atoms that mutually share a pair of electrons

Staudinger's colleague, Dr. Heinrich Wieland, told him to drop his idea of large molecule organic compounds and assured him that a sample of purified rubber would be shown eventually to be composed of low molecular weight compounds. During a lecture in Zurich in 1925, Staudinger was verbally attacked for advocating the idea of covalent bonding in macromolecules.

Despite the attacks, Staudinger was determined to convince his detractors that his ideas on the structures of macromolecules were sound. To prove his point he carried out a series of experiments designed to yield more understanding of the chemical and physical properties of polymers. He began with natural rubber. He and J. Fritschi hydrogenated the double bonds present in natural rubber polymer molecules in an autoclave and found that the isolated product had properties similar to those of the starting rubber. From this Staudinger concluded that natural rubber was not a colloidal substance, but a long-chain macromolecular substance.

formaldehyde: name given to the simplest aldehyde HC(O)H, incorporating the –C(O)H functional group

functional group: portion of a compound with characteristic atoms acting as a group

He gathered more evidence by synthesizing polymers from **formaldehyde** and from styrene. The homologous formaldehyde-derived polymers spanned the molecular size range, from small molecules to large macromolecules. From the results Staudinger concluded that polymers were molecules whose repeating units were linked by covalent bonds, and that they had characteristic **functional groups** at their ends. The polystyrene polymers were prepared under varying reaction conditions and had a range of molecular weights and physical properties. These data were also consistent with covalent bonding, but not with colloidal association.

Staudinger's ideas were gaining popularity, but it was a 1928 paper by Herman Mark and Kurt Meyer that finally convinced chemists that Staudinger had been right. Mark and Meyer used x-ray crystallography to probe the structure of a crystallized polymer and found that polymers were indeed long-chain molecules in which repeating units were linked by covalent bonds.

Staudinger spent the next twenty or so years building up macromolecular chemistry and helping to lay the foundation for today's multibillion-dollar polymer industry. He retired in 1951 and received the 1953 Nobel Prize in chemistry for his work on polymers. He died on September 8, 1965. SEE ALSO POLYMERS, NATURAL; POLYMERS, SYNTHETIC.

Thomas M. Zydowsky

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Steel

alloy: mixture of two or more elements, at least one of which is a metal

Steel is an **alloy** of iron with about 1 percent carbon. It may also contain other elements, such as manganese. Whereas pure iron is a relatively soft metal that rusts easily, steel can be hard, tough, and corrosion-resistant. Used to make almost everything from skyscraper girders, automobiles, and appliances to thumb tacks and paper clips, steel is one of the world's most vital materials. Among all the metals, iron is second only to aluminum in natural abundance, making up 4.7 percent of the earth's crust, and occurring mainly as its various oxides. The main product made from iron is steel, the least expensive and most widely used of all metals.

A steel worker is catching a sample of molten steel in a crucible during the manufacturing process.

History

It appears that ancient peoples were using iron as early as 4000 B.C.E. for making various tools, weapons, and other objects. They apparently obtained the iron from meteorites. The composition of those earliest iron artifacts was higher in nickel than native iron ores on Earth, in keeping with the composition of meteorites. In fact, the word "iron" comes from an ancient term meaning "metal from the sky." It is interesting to note that when Admiral Robert Peary visited Greenland in the 1890s, he found that the Inuit had for many years been making iron tools from a 30-ton iron meteorite that had fallen there centuries earlier.

While it is not known exactly when people learned how to remove iron from its ores, by 1200 B.C.E. iron ore was being mixed with burning wood or charcoal and turned into hot masses from which iron metal could be "wrought" by repeated hammering. Placing the iron back in burning charcoal seemed to make it harder and stronger. The iron picked up carbon from the charcoal, especially along its surface, turning it into the hard material that has come to be known as steel.

During the first millennium B.C.E. a highly superior steel product was made in India, in a region near Hyderabad. Well known for its strength and its wavy patterned surface, it was especially desirable for making sword blades. Some think that the ore found in that area just happened to have the right impurities to give the steel special properties. The hot iron was repeatedly forged and folded to produce a metal of extremely high quality that became famous all over the ancient world. It was especially sought after by Europeans, who called it “wootz”; by Moors living in Spain, who used it to make their Toledo blades; and by Arabs, who used it in their famous Damascus swords.

Making Steel

Over the years various countries have excelled in making steel. During the eighteenth century a relatively small amount of steel was made, but Sweden was the main producer. In the nineteenth century Great Britain became dominant. In the twentieth century the United States was the largest steel producer in the world until about 1970, when it was surpassed by the Soviet Union. At the start of the twenty-first century, China led the world in steel production.

Three primary installations in an integrated steel plant are the blast furnace, the steel furnaces, and the rolling mills. The blast furnace converts iron ore to pig iron; the steel furnaces convert the pig iron to steel; and the rolling mills shape the steel into sheets, slabs, or bars.

Blast furnace. A blast furnace is a chimney-like structure in which iron ores (mainly FeO, Fe_2O_3, and Fe_3O_4) are converted into iron metal. Iron ore, coke, and limestone are loaded into the top of the furnace, while air is blown in from below. The coke is converted to carbon monoxide (CO), which then acts as the reducing agent:

$$2\ C + O_2 \rightarrow 2\ CO$$

$$3\ CO + Fe_2O_3 \rightarrow 2\ Fe + 3\ CO_2$$

The molten iron falls to the bottom of the furnace, and the limestone reacts with silicate impurities to form a molten slag, which floats on top of the iron. The two layers are drawn off separately, and the iron is poured into molds. Because the molten iron yields ingots that resemble little pigs, the product is referred to as “pig iron.”

Steel furnaces. In the steel furnace, sulfur and phosphorus impurities and excess carbon are burned away, and manganese and other alloying ingredients are added. During the nineteenth century most steel was made by the Bessemer process, using big pear-shaped converters. During the first half of the twentieth century, the open hearth furnace became the main type of steel furnace. This gave way mid-century to the basic oxygen process, which used pure oxygen instead of air, cutting the process time from all day to just a few hours. In the twenty-first century, most new steel plants use electric furnaces, the most popular being the electric-arc furnace. It is cheaper to build and more efficient to operate than the basic oxygen furnace. In the electric-arc furnace a powerful electric current jumps (or arcs) between the electrodes, generating intense heat, which melts the iron scrap that is typically fed into it. The most modern process for making steel is the continuous process, which bypasses the energy requirements of the blast furnace. Instead of using coke, the iron ore is reduced by hydrogen and CO derived from natural gas. This direct reduction method is especially being used in developing countries where there are not any large steel plants already in operation.

TYPES OF STEEL

Carbon Steel. This is the most widely used kind of steel. Its carbon content is under 2 percent and is usually less than 1 percent. It often also contains a little manganese.

Stainless Steel. This is the most corrosion-resistant kind of steel. It normally contains at least 12 percent (and sometimes up to 30 percent) chromium, and it usually also contains nickel. A very popular stainless steel formulation is 18-8, 18 percent chromium and 8 percent nickel.

Alloy Steels. These contain a little carbon, and sometimes silicon, but they mainly contain added metals, such as manganese (hardness), nickel (strength), molybdenum (improved wear), tungsten (high temperature strength), chromium (corrosion resistance), and vanadium (toughness).

Galvanized Steel. This steel is coated with zinc to protect against corrosion. The coating is usually done by a hot dip process.

Electroplated Steel. This steel has a coating of another metal, usually tin, applied by the use of an electric current. Tin-plated steel is widely used for making cans and other containers.

Tool Steel. This is very hard steel made by tempering (heating to a very high temperature and then quickly cooling).

Damascus Steel. This was a very high quality ancient steel with a beautiful wavy surface pattern used in making sword blades. It seems to have come mainly from India.

Wootz Steel. This was actually a European mispronunciation of *ukku*, the very fine steel made in ancient India that they called "wook." (It is probably the same material as Damascus steel.)

Finishing processes. A final step in processing steel is shaping. Liquid steel can be cast into ingots or various other forms. They can then be sent to rolling mills. There are hot rolling mills and cold rolling mills. Various kinds of steel slabs are rolled into sheets, strips, bars, or other kinds of products. Sometimes the steel is forged into shape with hammers or presses, or the hot steel is extruded through dies to give it some desired shape. For example, steel wire is made by drawing hot steel rods through smaller and smaller dies. Some steel is finished by grinding or polishing, and some is coated with zinc or electroplated with tin.

World Steel Production

The three top steel producers in the world are China, the United States, and Japan, in that order. The United States and Japan each produce around 100 million tons (90 million metric tons) of steel per year, and China had an output in 2000 of about 140 million tons (127 million metric tons). Iron and steel make up approximately 90 percent of all the metal produced in the world. The largest steel company in the United States is United States Steel, which produces about 20 percent of the country's steel.

Steel plants vary widely in size. Some large integrated plants include coke ovens, blast furnaces, several kinds of steelmaking furnaces, and various mills for rolling the steel into sheets or slabs. Some companies dig their own ore and run their own coal mines and limestone quarries, and some even operate their own railroads and barges. Other steel plants consist of a single electric furnace for melting scrap with a small mill for turning the melted steel into bars. These scrap recycling plants are known as

A steel bridge in Portland, Oregon. Steel's strength and resistance to corrosion make it an alloy useful for many purposes.

"minimills," and they now account for about half of steel production in the United States. There were about 160 steel plants operating in the United States in 2003, and most of them were minimills. SEE ALSO IRON.

Doris K. Kolb

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Steroids

Steroids are a family of **lipid** molecules that includes cholesterol, steroid hormones, and bile salts. These amphipathic molecules (containing both **hydrophobic** and **hydrophilic** regions) are derived from two-carbon acetyl-CoA

lipid: a nonpolar organic molecule; fatlike; one of a large variety of nonpolar hydrophobic (water-hating) molecules that are insoluble in water

hydrophobic: a part of a molecule that repels water

hydrophilic: a part of a molecule having an affinity for water

units, whose combination leads to the formation of isoprenoids (five-carbon **isoprene** molecular units), and finally to the formation of a seventeen-carbon tetracyclic hydrocarbon, the steroid skeleton. Figure 1 shows the basic steroid skeleton structure, made up of three six-membered rings and one five-membered ring. The fused six-membered cyclohexane rings each have the **chair conformation**. Each member of the steroid family has a structure that differs from this basic skeleton in the degrees of unsaturation within the ring system and the identities of the hydrocarbon side chain substituents attached to the rings. These substituents are in most cases oxidized to alcohol, **aldehyde**, **ketone**, or **carboxylic acid functional groups**.

The general term *sterol* refers to a subgroup of steroids that contain an alcohol functional group, which is signified by the -ol ending. Steroids are found predominantly in **eukaryotic cells**, with cholesterol being the most abundant steroid molecule. It contains twenty-seven carbons, has an alcohol functional group at C-3, a methyl group at C-13, and a branched aliphatic hydrocarbon (eight carbons) unit at the C-17 carbon atom. It is the basic building block for all the other steroid molecules. The **biosynthesis** of other steroids from cholesterol yields molecules that have fewer carbons, are more polar and more oxidized, and have smaller and more oxidized hydrocarbon units at C-17. It should be emphasized that cholesterol and most steroids contain predominantly single (C–C) bonds and take on non-planar structures. Intracellular cholesterol is predominately found as part of (embedded in) the plasma cell membranes. Because of cholesterol's bulky structure, it does not embed well into the lipid bilayer structure of a membrane and as a result disrupts the order or regularity of the membrane. Increasing levels of embedded cholesterol, which can be as high as 25 percent of membrane volume, correlates with increasing the fluidity (as opposed to rigidity) of the membrane.

The level of extracellular cholesterol in blood serum correlates with the degree of advancement of atherosclerosis and the development of coronary heart disease. The serum cholesterol is obtained from diet and from biosynthesis, which occurs primarily in the liver of mammals. The usual metabolic pathway for cholesterol biosynthesis involves a sequence of more than twenty reactions, each catalyzed by a specific enzyme. The committed and the rate-limiting step in the sequence is the **synthesis** of a six-carbon molecule, mevalonate, catalyzed by the enzyme 3-hydroxy-3-methylglutaryl CoA reductase (HMG CoA reductase). The development of drugs that inhibit the activity of HMG CoA reductase (and that reduce levels of serum cholesterol), has led to a decline in coronary heart disease. These drugs have structures similar to that of mevalonate and serve as **competitive inhibitors** of HMG CoA reductase. The binding of a competitive inhibitor to the enzyme and of the substrate mevalonate to the same enzyme are mutually exclusive events. One of the most potent inhibitors of HMG CoA reductase is the drug lovastatin, which binds very strongly at the active site of the enzyme, and, as a result, serum cholesterol levels in humans are decreased by as much as 20 percent.

The hydrophobic, water-insoluble cholesterol is transported in blood to cells predominantly as part of high density and low density lipoprotein particles (HDLs and LDLs, respectively). LDLs transport cholesterol to extrahepatic tissues. The LDL particles bind to LDL **receptors** on the cell

isoprene: common name for 2-methyl-1,3butadiene, the monomer of the natural rubber polymer

chair conformation: arrangement of atoms in a cycle structure (usually a six-membered ring) that appears to be arranged like a chair (as opposed to the other conformation, which is described as a "boat")

aldehyde: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the RC(O)H functional group

ketone: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the RC(O)R functional group

carboxylic acid: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the $–CO_2H$ functional group

functional group: portion of a compound with characteristic atoms acting as a group

eukaryotic cell: cell characterized by membrane-bound organelles, most notably the nucleus, and that possesses chromosomes whose DNA is associated with proteins

biosynthesis: formation of a chemical substance by a living organism

synthesis: combination of starting materials to form a desired product

competitive inhibitor: species or substance that slows or stops a chemical reaction

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

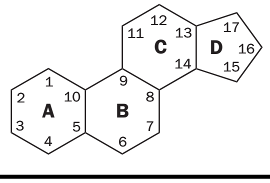

Figure 1. Steroid skeleton.

membranes, facilitating cholesterol deposition at the cells, for use primarily as a component of the membrane. HDLs carry out a similar transport function but also return cholesterol to the liver, where it can be metabolized. In this way HDLs decrease the levels of the cholesterol that contributes to the deposition of plaque in arteries and is implicated in heart disease. In a number of cases, patients have been found to have defective genes that **code** for the LDL receptors. In these cases the LDL particles cannot deposit the cholesterol at cell sites. The LDLs remain in the blood, and eventually their lipid molecules accumulate on the arterial walls, which can lead to blockage of arteries and a heart attack.

code: mechanism to convey information on genes and genetic sequence

metabolites: products of biological activity that are important in metabolism

nonpolar: molecule, or portion of a molecule, that does not have a permanent, electric dipole

emulsify: process of forming an emulsion; of suspending one phase of an immiscible pair of phases in the other

hydrolyze: to react with water

Cholesterol is the precursor of other important steroid **metabolites**, which include bile salts and steroid hormones. Bile salts, which are the major breakdown product of cholesterol, resemble detergents, which are amphipathic molecules (having both polar and **nonpolar** regions). Their primary function is to **emulsify** dietary lipids. This interaction between bile salt and lipid increases the surface area of exposed lipid, which greatly enhances the ability of lipase enzymes to get access to and **hydrolyze** lipid molecules, thereby promoting their absorption and digestion. Bile salts are synthesized and secreted by the liver, stored in the gall bladder, and pass through the bile duct and into the small intestine. Bile salts are the major metabolic product of cholesterol, their manufacture accounting for the consumption of approximately 800 mg/day of cholesterol in a normal human adult. (On the other hand, less than one-tenth that amount of cholesterol is utilized for steroid hormone synthesis.) A major bile salt is glycocholate.

glucocorticoid: class of hormones that promotes the breakdown of proteins to make amino acids available for gluconeogenesis; this elevates the blood sugar level and leads to glycogen synthesis in the liver

progesterone: steroid found in the female reproductive system: formula $C_{21}H_{30}O_2$

androgen: group of steroids that act as male sex hormones

Cholesterol is also the precursor of all the steroid hormones, which can be subdivided into five major classes. The first and second classes of hormones, the mineralocorticoids and the **glucocorticoids**, are synthesized in the adrenal cortex. The mineralocorticoids (e.g., aldosterone) regulate the body's ion balance by promoting the reabsorption of inorganic ions, such as Na^+, Cl^-, and $HCO3^-$, in the kidney. As a result, they are involved in the regulation of blood pressure. The glucocorticoids (e.g., cortisol) regulate gluconeogenesis and, in pharmacological doses, inhibit the inflammatory response. The third class includes **progesterone**, associated with the female reproductive cycle and synthesized in the cells of the corpus luteum; it prepares the lining of the uterus for implantation of the ovum and is essential for the maintenance of pregnancy. The sex hormones are synthesized in the male and female gonads and in the placenta. These hormones, the fourth and fifth classes, are **androgens** (primarily testosterone) and the estrogens (primarily estradiol). These two classes of hormones are associated with the development of the secondary sexual characteristics of males and females, respectively. They exert powerful physiological effects in humans because of their importance in the regulation of a variety of vital metabolic processes.

metabolism: the complete range of biochemical processes that take place within living organisms; comprises processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those that break down complex food molecules, thus liberating energy (catabolism)

micromolar: relating to a solution of a substance that is in the concentration range of micromoles per liter, or 10^{-6} moles per liter

Steroid hormones, like all hormones, are chemical messengers. They are synthesized in the cells of an endocrine gland, secreted by the cells into the bloodstream, and travel to target organs in which they direct cell-to-cell communication and the "global regulation" of **metabolism** in a multicellular organism such as humans. The levels of the steroid hormones are also highly regulated, with levels in the blood or in cells being very small, typically less than **micromolar** amounts. Because of their hydrophobic

The anabolic steroid Durabolin causes a muscle cell to store more nitrogen, facilitating muscle growth.

character, they must associate with carrier molecules for their transport in the blood.

In contrast to **polypeptide** hormones that bind to hormone receptor proteins embedded in the plasma membranes of cells, the hydrophobic steroid hormones pass from the bloodstream into cells readily via **passive diffusion** across the membrane. Although the steroid hormones can in principle enter all cells, the only cells that are responsive to steroid hormones are those cells that contain proteins called steroid hormone receptors. These receptors reside in an inactive state either in the cytoplasm or in the cell nucleus. There are specific hormone receptors for each of the hormone types: **estrogen**, androgen, progesterone, glucocorticoid, and mineralcorticoid. As a result of the hormone binding to the recognition site of its hormone receptor, an inactive receptor is transformed into a functionally active one. These active hormone-receptor complexes are **ligand**-activated **transcription** factors, which are then able to migrate to the **DNA** in the nucleus and bind to the promoter regions of a specific subset of genes. This stimulates the transcription of genes that are sensitive to the presence of the

polypeptide: compound containing two or more amide units—C(O)NH—produced by the condensation of two or more amino acids

passive diffusion: mechanism of transporting solutes across membranes

estrogen: female sex hormone

ligand: molecule or ion capable of donating one or more electron pairs to a Lewis acid

transcription: enzyme-catalyzed assembly of an RNA molecule complementary to a strand of DNA

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

expressed: made to appear; in biochemistry—copied

RNA: ribonucleic acid, a natural polymer used to translate genetic information in the nucleus into a template for the construction of proteins

anabolism: metabolic process involving building of complex substances from simpler ones, using energy

hormone. These genes are only **expressed** or transcribed when the hormone is present. The messenger **RNA** that is produced is then translated into a new set of proteins. As a result of this stimulation of gene expression, the metabolic character of the cell is dramatically changed.

Anabolic steroids are synthetic substances related to male sex hormones (androgens). Although it is illegal in the United States to possess or distribute anabolic steroids for nonmedical use, a "black market" for them exists, and many amateur and professional athletes take them to enhance performance. In many cases, the athletes take doses that are extremely high—perhaps 100 times the doses that might be prescribed for medical use. As a result, they put themselves in real danger of short-term and long-term health problems. Blood testing, as has been used in the Olympic Games, can detect, identify, and quantify the presence of anabolic steroids in the blood of athletes, which can lead to the disqualification of an athlete. SEE ALSO Cholesterol; Cortisone; Estrogen; Lipids; Testosterone.

William M. Scovell

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Stimulants

The substances referred to as stimulants are a variety of compounds that excite the central nervous system or alter the body's metabolic activity. Some stimulants enhance alertness and increase energy whereas others affect emotions and oppose psychological depression.

One way in which chemical stimulants function is to mimic or enhance the effects of hormones that prepare animals for "fight or flight" when they are faced with threatening situations. They bring about an increased heartrate, increased blood pressure, and an increased rate of respiration. One way in which such hormones (or their imitators) prepare the body for sudden action is to increase the breakdown of glycogen and **glucose** in order to meet the increased demand for energy. The best examples of these hormones are the catecholamines (epinephrine, also known as **adrenalin**, and norepinephrine, also known as noradrenalin). The hormones bind to **receptors** on target muscle cell membranes and prompt formation of cyclic adenosine monophosphate (cAMP), known as a "second messenger" because it transmits a signal to many intracellular molecules involved in **metabolism** (epinephrine and norepinephrine being first messengers). In order for a subsequent message to be received (and for intracellular alterations related to fight or flight to be maintained), hormones and second messengers must be rapidly removed from cell surfaces once they have delivered their messages. An enzyme classified as a phosphodiesterase degrades cAMP to a form that is inactive. Some of the most common stimulants, such as caffeine and related compounds in tea and chocolate, inhibit the phosphodiesterase enzyme so that cAMP levels remain high enough to maintain the alerted state.

glucose: common hexose monosaccharide; monomer of starch and cellulose; also called grape sugar, blood sugar, or dextrose

adrenalin: chemical secreted in the body in response to stress

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

metabolism: the complete range of biochemical processes that take place within living organisms; comprises processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those that break down complex food molecules, thus liberating energy (catabolism)

Speed is a stimulant that excites the central nervous system.

A second way in which stimulants exert their effects is by inhibiting the neurochemistry that involves the transmission of signals from one nerve cell to another. When a nerve cell receives a signal, that signal is propagated to the far end of the long nerve cell. In order for that signal to be transmitted to the next nerve cell, molecules called neurotransmitters are released into the spaces (synapses) between the cells. The neurotransmitters bind to specific receptors on the receiving cell, thus passing on the signal. In order to prepare for a new signal, neurotransmitters must be removed from the intercellular space through reuptake or degradation.

Cells can also recover from the signal for the fight or flight reaction by taking hormones that they have released back up into themselves. Cocaine interferes with the reuptake of adrenalin by cells in the cortex of the brain, thus intensifying the effects of adrenalin and producing a sense of euphoria and (sometimes) hallucinations. Cocaine use leads to psychological dependency and can cause convulsions, respiratory failure, and death.

Amphetamines are drugs that mimic the effects of epinephrine, or adrenalin. Because effects such as mental illness and brain damage can result from overuse of amphetamines, they currently have limited medical use. Metamphetamines are similar to amphetamines in structure and action but have fewer undesirable side effects. Ritalin (methylphenidate), commonly used to treat attention deficit disorder, has essentially the same mode of action as amphetamines. Ritalin abuse by middle and high school students has become a common concern.

amphetamine: class of compounds used to stimulate the central nervous system

Because of their adverse effects, the Food and Drug Administration (FDA) has taken action to remove two over-the-counter products that have amphetamine-like action: ephedrine, an agent with actions similar to those of epinephrine and the main active ingredient in the herb ephedra, used for weight loss and in energy-enhancement cold medicines; and weight loss products that contain phenylpropanolamine, which can raise blood pressure and increase the risk of stroke.

Opiates such as morphine and codeine are thought to enhance the release by neurons of the neurotransmitter dopamine; the release of dopamine leads to a sense of euphoria. These drugs are addictive and are often abused. In general, all antipsychotic medications work by blocking dopamine receptors in the forebrain. Nicotine mimics the action of the neurotransmitter **acetylcholine** at receptors having to do with the transmission of signals between autonomic nerve cells and skeletal muscle. SEE ALSO CAFFEINE; EPINEPHRINE; METHYLPHENIDATE; NEUROCHEMISTRY; NEUROTRANSMITTERS; NOREPINEPHRINE.

acetylcholine: neurotransmitter with the chemical forumula $C_7H_{17}NO_3$; it assists in communication between nerve cells in the brain and central nervous system

Sharron W. Smith

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Stoichiometry

Stoichiometry refers to the ratios of products and reactants in a chemical reaction. It is a fundamental concept in chemistry, and we shall give a more exact description later.

Early Stoichiometry

The masses of the starting materials and of the products of chemical reactions were of obvious interest to early chemists. The earliest measurements may have been made by prehistoric **metal** workers who weighed a metal ore with a primitive balance and compared the weight with that of the extracted metal. Weighing was the most common and most accurate measurement that chemists could make for many centuries. An early example is the work of Belgian chemist Johann van Helmont in the early seventeenth century. Van Helmont weighed a large pot containing a growing plant at intervals and tried to show that the gain in weight was fully accounted for by the water added. He did not measure the carbon dioxide gas taken up or the oxygen released by the plant and so his conclusion was not valid, although the measurements were roughly correct.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Whether or not pure substances have the same proportion by mass of their constituents was by no means initially obvious. Around 1800 two French chemists, Claude Berthollet and Joseph Proust, supported opposite views on this topic. If a metal such as lead is heated in air, there is a gradual color change as lead oxide is slowly formed. Berthollet argued for a combination of "indefinite proportions" as this transformation occurs: the reactant is lead, the product is lead oxide, and there is an indefinite number of **intermediates**. Proust argued for "definite proportions" in that the system would at all times consist only of lead mixed with lead oxide (for simplicity we can ignore that more than one oxide of lead exists). The ratio of lead to lead oxide would change as the reaction proceeded but the system would have only two components. The wide acceptance of English

intermediate: molecule, often short-lived, that occurs while a chemical reaction progresses but is not present when the reaction is complete

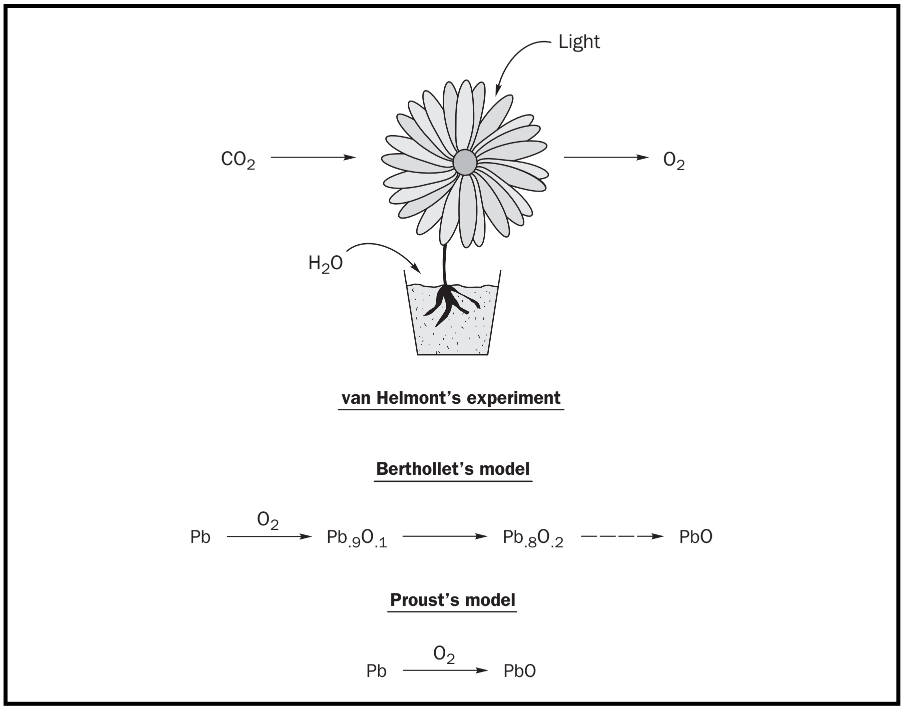

Figure 1. Early experiments to test the masses of reactants and products of chemical reactions.

chemist and physicist John Dalton's **atomic theory** a few years later convinced most chemists that Proust was right and that there was a Law of Definite Proportions for pure compounds.

atomic theory: physical concept that asserts that matter is composed of microscopically tiny particles called atoms and that various elements differ from each other by having different atoms

The term "stoichiometry" was devised by German chemist Jeremias Richter in 1792 to describe the measurement of the combining ratios of chemical elements by mass. The term has since been expanded to include the combining ratios of substances in any chemical reaction. Richter studied mathematics with philosopher Immanuel Kant and wrote a thesis on the use of mathematics in chemistry. He was convinced that all chemical changes could be described in terms of simple whole-number ratios. He put forward the Law of Reciprocal Proportions, stating that if two chemical elements unite separately with a third element, the proportion in which they unite with the third element will be the same or a multiple of the proportion in which they unite with each other. This law has disappeared from most chemistry textbooks, but a companion law, the Law of Multiple Proportions, has survived.

The Law of Multiple Proportions states that when two elements combine to form two or more different compounds, the weights of one compound that can combine with a given weight of the second compound form small whole number ratios. For example, consider one experiment in which 10.0 grams of sulfur is combined with 10.0 grams of oxygen to form an oxide of sulfur, and another experiment under different conditions in which 3.21 grams of sulfur is combined with 4.82 grams of oxygen to form a different oxide. For each 10.0 grams of sulfur used in the second experiment, 15.0 grams (4.82 × 10.0/3.21) of oxygen is used. The ratios of the masses of oxygen that combine with a fixed mass of sulfur are 10.0:15.0, which is equal to the whole number ratio 2:3. This conforms to the Law of Multiple Proportions. (See Figure 2.)

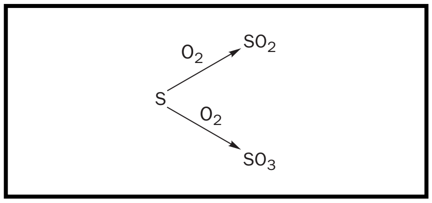

Figure 2.

The Laws of Reciprocal and Multiple Proportions have ceased to have predictive scientific value. Their importance lies in the fact that they provided evidence that Dalton needed in 1807 to postulate his atomic theory. The reason for Richter's whole number ratios has since become obvious: the simple ratios occur because atoms, although having different masses, react in simple ratios. Dalton's insistence that atoms cannot be split in chemical reactions holds true in modern chemistry.

Balancing Chemical Equations

Chemical equations are an indispensable way of representing reactions. They are routinely used to calculate masses of reactants and products. In the case of the examples used above for the Law of Multiple Proportions, the equations are:

$$S + O_2 = SO_2 \tag{1}$$

$$2S + 3O_2 = 2SO_3 \tag{2}$$

Note that we do not write the second equation as:

$$S + 3O = SO_3 \tag{3}$$

because O (an oxygen atom) means something very different from O_2 (an oxygen molecule). Chemical equations also introduce the concept of a limiting **reagent**, or the reactant that is used up first in a reaction, when one or more components are in excess of the stoichiometric amount.

reagent: chemical used to cause a specific chemical reaction

The balancing of chemical equations is a common exercise in elementary stoichiometry. It is not always appreciated, however, that some chemical equations are ambiguous in that they can be balanced in more than one way. Consider, for example, the following equation:

$$H^+ + ClO_3^- + Cl^- \rightarrow Cl_2 + ClO_2 + H_2O \tag{4}$$

where the dashed arrow signifies an unbalanced equation. It may be balanced as follows:

$$4H^+ + 2ClO_3^- + 2Cl^- = Cl_2 + 2ClO_2 + 2H_2O \tag{5}$$

Both sides of this equation have four H-atoms, six O-atoms, four Cl-atoms, and a total charge of zero. Equation 5 can also be balanced as:

$$16H^+ + 4ClO_3^- + 12Cl^- = 7Cl_2 + 2ClO_2 + 8H_2O \tag{6}$$

Here both sides have 16 H-atoms, 12 O-atoms, 16 Cl-atoms, and a total charge of zero. How can both equations balance, and which is correct? To answer the first question, many equations can be written as the sum of two or more component reactions. In this case the following related reaction can be used:

$$8H^+ + 2ClO_2 + 8Cl^- = 5Cl_2 + 4H_2O \tag{7}$$

If equation (5) is doubled and added to equation (7), the result is equation (6). Alternatively, equation (5) could be tripled and added to equation (7) to obtain yet another balanced equation with the same reactants and products in different stoichiometric amounts. There is therefore no limit to the number of balanced equations.

Deciding which equation is "correct" is often difficult because one of many competing pathways may take precedence in a reaction, depending on the energy requirements of the system (the thermodynamic limitations) and the speed of the reactions (the kinetics of the system). In the example above, analysis shows that equation (5) is thermodynamically unfavorable at room temperature while equation (6) is favorable.

Non-Stoichiometric Compounds

Most of chemistry is governed by simple whole-number ratios of molecules and atoms. Simple stoichiometry, although valid for the vast majority of mole ratios, is not universal: there are compounds with non-integral mole ratios. Substances such as **alloys** and glasses created problems for the initial acceptance of Dalton's atomic theory. There are, in addition, simple non-stoichiometric compounds that have varying ratios of constituent atoms. Such compounds are generally crystalline solids with defects in their crystal lattices; the lack of simple stoichiometry may give them important properties. Wustite, an oxide of iron, is an example of a non-stoichiometric compound. Its formula can be written $Fe_nO_{1.000}$, where n may have values varying from 0.88 to 1.00 and its physical and chemical properties will vary somewhat depending on the value of n.

alloy: mixture of two or more elements, at least one of which is a metal

Current Applications of Stoichiometry

Most chemical reactions are complex, occurring via many steps. In such cases, can an overall reaction be written that describes the stoichiometry of a system under consideration? Consider an example in which sulfur is burned in oxygen to simultaneously form sulfur dioxide (mostly) and some sulfur trioxide:

$$S + O_2 \rightarrow SO_2 \tag{8}$$

$$S + 1.5\ O_2 \rightarrow SO_3 \tag{9}$$

(Note that the "1.5" in reaction (9) means 1.5 moles, not 1.5 molecules.) If the two reactions are added, the resulting equation is: $2S + 2.5\ O_2 \rightarrow SO_2 + SO_3$. This representation of the reaction is plainly wrong because it states that one mole of SO_2 is obtained for every mole of SO_3, whereas most of the products consist of SO_2. The reason for this inconsistency is that the arrows in reactions (8) and (9) mean "becomes"; they are not equivalent to equals signs because they involve time dependence. In order to obtain an overall stoichiometric description of the reaction, both equations (8) and (9) are necessary, as is knowledge about their relative importance in the overall reaction.

Stoichiometry also has biochemical applications. In this case, the systems are biological networks. A typical biological network might be the central **metabolism** of a bacterium living in the gut under anaerobic conditions. This system consists of multiple processes that occur simultaneously involving reactions catalyzed by many enzymes. At the same time that reactants such as **glucose** are being consumed, many different metabolic products are being formed, and the combined reactions provide energy for the overall process. By doing experiments in which some genes in the bacterium have been deactivated, and then analyzing the "metabolic balance sheets," it becomes possible to identify which genes are essential for the overall process and which have no effect. It then becomes possible

metabolism: the complete range of biochemical processes that take place within living organisms; comprises processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those that break down complex food molecules, thus liberating energy (catabolism)

glucose: common hexose monosaccharide; monomer of starch and cellulose; also called grape sugar, blood sugar, or dextrose

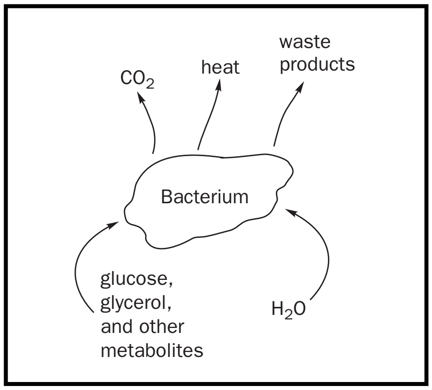

Figure 3. The stoichiometry of a complex reacting system like polluted air in sunlight is very complicated.

to predict the properties of mutants of the bacterium. SEE ALSO EQUATIONS, CHEMICAL.

Sidney Toby

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Storage Protein

Storage proteins serve as reserves of **metal** ions and amino acids, which can be mobilized and utilized for the maintenance and growth of organisms. They are particularly prevalent in plant seeds, egg whites, and milk.

Perhaps the most thoroughly studied storage protein is ferritin, which stores iron. Iron is a mineral required by all living things; it is a component of heme, which is found in the transport protein hemoglobin, as well as of cytochromes, molecules taking part in cell **metabolism** (including drug metabolism). Free iron in solution, on the other hand, is able to participate in free radical reactions that damage proteins, **lipids**, and nucleic acids. Therefore, within organisms, in addition to serving as an iron reserve, ferritin provides a safeguard against potentially harmful side effects of iron.

Ferritin is a complex of 24 **polypeptide** chains that form a nearly spherical shell around a core of up to 4,500 iron atoms stored as iron oxide–hydroxide (ferrihydrite) complexes. Ferritin is able to store and release iron in a controlled fashion.

Proteins are made from amino acids, and many storage proteins serve as reserves of amino acids in embryonic and developing organisms. This is true of both animals and plants. Two well-known storage proteins in animals are casein and ovalbumin. Casein, found in mammalian milk, and ovalbumin, found in egg white, both provide a developing organism with a ready source of amino acids and organic nitrogen.

Plant storage proteins are found in high concentrations in seeds, especially in leguminous plants, in which the storage proteins constitute up to 25 percent of the dry weight of the seed. These proteins have no known enzymatic function and often exist within separate **vesicles** (packets) in the seeds. In addition to their importance to the germinating seed, these plant storage proteins are a valuable source of human nutrition. SEE ALSO IRON; LIPIDS; NUCLEIC ACIDS; PROTEINS; TOXICITY; TRANSPORT PROTEIN.

Paul A. Craig

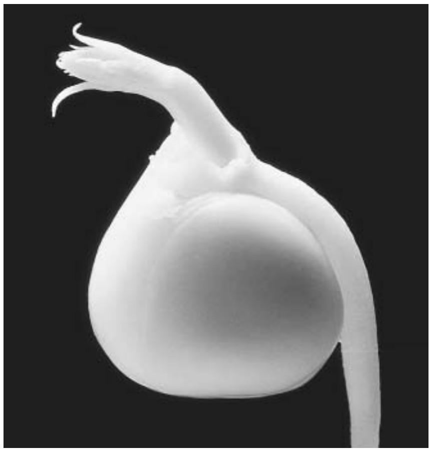
metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

metabolism: the complete range of biochemical processes that take place within living organisms; comprises processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those that break down complex food molecules, thus liberating energy (catabolism)

lipid: a nonpolar organic molecule; fatlike; one of a large variety of nonpolar hydrophobic (water-hating) molecules that are insoluble in water

polypeptide: compound containing two or more amide units—C(O)NH—produced by the condensation of two or more amino acids

vesicle: small compartment in a cell that contains a minimum of one lipid bilayer



Storage proteins are a source of amino acids for growing organisms, such as this germinating garden pea.

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Strontium

MELTING POINT: **769°C**

BOILING POINT: **1,383°C**

DENSITY: **2.54 g/cm^3**

MOST COMMON IONS: **Sr^{2+}**

38
Sr
STRONTIUM
87.62

Strontium is the thirty-eighth element in the Periodic Table and the sixteenth most abundant element in Earth's crust. It was first recognized by Adair Crawford in 1790, who named the substance "strontianite," after the Scottish town of Strontian where samples were originally obtained. However, it was Sir Humphrey Davy who actually isolated strontium in elemental form in 1808, using his electrolysis apparatus.

There are four stable **isotopes** of strontium that are found naturally. In addition there are about twenty radioactive isotopes, including strontium-90, a deadly by-product of **nuclear**-bomb detonations. The natural forms of strontium are relatively nontoxic. Similar to calcium both physically and chemically, elemental strontium is a soft, shiny **metal**. Like calcium and other alkaline earth metals, it is easily oxidized and thus not found naturally in its free elemental state. Instead, it almost always is found in the +2 **oxidation** state, forming such compounds as strontium oxide (SrO), strontium sulfate ($SrSO_4$, from the mineral celestite), strontium carbonate ($SrCO_3$, from the mineral strontianite), and strontium chloride ($SrCl_2$). Strontium nitrate, $Sr(NO_3)_2$, is used to produce the brilliant red color seen in some fireworks and signal flares and is also used in making "tracer bullets" that can be seen when fired at night. Other strontium compounds are sometimes used in the manufacture of special glasses. Yet overall, strontium is not a very important element industrially or commercially. SEE ALSO Davy, Humphry

isotope: form of an atom that differs by the number of neutrons in the nucleus

nuclear: having to do with the nucleus of an atom

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

David A. Dobberpuhl

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Strutt, John (Lord Rayleigh)

ENGLISH PHYSICIST
1842–1919

John William Strutt was born at Langford Grove in Essex, England, and was the first child of John James Strutt, the second Baron Rayleigh. In 1861 Strutt ventured to Cambridge University where he studied at Trinity College, the

English physicist John William Strutt, the third Baron Rayleigh, who discovered argon.

same institute attended by Isaac Newton. Strutt received his B.A. in 1865 and was elected a fellow of Trinity College.

Since in those days there were no university laboratory facilities, Strutt established his own at the family home, Terling Place. There he started research in electrodynamics, color vision, radiation scattering, acoustics, and other experimental phenomena that could be explained in terms of wave motion. In 1870 he published his classic paper "On the Theory of Resonance" that established Strutt's reputation as a serious scientist capable of handling both experimental and mathematical problems. In 1871 he followed up with his well-known theory of light scattering by small particles (now called Rayleigh scattering) and explained how this phenomenon is responsible for the blue color of the sky.

Upon the death of his father in 1873, Strutt inherited the family title and became the third Baron Rayleigh. With the exception of a short period (1879–1885) as the Cavendish Professor of Experimental Physics at the University of Cambridge, Lord Rayleigh spent the rest of his life working at Terling Place. He published a total of 446 publications covering many areas of physics.

inert: incapable of reacting with another substance

Strutt's best-known work, and one for which he was awarded the Nobel Prize in physics in 1904, was his unexpected discovery of the first rare **inert** gas argon. This element was discovered during his attempts to determine more reliable atomic weights by making very precise density measurements on gases. For nitrogen he found that when extracted from the atmosphere, it was heavier than nitrogen obtained by the decomposition of pure ammonia gas. He suspected that the nitrogen obtained from the air contained an impurity, and when Strutt published his density results, he requested suggestions on how to identify the impurity and correct it.

atomic weight: weight of a single atom of an element in atomic mass units (AMU)

William Ramsay, a professor of chemistry at University College, Bristol, took up the challenge, and, knowing that nitrogen could be removed from air by passing it over heated magnesium, he was able to isolate a pure sample of the material that was the cause of Rayleigh's difficulties. Also he showed, by its emission spectra, that it was a new species. Since the gas was found to be chemically inert, it was given the name argon, from the Greek word *argos*, meaning "inert." Ramsay and Rayleigh published a joint paper on the discovery of this new element in 1895, pointing out that its **atomic weight** of 40 and its properties did not fit into the Periodic Table current at that time. Ramsay went on to discover other inert gases now known as helium, neon, krypton, xenon, and radon and was honored for this work with the Nobel Prize in chemistry at the same time that Lord Rayleigh received the same award in physics. SEE ALSO ARGON; RAMSAY, WILLIAM.

John E. Bloor

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Substrate

A substrate is the substance upon which an enzyme acts in an enzymatic reaction. Enzymes are biological catalysts that increase the rate of chemical reactions by decreasing the activation energy required for that reaction. An enzyme catalyzes a chemical reaction converting a substrate reactant to a product. An individual enzyme generally has more than one substrate and may be specific to several reaction **intermediates** that are part of an overall reaction.

intermediate: molecule, often short-lived, that occurs while a chemical reaction progresses but is not present when the reaction is complete

The three-dimensional structure of an enzyme determines its substrate binding specificity. A simple hypothesis proposed by German chemist Emil Fischer in 1894 suggested that the specificity of an enzymatic reaction could be likened to a lock and key. In the lock and key hypothesis, the geometric **complementarity** of the structures of the enzyme (the lock) and the substrate (the key) accounts for the specificity of the reaction. Although scientists were not able to determine the actual three-dimensional structures of enzymes and substrates until many years later, the basic idea of the lock-and-key hypothesis has held. A more refined hypothesis, known as the induced fit hypothesis, proposes that the binding of the substrate by the enzyme changes the structure of the enzyme, resulting in an even greater affinity of the enzyme for the substrate. The site on an enzyme that binds the substrate (known simply as the substrate binding site) is most often a pocket or cleft in the approximately globular structure of the enzyme.

complementarity: basis for copying the genetic information, where each nucleotide base has a complementary partner with which it forms a base-pair

The term *substrate* has another meaning in chemistry. Some chemical syntheses are carried out in mixed phases; for example, the reactants exist in solution but the reaction itself occurs at the surface of a solid. The identity of the solid, specified in experimental protocols, influences the **synthesis** reactions, and the solid is referred to as the substrate. SEE ALSO Fischer, Emil Hermann.

synthesis: combination of starting materials to form a desired product

Robert Noiva

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Sugars ***See Carbohydrates.***

Sugar Substitutes ***See Artificial Sweeteners.***

Sulfa Drugs

Sulfa drugs were the first synthetic drugs with widespread antibiotic activity to be put into clinical use. In the 1930s German chemists observed that certain dyes used to stain bacteria stopped microbial growth. Gerhard Domagk, a pathologist at I. G. Farbenindustrie, performed a series of experiments on mice infected with streptococcus bacteria and observed that mice injected with an orange-red dye called Prontosil survived bacterial infection. Prontosil is an **azo dye** that had not shown antibacterial activity during

azo dye: synthetic organic dye containing an –N=N– group

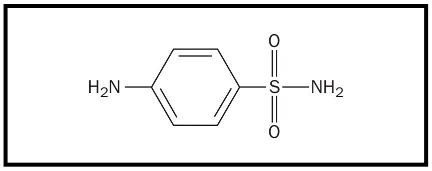

Figure 1. Structure of sulfanilamide.

in vitro: Latin, meaning “in glass” and applied to experiments done under artificial conditions, that is, in a test tube

in vivo: Latin, meaning “in life” and applied to experiments conducted in a living cell or organism

sulfonamides: first of a series of drugs used for the prevention and cure of bacterial infections in humans; sulfanomides are amides of sulfuric acids and contain the $-SO_2NRR_1$ group

biosynthesis: formation of a chemical substance by a living organism

folic acid: pteroylglutamic acid; one of the B complex vitamins

thymine: one of the four bases that make up a DNA molecule

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

earlier **in vitro** tests. However, **in vivo**, the dye is transformed into sulfanilamide, a compound with antimicrobial activity (see Figure 1). Domagk had such faith in Prontosil’s anti-infectious properties that he is reported to have injected the dye into his daughter when she had septicemia. In 1939 Domagk was awarded the Nobel Prize in physiology or medicine for his discovery.

Once sulfanilamide was recognized as an active antimicrobial agent, scientists synthesized thousands of **sulfonamides** to test for bactericidal activity. It was later realized that sulfonamides do not actually kill bacteria; they interfere with bacterial growth and replication. Sulfa drugs are bacteriostatic. They inhibit an enzyme necessary for the **biosynthesis** of **folic acid** in bacteria. Folic acid is necessary for the biosynthesis of **thymine** and the purine bases, the building blocks of **DNA**. Bacteria that are sensitive to sulfa drugs are unable to acquire folic acid from their environment and, in the presence of sulfonamides, are unable to synthesize the folic acid essential for cell growth and multiplication. Sulfonamides do not harm their human hosts, however, because, unlike susceptible bacteria, humans acquire folic acid from their diet and lack the enzyme necessary for synthesizing folic acid. SEE ALSO ALLOSTERIC ENZYMES; ANTIBIOTICS; INHIBITORS; PENICILLIN.

Nanette M. Wachter

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Sulfur

16
S
SULFUR
32.064

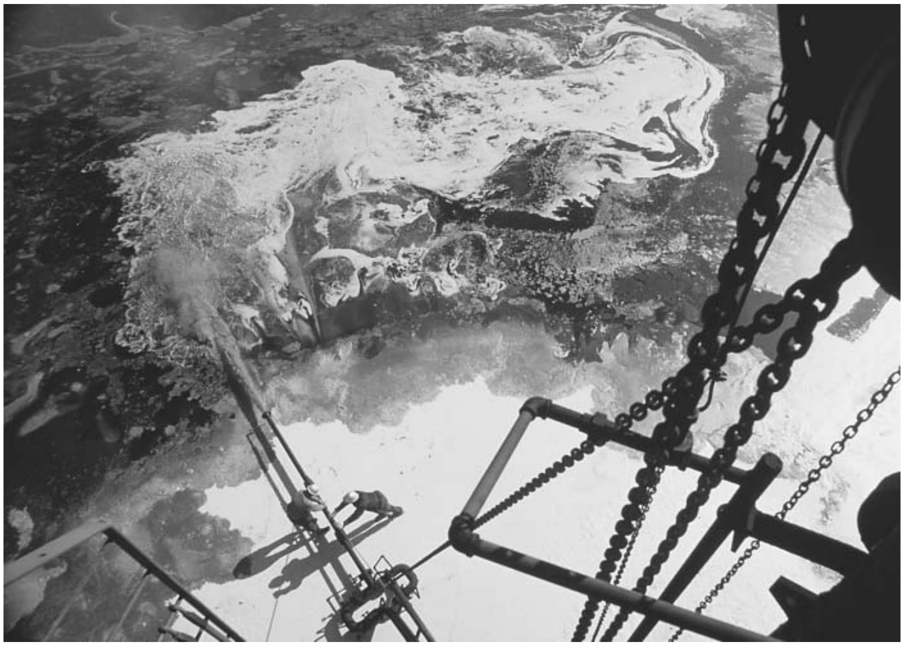
combustion: burning, the reaction with oxygen

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

MELTING POINT: 115.2°C
BOILING POINT: 444.6°C
DENSITY: 2.06 g/cm^3
MOST COMMON IONS: S^{2-}, $S_2O_3^{2-}$, SO_3^{2-}, $S_2O_6^{2-}$, SO_4^{2+}

Sulfur has been known since prehistoric times. Because it is flammable, alchemists regarded sulfur as essential to **combustion**. The chemical properties of sulfur and its compounds, including the reaction of sulfur with mercury (Hg) to form a red solid, mercuric sulfide (HgS), and the use of sulfuric acid (H_2SO_4) as a solvent of **metals**, were discovered at about C.E. 250–300. Gunpowder, a mixture of sulfur, charcoal, and potassium nitrate (KNO_3), was first used for military purposes in China in C.E. 904.

Sulfur is a tasteless, odorless, nonmetallic element. Sulfur along with selenium (Se) and tellurium (Te) are called chalcogens. The valences of sulfur are 2, 4, and 6, which can be represented by compounds such as hydrogen sulfide (H_2S), sulfur dioxide (SO_2), and barium sulfate ($BaSO_4$), respectively. Pure sulfur is insoluble in water. The most stable variety of sulfur, rhombic sulfur, is a yellow crystalline solid.



A vat of sulfur in Port Sulphur, Louisiana. Sulfur is an important crop nutrient and is the thirteenth most abundant element in Earth's crust.

In Earth's crustal composition, sulfur ranks thirteenth in abundance, with an estimated concentration of 0.05 percent. Sulfur exists in elemental form, as metallic sulfides, as sulfates, and, when combined with carbon and nitrogen, in organic forms. Most of the world's sulfur resource is located in North America. It is distributed, in descending order according to share of that resource, as follows: the United States and Canada have 26 percent and 22 percent, respectively, followed by Russia (11%), Saudi Arabia (5%), Japan (5%), Poland (4%), Germany (4%), and France (2%); the remaining 21 percent is distributed in other countries.

Sulfur is commercially important in the manufacture of chemicals such as sulfuric acid. The chemicals, in turn, are used in the manufacture of sulfa drugs, **vulcanized rubber**, acid batteries, dyes, and so on. In agriculture, sulfur is the fourth most important crop nutritive element, after nitrogen, phosphorus, and potassium. Its use in fertilizers is increasing rapidly. Sulfur is also used to manufacture poultry feed additives, pesticides, and parasiticides. SEE ALSO CHALCOGENS.

vulcanized rubber: chemical process of mixing rubber with other materials like sulfur; it strengthened rubber so it could be used under hot or cold conditions; discovered by Charles Goodyear

Guang Wen

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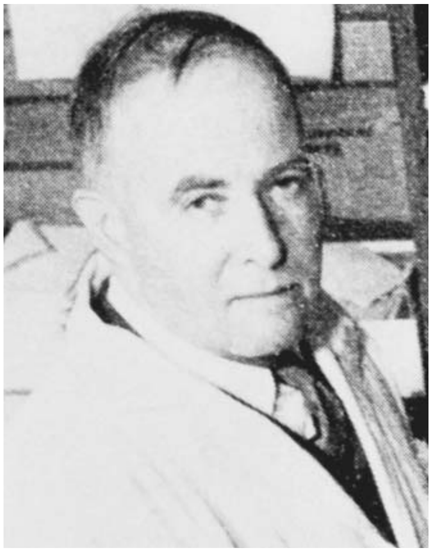
Sumner, James

AMERICAN BIOCHEMIST
1887–1955

James Sumner received the Nobel Prize in chemistry in 1946 (which he shared with John Northrop and Wendell Stanley), "for his discovery that



American biochemist James Batcheller Sumner, corecipient of the 1946 Nobel Prize in chemistry, "for his discovery that enzymes can be crystallized."

enzymes can be crystallized." In asserting that enzymes were proteins, Sumner had to battle the considerable opposition of European chemists for many years, particularly that of Richard Willstätter's group in Munich, who believed that enzymes belonged to an as yet unknown class of chemical compounds.

Sumner wrote in his Nobel Lecture: "I decided in 1917 to attempt to isolate an enzyme. . . . I desired to accomplish something of real importance. In other words I decided to take a 'long shot.' . . . Since the jack bean *Canavalia ensiformis* appeared to be extraordinarily rich in urease, I could see no reason why this enzyme could not be isolated in pure form and characterized chemically." The task took nine years.

Sumner's earliest research facilities were primitive. His laboratory did not even possess an ice chest. He noted, also in his Nobel Lecture: "I would leave cylinders of 30 percent alcoholic extracts on window ledges and pray for cold weather." (He frequently became discouraged.)

Treatment of the jack bean meal with 30 percent alcohol dissolved most of its urease but failed to dissolve other proteins, hence he achieved a considerable purification. Sometime in 1926, it occurred to him that he might achieve even greater purification by using dilute acetone instead of alcohol. A filtered acetone extract, chilled overnight, contained no visible precipitate. However, there was precipitate. In Sumner's own words: "Upon observing a drop of the liquid under the microscope it was seen to contain many tiny crystals. . . . I centrifuged off some of the crystals and observed that they dissolved readily in water. I then tested this water solution. It gave tests for protein and possessed a very high urease activity. I then telephoned to my wife, 'I have crystallized the first enzyme.'"

Willstätter and his collaborators challenged Sumner's claim that urease was a pure protein. After 1926 Sumner and collaborators provided further evidence that urease was indeed a protein molecule and that Willstätter's objections were based on incorrect experimentation. In 1930 Northrop had shown that pepsin was a protein, and in 1937 Sumner isolated catalase in pure crystalline condition. Sumner's initially controversial claims were thus fully vindicated.

James Batcheller Sumner was born in Canton, Massachusetts, in 1887. As a young man of seventeen he suffered a tragic misfortune. While he was out hunting with a companion, the companion accidentally shot him in the left arm, which had to be amputated above the elbow. (Sumner was left-handed.) With amazing courage and determination he taught himself to get along with one arm, and to use his right in activities for which he had previously used only his left. He continued on as a keen sportsman and, despite his disability, came to excel in tennis.

In 1906 Sumner entered Harvard College, graduating in 1910 with a degree in chemistry. He earned a Ph.D. in biological chemistry in 1914 for research carried out under Otto Folin on the formation of urea in animals. When Sumner first applied to do graduate work, Folin suggested he take up law, as he would never be able to carry out laboratory assignments as a one-armed man. Thus challenged, Sumner went on to show how skilled an experimentalist he could become.

In 1914 Sumner became an assistant professor of biochemistry at the Ithaca division of the Cornell University Medical College and was promoted to full professor in 1919. In 1938 he moved to the Cornell School of Agriculture, where in 1947 a laboratory of enzyme chemistry was established under his direction. Active to the last, he died in 1955 of cancer, aged sixty-seven. SEE ALSO Proteins; Willstätter, Richard.

Keith L. Manchester

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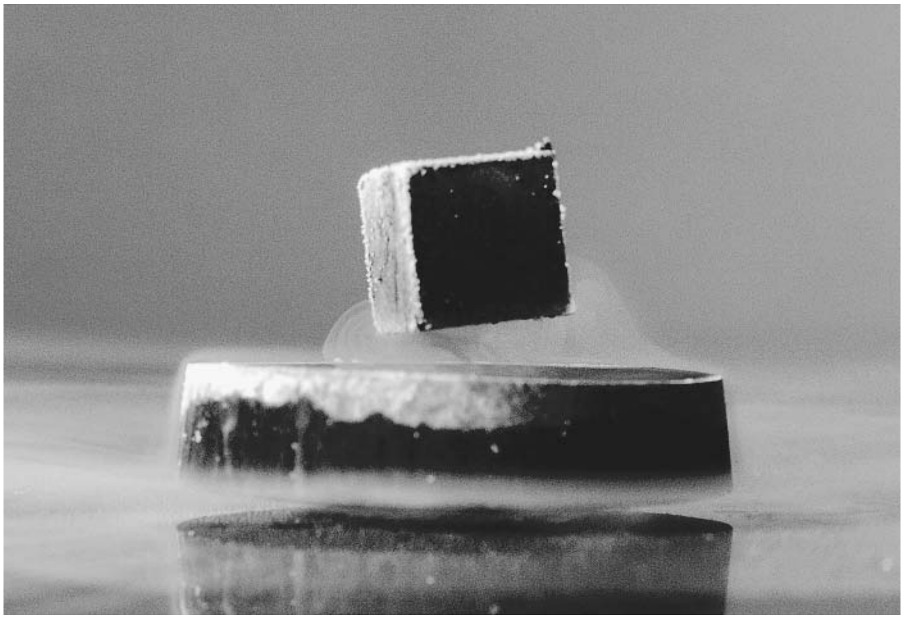
Superconductors

Superconductivity, which is defined as the absence of resistance in a conducting material to a continuously flowing electric current, is a special property that a sizable number of substances attain suddenly at very low temperatures. The substances (called superconductors) include elements, **alloys**, compounds, and nonstoichiometric ceramic materials. Superconductors also exhibit perfect diamagnetism; that is, magnetic fields cannot penetrate them (the Meissner effect), and small powerful magnets actually float (levitate) above flat superconductor surfaces. A superconductor's critical transition temperature, T_C, is the temperature above which no superconductivity can be obtained. For elements, alloys, and simple compounds, very low critical transition temperatures (T_C 23 K) mean that the cooling effects of liquid helium (b.p. = 4 K) are needed to bring about and to maintain their superconductivity. The discovery in 1986 that nonstoichiometric ceramics containing copper and oxygen can have much higher T_C values has provided a new impetus for developing superconducting materials.

alloy: mixture of two or more elements, at least one of which is a metal

High Temperature Superconductors

In April 1986, K. Alex Müller and J. Georg Bednorz (with IBM in Switzerland) reported the superconductivity of a nonstoichiometric ceramic oxide of lanthanum, barium, and copper, $La_{2-x}Ba_xCuO_{4-y}$, with the then record high T_C of 35 K. Further experiments conducted by Müller, Bednorz, and others showed that slight modifications made to $La_{2-x}Ba_xCuO_{4-y}$ (x 0.2 and y is even smaller) could yield materials having T_Cs of 50 K. By early 1987, Paul C. W. Chu (at the University of Houston), Maw-Kuen Wu (at the University of Alabama), and their coworkers synthesized another ceramic oxide material, $YBa_2Cu_3O_{7-y}$, and observed that superconductivity in the material was attainable by cooling it with liquid nitrogen (b.p. = 77 K). This "high temperature superconductor" made possible



A magnet is hovering over a superconductor, demonstrating that magnetic fields cannot penetrate the superconductor, known as the Meissner effect.

superconductor applications that were impractical with the low temperature superconductors. (See Figure 1.)

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

Other nonstoichiometric ceramic oxides that contain copper in nonintegral **oxidation** states have been synthesized and evaluated. Several of these materials have even higher T_C's than that of $YBa_2Cu_3O_{7-y}$. The BSCCO series $Bi_2Sr_2Ca_n-1Cu_nO_{2n}+4+y$ (for $n = 1$ to 4) reaches a T_C maximum of 110 K for $Bi_2Sr_2Ca_2Cu_3O_{10+y}$; a similar $Tl_2Ba_2Ca_n-1Cu_nO_{2n}+4+y$ series reaches a maximum of 122 K for $Tl_2Ba_2Ca_2Cu_3O_{10+y}$; $HgBa_2Ca_2Cu_3O_{8+y}$ has a T_C of 135 K at ambient pressure; and $Hg_{0.8}Tl_{0.2}Ba_2Ca_2Cu_3O_{8.33}$ has a T_C of 138 K. Also, the T_C of $HgBa_2Ca_2Cu_3O_{8+y}$ has been reported to increase to 153 K at a pressure of 150,000 atmospheres and to 160 K at 280,000 atmospheres. Even higher T_C values have been claimed for portions of multiparticle ceramics, but no macroscopic material has shown unambiguous superconductivity at these higher temperatures (above 160 K).

MEISSNER EFFECT

The Meissner effect is the repulsion of a magnetic field from the interior of a superconductor below its critical temperature. Whereas a weak magnetic field is totally excluded from the interior of a superconductor, a very strong magnetic field will penetrate the material and concurrently lower the critical transition temperature of the superconductor. W. Meissner and R. Ochsenfeld discovered the Meissner effect in 1933.

Other new classes of superconductors that are being investigated include intermediate temperature range superconductors, such as magnesium diboride ($T_C = 39$ K), alkali-doped C_{60} (M_3C_{60} has a T_C of 33 K), and hole-doped C_{60} ($T_C = 52$ K). The latter result led Jan Hendrik Schon, Christian Kloc, and Bertram Batlogg (of Bell Labs) to the newer haloform-intercalated, high temperature C_{60} superconductors $C_{60} \cdot 2CHCl_3$ and $C_{60} \cdot 2CHBr_3$, with T_C values of 80 K and 117 K, respectively.

The theoretical interpretation of the high temperature superconductors is still under development. The copper oxide ceramic superconductors obtain their paired conducting electrons from copper in mixed oxidation states of I and II or II and III, depending on the particular system. The paired conducting electrons are called Cooper pairs, after Leon N. Cooper. Cooper's name also gives us the C of BCS; the BCS theory is an interpretation of superconductivity for low temperature superconductors (having T_C's of less than 40 K).

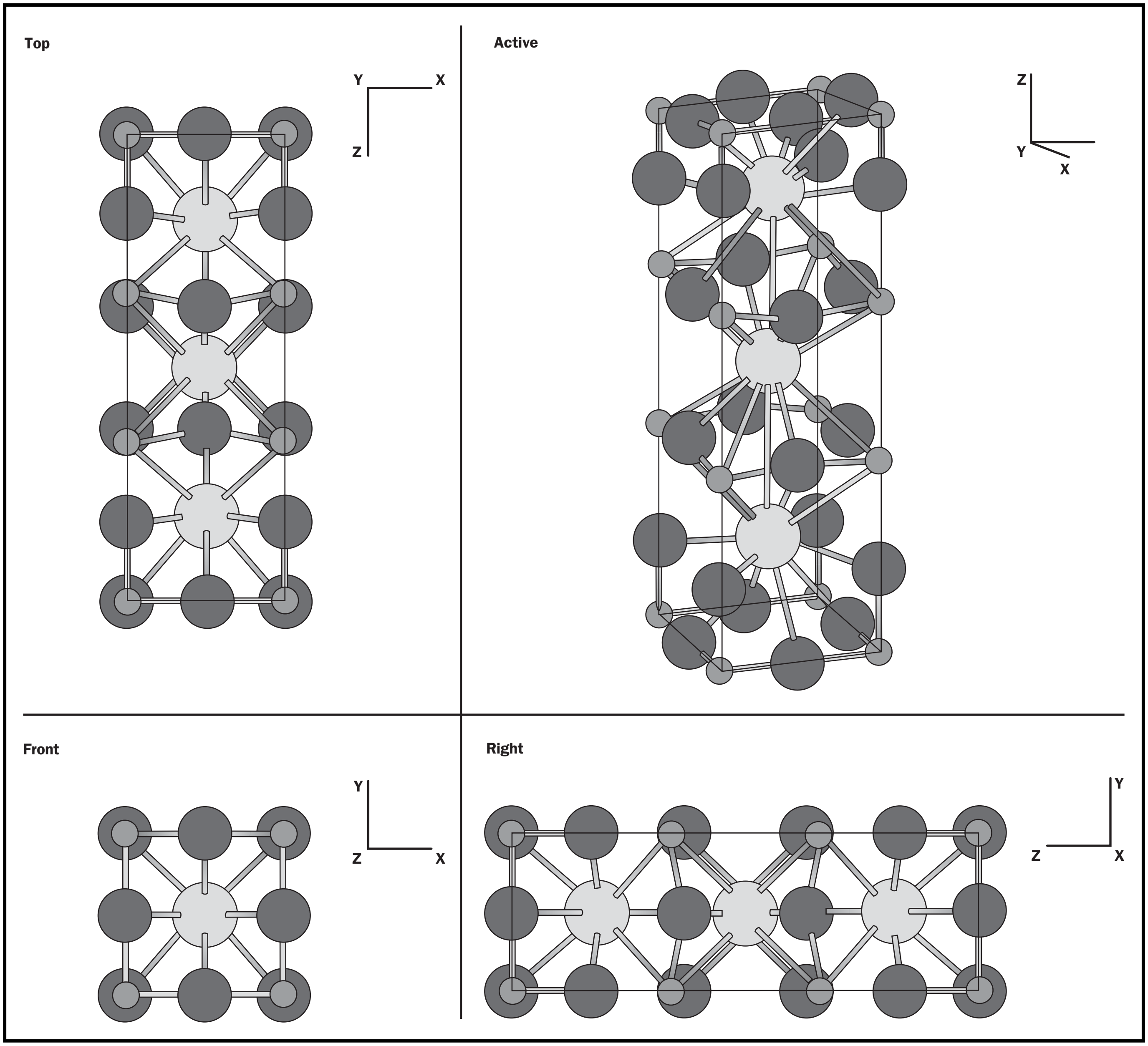


Figure 1. The crystal structure of $YBa_2Cu_3O_{7-y}$. Redrawn from Naval Research Laboratory. Available from <http://cst-www.nrl.navy.mil/lattice/struk.picts/>.

Applications

Applications for superconducting materials include strong superconducting magnets without iron cores, which in turn have a variety of uses. These superconducting magnets are used in particle accelerators, **nuclear** magnetic resonance and magnetic circular dichroism instruments, magnetic resonance imaging devices in medicine, levitating trains, magnetic refrigerators, magnetic energy storage, and SQUIDS (superconducting quantum interference devices) for very sensitive magnetic field measurements (including biomedical magnetoencephalography). Most magnetic applications were developed with and still use the older low temperature superconductors, such as niobium-titanium alloy superconducting wire, which must be cooled with liquid helium. For example, the Fermilab Tevatron (1983) uses 1,000 liquid helium–cooled superconducting magnets in its four-mile (circumference)

nuclear: having to do with the nucleus of an atom

BCS THEORY

BCS theory, developed by John Bardeen, Leon Cooper, and Robert Schrieffer, provides complicated mathematical equations that satisfactorily explain the superconductivity of the classical low temperature superconductors with critical transition temperatures below 40 K. The theory includes Cooper pairs of electrons but does not explain the high critical transition temperatures of the newer ceramic superconductors.

proton-antiproton collider. The sudden quenching of superconducting magnets by vibrations, external fields, or accidental warming can be a serious problem, and the associated heat can cause extensive helium loss.

Cooling with liquid nitrogen rather than liquid helium is much more economical. The difficulty in molding the high temperature superconductors into strong and flexible forms (e.g., filaments or wires) and the greater T_C lowering that accompanies greater magnetic field strength have limited their use up to the present time. Several firms have developed methods to improve the transfer of charge among superconducting particles; and it appears that the best superconductors may be impure ones that allow (the more disordered) ceramic glass formation rather than ceramic crystallite formation. BSCCO superconducting transmission lines are being manufactured (by American Superconductor, Pirelli, and Intermagnetics General) but are currently competitive only when space or weight limitations are important. Superconducting filters for cellular communications, in which the lack of resistance provides filters that have minimal signal loss and are more discriminating in frequency tuning, are being marketed (by Superconductor Technologies, Illinois Superconductor [ISCO], and Conductus), and superconducting motors (American Superconductor) and generators (General Electric) are under development. SEE ALSO CERAMICS; CRYOGENICS; MAGNETISM.

Ronald D. Archer

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Surface Chemistry

Wolfgang Pauli once stated that "the surface was invented by the devil," illustrating the complexity and difficulty of studying the surfaces of materials. This prompts a fundamental question: What is the surface of a material? The simplest definition is that the surface is the boundary at which the atoms that make up one material terminate and interface with the atoms of a new material. If the surface is considered to be just the outermost layer of atoms of a material, then it comprises on average only 10^{15} atoms per square centimeter (1 square centimeter equals 0.155 square inch), as compared to the bulk of the material, which consists of approximately 10^{23} atoms per cubic centimeter. Surface chemistry is important in many critical chemical processes, such as enzymatic reactions at biological interfaces found in cell walls and membranes, in electronics at the surfaces and interfaces of microchips used in computers, and the **heterogeneous catalysts** found in the catalytic converter used for cleaning emissions in automobile exhausts.

heterogenous: composed of dissimilar parts

catalyst: substance that aids in a reaction while retaining its own chemical identity

The development of modern surface chemistry did not begin until the early 1960s as the tools needed to detect the small numbers of surface atoms relative to the bulk atoms (predominately through electron-based spectroscopies) became available. Almost thirty years later, the study of surface chemistry received another boost with the development of a new class of tools called scanned probe microscopies, which provide the ability to view the chemical changes of surfaces under different environmental conditions. Such tools were the first to allow for the direct three-dimensional mapping of positions of atoms at surfaces. These techniques changed the view of surfaces by offering scientists and engineers the ability to directly examine and modify surface chemistries at the atomic and molecular levels.

Seeing Is Believing: The Scanning Tunneling Microscope

In 1981 the first direct visualization of surface atoms was made using a new tool, the Scanning Tunneling Microscope (STM). This tool and the offshoots of its development, including the Atomic Force Microscope (AFM) and Near-field Scanning Optical Microscope (NSOM) have revolutionized the field of surface chemistry. For the first time many processes that occurred at surfaces and interfaces, such as catalytic reactions, could be directly probed. This revolution was so important that the inventors, German physicist Gerd Binnig and Swiss physicist Heinrich Rohrer, received the Nobel Prize in physics only five years later in 1986.

quantum mechanics: theoretical model to describe atoms and molecules by wave functions

TUNNELING

Tunneling is the process in which electrons can pass from one metal to another, even though they are not in contact. This process occurs by coupling of the electronic states between the two surfaces.

The STM utilizes the **quantum mechanical** phenomenon of tunneling to visualize the positions of atoms on surfaces. A sharp metal tip is attached to a piezoelectric translator, which can position the tip with angstrom (1 Å = 1 x 10^{-10} meters) precision. As the tip is scanned over the surface, electrons move between the tip and sample and a tunneling current is produced. This current is very sensitive to (i.e., exponentially dependent upon) the

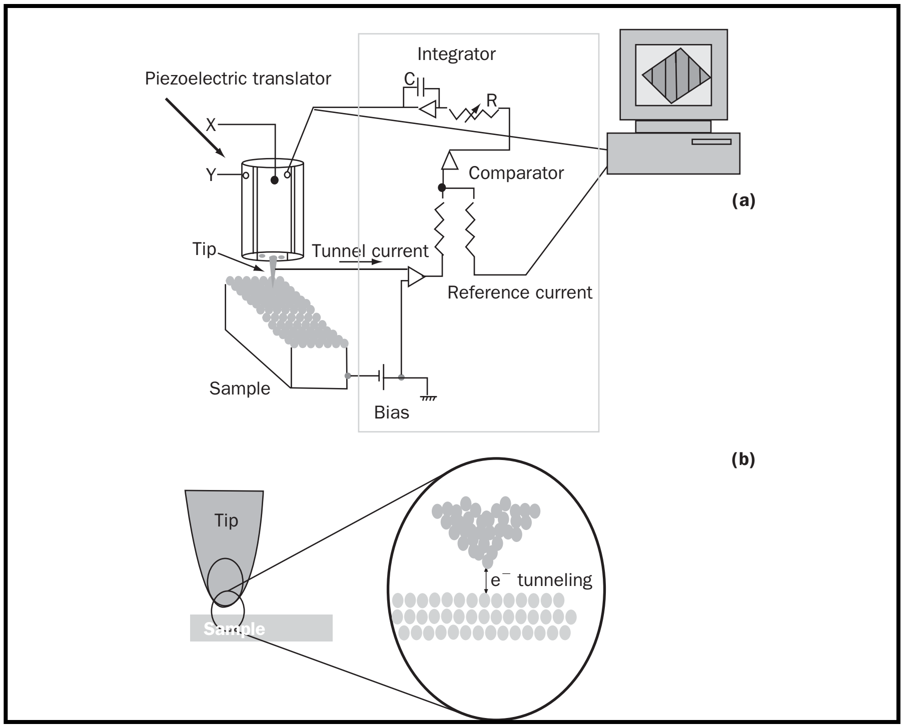

Figure 1. (a) A schematic of a scanning tunneling microscope (STM) showing the primary components including: the piezoelectric tip translator, the sample, the feedback loop, and the computer. (b) Because of the exponential distance dependence of the tunneling current, the majority of the tunneling between the tip and surface is through the closest atoms between the two.

distance between the tip and sample. By attempting to maintain a constant current using a feedback loop monitored by a computer, the piezoelectric receives a signal from the computer to raise or lower the tip as it scans over the surface (Figure 1). Plotting the changes in tip height and position produces a three-dimensional image of the surface, yielding the ability to view the locations of single atoms and to manipulate their atomic positions.

Numerous areas of research have benefited from this technique, including semiconductor technology, growth of metals, and heterogeneous catalysis. Shown in Figure 2 is an atomic resolution image of sulfur atoms on a rhodium surface. Because of the crystalline nature of the Rh surface, the S atoms position themselves in an ordered arrangement as they bond to the metal. Similarly, for surfaces such as silicon, the atomic positions can be viewed. STM revealed for the first time the organization of the structure of atoms on silicon surfaces, having a significant impact on the design of semiconductor devices. Shown in Figure 3 is an image of the Si(111)-(7×7) restructured surface as viewed by STM. Imaging of semiconductors such as Si as a function of voltage between the tip and sample allows for direct visualization of the occupied and unoccupied states, a direct view into the chemistry of the surface atoms.

PIEZOELECTRIC

A piezoelectric is a ceramic material (typically a mixture of Pb, Zr, Ti, and O) that changes size with applied voltage. Quartz is an example of a naturally occurring piezoelectric. Piezoelectric materials are used to control the tip position in scanned probe microscopes because the changes in the piezoelectric dimensions can be controlled with sub-angstrom precision.

Seeing the Rest of the World: Atomic Force Microscopy

While STM gave researchers the ability to probe atomic scale events at metal and semiconducting surfaces, many of the materials of interest to surface scientists fall outside these classes of materials, such as the surfaces of oxides and biological materials that lack conductivity. AFM is a tool that provides similar surface mapping of materials as STM, but can be used for systems that are nonconductive as well.

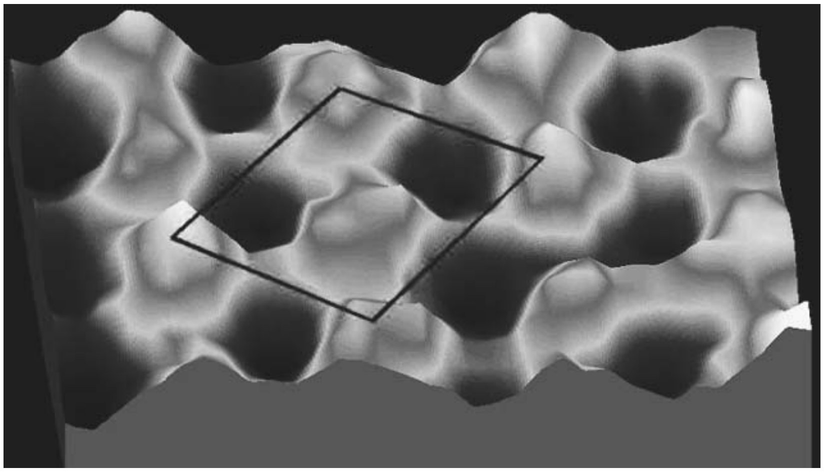

Figure 2. STM image of S atoms on a Rh surface (15 Å × 7 Å × 1.5 Å).

In AFM, a sharp tip on a cantilever is placed in contact with a surface. The forces acting between the tip and surface cause the cantilever to bend. Using a feedback loop, this force is held fixed as the tip is scanned and "feels" its way over the surface, producing an image of the surface topography (Figure 4). AFM measurements can be made in air or under liquids, which allows imaging of biologically important molecules and surfaces, within the nanoscale regime, under natural physiological conditions. AFM has also become an important tool in the measurement of surface properties ranging from basic structure to nanoscale mechanical properties such as friction, adhesion, and elasticity. The details of friction and adhesion are crucial at the nanoscale level, especially with the drive to move technology to even smaller length scales, leading to the development of microelectromechanical systems (MEMS) devices such as microscale motors, actuators, and switches. MEMS devices are currently used in critically important technologies such

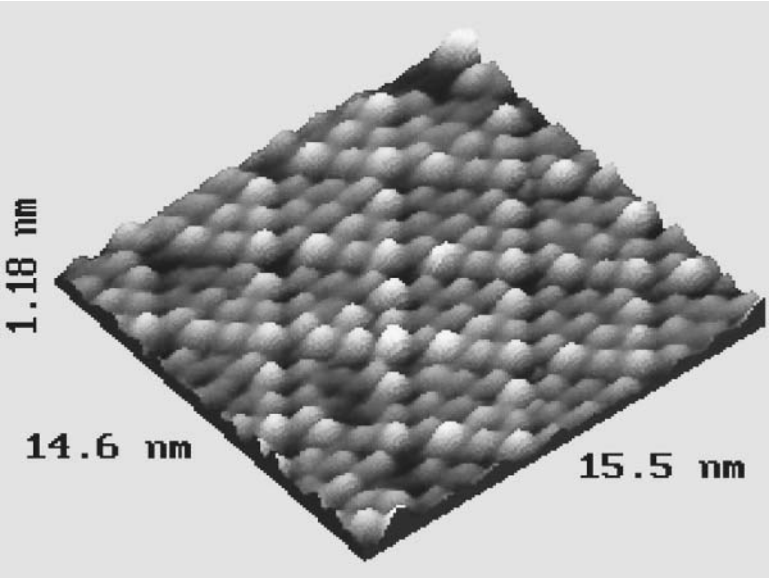

Figure 3. Topographic image (14.6 nm x 15.5 nm x 1.18 nm, 1 nm =10 Å) of a reconstructed Si(111) surface, showing the new outermost atomic positions.

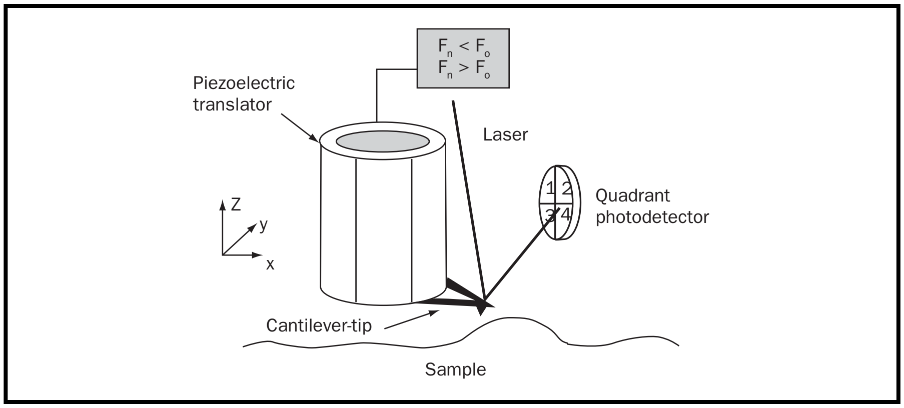

Figure 4. A schematic of an atomic force microscope (AFM), showing the primary components including: the piezoelectric translator, the sample, the cantilever-tip assembly, and the photodetector. In its simplest operating mode (contact mode), the feedback loop of the AFM maintains a constant force between the tip and sample. The force is monitored by measuring the deflection of the cantilever-tip assembly using a laser beam scattered into a quadrant photodetector.

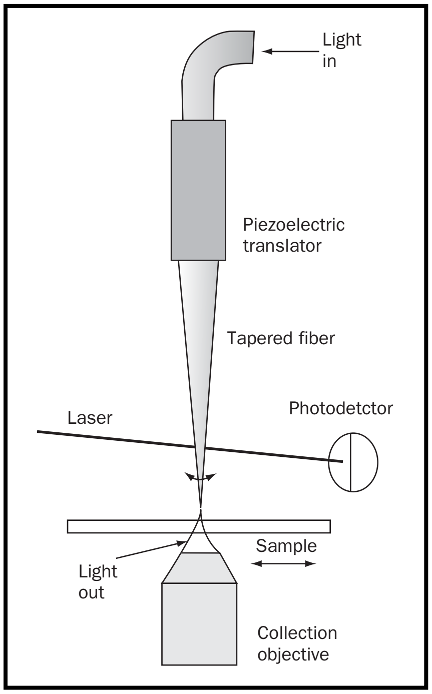

Figure 5. A schematic of a near-field scanning optical microscope, showing the primary components including: the piezoelectric tip translator, the sample, the fiber optic probe, and the photodetector. The fiber is oscillated from side to side and its oscillation measured in the photodetector to control the position of the fiber over the surface. The light leaving the end of the tip passes through the sample and is then collected in a typical microscope objective. The sample is scanned by moving it from side to side under the tip.

as shock sensors for the deployment of airbags in automobiles. The surfaces of these devices are typically covered with silicon dioxide (glass); controlling the surface chemistry is essential in order to ensure the successful operation of the device.

Studies of adhesion by AFM have led the way to probing local chemical forces at surfaces allowing for the fundamental molecular forces between molecules to be measured directly. Other unique aspects of surface chemistry that AFM has been used to explore include the imaging of liquid surfaces. Modification of the AFM tip with metals allows for the local electric field between the tip and sample to be monitored. Changes in the dielectric properties such as the large contrast between water and many solid surfaces allow for the position of liquid droplets to be observed and for the structures of thin films of water to be probed. Due to the ubiquitous nature of water, the details of the surface chemistry of water are of key concern in a wide range of systems including the chemistry occurring in the stratosphere where ozone-depleting chemical reactions occur on ice surfaces.

Squeezing Light: Near-field Scanning Optical Microscopy

The images that are generated by STM and AFM show structure but no true chemical composition. The details of the local chemistry on surfaces at the nanoscale level, however, are very important to understanding surface properties. Optical spectroscopy and microscopy provide a means of chemically identifying materials; in conventional microscopy, however, the resolution limit is approximately half the wavelength of the light used to illuminate the sample. Thus, spatial resolutions are typically limited to approximately 200 nanometers (7.9×10^{-6} inches) in the visible and approximately 5,000 nanometers (2.0×10^{-4} inches) in the infrared parts of the electromagnetic spectrum.

Near-field Scanning Optical Microscopy (NSOM) overcomes these limitations by "squeezing" the light through an aperture of approximately 50 nanometers (2.0 x 10^{-6} inches), typically using a tapered optical fiber just as is used in most telecommunications signal transmissions. By bringing the tapered fiber to within about 10 nanometers (3.9 x 10^{-7} inches) of a surface, the photons see only the local region of the surface where the tip is positioned (Figure 5). When the light is transmitted through the sample it is collected with a conventional microscope objective, spectroscopic as well as structural images of the materials on a surface can be observed. This approach has paved the way for single molecule spectroscopy and is opening new possibilities for the analysis of material properties at the nanometer scale. Technology is advancing into the infrared and microwave regions of the spectrum, allowing for the chemical composition and dielectric properties of materials to be probed with high spatial resolution. Figure 6 shows a near-field optical image of a polymer blend of polystyrene and polyethylacrylate, taken in the infrared region of the spectrum showing high spatial resolution spectroscopy.

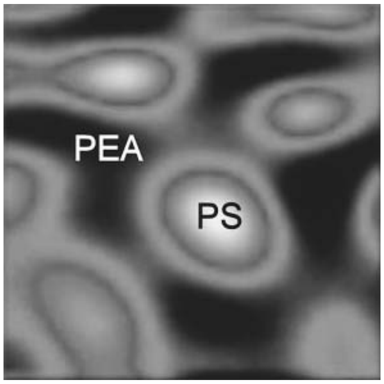

Figure 6. Infrared-NSOM image of a blended polystyrene/polyethylacrylate film (~1 micron thick) on Si. The image (8 μm x 8 μm), collected at 3125 cm^{-1}, shows the domains of polystyrene (PS) embedded within the polyethylacrylate (PEA). This chemical map of the surface has ~10 times higher spatial resolution than a conventional optical infrared microscope image. (Courtesy of Dr. Chris Michaels and Dr. Stephan Stranick, NIST.)

Nanostructures on Surfaces

The design of nanostructures on surfaces using scanned probe microscopies enables the custom design and manipulation of matter on the atomic and molecular level. An STM or AFM tip can be used as a "nanowriter," placing and pushing around atoms and molecules on surfaces to make organized structures. Single atom positioning heralded by American physicist Donald Eigler at IBM showed the way in which atoms could be placed in complex structures using an STM to carry and position atoms on a surface with high precision. In 1987, using xenon atoms deposited on a nickel surface, researchers at IBM used the STM to write "I," "B," and "M" on a surface (Figure 7). Given the ability to write structures at this length scale, the entire Library of Congress could be written on the head of a pin. Although the timescale needed to write structures atom-by-atom makes this prohibitive as a general tool for large-scale lithography, the feasibility has been shown. This burgeoning area of nanotechnology has surface chemistry at its heart, as the detailed control of matter at the molecular level on surfaces is viewed as part of the next technological revolution.

The generation of nanostructures with AFM using dip-pen and nanografting patterning methods has shown great utility in the writing of complex molecules onto surfaces for use in nanoscale devices and sensors.

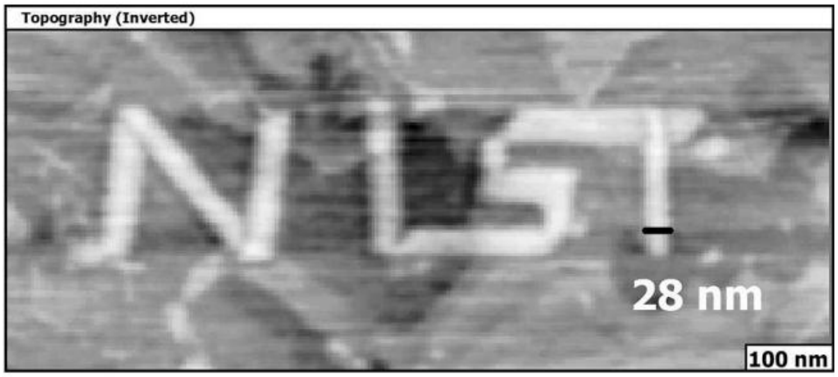

Figure 7. Nanowriting of a mercaptbenzoic acid layer into a background layer of dodecanethiol using nanografting. The height contrast is inverted to make the "nist" appear bright. The thickness of the "t" is only 28 nm. (Courtesy of Dr. Jayne Garno, NIST).

In dip-pen lithography an AFM tip "inked" with molecules is scanned along a surface in a controlled pattern. Under the appropriate conditions the molecules transfer from the tip to the surface, much as a fountain pen writes on a piece of paper.

Nanografting provides another means by which structures may be prepared on surfaces. In nanografting, a background layer of alkanethiols on gold is initially formed as a support matrix. When this surface is imaged in a background solution of a different molecule than the matrix, as the AFM tip scans through the matrix molecules, they are scraped away (mechanically removed) and replaced by the new molecules present in solution (Figure 8). This methodology has been successful in creating structures ranging from a few nanometers to tens of nanometers in dimension. Both of these approaches (and modifications thereof) are rapidly advancing the methodology of "nanowriting." SEE ALSO CATALYSIS AND CATALYSTS; NANOCHEMISTRY.

James D. Batteas
James M. Helt

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Sustainable Energy Use

Most people agree that sustainable energy is energy that is derived from a fuel that is renewable or will never run out and that results in minimal environmental impact. Consequently, the fossil fuels coal, oil, and natural gas clearly do not provide sustainable energy. Once used, those fuels are not replenished, and while they are burned they contribute to various forms of air pollution.

An example of a renewable energy source is one derived from plant materials, such as wood or grain. Plants can be regrown to replace those used for energy. However, plants are sustainable energy sources only if they can be replaced as quickly as they are used. In many areas of the world, trees are being cut for lumber or fuel at a much faster pace than they can be regrown. Such practices are not sustainable.

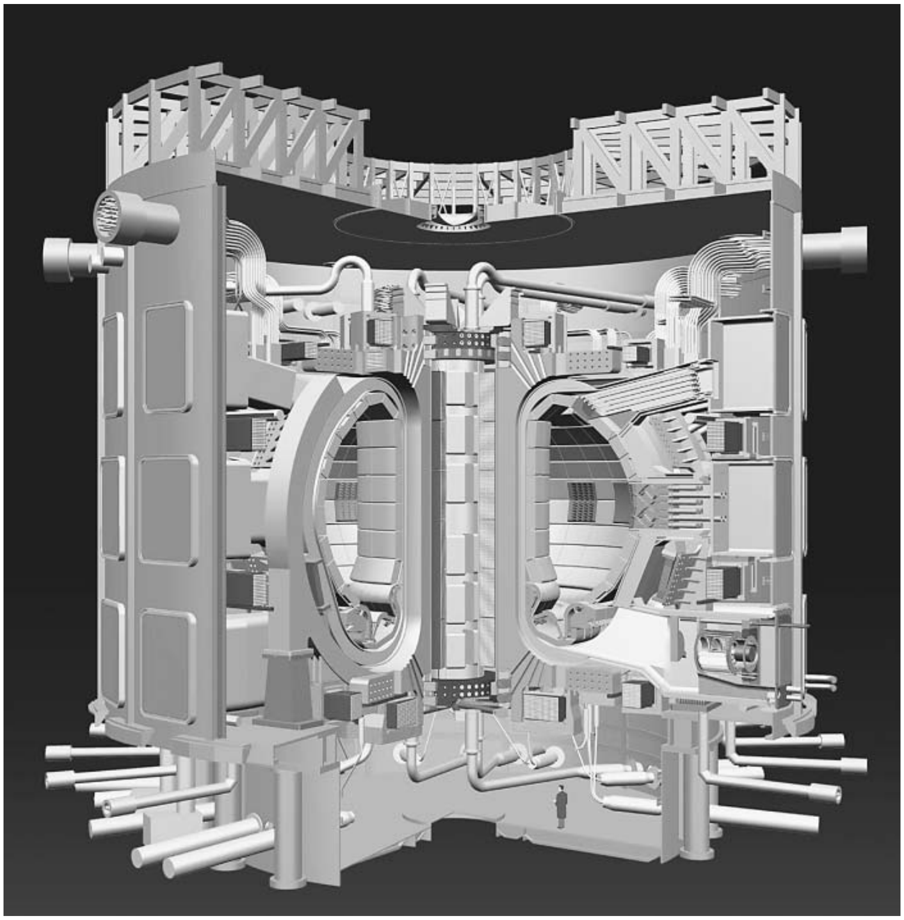
Plant materials, called **biomass**, are renewable and sustainable in the following examples:

biomass: collection of living matter

1. Anaerobic bacteria convert waste plant materials or animal manure to methane gas, and the methane gas (also present in natural gas) is burned either for heat or to make electricity (water is boiled and the steam turns a turbine).
2. Grain, such as corn, is converted to ethanol through a sugar fermentation process. Ethanol is then mixed with gasoline, a fossil fuel, before being burned in an automobile.

The sun and wind are major sustainable energy sources that do not directly use a "fuel." Solar energy is used for direct heating of homes and water, or it is converted directly to electricity using photovoltaic cells. Several large demonstration plants using various techniques to concentrate the solar energy have been built to convert solar energy into electric energy.

Wind is a sustainable source of energy in that it does not diminish with use like fuels.



A cutaway of the ITER tokamak device. A goal of the ITER project is to create sustainable energy by means of fusion.

The conversion of wind energy to electricity, using wind turbines, is now cost competitive with fossil-fuel sources of energy such as natural gas. Wind-turbine farms have been built in Europe and the United States. The land around them is still available for agricultural use. However, people have begun to resist the placement of wind farms in certain locations, citing noise, bird kills, and unsightly visual effects.

A future renewable energy source is hydrogen gas, which can be burned like natural gas or used in a fuel cell along with oxygen to make electricity, with only water as the final waste product. Hydrogen could replace natural gas if an economical method is found to extract it from water. The best future method is to use solar energy directly to "split" water to make hydrogen, and is a current area of research. An intermediate method, but still not used as of 2003, is to use photovoltaic cells to make electricity, which is used to electrolyze water to produce hydrogen. An unsustainable and energy-inefficient method is to use coal to make the electricity to electrolyze the water. As of 2003, fossil fuels, such as natural gas, are used to make hydrogen, which also is clearly unsustainable.

Some people have suggested fusion as a future energy source, based upon abundant supplies of deutrium in water and tritium from lithium and water. Technical problems have so far prevented this from occurring. SEE ALSO AIR POLLUTION; FOSSIL FUELS.

Charles E. Ophardt

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Svedberg, Theodor

SWEDISH CHEMIST
1884–1971

Swedish chemist Theodor Svedberg, recipient of the 1926 Nobel Prize in chemistry "for his work on disperse systems."

Theodor Svedberg was a physical chemist whose work significantly affected the development of biochemistry in the twentieth century. He was born in Flerang, Valbo, in Sweden on August 30, 1884. He was educated at the Koping School and Orebro High School and earned B.A., M.S., and Ph.D. degrees at Uppsala University (the latter in 1908). His hobbies were painting and botany. He chose chemistry as his life's work because he believed chemistry to be a means of greater understanding of biological systems. Svedberg spent his entire professional life associated with Uppsala University, first as an assistant at the Chemical Institute in 1905 and then as a professor of physical chemistry starting in 1912. He was awarded a number of international prizes, including the Nobel Prize in chemistry in 1926. This honor was awarded for his groundbreaking work in the chemistry and physics of **disperse systems**.

disperse system: two-phase system in which one phase, the disperse phase, is distributed in the second phase, the dispersion medium

Svedberg's primary focus as a physical chemist was the field of colloid chemistry. Colloids are mixtures of very small particles that when dispersed in solvents are not dissolved, but are held in suspension by various actions of the solvent. Svedberg and his collaborators studied the interaction of colloid suspensions with light and their sedimentation processes. These studies showed that the gas laws could be applied to colloidal systems. Svedberg's Ph.D. thesis on the diffusion of platinum colloidal particles elicited a response from Albert Einstein, since it supported Einstein's theory concerning the **Brownian motions** of colloidal particles.

Brownian motion: random motion of small particles, such as dust or smoke particles, suspended in a gas or liquid; it is caused by collisions of the particle with gas or solvent molecules, which transfer momentum to the particle and cause it to move

A more detailed study of the sedimentation of colloidal disperse systems required Svedberg's 1921 invention of the ultracentrifuge. This centrifuge is similar in principle to a regular laboratory centrifuge except that it rotates at very high angular velocities to provide centrifugal forces as high as 1,000,000 times the force of Earth's gravity. This force is capable of causing colloidal particles to separate into sedimentation bands of varying distances from the center of the centrifuge according to particle size. These bands are observed while the machine is running by photographing the bands, a technique called Schlieren photography. The sedimentation process of colloidal dispersions under these conditions is related to both the shape and mass of the particles. **Homogeneous solutions** of very large molecules such as carbohydrates, proteins, nucleotides (such as **DNA**), and manmade polymers also respond to high forces according to shape and molecular mass.

homogeneous solution: mixture of molecules that forms a single phase (solid, liquid, or gas)

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

In the early days of modern biochemical studies, the overall structure of proteins was not well understood. There were two major schools of thought. One theory posited that proteins are agglomerations of small molecules (Svedberg's theory, consistent with his colloid studies), and the second theory was that proteins are very large molecules. In 1921 Edwin Cohn of Harvard University, who subscribed to the large molecule theory, challenged Svedberg to subject a purified protein to the ultracentrifuge. If the protein were made up of smaller molecules, it would separate into a number of fractions with small molecular weights. If the protein was composed of only one type of very large molecule, the ultracentrifuge would show only one fraction of very high molecular weight. To Svedberg's surprise, the experiment showed that there was only one type of molecule and that proteins are, in fact, made up of a single sort of large molecule. This was a very important result in the understanding of proteins and other large molecules.

Although Svedberg is remembered for his very important work in colloids and artificial rubber, he must also be remembered as a scientist who was willing to test his own theory rigorously and change his point of view when experiment indicated a theory to the contrary. SEE ALSO COLLOIDS; EINSTEIN, ALBERT; PROTEINS.

Lawrence H. Brannigan

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Sweeteners *See Artificial Sweeteners; Disaccharides.*

Synge, Richard Laurence Millington

ENGLISH BIOCHEMIST
1914–1994

Richard Laurence Millington Synge's fascination with biochemistry came into being when he was a young man. In his 1952 Nobel Lecture, he revealed that, at the age of nineteen, after reading Sir Frederick Hopkins's presidential address to the British Association for the Advancement of Science, he suddenly realized "that living things must have wonderfully precise and complicated working parts on the molecular scale, and that biochemists had the best chance of finding out how these are put together and do their work" (Synge, "Applications of Partition Chromatograpy"). It was his desire to unravel the complicated molecules of biochemical importance that ultimately led to his collaboration with Archer J. P. Martin and to their development of liquid-liquid partition **chromatography**.

chromatography: the separation of the components of a mixture in one phase (the mobile phase) by passing it through another phase (the stationary phase) making use of the extent to which the components are absorbed by the stationary phase

Having completed his undergraduate training in biochemistry and having acquired a familiarity with biochemical techniques, Synge launched into a chemical study of glycoproteins. A short time later he changed course: "Soon I found that my knowledge both of carbohydrate and protein chemistry was inadequate to the task" (Synge, "Applications of Partition Chromatography"). Synge moved on to work with Dr. D. J. Bell, under whose instruction he came to appreciate the power of liquid-liquid extraction as a method of separating the components of chemical mixtures.

It was as a graduate student at Cambridge University that Synge came into contact with Dr. Hedley R. Marston, who advised Synge to study the amino acid composition of wool. The acetylamino acids that were generated during the course of Synge's analysis of wool proteins were partitionable between chloroform and water. Synge was encouraged to consult with Martin on how best to achieve this partitioning.

The collaboration between Martin and Synge eventually culminated in a demonstration of partition chromatography to the Biochemical Society at its meeting at the National Institute for Medical Research in London, on June 7, 1941, followed by the publication of their results in *Biochemical Journal* (1941).

Although Synge did not pursue the further development of chromatographic methods with Martin, he did employ techniques that had been developed by Martin to investigate large peptides. From 1942 to 1948 Synge worked almost exclusively with antibiotic peptides of the gramicidin group, employing paper chromatography to elucidate their primary structures (amino acid sequences). Breaking up these peptides into dipeptide and tripeptide fragments, Synge recognized that identification of these fragments led back to the original sequences. That is, an A–B–C–D–E chain will give rise to the fragments A–B, B–C, C–D, and D–E, from which the original sequence can be unequivocally reconstructed. SEE ALSO GLYCOPROTEIN; MARTIN, ARCHER JOHN PORTER; PRIMARY STRUCTURE.

Todd W. Whitcombe

British chemist Richard Laurence Millington Synge, co-recipient, with Archer John Porter Martin, of the 1952 Nobel Prize in chemistry, "for their invention of partition chromatography."

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Synthesis, Chemical

Over twenty-one million chemical compounds were known as of 2003. Most have been synthesized by chemists; only a small fraction of these are compounds isolated from natural sources. The final proof of a naturally occurring compound's structure is established by synthesizing the compound from simpler molecules by means of identifiable and reproducible reactions.

Protecting Groups

When synthesizing a molecule with more than one functional group, it may be difficult to carry out a reaction with one group without unintentionally

Figure 1. Protecting-group use.

$$BrCH_2CH_2CHO + 2CH_3OH + H^+ \longrightarrow BrCH_2CH_2CH(OCH_3)_2 + H_3O^+ \qquad (1)$$

$$BrCH_2CH_2CH(OCH_3)_2 + OH^- \longrightarrow CH_2{=}CHCH(OCH_3)_2 + Br^- + H_2O \qquad (2)$$

$$CH_2CHCH(OCH_3)_2 + H_3O^+ \longrightarrow CH_2{=}CHCHO + 2CH_3OH + H^+ \qquad (3)$$

interfering or reacting with another group. Use of a protecting group helps to prevent this. The protecting group must be removed after the desired reaction is completed. In the simple example shown in Figure 1, HBr could not be eliminated from the bromopropionaldehyde because the aldehyde group would react with the base. Protecting the aldehyde group by converting it to an acetal allows the HBr elimination to take place. Other examples can be noted: alcohols or phenols can be converted to esters or ethers, aldehydes or ketones to acetals, carboxylic acids to esters, and amino groups to amides.

Retrosynthetic Analysis

For synthesis of fairly complicated molecules, the concept of retrosynthetic analysis (also called the disconnection approach), stated formally as a principle by American chemist E. J. Corey, is generally employed. In this approach, the molecule is broken up into two or more parts called synthons. A symbol used to indicate a retrosynthetic step is an open arrow written from product to suitable precursors or fragments of those precursors (Figure 2). Each synthon is similarly broken up and the process repeated until the fragments are available starting molecules. The synthesis is essentially worked backwards to the actual process followed in the laboratory. Beginning in the 1960s the strategy of organic synthesis became sufficiently systematic that computers could be used for syntheses planning.

Some of the better-known compounds synthesized by retrosynthetic analysis are strychnine, penicillin, prostaglandins, progesterone, vitamin B12, biotin, L-hexoses, menthol, and taxol.

Coordination Compounds

A coordination compound or complex refers to the grouping that is formed when a metal ion or atom accepts a pair of electrons from a molecule or ion. Metal ions—even in very low concentrations—function as powerful catalysts in many important industrial organic processes, as well as with enzymes (catalysts in living tissues). The total number of electron-donor atoms or donor pairs bonded to a given metal atom or metal cation is referred to as the coordination number. The coordination number of a compound can range from two to twelve and determines geometrical shape and physical properties.

Coordination number zero corresponds to an isolated atom; coordination number one occurs for very simple molecule combinations such as Ni-NN that are stable only in very cold matrices such as argon. Coordination

$$\text{Target molecule} \Longrightarrow \text{Precursors}$$

Figure 2. Retrosynthetic analysis.

number three is fairly rare since the metal can still serve as acceptor to more Lewis bases. Coordination number four refers to the smallest number of ligands commonly found in transition metal complexes. Coordination number five was thought to be nonexistent or rare at one time; more recently, studies have revealed stable five-coordinate complexes. Most transition metal complexes have a coordination number of six and show octahedral geometry, although other geometry is possible. Coordination numbers greater than six are rare because of high ligand-ligand steric repulsion. Only small ligand atoms such as fluorine (F) and oxygen (O) have low enough repulsion to form stable seven-coordinate complexes. For coordination number eight, the number of examples is limited because of high ligand-ligand repulsion; most examples involve small ligand atoms. However, eight is a relatively favorable number for complexes of f-block elements (the lanthanides and actinides), since these are large in size and also have a larger number of valence orbitals. Higher coordination numbers of nine and ten are known that also involve f-block elements.

In 1937 English chemist Nevil V. Sidgwick suggested a rule (the octet rule for first-row p-block elements) for complex formation under which a metal can acquire ligands until the total number of electrons around it is equal to the number surrounding the next noble gas. This rule was later expanded as the eighteen-electron rule under which a d-block transition metal atom has eighteen electrons in its nine valence orbitals [five n d; one (n + 1) s, and three (n + 1) p] and will form the stablest compounds when engaged in nine bonding molecular orbitals containing eighteen electrons.

Catalysts

Catalytic processes abound in nature. From enzymes to mineral surfaces, catalysts increase the rate of a given reaction, often by reducing the activation energy that the reactants must overcome before they go on to form products. Catalysts have been developed for a wide spectrum of reactions; a common example is the catalytic converter, used in cars to reduce toxic emissions. Inexpensive transportation fuels, high-temperature lubricants, chlorine-free refrigerants, high-strength polymers, stain-resistant fibers, cancer treatment drugs, and many thousands of other products would not be possible without the existence of catalysts. Catalysts are also essential for the reduction of air and water pollution, contributing to the reduction of product emissions that are harmful to human health and the environment.

catalytic: the action or effect of increasing the rate of a reaction without itself being converted

Most catalysts can be described as either **homogeneous** or **heterogeneous**. Homogeneous catalysts are molecularly dispersed with the reactants in the same phase, which provides easy access to the catalytic site but can make the separation of catalyst and products difficult. Heterogeneous catalysts—usually solids—are in a different phase from the reactants, reducing separation problems but providing more limited access to the catalytic site. Approaches to dealing with these disparate properties include anchoring the catalyst to a soluble or insoluble support, effectively "heterogenizing" the catalyst, or designing the catalyst so that it is soluble in a solvent that, under some conditions, does not mix with the reaction product. Some reactions will not take place (or will take place at a slower rate) without a catalyst being present. Actually an intermediate reaction of one of the reagents with

homogenous: made of similar parts

heterogenous: made of dissimilar parts

This organic chemist is synthesizing a chemotherapy agent, which is among the chemical compounds that do not occur naturally.

the catalyst (or catalyst surface) takes place at a faster rate than without it being present.

Enantiomers. Different enantiomers (mirror image forms) of a given biomolecule can exhibit dramatically different biological activities. Enzymes have evolved to catalyze reactions with selectivity for the formation of one enantiomeric form over the other. Chemists have developed various synthetic small-molecule catalysts that can achieve levels of selectivity approaching (and in some cases matching) those observed in enzymatic reactions. American chemist William S. Knowles pointed out in his 2001 Nobel Prize address that the best synthetic catalysts demonstrate useful levels of enantioselectivity for a wide range of substrates. Such catalysts have been called "privileged chiral catalysts." Such generality of scope is not observed in enzymatic catalysis. SEE ALSO ACID-BASE CHEMISTRY; CATALYSIS AND CATALYSTS; COORDINATION COMPOUNDS; INORGANIC CHEMISTRY; ORGANIC CHEMISTRY.

A. G. Pinkus

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Synthetic Fibers ***See Fibers; Polyesters; Polymers, Synthetic.***

Szent-Györgyi, Albert

HUNGARIAN-BORN AMERICAN BIOCHEMIST
1893–1986

Albert Szent-Györgyi was surely one of the most important scientists of the twentieth century. His research interests included **vitamins**, enzymatic **oxidation** mechanisms, muscle contraction, and cancer. He won the 1937 Nobel Prize in physiology or medicine for his discovery of vitamin C and for his studies on the Krebs, or citric acid, cycle.

vitamins: organic molecules needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

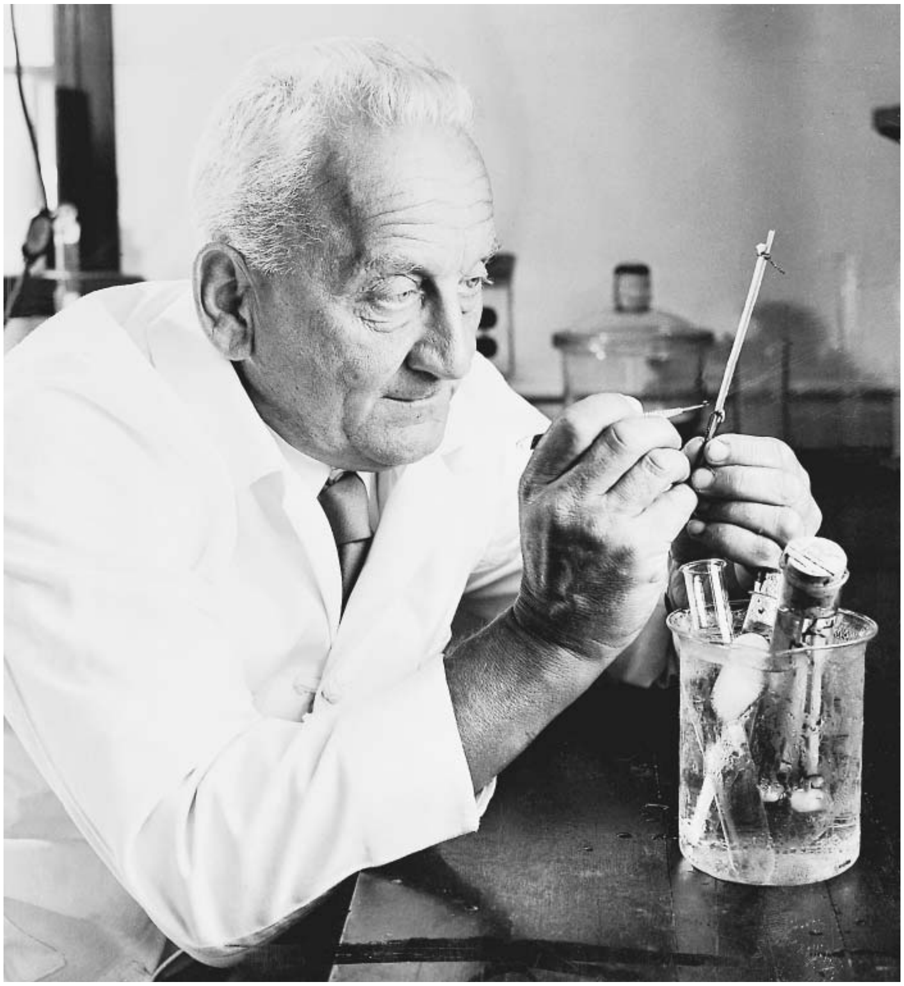
oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

Szent-Györgyi was born in Budapest, Hungary, on September 16, 1893. His father, Nicholas von Szent-Györgyi, was a prominent landowner. His mother, Josefine Lenhossek, belonged to a highly educated family: Her father and brother were both professors of anatomy at the University of Budapest.

Szent-Györgyi entered the University of Budapest in 1911. He stayed there until the outbreak of World War I, at which time he was drafted into the Hungarian army. Subsequently he served on the Italian and Russian fronts. After being wounded in action, Szent-Györgyi received a medal for bravery and was discharged. He completed his studies in Budapest and during the next decade worked at some of the world's leading academic research centers, including the University of Groningen, Cambridge University, and the Mayo Clinic.

In 1930 Szent-Györgyi returned to Hungary as a professor of medicinal chemistry. He joined the anti-Nazi resistance movement in Hungary during World War II and was for a while exposed to constant danger. He left Hungary in 1947 to join the staff of the Marine Biological Laboratory at Woods Hole, Massachusetts.

During his stay at Groningen, Szent-Györgyi identified a compound present in plant and animal tissues that blocked the enzyme-catalyzed oxidation of fruits and vegetables (the browning of a sliced apple exposed to air is the result of an enzyme-catalyzed oxidation). At Cambridge, he continued his work on this reducing substance and managed to isolate minute



Hungarian scientist Albert von Szent-Györgyi, recipient of the 1937 Nobel Prize in physiology or medicine, "for his discoveries in connection with the biological combustion processes, with special reference to vitamin C and the catalysis of fumaric acid."

quantities of it from adrenal glands. Upon his return to Hungary, he discovered that the reducing substance cured scurvy.

The discovery prompted Szent-Györgyi to search for a more abundant and reliable source of the compound, and eventually he was able to isolate kilograms of it from paprika (the dried, ground fruit of the pepper plant *capsicum annuum*). He named the new compound ascorbic acid, which means the acid that cures or prevents scurvy. (It also goes by the name of vitamin C.) Turkish invaders introduced paprika into Hungary in the sixteenth century and, historically, Hungary has been one of the world's leading exporters of paprika. Presumably large quantities of it were available to Szent-Györgyi, explaining why he looked to paprika to solve his supply problem.

Wanting to know the chemical structure of ascorbic acid, Szent-Györgyi gave a sample to Walter Haworth, a chemistry professor at the University of Birmingham in England and an expert in carbohydrate (sugar) chemistry. Haworth determined the complete chemical structure of ascorbic acid and shared the 1937 Nobel Prize in chemistry for his work.

An originator of many interesting and thought-provoking ideas, Szent-Györgyi died at Woods Hole on October 22, 1986. SEE ALSO ASCORBIC ACID.

Thomas M. Zydowsky

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Tantalum

73
Ta
TANTALUM
180.9479

MELTING POINT: **2,996°C**
BOILING POINT: **5425°C**
DENSITY: **16.65 g/cm^3**
MOST COMMON IONS: **Ta^{3+}, Ta^{4+}**

Tantalum was discovered in 1802 by Swedish chemist Anders Gustav Ekeberg while analyzing Scandinavian minerals. He named the third-row early **transition metal** after the Greek god Tantalus, the son of Zeus, because the oxide was difficult to dissolve in strong acids.

Impure tantalum was isolated in 1825 by Swiss chemist Jean-Charles-Galissard de Marignac and, in purer form, by Heinrich Rose in 1844. It is found, in combination with its **congener** niobium, in tantalite/columbite $(Fe, Mn)(Ta, Nb)_2O_6$ ore, with tantalite containing more tantalum than niobium. Its crustal abundance is 1.7 parts per million, with major deposits in Australia, Brazil, China, Africa, the former Soviet Union, and Canada. The ore is concentrated, refined to the oxide Ta_2O_5, converted to K_2TaF_7, and reduced to the **metal**.

Tantalum is a hard, **ductile**, dense, steel-blue (when unpolished) metal with the fourth highest melting point of all metals. It crystallizes in a body-centered cubic **lattice** with an atomic radius of 146 picometers. Tantalum has one stable **isotope**, ^{181}Ta; ^{180}Ta is a long-lived (half-life 1.2 x 10^{15} years) isotope.

Tantalum is not attacked at 25°C (77°F) by concentrated bases or acids (other than hydrofluoric acid or fuming sulfuric acid) because of its adhering, corrosion-resistant oxide film. Important compounds, spanning the **oxidation** state range of –3 to +5, include tantalum oxide, Ta_2O_5; the hard, refractory ceramic carbide TaC; the pentachloride $TaCl_5$; the refractory nitride TaN; reactive **organometallic compounds** with unusual molecular structures; and an interesting series of tantalum-tantalum bonded halide clusters (e.g., $Ta_6Cl_{18}^{4-}$) consisting of an octahedron of six tantalums with terminal and **octahedral** edge-bridging halides.

In 2000, 2,267 metric tons (5 million pounds) were produced for various applications, including: (1) electronic devices (79%), especially in capacitors for cell phones, portable computers, and video cameras where high volumetric efficiency and reliability are essential (the oxide coat on tantalum has a high dielectric constant and resistivity); (2) corrosion-resistant chemical process equipment; (3) filaments for evaporating metals; (4) high-temperature superalloys for gas turbines and jet engines; (5) high refractive-index optical lenses; (6) cutting tools; (7) screws and clips for surgical bone

transition metals: elements with valence electrons in d-sublevels; frequently characterized as metals having the ability to form more than one cation

congener: an element or compound belonging to the same class

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

ductile: property of a substance that permits it to be drawn into wires

lattice: systematic geometrical arrangement of atomic-sized units that describe the structure of a solid

isotope: form of an atom that differs by the number of neutrons in the nucleus

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

organometallic compound: compound containing both a metal (transition) and one or more organic moieties

octahedral: relating to a geometric arrangement of six ligands equally distributed around a Lewis acid; literally, eight faces repair because of its biological inertness; and (8) radioluminescent x-ray image-intensifying phosphors for medical imaging.

Louis Messerle

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Taste Receptors

Two categories of chemical senses (gustation or taste and olfaction or smell) are important for organisms to respond appropriately to their environments. The sensation of taste detects environmental chemicals and may have initially helped organisms distinguish between new sources of food and potential poisons. There are five different tastes that humans recognize: saltiness, sourness, sweetness, bitterness, and *umami* (the meaty flavor of monosodium glutamate or parmesan cheese). The chemistry of stimuli is described here, as well as their interactions with proteins in the membranes of taste **receptor** cells. These initiate nervous signals traveling via the gustatory nucleus of the brain stem to the cerebral cortex where conscious recognition of taste occurs.

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

Humans have 2,000 to 5,000 taste buds found scattered over the surface of the tongue in small projections known as papillae (bumps). Each taste bud contains about 50 to 150 taste receptor cells that are relatively selective for the taste that they sense. Chemical stimuli interact with the membranes of taste receptor cells either by binding to membrane receptors (proteins with selective binding sites) or by directly changing the number of ions flowing across the membrane.

Ionic Taste Stimuli

Saltiness is sensed by taste receptor cells that respond primarily to sodium chloride. The proteins in the cell membranes involved in transforming the presence of salt into nervous signals are **epithelial** sodium channels that allow the sodium ions to enter the cells, initiate the release of chemical **neurotransmitters**, and stimulate adjacent gustatory afferent axons (nerve cells that carry taste information to the brain). Sourness (hydrochloric acid, citric acid, or acetic acid) is likewise sensed by taste receptor cells in ways that directly affect ion channels. Protons either enter via the epithelial sodium channels or block epithelial potassium channels to initiate the cellular response. The bitterness of quinine and calcium is also sensed by blocking potassium channels in taste receptor cell membranes.

epithelial: related to a tissue type characterized by thin sheets and usually serving a protective or secretory function

neurotransmitters: molecules released by one neuron to stimulate or inhibit another neuron or cell

Membrane Receptor Taste Stimuli

In contrast, other tastes including sweetness (as in sucrose, fructose, and artificial sweetener) are sensed by actually binding to specific membrane receptor proteins in taste receptor cells. The chemicals sensed as sweet bind to selective sites on a membrane receptor in a “lock-and-key” fashion (implying that only chemicals of a particular shape can fit in the binding site and initiate the response). Once the sweet chemical is bound, the membrane receptor initiates a series of chemical reactions inside the cell, leading eventually to a change in the flow of ions across the membrane and the release of neurotransmitter. Likewise, the bitterness of some chemicals is sensed by binding to other membrane receptors and then initiating a response. The taste of some amino acids is initiated by binding to a specific site on **chemical-gated** ion channels (channels that open when a chemical is bound) where the amino acid (the chemical) acts as the key. The *umami* taste of monosodium glutamate is sensed by binding to another type of membrane receptor (similar to the synaptic glutamate receptors of the brain) that allows ions to cross cell membranes.

chemical-gated: of a membrane protein whose action to open a pore in the membrane occurs only after a substrate has been binded to the protein or a cofactor

Taste and smell are well-known chemical senses; however, the specific genes and proteins involved in some tastes have not yet been fully identified. SEE ALSO Artificial Sweeteners; Molecular Structure; Neurotransmitters.

Barbara E. Goodman

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Technetium

MELTING POINT: 2,157°C
BOILING POINT: 4,265°C
DENSITY: 11.5 g/cm^3
MOST COMMON IONS: TcO_5^{2-}, TcO_3^{-}, TcO_4^{2-}, TcO_4^{-}

43
Tc
TECHNETIUM
98.906

The discovery of technetium in 1937 by the Italian scientists Carlo Perrier and Emilio Segré was an important affirmation of the configuration of the Periodic Table. The table had predicted the existence of an element with 43 protons in its nucleus, but no such element had ever been found. (In fact, technetium does not occur naturally on Earth, as all of its known **isotopes** are radioactive and decay to other elements on a timescale that is relatively small when compared with the age of the earth.) Perrier and Segré were able to observe technetium from molybdenum that had been bombarded with deuterons. They named the element technetium, from the Greek word *technetos*, meaning artificial. Technetium is produced in relatively large quantities during **nuclear fission**, so there is currently an ample supply of the element from nuclear reactors and nuclear weapons production.

isotope: form of an atom that differs by the number of neutrons in the nucleus

nuclear: having to do with the nucleus of an atom

fission: process of splitting an atom into smaller pieces

Technetium looks like most other **metals**, silver-gray in color, but it is usually produced as one of its oxides, pertechnetate (TcO_4^{-}). Technetium has great chemical flexibility, and a wide variety of its compounds have been

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

prepared, generally paralleling the known compounds of rhenium. Technetium's radioactive nature and varied chemistry have helped to make it the most important element that is used in nuclear medicine. For diagnostic purposes, a compound containing technetium is prepared and injected into a patient, and then a large camera, typically made up of several gamma ray detectors, is passed over the patient. The technetium compound will have localized in specific organs, providing valuable information about organ function or the presence of abnormalities. The radiation dose to the patient is low, and the diagnostic procedure is considered less risky than exploratory surgery. Every year, millions of medical diagnostic scans that employ technetium are performed. SEE ALSO NUCLEAR FISSION; RHENIUM.

Jeffrey C. Bryan

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52
Te
TELLURIUM
127.60

Tellurium

MELTING POINT: 449.5°C
BOILING POINT: 990°C
DENSITY: 6.25 g/cm^3
MOST COMMON IONS: Te^{2-}, Te_2^{2-}, Te^{4+}, TeO_5^{2-}, TeO_4^{2-}

Tellurium was discovered in gold ores by Franz Joseph Müller von Reichenstein, the chief inspector of mines in Transylvania (Romania), in 1782. Tellurium was named, however, by M. Klaproth, who continued Müller von Reichenstein's work and isolated the element in 1798. Its name originates from the Latin *tellus*, which means "earth."

SOME BINARY COMPOUNDS OF TELLURIUM

	Compound	Chemical formula
Hydrides	tellurium hydride	H_2Te
Fluorides	tellurium (IV) fluoride	TeF_4
	tellurium (VI) fluoride	TeF_6
Chlorides	tellurium chloride	Te_2Cl
	tellurium (II) chloride	$TeCl_2$
	tellurium chloride	Te_3Cl_2
	tellurium (IV) chloride	$[TeCl_4]_4$
Bromides	tellurium bromide	Te_2Br
	tellurium (II) bromide	$TeBr_2$
	tellurium (IV) bromide	$[TeBr_4]_4$
Iodides	tellurium (I) iodide	TeI
	tellurium iodide	Te_2I
	tellurium (I) iodide	Te_4I_4
	tellurium (IV) iodide	$[TeI_4]_4$
Oxides	tellurium (II) oxide	TeO
	tellurium (IV) oxide	TeO_2
	tellurium (VI) oxid	TeO_2

Some binary compounds of tellurium.

Tellurium is used in photocopiers to enhance picture quality.

Tellurium is a comparatively rare element, is seventy-third in order of crustal abundance (approximately 0.001 ppm), and is occasionally found as the native **metal**. Many of its minerals occur together with the sulfides of chalcophilic metals (e.g., Cu, Ag, Au, Zn, Cd, Hg, Fe, Co, Ni, Pb, As, Bi). It is obtained from anode slime produced in the electrolytic refining of Cu. Tellurium has eight naturally occurring **isotopes**; the most abundant ones are ^{130}Te (33.8%) and ^{128}Te (31.7%). Crystalline tellurium has a silvery-white appearance and exhibits a metallic luster but is usually obtained as a dark gray powder. It is brittle and easily pulverized. Tellurium is a p-type semiconductor and shows varying conductivity with crystal alignment (its electrical resistivity is approximately 1 ohm cm at 25°C). Its conductivity increases slightly with exposure to light. It can be **doped** with silver, copper, gold, tin, and other elements. Other **nuclear** and physical properties include: atomic radius: 160 pm; ionic radius: 221 pm (Te^{2-}); 97 pm (Te^{4+}); 56 pm (Te^{6+}); and **ionization** energy: 869 kJ/mol.

The main uses of tellurium are: as semiconductors; in the formation of **alloys** with lead (to prevent corrosion), cast iron (to improve machinability), copper, and stainless steel; in ceramic materials; tinting glass. SEE ALSO Chalcogens.

Thomas M. Klapotke
M. J. Crawford

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

isotope: form of an atom that differs by the number of neutrons in the nucleus

dope: to add a controlled amount of an impurity to a very pure sample of a substance, which can radically change the properties of the substance

nuclear: having to do with the nucleus of an atom

ionization: dissociation of a molecule into ions carrying + or − charges

alloy: mixture of two or more elements, at least one of which is a metal

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Temperature

In everyday terms, temperature is a measure of the "hotness" or "coldness" of a substance. More technically, temperature indicates the direction in which energy flows (as heat) when two objects are in thermal contact: energy flows as heat from a high temperature region to a low temperature region. In other words, temperature is simply an indicator of the expected direction of flow of energy as heat.

Temperature is not heat. Heat is energy in transition; temperature is the signpost of the expected direction of that transition. A large quantity of energy can flow as heat from one region to another even though the temperature difference between the regions is minute.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Temperature is not energy. A very large, cold block of **metal** will have a low temperature but may contain a very large amount of energy. A small block of the same material having the same temperature will contain less energy. This distinction is expressed by saying that temperature is an intensive property, a property independent of the size of the sample; whereas energy content is an extensive property, a property that does depend on the size of the sample. Thus, a sample taken from a tank of hot water will have the same temperature regardless of the size of the sample, but the energy content (more formally, the internal energy) of a large sample is greater than that of a small sample.

At a molecular level, the temperature of a system indicates the distribution of "populations" of energy levels within the system: the higher the temperature, the greater the proportion of molecules in a state of high energy. If the numbers of molecules in two energy states, separated by an energy difference ΔE, are N_{upper} and N_{lower}, then the temperature is

$$T = (\Delta E/k)\ln(N_{\text{lower}}/N_{\text{upper}}) \tag{1}$$

where k is Boltzmann's constant, a fundamental constant of nature. We see that the greater the ratio $N_{\text{lower}}/N_{\text{upper}}$ for a given energy difference, the higher the temperature. This molecular interpretation has a special significance in cases in which the only contribution to the overall energy is kinetic energy, which is the case in a perfect (ideal) gas. In that case, high temperature corresponds to a higher average speed of the molecules and a wider range of speeds in the sample. The average speed c of molecules of mass m at a temperature T is

$$c = (8kT/\pi m)^{1/2} \tag{2}$$

and so the average speed increases with the square root of the temperature.

Temperature is measured with a thermometer, a device in which a physical property of some component of the device changes when the device is put in thermal contact with a sample. That property may be the volume of a liquid (as in a mercury-in-glass thermometer) or an electrical property such as resistance. Electronic probes based on resistance changes in a semiconductor material are also used to measure temperature.

Three scales of temperature are still commonly encountered. The Fahrenheit scale is used in the United States for domestic purposes. On this

A woman is checking a baby's temperature. A high temperature indicates more energy in the body and possibly an illness.

scale, the freezing point of water is 32°F and its boiling point is 212°F. This scale has been discarded by virtually all other countries in favor of the Celsius scale, which is used for all scientific work. On the Celsius scale, the freezing point of water corresponds to 0°C and the boiling point corresponds to 100°C. A more fundamental scale is the Kelvin scale, which sets 0 at the absolute zero of temperature (corresponding to −273.15°C), and adopts a scale in which the triple point of water (the temperature at which ice, water, and water vapor coexist at **equilibrium**) is exactly 273.16 K. This scale ensures that the magnitude of the kelvin (as the unit for the Kelvin scale is called) is the same as that of the Celsius degree.

equilibrium: condition in which two opposite reactions are occurring at the same speed, so that concentrations of products and reactants do not change

The Kelvin scale is used to express the thermodynamic temperature, denoted T, with $T = 0$ as the lowest possible temperature (when all motion has ceased). Temperatures on the Celsius and Fahrenheit scales are denoted θ (theta). Two important conversions are:

$$\theta/°\mathrm{C} = \tfrac{5}{9}(\theta/°\mathrm{F} - 32) \quad (3)$$

$$T/K = \theta/°\mathrm{C} + 273.15 \quad (4)$$

In chemistry, it is often necessary to keep a system at a constant temperature, for otherwise observations and measurements would provide a reading that was an average of a temperature-dependent property, such as reaction rate. One way to achieve a constant temperature is to immerse the system in a water bath containing a large volume of water, the temperature of which is controlled by a heater and a thermostat. A thermostat is a device for switching a current on and off according to whether the temperature of the system is above or below a selected value. It incorporates a temperature probe (a thermometer with an electric output) and electronic devices for interpreting the temperature and effecting the switching. The same principle is the basis of the thermostat that is used in homes.

phase: homogeneous state of matter

The chemical effects of greater temperature include changes in the rate of reaction and the position of chemical equilibrium. Almost all reactions proceed more rapidly at higher temperatures because the molecules (in the gas **phase**) collide more vigorously at higher temperatures. A thermodynamic consequence of changing temperature is that the equilibrium constant of an exothermic reaction decreases as the temperature is raised, so reactants are more favored at low temperatures than at high. This dependence is sometimes referred to as Le Chatelier's principle, but it is better to regard it as a consequence of thermodynamics and in particular of the second law of thermodynamics.

Although $T = 0$ is the lowest attainable temperature, it is possible to achieve negative temperatures. This seemingly paradoxical remark is resolved as follows. When a system has only two energy levels, all finite temperatures correspond to a distribution of populations in which more molecules occupy the lower state than the upper. However, it is possible by artificial means to invert the populations, so that briefly there would be more molecules in the upper state than the lower. It follows from equation 1 that T is then negative.

The thermodynamic justification for introducing the temperature into science is the Zeroth Law, which states that if system A is in thermal equilibrium with system B, and system B is in thermal equilibrium with system C, then A and C would also be in thermal equilibrium with each other, if they were put in contact. The third law of thermodynamics is also relevant here: it states that absolute zero ($T = 0$) is not attainable in a finite number of steps. SEE ALSO CHEMISTRY AND ENERGY; ENERGY; HEAT; PHYSICAL CHEMISTRY; THERMODYNAMICS.

Peter Atkins

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Teratogen

Teratogen means, in Greek, "monster forming." Teratogens are chemicals that cause abnormalities in embryos. The most well-known is thalidomide, a drug originally designed to combat morning sickness in pregnant women. It caused the long bones in the arms or legs of fetuses to not develop properly, resulting in babies with severely stunted arms or legs.

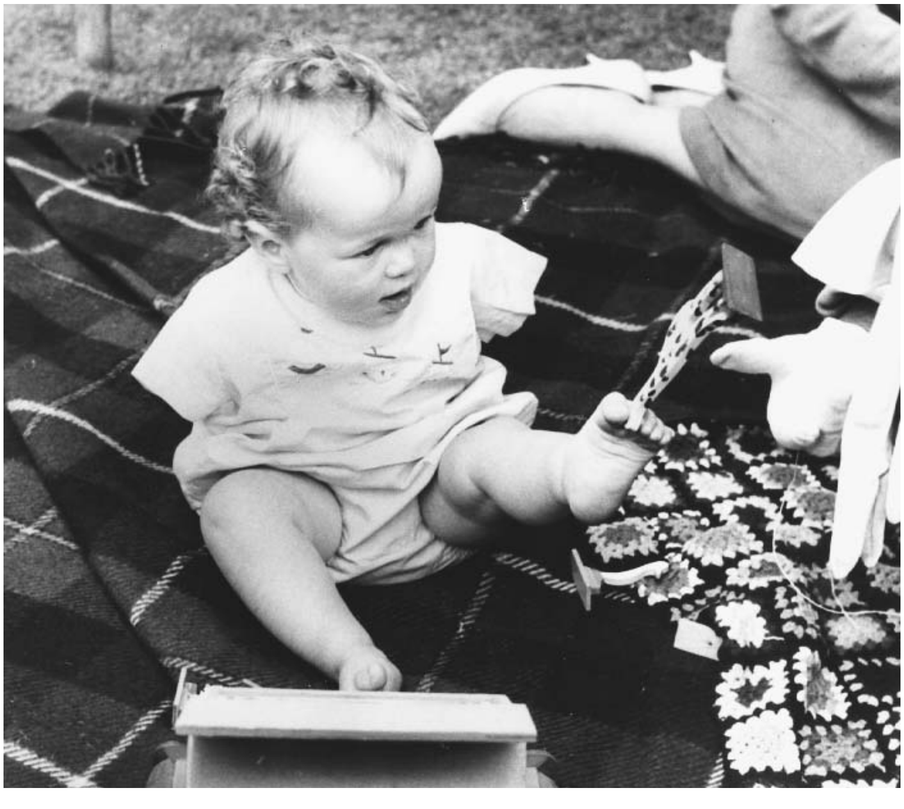
Teratogen is a type of mutagen that causes mutations in **somatic cells** (cells that are not part of the reproductive system). Mutagens induce mutations of deoxyribonucleic acid (**DNA**), the hereditary material in cells. The damage of DNA may either kill the cells or, when misrepaired, produce abnormal sequences that will be passed on to daughter cells. This may result in birth defects by injuring developing organs or by disorganizing growth and differentiation.

somatic cell: cells of the body with the exception of germ cells

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

Apart from thalidomide, the steroid hormones have also been identified as teratogens. The use of male sex hormones as a treatment for breast cancer has resulted in the masculinization of a number of female fetuses when such treatment was commenced prior to the twelfth week of gestation. In addition, the accepted practice of using **progesterone** from natural sources for the treatment of miscarriage led to the widespread use of synthetic hormones between 1950 and 1960. The result was the birth of more than 600 female babies with equivocal or frankly masculinized external genitalia. It

progesterone: steroid found in the female reproductive system: formula $C_{21}H_{30}O_2$



The teratogen thalidomide causes stunted arms and legs in babies. It was commonly used by pregnant women to combat morning sickness.

was found later that these synthetic compounds had appreciable androgenic (related to the male sex hormone) activity.

There are other chemicals suspected of being teratogenic because they are occasionally associated with malformations in the offspring of women treated during pregnancy. These include anticonvulsants and some oral hypoglycemics when taken at high doses during pregnancy. It is, however, very difficult to determine the teratogenesis of a drug. Long and costly surveys must be done on a very large population to associate a particular drug with birth defects. SEE ALSO Deoxyribonucleic Acid; Kelsey, Frances Kathleen Oldham; Mutagen; Toxicity.

Joseph Bariyanga

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Terbium

MELTING POINT: **1,356°C**
BOILING POINT: **2,480°C**
DENSITY: **8.253 g/cm^3**
MOST COMMON IONS: **Tb^{3+}, Tb^{4+}**

In 1787, near Ytterby, Sweden, Swedish army officer Karl Axel Arrhenius discovered a mineral that he named ytterite. In 1794 Finnish chemist Johan Gadolin, working with ytterite, isolated a mixture of oxides (yttria) from which Carl G. Mosander in 1843 isolated three fractions: the oxide of the element yttrium (Y) and two other mixtures of oxides (old erbia and old terbia). In 1878 Swiss chemist Marc Delafontaine worked with "old erbia" but called it new new terbia. Also in 1878 J. C. Galissard de Marignac and Delafontaine, working with "new terbia," isolated an oxide of a new element, terbium. The element has an abundance of 0.91×10^{-5} percent (by weight) in the igneous rocks of Earth's crust. Terbium's ground state electronic configuration is $[Xe]4f^9 6s^2$. It has an atomic radius of 1.782 angstroms. Terbium has two crystallographic structures: α-Tb (room temperature to 1,310°C) and β-Tb (> 1,310°C). Bastnasite (fluorocarbonates), monazite, and xerotime (phosphates) are the principal terbium-containing minerals.

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

Terbium has two **oxidation** states: 3+, the most important, and 4+. Tb^{4+} is a strong oxidizing agent. Tb^{3+} salts are generally colorless or very pale pink. The Tb^{3+} halides, except the fluoride compound, are soluble in water as well as in nitric acid, perchloric acid, and acetic acid. The hydroxide, oxide, phosphate, carbonate, and oxalate compounds are insoluble. A Tb^{4+} oxide with a composition approaching Tb_4O_7 (brown) is obtained via the **calcination** of several salts: carbonate, nitrate, and oxalate. The Tb^{4+} compounds TbO_2, with a fluorite-type **lattice**, and TbF_4 also exist.

calcine: to heat or roast to produce an oxide

lattice: systematic geometrical arrangement of atomic-sized units that describe the structure of a solid

Tb^{3+} compounds and complexes in most cases exhibit strong luminescence in the green portion of visible light. Ternary compounds such as

$La_{1-x}-yCe_xTb_yPO_4$ exhibit strong green emission radiation. Such kinds of compounds are called "phosphors" and are used to display color in television. Terbium is also used as an **alloy** material in compact discs. SEE ALSO Cerium; Dysprosium; Erbium; Europium; Gadolinium; Holmium; Lanthanum; Lutetium; Neodymium; Praseodymium; Promethium; Samarium; Ytterbium.

alloy: mixture of two or more elements, at least one of which is a metal

Lea B. Zinner
Geraldo Vicentini

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Terpenes

If you walk into a garden in bloom and breathe deeply, you are likely to encounter great smells. In many cases, the molecules that bring those scents to your nose are terpenes. Terpenes are a class of molecules that typically contain either ten or fifteen carbon atoms built from a five-carbon building block called **isoprene**. It is important to note these molecules are **volatile**—they tend to evaporate relatively easily—which allows them to reach one's nose and trigger the olfactory senses. Figure 1 shows the structure of several molecules in this category and identifies the plant from which they are derived.

isoprene: common name for 2-methyl-1,3butadiene, the monomer of the natural rubber polymer

volatile: low boiling, readily vaporized

Because they share the common building block of isoprene, terpenes can be categorized based on how many terpene units they include. The "base" of this system is a two-isoprene unit, so monoterpenes have ten carbons. This category includes molecules such as camphor, menthol, and pinene. If three isoprenes are present, as in farnesol (shown in Figure 1), the category is called sesquiterpenes.

In plants, terpenes are typically found as a component of the essential oils. The name of this fluid suggests an important characteristic of this class of molecules. If humans have found these oils important enough to refer to them as essential, there is a reasonable chance that they have useful properties. Many terpenes such as menthol (shown in Figure 1) and camphor have medicinal values. You may have used a throat lozenge with menthol to help clear your sinuses the last time you had a cold.

Another use of terpenes may be found in coatings such as varnish. Varnish for musical instruments like violins can be made largely from the terpene pinene. The key to generating a coating such as varnish is to allow polymerization to occur. The fact that terpenes are built up from isoprene building blocks, much like any other polymer, suggests that polymerization is a possibility. When pinene (present in pine tree and made into turpentine) is exposed to air and sunlight, it will slowly polymerize and make a fine finish for wood.

β-carotene is a tetraterpene (structure shown in Figure 1); it has four isoprene units. This molecule, found in abundance in carrots, is useful in

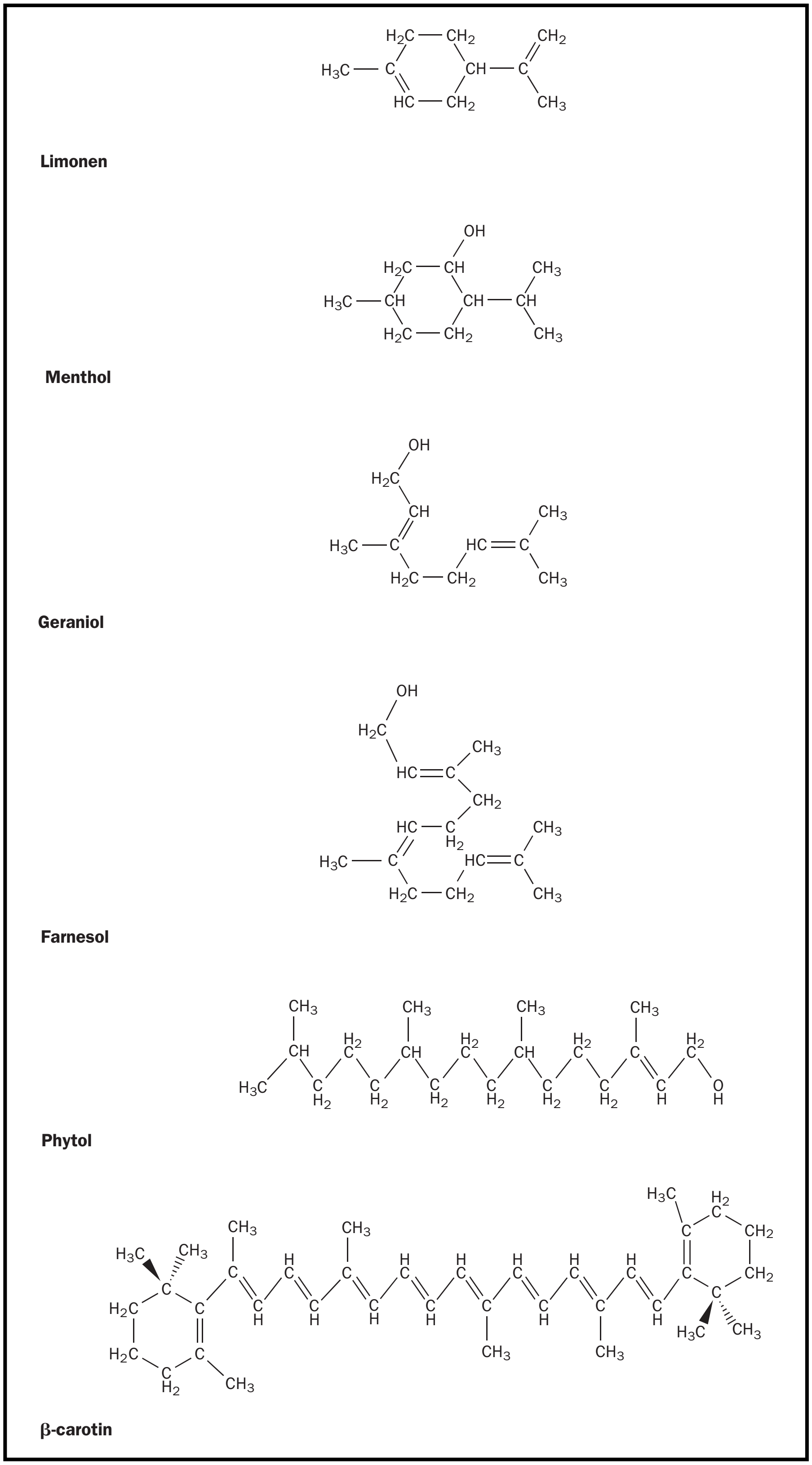

Figure 1. The structures of several terpene molecules and the plants from which they are derived.

human diets because it can be converted into **vitamin** A in the body. It also plays an important role in plants because it is among the pigments that absorb light in **photosynthesis**. When leaves change color in the fall, β-carotene is often responsible for this effect. SEE ALSO Lipids; Membrane.

Thomas A. Holme

vitamins: organic molecules needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

photosynthesis: process by which plants convert carbon dioxide and water to glucose

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Tertiary Structure

The tertiary structure is the complete three-dimensional structure of a **polypeptide** chain. Many polypeptides fold into compact, globular structures in which amino acid residues that are distant from each other in primary structure come into close proximity in the folded structure. Because of efficient packing, most water molecules are excluded from the protein's interior. It is the different interactions between the side chains of the amino acids that stabilize the tertiary structure. A major force stabilizing the tertiary structure is the **hydrophobic** interaction among **nonpolar** side chains in the core of the protein.

Additional stabilizing forces include **electrostatic interactions** between ionic groups of opposite charge, **hydrogen bonds** between polar groups, and **disulfide bonds**. Disulfide (S–S) bonds are formed between the thiol (S–H) groups of two cysteine side chains resulting in a **covalent bond** between the two side chains. Many physical and chemical agents, including heat, detergents, salts, **heavy metals**, strong acids and bases, organic solvents, and mechanical stress, can disrupt or destroy the three-dimensional structure of a protein. This process of destroying the three-dimensional protein structure is called denaturation. SEE ALSO Primary Structure; Quaternary Structure; Secondary Structure.

Elizabeth S. Roberts-Kirchhoff

polypeptide: compound containing two or more amide units—C(O)NH—produced by the condensation of two or more amino acids

hydrophobic: water repelling

nonpolar: molecule, or portion of a molecule, that does not have a permanent, electric dipole

electrostatic interaction: force that arises between electrically charged particles or regions of particles

hydrogen bond: interaction between H atoms on one molecule and lone pair electrons on another molecule that constitutes hydrogen bonding

disulfide bond: bond that involves two bonding sulfur atoms, –S–S–

covalent bond: bond formed between two atoms that mutually share a pair of electrons

heavy metal: by convention, a metal with a density greater than 5 g/cm^3; 70 elements are thus classified as heavy metals

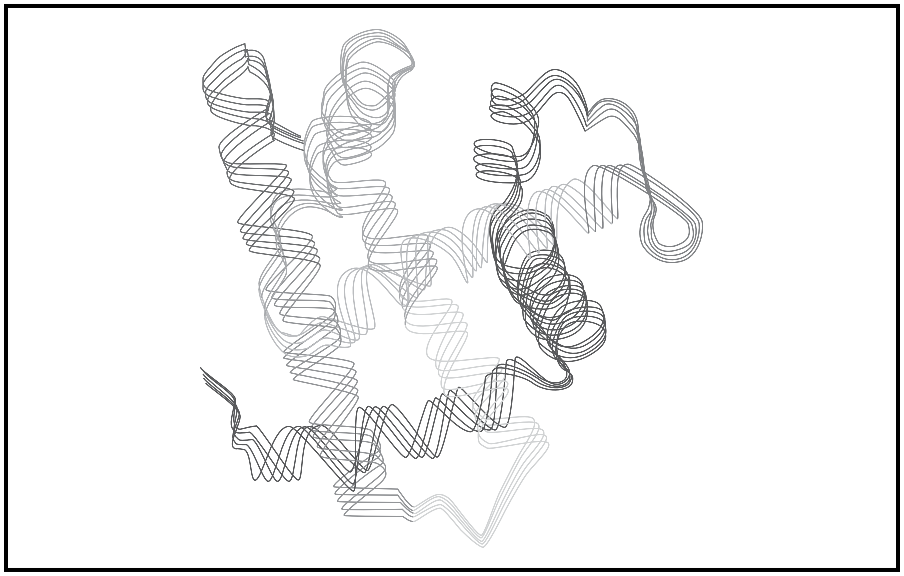

Figure 1. This structure of myoglobin illustrates a typical tertiary structure.

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Testosterone

androgen: group of steroids that act as male sex hormones

estrogen: female sex hormone

synthesis: combination of starting materials to form a desired product

Testosterone is a male sex hormone, one of a class of compounds known as **androgens**. Included in this group are testosterone, dihydrotestosterone, and androstenedione. Androgens are synthesized from cholesterol and are considered steroid hormones, a category of hormones that includes female sex hormones such as **estrogen**. The isolation and **synthesis** of testosterone were reported in 1935. Chemists Adolf Butenandt and Leopold Ruzicka later received the Nobel Prize in chemistry (in 1939) for this work and related discoveries.

basal metabolism: the process by which energy to carry out involuntary, life-sustaining processes is generated.

Testosterone (which is also present in small amounts in females) stimulates the growth of the male reproductive organs and promotes the development of the male secondary sex characteristics. It also affects body hair distribution, baldness, voice, and skin thickness and promotes each of the following: the formation of spermatozoa, protein formation, muscle development, bone growth, the retention of calcium, the rate of **basal metabolism**, and the number of red blood cells in the body.

excrete: to eliminate or discharge from a living entity

In males testosterone is manufactured and secreted overwhelmingly by the testes. After secretion, 97 percent of testosterone is bound by protein carriers in blood and circulates in the body for thirty to sixty minutes. At this point, it has either been absorbed by various tissues or degraded to inactive molecules. Much of the testosterone absorbed by tissues is reduced to dihydrotestosterone, a step that is essential for the actualization of some of testosterone's effects. Testosterone not absorbed by tissues will be degraded by the liver, and the products of this degradation will be **excreted** from the body. SEE ALSO ESTROGEN; STEROIDS.

Matthew A. Fisher

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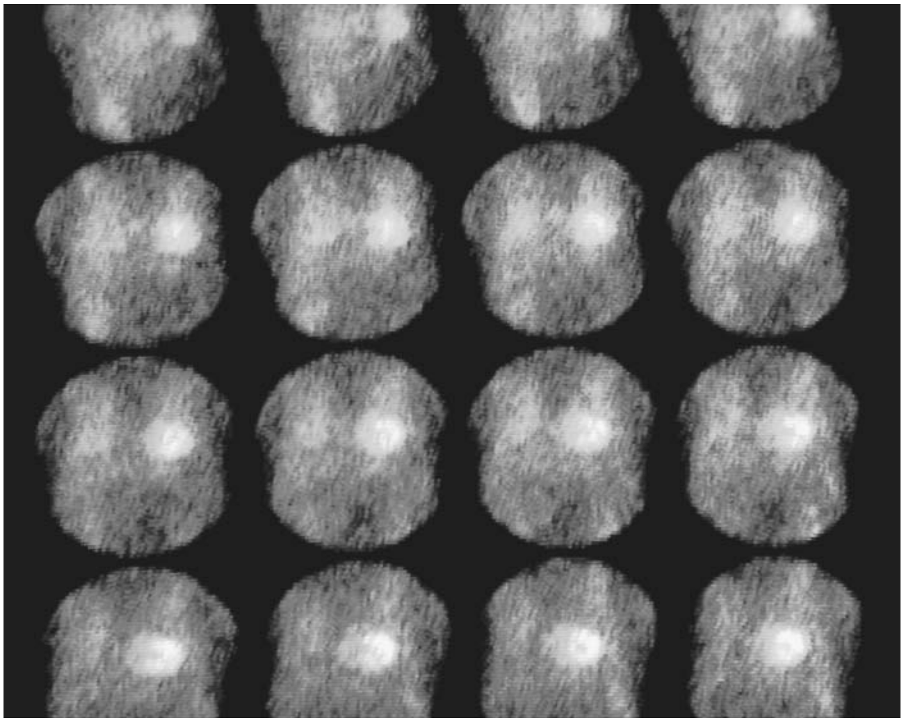
Thallium

81
Tl
THALLIUM
204.383

MELTING POINT: 302°C
BOILING POINT: 1,457°C
DENSITY: 11.8 g/cm^3
MOST COMMON IONS: Tl^+, Tl^{3+}

spectroscopy: use of electromagnetic radiation to analyze the chemical composition of materials

Thallium was discovered in 1861 by the British chemist Sir William Crookes. While attempting a **spectroscopic** analysis of materials that contained tellurium, Crookes observed a previously unknown bright green line



The soft metal thallium is used in heart scans to evaluate the blood supply to the heart.

on his spectroscope (a machine that identifies the kinds of light emitted by elements at high temperatures). The name thallium comes from the Greek word *Thallos*, meaning "green twig," and was chosen by Crookes because the **spectral line** he had observed reminded him of a fresh green shoot.

spectral line: line in a spectrum representing radiation of a single wavelength

The abundance of thallium in Earth's crust is estimated to be between 0.1 and 1 mg/kg (ppm). It is widely dispersed and is often associated with potassium minerals. Small deposits of the thallium-bearing minerals such as lorandite and the aptly named crookesite exist in Greece and Sweden, respectively.

Thallium **metal** is so soft that it can easily be cut with a knife. It has a metallic luster that slowly tarnishes upon exposure to air to give the metal a bluish-gray appearance (caused by the formation of Tl_2O_3). The thin layers of surface oxide prevent further **oxidation**. However, in moist air or water, the soluble hydroxide TlOH is formed. Thallium can exist in two oxidation states, (I) and (III). When heated in air, the metal oxidizes to Tl_2O. Thallium reacts vigorously with the **halogens**, forming dihalides of composition $2TlX_3$ where X = fluorine, chlorine, or bromine. Thallium is rapidly dissolved in nitric acid but rendered passive in sulfuric and hydrochloric acids due to the formation of insoluble Tl(I) salts.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

In biological systems, thallium is nonessential, (i.e., not required for organisms to complete their life cycles) and toxic at high concentrations. Thallium(I) mimics potassium. In humans it affects potassium-activated enzymes in the brain, muscles, and skin. Symptoms of thallium poisoning can easily be attributed to other causes, which in the past has made this element popular for homicides!

Currently, thallium is used in some electronic devices, in low melting point glass, and in the creation of low melting point **alloys**. SEE ALSO HALOGENS; POTASSIUM.

alloy: mixture of two or more elements, at least one of which is a metal

Brett Robinson

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Theoretical Chemistry

Theoretical chemistry is the discipline that uses quantum mechanics, classical mechanics, and statistical mechanics to explain the structures and dynamics of chemical systems and to correlate, understand, and predict their thermodynamic and kinetic properties. Modern theoretical chemistry may be roughly divided into the study of chemical structure and the study of chemical dynamics. The former includes studies of: (1) electronic structure, potential energy surfaces, and force fields; (2) vibrational-rotational motion; and (3) **equilibrium** properties of condensed-phase systems and macromolecules. Chemical dynamics includes: (1) bimolecular kinetics and the collision theory of reactions and energy transfer; (2) unimolecular rate theory and metastable states; and (3) condensed-phase and macromolecular aspects of dynamics.

equilibrium: condition in which two opposite reactions are occurring at the same speed, so that concentrations of products and reactants do not change

A critical issue crossing all boundaries is the interaction of matter and radiation. Spectroscope experiments are used as both structural and dynamic probes and to initiate chemical processes (as in photochemistry and laser-induced chemistry), and such experiments must be understood theoretically. There are also many subfields of theoretical chemistry—for example, biomedical structure-activity relationships, the molecular theory of nuclear magnetic resonance spectra, and electron-molecule scattering—that fit into two or more of the areas listed.

Another source of overlap among the categories is that some of the techniques of theoretical chemistry are used in more than one area. For example, statistical mechanics includes the theory and the set of techniques used to relate **macroscopic phenomena** to properties at the atomic level, and it is used in all six subfields listed. Furthermore, the techniques of **quantum mechanics** and classical-mechanical approximations to quantum mechanics are used profitably in all six subfields as well. Condensed-phase phenomena are often treated with gas-phase theories in instances in which the effects of liquid-phase solvent or solid-state **lattice** are not expected to dominate. There are many specialized theories, models, and approximations as well.

macroscopic phenomena: events observed with human vision unassisted by instrumentation

quantum mechanics: theoretical model to describe atoms and molecules by wave functions

lattice: systematic geometrical arrangement of atomic-sized units that describe the structure of a solid

Because quantum and statistical mechanics are also parts of physics, theoretical chemistry is sometimes considered a part of chemical physics. There is no clear border between theoretical physical chemistry and theoretical chemical physics.

Three Modes of Science

Modern science is sometimes said to proceed by three modes—experiment, theory, and computation. This same division may be applied to chemistry. From this point of view, theoretical chemistry is based on analytical theory, whereas computational chemistry is concerned with predicting the properties of a complex system in terms of the laws of quantum mechanics (or classical approximations to quantum mechanics, in the domains in which such classical approximations are valid that govern the system's constituent atoms or its constituent nuclei and electrons, without using intermediate levels of analytical chemical theory. Thus, in principle, computational chemistry assumes only such basic laws as the Schrödinger equation, Newton's laws of motion, and the Boltzmann distribution of energy states. In practice, though, computational chemistry is a subfield of theoretical chemistry, and predictions based on approximate theories, such as the dielectric continuum model of solvents, often require considerable computer programming and number crunching. The number of subfields of chemistry in which significant progress can be made without large-scale computer calculations is dwindling to zero. In fact, computational advances and theoretical understanding are becoming more and more closely linked as the field progresses. Computational chemistry is sometimes called molecular modeling or molecular simulation.

Electronic Structure

Perhaps the single most important concept in theoretical chemistry is the separation of electronic and nuclear motions, often called the Born-Oppenheimer approximation, after the seminal work of Max Born and Robert Oppenheimer (1927), although the basic idea must also be credited to Walter Heitler, Fritz London, Friedrich Hund, and John Slater. The critical facts that form a basis for this approximation are that electrons are coupled to nuclei by Coulomb forces, but electrons are much lighter—by a factor of 1,800 to 500,000—and thus, under most circumstances, they may be considered to adjust instantaneously to nuclear motion. Technically we would describe the consequence of this large mass ratio by saying that a chemical system is usually electronically adiabatic. When electronic adiabaticity does hold, the treatment of a chemical system is greatly simplified. For example, the H2 molecule is reduced from a four-body problem to a pair of two-body problems: one, called the electronic structure problem, considers the motion of two electrons moving in the field of fixed nuclei; and another, called the vibration-rotation problem or the dynamics problem, treats the two nuclei as moving under the influence of a force field set up by the electronic structure. In general, because the energy of the electronic subsystem depends on the nuclear coordinates, the electronic structure problem provides an effective potential energy function for nuclear motion. This is also called the potential energy hypersurface. The atomic force field (i.e., the set of all the forces between the atoms) is the gradient of this potential energy function.

Thus, when the Born-Oppenheimer approximation is valid and electronic motion is adiabatic, the end result of electronic structure theory is a potential energy function or atomic force field that provides a starting point for treating vibrations, equilibrium properties of materials, and dynamics. Robert Mulliken, Road Hoffman, Kenichi Fukui, John Pople, and Walter Kohn won Nobel Prizes in chemistry for their studies of electronic structure, including molecular orbital theory. Some important problem areas in which the Born-Oppenheimer separation breaks down are photochemical reactions involving visible and **ultraviolet radiation** and electrical conductivity. Even for such cases, though, it provides a starting point for more complete treatments of electronic-nuclear coupling.

ultraviolet radiation: portion of the electromagnetic spectrum with wavelengths shorter than visible but longer than x rays

Dynamics

In the subfield of theoretical dynamics, the most important unifying concept is transition state theory, which was developed by Henry Eyring, Eugene Wigner, M. G. Evans, and Michael Polanyi. A transition state is a fleeting intermediate state (having a lifetime on the order of 10 femtoseconds) that represents the hardest-to-achieve configuration of a molecular system in the process of transforming itself from reactants to products. A transition state is sometimes called an activated complex or a dynamical bottleneck. In the language of quantum mechanics, it is a set of resonances or metastable states, and in the language of classical mechanics, it is a hypersurface in phase space. Transition states are often studied by semiclassical methods as well; these methods represent a hybrid of quantum mechanical and classical equations. Transition state theory assumes that a good first approximation to the rate of reaction is the rate of accessing the transition state. Transition state theory is not useful for all dynamical processes, and in a more general context a variety of simulation techniques (often called molecular dynamics) are used to explain observable dynamics in terms of atomic motions.

Predictive Power

In the early days of theoretical chemistry, the field served mainly as a tool for understanding and correlating data. Now, however, owing to advances in computational science, theory and computation can often provide reliable predictions of unmeasured properties and rates. In other cases, where measurements do exist, theoretical results are sometimes more accurate than measured ones. Examples are the properties of simple molecules and reactions such as $D + H_2 \rightarrow HD + H$, or the heats of formation of reactive species. Computational chemistry often provides other advantages over experimentation. For example, it provides a more detailed view of phenomena such as the structure of transition states or a faster way to screen possibilities. An example of the latter is provided in the field of drug design, in which thousands of candidate molecules may be screened for their likely efficiency or bioavailability by approximate calculations—for example, of the electronic structure or free energy of desolvation—and, relying on the results of these calculations, candidates may be prioritized for **synthesis** and testing in laboratory studies. In conclusion, theoretical chemistry, by combining tools of quantum mechanics, classical mechanics, and statistical mechanics, allows chemists to predict materials' properties and rates of chemical processes, even in many cases in which they have not yet been measured or even observed in the laboratory; whereas for processes that have been observed, it provides a deeper level of understanding and explanations of trends in the data. SEE ALSO COMPUTATIONAL CHEMISTRY; MOLECULAR MODELING; QUANTUM CHEMISTRY.

synthesis: combination of starting materials to form a desired product

Donald G. Truhlar

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Thermochemistry

Thermochemistry is the study of the heat released or absorbed as a result of chemical reactions. It is a branch of thermodynamics and is utilized by a wide range of scientists and engineers. For example, biochemists use thermochemistry to understand bioenergetics, whereas chemical engineers apply thermochemistry to design manufacturing plants. Chemical reactions involve the conversion of a set of substances collectively referred to as "reactants" to a set of substances collectively referred to as "products." In the following balanced chemical reaction the reactants are gaseous methane, CH_4(g), and gaseous molecular oxygen, O_2(g), and the products are gaseous carbon dioxide, CO_2(g), and liquid water H_2O(l):

$$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l) \quad (1)$$

Reactions in which a fuel combines with oxygen to produce water and carbon dioxide are called **combustion** reactions. Because natural gas consists primarily of methane, it is expected that reaction (1) will liberate heat. Reactions that liberate heat are termed exothermic reactions, and reactions that absorb heat are termed endothermic reactions.

combustion: burning, the reaction with oxygen

The heat associated with a chemical reaction depends on the pressure and temperature at which the reaction is carried out. All thermochemical data presented here are for reactions carried out under standard conditions, which are a temperature of 298 K (24.85°C) and an applied pressure of one **bar**. The quantity of heat released in a reaction depends on the amount of material undergoing reaction. The chemical formulas that appear in a reaction each represent 1 mole (see article on "Mole Concept") of material; for example, the symbol CH_4 stands for 1 mole of methane having a mass of 16 grams (0.56 ounces), and the 2 O_2(g) tells us that 2 moles of oxygen are required. Thermochemistry also depends on the physical state of the reactants and products. For example, the heat liberated in equation (1) is 890

bar: unit of pressure equal to one million dynes per square centimeter

phase: homogeneous state of matter consisting of gases, liquids, or solids

kilojoules (kJ); if, however, water in the gas **phase** is formed, $H_2O(g)$, the heat released is only 802 kJ. Reversing a reaction like (l), which liberates heat, yields a reaction wherein heat must be supplied for the reaction to occur. The following reaction absorbs 890 kJ.

$$CO_2(g) + 2\ H_2O(l) \rightarrow CH_4(g) + 2\ O_2(g) \qquad (2)$$

Energy and Enthalpy

Thermochemical changes are often discussed in terms of the "system" and the "surroundings." The system is regarded as the reaction products and reactants, whereas the surroundings consist of everything else in the universe. A boundary separates the system from the surroundings. The first law of thermodynamics relates the energy change belonging to a system to the amount of work and heat crossing the boundary. A statement of the first law applied to chemical reactions in which only heat and work cross the boundary is given by the expression:

$$U_{\text{products}} - U_{\text{reactants}} = \Delta U = q + w \qquad (3)$$

Here U_{products} represents the energy of the products and $U_{\text{reactants}}$ represents the energy of the reactants. The heat associated with the reaction is given as q, and w represents work done during the transformation of reactants to products. If the volume of the system changes during the reaction and the applied pressure remains constant, the work carried out is termed pressure-volume work. For example, reaction (2) converts one mole of gas and two moles of liquid to a total of three moles of gas. The volume of the system increases during the reaction because, under standard conditions, a mole of gas occupies more volume than a mole of liquid. The work of expanding a system against atmospheric pressure is experienced when one inflates a balloon, and this work can be shown to be equal to $-P\Delta V$. Here P represents the atmospheric pressure and ΔV represents the change in volume of the system.

The first law of thermodynamics also states that U is a state function. State functions are very important in thermodynamics; they depend only on the present state of a system and not on its past history. Neither q nor w are state functions. An understanding of the concept of state function is furthered by considering the example of one's taking a trip from San Diego, California, to Denver, Colorado. The change in altitude that one experiences during this trip does not depend on the route taken and, thus, is similar to a state function. In comparison, the distance traveled between the two cities does depend on the route one follows; similarly, q and w are path-dependent quantities.

If a process such as a chemical reaction is carried out at a constant pressure in a way that involves only pressure-volume work, then $-P\Delta V$ can be substituted for the work term in equation (3). Thus, we have:

$$\Delta U + P\Delta V = q_p \qquad (4)$$

The symbol q_p represents the heat accompanying a chemical change carried out at constant pressure; in our previous example this would be equivalent to our specifying the exact route of travel between the two cities. The **enthalpy** of a system H is related to the energy of a system by the expression:

enthalpy: the sum of the energy in a system added to the product of its volume and pressure

$$H = U + PV \tag{5}$$

For a process or reaction carried out at constant pressure:

$$\Delta H = \Delta U + P\Delta V = q_p \tag{6}$$

Enthalpy, like energy, is a state function. Thus, equation (6) shows that, for a reaction carried out at constant pressure, q_p depends only on the reactants consumed and the products formed. The enthalpy change associated with a reaction carried out under standard conditions is termed the heat of reaction and is given the symbol ΔH^0, with the superscript denoting standard conditions. Endothermic reactions have a positive ΔH^0 whereas exothermic reactions have a negative ΔH^0. The change in enthalpy accompanying the conversion of reactants to products in a chemical reaction determines the amount of heat liberated or absorbed by the reaction. For a reaction carried out at constant pressure the enthalpy change depends only on the reactants and products.

Hess's Law

Because enthalpy is a state function, the heat associated with a reaction does not depend on whether the reaction proceeds from reactants to products in a series of steps or in a single step. This is the basis for Hess's law, which states that if two reactions are combined to yield a third reaction, the sum of the ΔH^0s for the first two reactions is equal to the ΔH^0 for the third. For example, consider the conversion of gaseous methane to liquid methanol:

$$CH_4(g) + 1/2\ O_2(g) \rightarrow CH_3OH\ (l) \tag{7}$$

and the subsequent combustion reaction:

$$CH_3OH(l) + 3/2\ O_2(g) \rightarrow 2\ H_2O(l) + CO_2(g) \tag{8}$$

Combining reactions (7) and (8) by adding them together gives reaction (1). Thus, the ΔH^0 for combined reactions (7) and (8) must equal −890kJ. If the ΔH^0 for reaction (8) is known to be −681 kJ, then the ΔH^0 for reaction (7) can be calculated by Hess's law to equal −209 kJ. Born-Haber cycles represent an application of Hess's law to reactions associated with the formation of salts, such as potassium chloride. Born-Haber cycles can be used to determine the enthalpy change accompanying the breakup of the potassium chloride **lattice** into isolated potassium and chlorine ions. SEE ALSO Energy; Heat; Physical Chemistry; Temperature; Thermodynamics.

lattice: systematic geometrical arrangement of atomic-sized units that describe the structure of a solid

Michael Eastman

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Thermodynamics

Thermodynamics is the science of heat and temperature and, in particular, of the laws governing the conversion of thermal energy into mechanical, electrical, or other forms of energy. It is a central branch of science that has important applications in chemistry, physics, biology, and engineering.

Thermodynamics is a logical discipline that organizes the information obtained from experiments performed on systems and enables us to draw conclusions, without further experimentation, about other properties of the system. It allows us to predict whether a reaction will proceed and what the maximum yield might be.

quantum mechanics: theoretical model to describe atoms and molecules by wave functions

Thermodynamics is a macroscopic science that deals with such properties as pressure, temperature, and volume. Unlike **quantum mechanics**, thermodynamics is not based on a specific model, and therefore it is unaffected by our changing concepts of atoms and molecules. By the same token, equations derived from thermodynamics do not provide us with molecular interpretations of complex phenomena. Furthermore, thermodynamics tells us nothing about the *rate* of a process except its likelihood.

energy: the capacity to do work

entropy: measure of the amount of energy unavailable for work in a closed system

Applications of thermodynamics are based on three fundamental laws that deal with **energy** and **entropy** changes. The laws of thermodynamics cannot be derived; their validity is based on the fact that they predict changes that are consistent with experimental observations.

The first law of thermodynamics is based on the law of conservation of energy, which states that energy can neither be created nor destroyed; therefore, the total energy of the universe is constant. It is convenient for scientists to divide the universe into two parts: the system (the part of the universe that is under study—for example, a beaker of solution) and the surroundings (the rest of the universe). For any process, then, the change in the energy of the universe is zero. Chemists are usually interested only in what happens to the system. Consequently, for a given process the first law can be expressed as

$$\Delta U = q + w \tag{1}$$

where ΔU is the change in the internal energy of the system, q is the heat exchange between the system and the surroundings, and w is the work done by the system or performed on the system by the surroundings. The first law is useful in studying the energetics of physical processes, such as the melting or boiling of a substance, and chemical reactions—for example, **combustion**. The heat change occurring as part of a process is measured with a calorimeter. For a constant-volume process, the heat change is equated to the change in the internal energy ΔU of the system; for a constant-pressure process, which is more common, the heat change is equated to the change in the enthalpy ΔH of the system. Enthalpy H is a thermodynamic function closely related to the internal energy of the system, and is defined as

combustion: burning, the reaction with oxygen

$$H = U + PV \tag{2}$$

where P and V are the pressure and volume of the system, respectively.

The first law of thermodynamics deals only with energy changes and cannot predict the direction of a process. It asks, for example: Under a given set of conditions of pressure, temperature, and concentration, will a specific reaction occur? To answer the question we need a new thermodynamic function called entropy S. To define entropy, we need to use a quantum mechanical concept. The entropy of a system is related to the distribution of energy among the available molecular energy levels at a given temperature.

The greater the number of energy levels that have significant occupation, the greater the entropy.

The second law of thermodynamics states that the entropy of the universe increases in a spontaneous process and remains unchanged in an equilibrium process. The mathematical statement of the second law of thermodynamics is given by

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \geq 0 \qquad (3)$$

where the subscripts denote the universe, the system, and the surroundings, respectively. The greater than portion of the "greater than or equal to" sign corresponds to a spontaneous process, and the equal portion corresponds to a system at equilibrium. Because processes in the real world are spontaneous, the entropy of the universe therefore constantly increases with time.

As is not the case with energy and **enthalpy**, it is possible to determine the absolute value of entropy of a system. To measure the entropy of a substance at room temperature, it is necessary to add up entropy from the absolute zero up to 25°C (77°F). However, the absolute zero is unattainable in practice. This dilemma is resolved by applying the third law of thermodynamics, which states that the entropy of a pure, perfect crystalline substance is zero at the absolute zero of temperature. The increase in entropy from the lowest reachable temperature upward can then be determined from heat capacity measurements and enthalpy changes due to phase transitions.

enthalpy: the sum of the energy in a system added to the product of its volume and pressure

Because it is inconvenient to use the change in entropy of the universe to determine the direction of a reaction, an additional thermodynamic function, called the Gibbs free energy (G), is introduced to help chemists to focus only on the system. The Gibbs free energy of a system is defined as $G = H - TS$, where T is the absolute temperature. At constant temperature and pressure, ΔG is negative for a spontaneous process, is positive for an unfavorable process, and equals zero for a system at equilibrium. The change in Gibbs free energy can be related to the changes in enthalpy and entropy of a reaction, and also to the equilibrium constant of the reaction, according to the equation $\Delta G° = -RT \ln K$, where $\Delta G°$ is the change in Gibbs free energy under standard-state conditions (1 bar), R is the gas constant, and K is the equilibrium constant.

Many chemical reactions can be classified as either **kinetically** controlled or thermodynamically controlled. In a kinetically controlled process the products are thermodynamically more stable than the reactants, hence the reaction is favorable. However, the rate of reaction is often very slow due to a high activation energy barrier. The conversion of the less stable **allotropic** form of carbon, diamond, to the more stable graphite is an example: The process can take millions of years to complete. In a thermodynamically controlled reaction the reactants may have a number of kinetically accessible routes to follow to form different products, but what is eventually formed is governed by relative thermodynamic stability. In protein folding, for example, a denatured protein may have many possibilities of **intermediate** conformation; however, the conformation it finally assumes, which corresponds to the physiologically functioning protein, is the most stable state thermodynamically. SEE ALSO CHEMISTRY AND ENERGY; ENERGY; HEAT; KINETICS; PHYSICAL CHEMISTRY; TEMPERATURE.

Raymond Chang

allotrope: a different physical form of an element in the same state of matter

intermediate: molecule, often short-lived, that occurs while a chemical reaction progresses but is not present when the reaction is complete

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Thiamin

B **vitamins** are complex, water-soluble organic chemicals, often containing heterocyclic ring systems (containing one or more atoms other than carbon atoms); they cannot be synthesized by humans and are, therefore, required nutrients. Each of these vitamins is converted by the body into a coenzyme. Coenzymes are cofactors essential to the **catalytic** activity of enzymes.

Thiamin is also known as vitamin B_1. In the body it is converted to thiamin pyrophosphate (TPP), an essential coenzyme serving enzymes involved in the breakdown of nutrient molecules for energy. Thiamin deficiency in its severest form causes beriberi.

Thiamin is converted to TPP via the transfer of a pyrophosphate group to thiamin from **adenosine triphosphate (ATP)**.

In animals TPP-dependent decarboxylation reactions are essential to the production of energy needed for cell **metabolism**. In these reactions α-ketoacids are converted to acyl CoA molecules and carbon dioxide. The reactions (e.g., the conversion of **pyruvate** to acetyl CoA) are an important part of the breakdown of carbohydrates, and of the conversion of several classes of molecules (carbohydrates, fats, and proteins) to energy, carbon dioxide, and water in the citric acid cycle. In other organisms, in addition to its participation in the above reactions, TPP is a required coenzyme in alcohol fermentation, in the carbon fixation reactions of **photosynthesis**, and in the **biosynthesis** of the amino acids leucine and valine.

Major food sources of thiamin are fortified breads, cereals, pasta, whole grains (especially wheat germ), lean meats (especially pork and liver), fish, peanuts, dried beans, peas, and soybeans. Fruits and vegetables are not high in thiamin but are a significant source of thiamin if they are consumed in large enough amounts. The daily value (DV) of thiamin for adults is 1.5 milligrams (5.3×10^{-5} ounces). Thiamin deficiency virtually does not occur in North America. Because thiamin is water-soluble and easily removed from the body there is no known toxicity.

Beriberi has been found in people who eat polished rice (with husks discarded) and few other foods, as thiamin is in the husks of grains. Beriberi is associated with damage to the nervous system, brain, heart, and blood vessels. It is fatal if not treated with adequate amounts of thiamin. Lesser deficiencies of thiamin lead to weakness and fatigue. These lesser deficiencies respond rapidly to thiamin unless they are complicated by another condition, for example, alcoholism. SEE ALSO COENZYME.

Vivienne A. Whitworth

vitamins: organic molecules needed in small amounts for the normal function of the body; often used as part of an enzyme-catalyzed reaction

catalysis: the action or effect of a substance in increasing the rate of a reaction without itself being converted

adenosine triphosphate (ATP): molecule formed by the condensation of adenine, ribose, and triphosphoric acid, HOP(O)OH–O–(O)OH–OP(O)OH–OH; it is a key compound in the mediation of energy in both plants and animals

metabolism: the complete range of biochemical processes that take place within living organisms; comprises processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those that break down complex food molecules, thus liberating energy (catabolism)

pyruvate: anion of pyruvic acid produced by the reaction of oxygen with lactic acid after strenuous exercise

photosynthesis: process by which plants convert carbon dioxide and water to glucose

biosynthesis: formation of a chemical substance by a living organism

CASIMIR FUNK (1884–1967)

Beriberi, a fatal disease, was prevalent at the turn of the nineteenth century among groups who ate large quantities of polished rice. Casimir Funk correctly theorized that the discarded polishings contained some nutrient for disease prevention. Funk isolated this item and called it a "vitamine," combining *vite,* meaning life, and amine.

—Valerie Borek

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Thomson, Joseph John

ENGLISH PHYSICIST
1856–1940

Joseph John Thomson, always known as "J. J.," was born in Manchester, England, on December 18, 1856. His fame derives primarily from his discovery of the electron in 1897. He studied physics and mathematics, first in Manchester, and in 1876 went to Trinity College, Cambridge University, and never left. He graduated in 1880 and in 1884 succeeded Lord Rayleigh as professor of physics and director of the Cavendish Laboratory. (When he retired from Cavendish in 1919 he passed the baton to Ernest Rutherford). Thomson made Cambridge a world center for atomic physics. He won the Nobel Prize for physics in 1906 for his work on the electron, and seven of his research associates went on to win Nobel Prizes. The electron could almost be said to have been a family heirloom, as his son, George Paget Thomson, won the Nobel Prize for physics (in 1937) for showing the wave nature of the electron.

His early work in electromagnetism led him to say, in 1893: "There is no other branch of physics which affords us so promising an opportunity of penetrating the secret of electricity." He turned his attention to cathode rays, and his subsequent investigations of these rays led him to the idea that they consisted of bodies smaller than atoms. Thomson's main contribution to science was the clear identification of the electron and its characterization as an elementary, subatomic particle in 1897. He showed that cathode rays were deflected by both magnetic and electric fields, and he was able to measure a cathode ray's charge/mass (*e/m*) ratio. Figure 1 is a schematic of diagram of his apparatus, showing how a beam of electrons can be subjected to opposing electric and magnetic fields, which can be adjusted until their effects balance. This enabled him to estimate the mass of the electron as 1/1,837 of a hydrogen atom. The electron was the first subatomic particle to be discovered, and he made the inspired guess that it was a universal constituent of matter. He said: " . . . [W]e have in the cathode rays matter in a new state, a state in which the subdivision of matter is carried very much

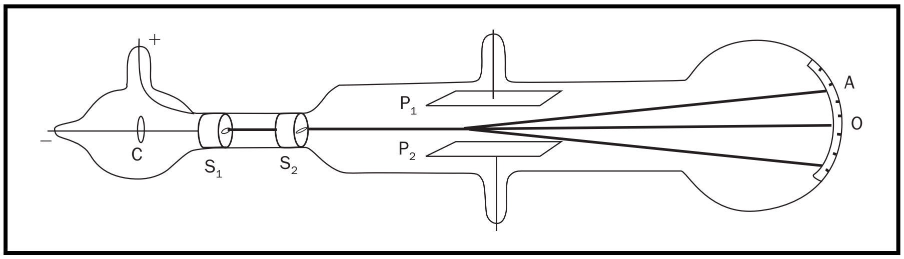
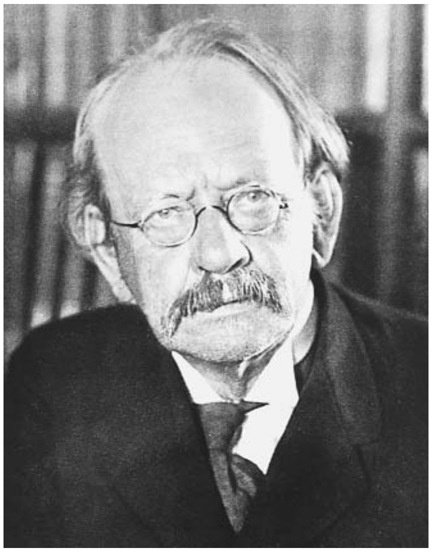


Figure 1. Basic features of Thomson's apparatus.

further than in the ordinary gaseous state: a state in which all matter . . . is of one and the same kind; this matter being the substance from which all the chemical elements are built up." He announced his discovery in the course of a public lecture at the Royal Institution in London, on April 30, 1897, in which he said: "Could anything at first sight seem more impractical than a body which is so small that its mass is an insignificant fraction of the mass of an atom of hydrogen?" Thomson referred to electrons as "corpuscles" (even in his 1906 Nobel lecture).



English physicist Sir Joseph John Thomson, recipient of the 1906 Nobel Prize in physics, "in recognition of the great merits of his theoretical and experimental investigations on the conduction of electricity by gases."

nuclear: having to do with the nucleus of an atom

isotope: form of an atom that differs by the number of neutrons in the nucleus

Thomson devised the famous plum pudding model of the atom, in which electrons were compared to negative plums embedded in a positively charged pudding. The idea was wrong, and his successor at Cambridge, Ernest Rutherford, was soon to develop the **nuclear** model of the atom.

Thomson investigated positive rays, which consist of ionized atoms, beginning in 1906. He was able to use a combination of electric and magnetic fields to separate different charged atoms of elements on the basis of their charge/mass ratios. He was the first to show that neon contained two atoms of slightly different masses, in a paper published in 1913. As part of the conclusion of the paper he wrote: "There can, therefore, I think, be little doubt that what has been called neon is not a simple gas but a mixture of two gases, one of which has an atomic weight about 20 and the other about 22. The parabola due to the heavier gas is always much fainter than that due to the lighter, so that probably the heavier gas forms only a small percentage of the mixture." The two forms of neon were called **isotopes** by Frederick Soddy. One of Thomson's students, Frederick Aston, developed Thomson's idea of multiple species of an element, and in 1919 Aston produced the first mass spectrograph (an instrument that determined isotopic ratios), ancestor of today's mass spectrometer.

Thomson was a great advocate of pure research, in contrast to applied research, declaring: "[R]esearch in applied science leads to reforms, research in pure science leads to revolutions, and revolutions, whether political or industrial, are exceedingly profitable things if you are on the winning side." Thomson was knighted in 1908 and received many awards and honors. He died during the early part of World War II, on August 30, 1940, and is buried in Westminster Abbey near Sir Isaac Newton, in recognition of his great contributions to science. SEE ALSO MAGNETISM; SPECTROSCOPY.

Peter E. Childs

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Thorium

90
Th
THORIUM
232.0381

MELTING POINT: 1,750°C
BOILING POINT: 4,820°C
DENSITY: 11.724 g/cm^{-3}
MOST COMMON IONS: Th^{4+}

Thorium is a radioactive chemical element that belongs to the actinide series. Its ground state electronic configuration is $[Rn]5f^0 6d^2 7s^2$. Thorium was discovered by Jöns Jacob Berzelius in 1828. Its name is derived from "Thor," the god of war in the Scandinavian mythology. Thorium chemistry is dominated by the tetravalent thorium ion (Th^{4+}). Its ionic radius is very similar to that of the trivalent cerium ion (Ce^{3+}). For that reason it is no surprise that thorium occurs in nature together with the **rare earth elements**. Thorium is recovered commercially from the rare earth ore monazite (mainly $CePO_4$), which contains up to 9 percent ThO_2. Other thorium-containing minerals are thorite and thorianite. The most abundant **isotope** is ^{232}Th, with a half-life of 1.4×10^{10} years. None of the twenty-five known isotopes of thorium (with atomic masses ranging between 212 and 236) is stable.

rare earth elements: older name for the lanthanide series of elements, from lanthanum to lutetium

isotope: form of an atom that differs by the number of neutrons in the nucleus

Pure thorium is a silvery-white **metal** (melting point 1,750°C) that tarnishes upon exposure to air. Its density is 11.724 g/cm^{-3} at 25°C (77°F), similar to that of lead. The best-known application of thorium is its use in incandescent mantles for gas lamps. These mantles consist of a metal oxide skeleton (99% ThO_2 and 1% CeO_2). Thorium(IV) oxide is used by chemists

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Thorium is used in incandescent mantles for gas lamps.

catalyst: substance that aids in a reaction while retaining its own chemical identity

nuclear: having to do with the nucleus of an atom

noble gas: element characterized by inert nature; located in the rightmost column in the Periodic Table

as a **catalyst** in different organic reactions, and in the conversion of ammonia to nitric acid. Thorium is about three times as abundant as uranium, and therefore it may become an important **nuclear** fuel in the future. Because one of the disintegration products of thorium is the radioactive **noble gas** radon (^{220}Rn), good ventilation of areas and places where thorium is stored or handled is necessary. SEE ALSO Actinium; Berkelium; Einsteinium; Fermium; Lawrencium; Mendelevium; Neptunium; Nobelium; Plutonium; Protactinium; Rutherfordium; Uranium.

Koen Binnemans

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69
Tm
THULIUM
168.93421

Thulium

MELTING POINT: 1,545°C
BOILING POINT: 1,950°C
DENSITY: 9.32 g/cm^3
MOST COMMON ION: Tm^{2+}, Tm^{3+}

Thulium is a silver-grey metal with a bright luster. Swedish chemist Per Theodor Cleve discovered the metal in 1879 while processing the ore erbia. One of the materials Cleve extracted from the ore was a green substance he named "thulia"—a thulium oxide. The element's name is derived from an ancient name for northern Europe, Thule.

Thulium is the least abundant of the naturally occurring rare earth elements, although it is believed to have a natural abundance similar to gold,

An army medic takes an x ray of a simulated injury during a field test of an atom-powered portable x-ray unit. Portable x-ray units are powered by thulium, obviating the need for electricity.

silver, and cadmium. Its abundance in the earth's crust is approximately 0.52 milligrams per kilogram. Thulium is commercially extracted from monazite (which is composed of up to 0.007 percent thulium) using ion exchange and solvent extraction techniques. It is also found in the minerals gadolinite, euxenite, and xenotime.

The most common isotope of thulium is ^{169}Tm, which has a natural abundance of 100 percent and is the only stable isotope. Other isotopes range from ^{145}Tm to ^{179}Tm and have half-lives ranging from 0.36 milliseconds (^{147}Tm) to 1.92 years (^{171}Tm). Examples of thulium compounds include thulium iodide (TmI_3), thulium fluoride (TmF_3), and thulium oxide (Tm_2O_3).

Thulium metal is soft, ductile, and malleable and can be cut with a knife. It tarnishes when in contact with air and reacts with water. Thulium has very few commercial uses. Radioactive thulium can be utilized as a power source for portable x-ray machines and is produced by irradiating the element in a nuclear reactor. Thulium may also be utilized to make magnetic ceramic materials found in microwave equipment. SEE ALSO Cleve, Per Theodore.

Stephanie Dionne Sherk

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Thymine *See Nucleotide.*

Tin

MELTING POINT: **231.9°C**
BOILING POINT: **2,270.0°C**
DENSITY: **7.31 g/cm^3**
MOST COMMON IONS: **Sn^{2+}, Sn^{4+}**

50
Sn
TIN
118.71

Tin makes up only about 0.001 percent of the earth's crust, but it was well known in the ancient world. Named after the Etruscan god Tinia, tin has the symbol Sn, which comes from the Latin word for tin, *stannum*, which is related to the word *stagnum* (dripping), because tin melts easily. Tin is primarily obtained from the mineral cassiterite (SnO_2) and is extracted by roasting cassiterite in a furnace with carbon.

Tin is a soft, pliable **metal**, but it is not used as such, because below 13°C, it slowly changes to a different allotype and forms a powder. Steel is plated with tin to make cans for food, and tin is also used in solders. Some tin compounds have been employed as antifouling agents in paint for ships and boats to prevent barnacles. However, even at low concentrations, these compounds are deadly to marine life, especially to oysters. Tin is thought to be an essential element for some living things, and this may also be true for humans.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

A major use of tin has been as a constituent of **alloys**—such as bronze (tin and copper); pewter (tin and lead); superconducting wire (tin and nio-

alloy: mixture of two or more elements, at least one of which is a metal

bium); Babbitt metal (tin, copper, and antimony); Bell metal (tin and copper); and fusible metal (tin, bismuth, and lead).

Stannous fluoride (SnF_2), a compound of tin and fluorine, is used in some toothpastes to decrease the incidence of caries.

George H. Wahl Jr.

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22
Ti
TITANIUM
47.88

Titanium

MELTING POINT: 1,668°C
BOILING POINT: 3,287°C
DENSITY: 4.54 g/cm^3
MOST COMMON IONS: Ti^{2+}, Ti^{3+}, TiO^{2+}

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Titanium is a strong, lightweight, silver-white **metal**. It was discovered in 1791 by Reverend William Gregor, a British cleric who established its presence in the mineral menachanite. The German chemist Martin Heinrich Klaproth named the element after the Titans, the sons of the earth goddess in Greek mythology. Pure titanium was not isolated until 1910, when American metallurgist Matthew A. Hunter heated titanium (IV) chloride ($TiCl_4$) with sodium at temperatures between 700°C and 800°C.

rutile: common name of TiO_2; also a common structural type for compounds with the general composition AB_2

As the ninth most common element in the earth's crust, titanium occurs at an abundance of 6,600 parts per million (ppm) or 5.63 grams per kilogram. Its chief sources are the minerals ilmenite ($FeTiO_3$), **rutile** (TiO_2), and sphene ($CaTiSiO_5$); ilmenite is the source of approximately 90 percent of titanium produced. Titanium is largely produced in the United States, Canada, Russia, Japan, Kazakhstan, Germany, France, and Spain.

isotope: form of an atom that differs by the number of neutrons in the nucleus

The most common **isotope** of titanium is ^{48}Ti, which has a natural abundance of 73.72 percent. Four other stable isotopes exist: ^{46}Ti (8.25%), ^{47}Ti (7.44%), ^{49}Ti (5.41%), and ^{50}Ti (5.18%). Most titanium is used in its dioxide (TiO_2) or metallic form.

alloy: mixture of two or more elements, at least one of which is a metal

Titanium's physical properties (high melting temperature, resistance to corrosion, strength, light weight) make it an ideal additive to **alloys** used by the aerospace industry in rockets and jet aircraft, for ship components that are exposed to seawater, and for biomedical implants such as artificial joints or pacemakers. Titanium dioxide is utilized as a white pigment in paint, paper, plastics, and cosmetics. It is also used in some sunscreens because of its ability to absorb ultraviolet (UV) light.

Stephanie Dionne Sherk

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Todd, Alexander

BRITISH CHEMIST
1907–1997

Alexander R. Todd was born in Glasgow on October 2, 1907. His father was a businessman. Young Todd was educated at the Allan Glen School and Glasgow University. There he earned a B.S. and in 1928 left for the University of Frankfurt-am-Main, where he earned a Ph.D. in 1931 for his work on bile acids with W. Borsche. He returned to England that same year to study with Sir Robert Robinson; it was during this period that he completed very successful work on the colored materials of fruits, the anthocyanins. Todd journeyed home to Scotland in 1934 to join the staff of Edinburgh University. In 1938 he was appointed Sir Samuel Hall Professor of Chemistry and director of the Chemical Laboratories at the University of Manchester, posts he held until 1944. He then accepted a position as professor of organic chemistry at Cambridge University and became a fellow of Christ's College. He was named chancellor of the University of Strathclyde in 1975 and was a visiting professor at Hatfield Polytechnic until 1986.

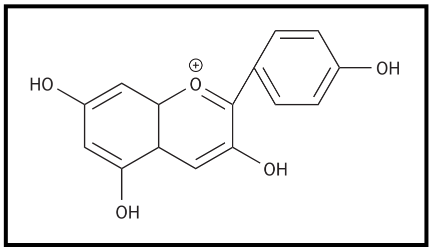

Figure 1. Red form of cranberry anthocyanin.

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

RNA: ribonucleic acid, a natural polymer used to translate genetic information in the nucleus into a template for the construction of proteins

adenine: one of the purine bases found in nucleic acids, $C_5H_5N_5$

synthesis: combination of starting materials to form a desired product

vitamins: organic molecules needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

alkaloid: alkaline nitrogen-based compound extracted from plants

The anthocyanin dyes that Todd researched while working with Robinson are important substances because they are part of the mechanism for protecting the plants' **DNA** from the deleterious effects of UV radiation during pollination and act as insect attractants during the pollination season. The structure for the red substance of cranberries is given in Figure 1.

While at Manchester, Todd began his work on nucleotides. These compounds are the structural units of the nucleic acids DNA and **RNA**. In 1949, while at Cambridge, he synthesized adenosine triphosphate (ATP; Figure 2) and later that same year flavin **adenine** dinucleotide (FAD). These nucleotides are the molecules that carry and transfer energy in virtually all living organisms. These discoveries are not only important in the elucidation of the energy transfer mechanisms, but they also set a precedent for the **synthesis** of nucleotides and the precursors of DNA and RNA. These accomplishments required the utmost skill in the art of organic synthesis because nucleotides are very difficult substances to prepare and characterize.

Todd also did significant work on the structure and synthesis of **vitamin** B_{12}, vitamin E, and a number of **alkaloids**. The most noteworthy of these contributions was the elucidation of the structure of tetrahydrocannabinol (THC), the active component of marijuana.

Todd was named president of the Royal Academy in 1975. He was also a member of the National Academy of Sciences (USA), the American Academy of Arts and Sciences, and several prestigious European societies. Todd served as the chairman of the British government's advisory committee on scientific policy from 1952 until 1964. He was awarded the Nobel Prize in chemistry in 1957 for his work on nucleotides and nucleotide coenzyme studies. He was knighted in 1954 and died in 1997. SEE ALSO Nucleotide.

Lawrence H. Brannigan

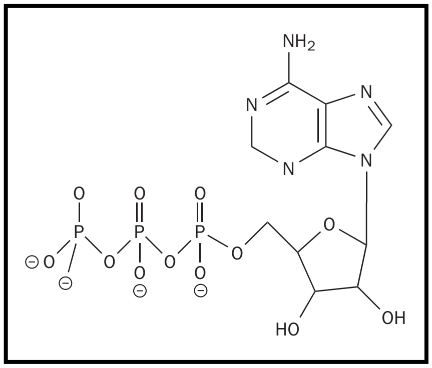

Figure 2. Structure of ATP.

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Toxicity

Toxicity is the capacity of a substance to poison. Swiss physician Paracelsus (1493–1541) defined poison as follows: "What is there that is not a poison? All things are poison and nothing without poison. Solely the dose determines that thing is not a poison." The toxicity of a substance is therefore not an inherent property but the detrimental manifestation of its biochemical effect in a living system. The severity of a substance's toxicity is the function of its interaction with the physiology of a particular organism. For example, chocolate is moderately toxic to canines but minimally to other animals. Ingested in very large quantities, even **vitamins** can exhibit toxicity in humans.

vitamins: organic molecules needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

The comparison of two substances in terms of their relative toxicity is difficult because every substance has its own mode of action and target organ(s). Hence, the short-term poisoning potential (acute toxicity) of a substance is measured by the amount needed to kill half the population of a test species, called the LD50 (lethal dose for 50 percent). The measurement is expressed as milligrams per kilogram of body weight (mg/kg). For example, administering to mice a substance with an LD50 for mice of 10 mg/kg would kill 50 percent of a population of mice. In environmental studies, the term used to measure toxicity in air or water is LC50 (lethal concentration for 50 percent), defined similarly to LD50 and expressed as parts per million, parts per billion, or milligrams per liter (mg/l).

metabolism: the complete range of biochemical processes that take place within living organisms; comprises processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those that break down complex food molecules, thus liberating energy (catabolism)

The route of entry of a toxicant affects its LD50 value. Since the lethality of a substance is related to its ability to block vital cellular functions by interacting with specific biomolecules, the site of exposure, its dissemination speed, and the physiological importance of the target tissue all factor into its toxicity. For example, the common household pesticide dichlorovos has an LD50 for rats of 56 mg/kg if taken orally (through the mouth) and an LD50 of 15 mg/kg if injected intraperitoneally (into the abdominal cavity).

The toxicity of a chemical also varies from one animal to the next. The LD50 for the common insecticide Diazinon is 300 to 400 mg/kg in rats, while in birds it is 2.75 mg/kg. Theobromine, a chemical found in chocolate, is toxic to dogs but not to rodents. Although largely extrapolated from animal tests, a rating system for acute chemical toxicity for humans has been devised and is presented in Table 1.

Chronic or cumulative toxicity is manifested as a result of continuous exposure to a chemical. A common example is the "genotoxicity" of benzene, a chemical present in car exhausts and cigarette smoke. The **metabolism** of benzene in the liver results in the formation of highly reactive free-radicals. These in turn may cause damage to the genetic material of a cell, in some cases leading to cancer.

LD50

LD50 is the amount of a hazardous substance that results in the death of 50 percent of the individuals exposed. LD50 is commonly measured by exposing rats or mice to increasing amounts of the toxic substance until a dosage is reached that kills half the exposed animals within a certain time period (usually fourteen days).

—Dan M. Sullivan

TOXICITY RATING FOR HUMANS (70 KG BODY WEIGHT)

Rating/Class	Dose
6. Super toxic	<5 mg/kg
5. Extremely toxic	5–50 mg/kg
4. Very toxic	50–500 mg/kg
3. Moderately toxic	0.5–5 g/kg
2. Slightly toxic	5–15 g/kg
1. Practically nontoxic	>15 g/kg

SOURCE: Gosselin, et al. (1984). *Clinical Toxicology of Commercial Products.* Baltimore: Williams & Wilkens.

Table 1. Toxicity rating for humans (70 kg [154 lb.] body weight).

Although traditional investigations into the toxicity of chemicals in the natural environment have focused on animals, the toxicity of agrichemical and environmental pollutants to plants (phytotoxicity) has gained interest. Despite being well documented in literature, phytotoxicity is measured in various ways by agronomists and plant scientists; a standard quantification unit is therefore difficult to devise. SEE ALSO VENOM.

Hiranya S. Roychowdhury

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Transactinides

The term "transactinides" is used to refer to all elements beyond the actinides—that is, those elements with atomic numbers larger than 103. Lawrencium, with atomic number 103 and a full inner 5f electron shell, ends the actinide series. According to atomic relativistic calculations, the filling of the 6d electron shell takes place in the first nine of the transactinide elements (those with atomic numbers 104 through 112). They are placed as a 6d transition series under the 5d transition series in the Periodic Table of the chemical elements.✷ As of 2003 the discoveries of elements 104 through 111 had been confirmed, and element 112 was reported but not yet confirmed. The date of discovery and the names and symbols approved for each of these elements by the International Union of Pure and Applied Chemistry (IUPAC) in August 1997 and in August 2003 are given in Table 1, as is the date of discovery of the element that has been reported but not yet named. The naming of element 112 awaits a final IUPAC decision that there has been sufficient confirmation of its discovery to ask the discoverers to propose a name and symbol for consideration.

✷See Periodic Table in the For Your Reference section at the beginning of this volume.

All the known transactinides were first positively identified using physical rather than chemical techniques because of their very short half-lives

TRANSACTINIDE NAMES APPROVED BY IUPAC ON AUGUST 30, 1997, IN GENEVA, SWITZERLAND AND ON AUGUST 16, 2003 IN OTTAWA CANADA

Element	Name	Symbol	Year of Discovery#
104	Rutherfordium	Rf	1969
105	Dubnium (Hahnium)*	Db (Ha)*	1970
106	Seaborgium	Sg	1974
107	Bohrium	Bh	1981
108	Hassium	Hs	1984
109	Meitnerium	Mt	1982
110	Darmstadtium**	Ds**	1995
111***	__________	___	1995
(112)	__________	___	1996

Year of publication of discovery experiment.
* Many publications of chemical studies prior to 1997 use hahnium (Ha) for element 105.
** Name and symbol approved by IUPAC, August 16, 2003, Ottawa, Canada.
*** IUPAC has deemed evidence for discovery of this element sufficient and has asked the discovers to propose a name.

Table 1.

nuclear: having to do with the nucleus of an atom

isotope: form of an atom that differs by the number of neutrons in the nucleus

and small production rates. Production rates decrease from a few atoms per minute for element 104 to only a few atoms per week for element 111. Methods other than the classical chemical separation techniques for determining the atomic number (proton number) of a new element had to be developed. The production and study of both the chemical and **nuclear**-decay properties of the transactinides require special facilities and capabilities. These include preparation and handling of radioactive targets, access to an accelerator that can furnish high-intensity beams of the required light-to-heavy ions for irradiating the targets, and a method for rapidly transporting the desired short-lived **isotopes** to a suitable chemical or physical separation system. In the 1960s such facilities were available in Russia at the cyclotron at the Joint Institutes for Nuclear Research in Dubna and in the United States at the Heavy Ion Linear Accelerator (HILAC) at the Lawrence Berkeley Laboratory in California.

fission: process of splitting an atom into smaller pieces

From the mid-1960s to the early 1970s, the Russian and U.S. groups reported conflicting claims concerning the discoveries of elements 104 and 105, primarily due to the difficulty in positively determining the atomic number of the short-lived isotopes involved. Different techniques were used by the groups to attempt to provide positive proof of the discoveries. The U.S. group used an alpha-alpha correlation technique to identify the atomic number of alpha-decaying isotopes (alpha-decay is the emission of a $^{4}He^{2+}$ nucleus) of elements 104 and 105 by observing the time correlations between alpha-particles emitted by the parent element and those of the already known element 102 (nobelium) or 103 (lawrencium) daughter activities. The Russian group relied primarily on the detection of spontaneous **fission** (SF) decay. Spontaneous fission is one of the modes of decay found in elements of higher atomic number than actinium; in this process the nucleus "spontaneously" splits into two large "fission fragments." Half-lives for SF decay range from microseconds to billions of years (e.g., the SF-decay branch in plutonium-244 has a half-life of nearly 100 billion years). Detection of SF fragments is a very sensitive method, but the atomic number and mass of the fissioning nucleus are effectively destroyed in the fission process, so it is extremely difficult to identify the fissioning element with certainty. In the case of element 105, the Dubna group also performed an alpha-alpha correlation experiment, but these experiments were rather inconclusive and did not agree with later confirmatory experiments. They also measured SF decay that they attributed to element 105 based on its half-life, proposed production reaction based on data from other experiments, and angular distribution of the products of the nuclear reaction. Chemical separations, even if rapid enough, are not definitive without some independent positive determination of atomic number, since the unknown chemistry of a new element cannot be used to prove its atomic number. The U. S. and Russian groups proposed different names for these elements, and the controversy was not resolved until the compromise set of names shown in Table 1 was finally approved by IUPAC in 1997. Element 106 was produced and identified at the SuperHILAC by the Berkeley group in 1974 and confirmed by an independent group in 1994. The name seaborgium (Sg) in honor of Professor Glenn T. Seaborg was then proposed by the discovery group. After initially being rejected because Seaborg was still alive, the name was approved.

In the 1970s the Separator for Heavy Ion Reactions (SHIP) was constructed by a group at the Universal Linear Accelerator (UNILAC) at the Gesellschaft für Schwerionenforschung (GSI) in Darmstadt, Germany. The researchers hoped that SHIP might take them to the long-sought island of SuperHeavy Elements (SHEs) in the predicted region of extra stability around the "magic" numbers of 112 to 114 protons and 184 neutrons. SHIP was designed to separate the "slow" **fusion** products created in the nuclear reactions from the "fast" heavy-ion beams that produced them by using a combination of electric and magnetic fields. The reaction products were then implanted in a detector system some distance away from the target. The time, energy, and position of the implant and all subsequent decays and other information were recorded by a computer system. The original event was then correlated unambiguously with its decay to already known properties of many generations of known daughter isotopes, and its atomic number and mass were unequivocally determined.

fusion: process of combining atomic nuclei

Discovery of elements 107 through 109 was reported by the SHIP group between 1981 and 1984. After some improvements were made in SHIP, elements 110 through 112 were produced and identified in 1995 and 1996. However, the most neutron-rich of the isotopes first reported for elements 110 through 112 contain only 165 neutrons or fewer, far from the predicted SHE region. Their half-lives are milliseconds or shorter, and most scientists do not consider them to be SHEs. Even though the attempt to produce element 113 was unsuccessful, these results gave researchers new hope that the SHEs might yet be reached, sparking a renaissance of interest in their production. Between 2000 and 2002, the production of element 114 with 174 neutrons and a half-life of about 3 seconds and element 116 with 176 neutrons and a half-life of 50 milliseconds was reported by a Dubna/LLNL collaboration using the on-line separator at the Dubna cyclotron. The group used beams of the heaviest stable calcium isotope (mass 48) and either ^{244}Pu or ^{248}Cm targets, to make element 114 or 116, respectively. They have proposed that these should be called SHEs, although they are still far from the 184-neutron shell. The element 112 and 110 daughters resulting from the element 116 and 114 alpha-decay chains were reported to have half-lives on the order of 10 seconds. It is extremely im-

The Stanford Linear Accelerator Center has three giant particle spectrometers, which are used to detect subatomic particles of different energies. This is the largest linear accelerator in the world.

portant to confirm these results, as investigations of their chemical properties could then be considered.

Chemical Studies

homologues: members of a group of organic compounds that have the same functional group and a regular structural pattern so that a member of the group differs from the next member by a fixed number of atoms

chromatography: the separation of the components of a mixture in one phase (the mobile phase) by passing it through another phase (the stationary phase) making use of the extent which the components are absorbed by the stationary phase

A primary goal of the chemical studies of the transactinides is to determine their placement in the Periodic Table by comparing their properties with those of their lighter **homologues** and with theoretical predictions. These studies seek to probe the uppermost region of the Periodic Table, where the influence of relativistic effects on chemical properties should be strongest and where deviations from simple extrapolation of known trends within chemical groups in the Periodic Table have been observed. There are many challenges for chemical studies in addition to those already outlined for physical separation techniques: An isotope with a half-life of at least a second must be known. Its decay characteristics must be well established and must furnish a positive "signature" so that it can be shown that the desired element is actually being studied. Again, the method of measuring time-correlated "mother-daughter" alpha-decay chains is most definitive. Because the production rates are so low, the results of many separate identical experiments must often be combined. Very efficient separation methods must be devised that reach equilibrium rapidly and can be conducted in a length of time that is short compared to the half-life. These separations should give the same results on an "atom-at-a-time" basis as they would for the usual macro-scale laboratory experiments conducted with milligram quantities. Both aqueous- and gas-phase **chromatographic** methods have been shown to meet these criteria. A rapid and efficient method for transporting these atoms from the production site to a suitable chemical separation system is needed. Computer-controlled automated systems have been developed for these studies.

Typically, the isotope with the longest half-life and largest production rate is chosen. This is not necessarily the first isotope discovered. The half-lives of the isotopes used in the first definitive chemical studies of the transactinides were: 75-second ^{261}Rf; 34-second ^{262}Db; 21-second ^{266}Sg; 17-second ^{267}Bh; and approximately 14-second ^{269}Hs. Their well-known alpha-decay properties were used for positive identification. As of 2003, 0.04-second ^{268}Mt was the longest-known isotope of Mt, and studies of its chemical properties awaited discovery of a longer-lived isotope.

From 1969 to 1976 researchers at Dubna reported studies of the volatilities of the halides of elements 104 and 105, suggesting that the halides of these elements behaved similarly to those of their lighter group-4 and group-5 homologues. Because only spontaneous fission was detected, the identity of the species being measured could not be positively attributed to element 104 or 105.

The first study of the solution chemistry of Rf was performed at Berkeley in 1970 and showed that Rf had a stable tetravalent state with properties similar to the group-4 elements Zr and Hf and different from Lr and the other trivalent actinides. This established that Rf should be placed in the Periodic Table as the heaviest member of group 4 and the first member of a new 6d transition series. It also confirmed the 1945 prediction of Seaborg that the actinide series should end with element 103. The first studies of the solution chemistry of element 105, conducted at the 88-Inch Cyclotron at Berkeley, were reported in 1988 and showed that the element behaved similarly to the group-5 elements Nb and Ta in its sorption properties, but differently from the group-4 elements. However, in extractions into certain organic solvents, Db(Ha) and Ta extracted but Nb did not, creating a renaissance of interest in more detailed studies of the behavior of element 105.

Subsequently, extensive studies of both the aqueous- and gas-phase chemistry of elements 104 and 105 were conducted using manual and sophisticated computer-controlled automated systems. Although in general these studies confirmed that the elements' chemical properties are similar to those of the group-4 and group-5 elements, respectively, unexpected deviations from simple extrapolation of known trends within the groups were found. Theoretical investigations based on molecular relativistic calculations can explain these results and provide guidance for experimentalists in designing the sophisticated and resource-intensive experiments required for future experiments. With this guidance and further improvement in experimental techniques, chemical studies were extended to Sg, Bh, and Hs. Aqueous- and gas-phase studies of Sg were conducted between 1995 and 1998 by an international team of researchers working at the UNILAC at GSI. Gas-phase studies of an oxychloride of Bh were reported in 2000, and separation of Hs as a volatile oxide similar to that of osmium tetroxide was reported in 2002. It appears that all of these elements should be placed in the Periodic Table as members of the 6d transition series under groups 4 through 8 of the Periodic Table and that the trends in properties within the groups can be described by relativistic calculations. No investigations of the solution chemistry of Bh and Hs has been conducted as of mid-2003 because the aqueous chemistry and preparation of samples suitable for measuring alpha-particles or fission fragments is too slow. Very fast liquid-liquid extraction systems followed by direct incorporation of the activity in a flowing liquid scintillation detection system have been used for elements 104 and 105 and may prove applicable.

The improvement in experimental techniques for atom-at-a-time studies of elements with both short half-lives and small production rates has permitted chemical studies of both aqueous- and gas-phase chemistry of the transactinides through Sg, and gas-phase studies of Bh and Hs have been conducted. Extending the solution-chemistry studies will depend on the development of faster systems. Studies of elements beyond Hs await discovery of longer-lived isotopes with definitive decay properties and production rates that are larger than a few atoms per week. If isotopes with half-lives of years or more are discovered, then techniques for "stockpiling" them might be envisioned. The synergistic interactions between theory and experiment are leading to a better understanding of the chemistry of the transactinides and the role and magnitude of relativistic effects. SEE ALSO ACTINIDES; ACTINIUM; AMERICIUM; BERKELIUM; CALIFORNIUM; EINSTEINIUM; FERMIUM; LAWRENCIUM; MENDELEVIUM; NEPTUNIUM; NOBELIUM; NUCLEAR CHEMISTRY; NUCLEAR FISSION; PLUTONIUM; PROTACTINIUM; RADIOACTIVITY; RUTHERFORDIUM; SEABORG, GLENN THEODORE; THORIUM; TRANSMUTATION; URANIUM.

Darleane C. Hoffman

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Transmembrane Protein

lipid: a nonpolar organic molecule; fatlike; one of a large variety of nonpolar hydrophobic (water-hating) molecules that are insoluble in water

The membrane of a cell is not only a border; it is also an interface. The most critical molecules involved in interface functioning are proteins that are embedded within the membrane. Many of these proteins span the distance from the outside to the inside of the cell (in part because they are much larger than the **lipids** that make up the membrane) and are referred to as transmembrane proteins. Transmembrane proteins are a class of integral proteins (i.e., proteins that penetrate into or through the membrane bilayer).

The lipid molecules of the membrane bilayer are predominantly **hydrophobic** (i.e., they do not interact strongly with polar water molecules). The portion of the transmembrane protein that is embedded in the bilayer must therefore have residues that are not polar. Commonly, these residues form a coil, or **helix**, that is hydrophobic and therefore stable within the bilayer.

hydrophobic: relating to a region of a molecule that will, in solution with water, tend to be in contact with few water molecules; if an entire molecule is hydrophobic, it will not dissolve in water

helix: form of a spiral or coil such as a corkscrew

Transmembrane proteins have three regions or domains that can be defined: the domain in the bilayer, the domain outside the cell (called the extracellular domain), and the domain inside the cell (called the intercellular domain). Even though a cell membrane is somewhat fluid, the orientation of transmembrane proteins does not change. The proteins are so large that the rate for them to change orientation is extremely small. Thus, the extracellular part of the transmembrane protein is always outside the cell and the intercellular portion is always inside.

Transmembrane proteins play several roles in the functioning of cells. Communication is one of the most important roles: The proteins are useful for signaling to the cell what the external environment contains. **Receptors** are capable of interacting with specific substrate molecules on the extracellular domain. Once a protein binds to substrate, a change in the geometry near the binding site results in subsequent changes in the structure of the intercellular domain. These changes result in a cascade effect—another protein in the cell changes, affecting the next protein, and so on. Thus, transmembrane proteins are capable of initiating signals that are responsive to the external environment of the cell but ultimately lead to actions that take place in other structures of the cell.

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

In addition to serving as a way for the cell to gather information about the external environment, transmembrane proteins are associated with controlling the exchange of materials across the membrane. The proteins most involved in this process are called porins. These molecules appear in clusters that create pores (or channels) within the membrane. In many cases the pores are controlled (or regulated) by other proteins so that they are open under some circumstances and closed under others.

Nerve cell signaling provides a good example of this functionality. Nerve cells propagate electrical signals called action potentials by using the flow of ions across the membrane. The channels that allow the flow of ions are usually closed in their resting state but open when a signal occurs. These proteins form voltage-gated channels. When one nerve cell interacts with another, a different mechanism opens the channels. In this case, a receptor protein binds a neurotransmitter; this interaction affects the channel proteins so that they are opened for ion flow. This structure is referred to as a ligand-gated channel. The ligand is the neurotransmitter in this case, but other ligand-gated channels also exist and all use transmembrane proteins. SEE ALSO PROTEINS; NEUROTRANSMITTERS.

Thomas A. Holme

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Transmutation

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

nuclear: having to do with the nucleus of an atom

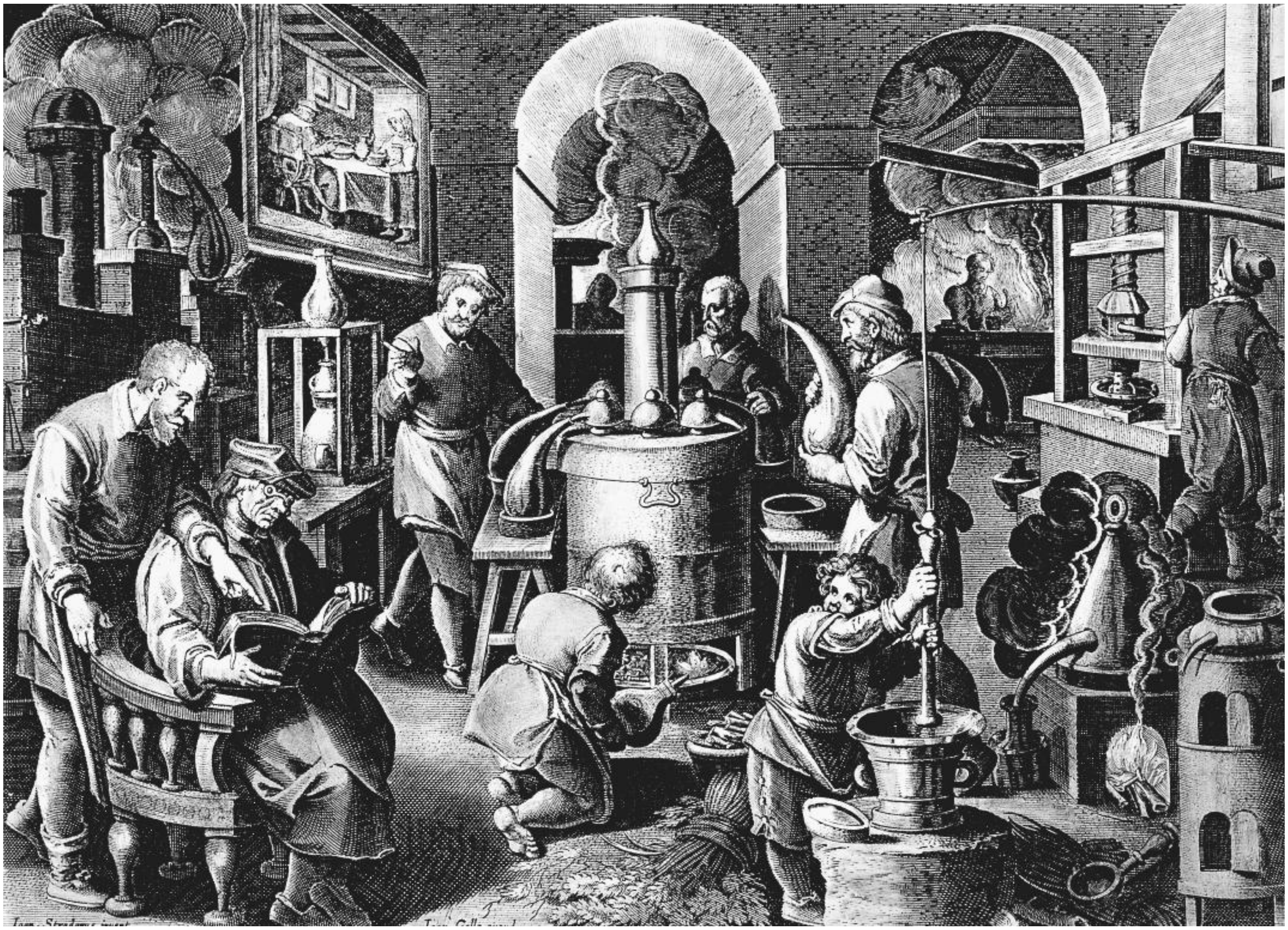
Transmutation is the act of changing a substance, tangible or intangible, from one form or state into another. To the alchemists of old, this meant the conversion of one physical substance into another, particularly base **metals** such as lead into valuable silver and gold. To the modern scientists, this means the transformation of one element into another by one or a series of **nuclear** decays or reactions.

Although people worked with gold, silver, copper, iron, tin, lead, carbon, sulfur, and mercury in ancient times, they had little understanding of chemistry and could write little about it. At this time chemistry was an art, not a science. The Egyptians were the first to produce extensive written documentation of chemical procedures, at the beginning of the Christian era, and Egypt is generally identified as the birthplace of chemistry. These writings indicate that the development of methods for transmuting one substance into another was one of the principal early goals of their investigations. During the several hundred years that followed these writings, the alchemists attempted to develop schemes to transmute base metals into gold and silver through various chemical manipulations of mixtures and distillations. The alchemists were spurred on by what appeared to be some success—for example, production of very small amounts of gold from lead ore by their chemical procedures. (This gold was undoubtedly present in trace amounts in the original ores and was not produced by transmutation.) The ultimate folly of the alchemists turned up during the Middle Ages with the search for the philosopher's stone, a substance that could be mixed with base metals and, through purification, convert them into gold. It was never found.

Because each element has a different but fixed number of protons in the nucleus of the atom, which is the atomic number, the transmutation of one chemical element into another involves changing that number. Such a nuclear reaction requires millions of times more energy than was available through chemical reactions. Thus, the alchemist's dream of transmuting lead into gold was never chemically achievable.

Although the alchemists failed to find a method for the transmutation of base metals into precious metals, a number of important chemical processes resulted from their efforts. For example, they extracted metals from ores; produced a number of inorganic acids and bases that later became commercially important; and developed the techniques of fusion, calcination, solution, filtration, crystallization, sublimation, and, most importantly, distillation. During the Middle Ages, they began to try to systematize the results of their primitive experiments and their fragments of information in order to explain or predict chemical reactions between substances. Thus the idea of chemical elements and the first primitive forms of the chemical Periodic Table appeared.

Ironically, nuclear transmutations were taking place virtually under the noses of the alchemists (or under their feet), but they had neither the methods to detect nor the knowledge to use these happenings. The discovery of the nuclear transmutation process was closely linked to the discovery of radioactivity by Henri Becquerel in 1896. Nuclear transmutations occur during the spontaneous radioactive decay of naturally occurring thorium and uranium (atomic numbers 90 and 92, respectively) and the radioactive



Alchemists considered transmutation as the conversion of one physical substance to another, such as base metals into valuable metals.

daughter products of their decay, namely the natural decay series. As an example, the ^{232}Th decay series is shown in Figure 1. The superscript 232 represents the atomic mass, which is the total number of protons and neutrons in the nucleus of the atom. In this decay series, a ^{232}Th nucleus starts the process by spontaneously emitting an α-particle (a He nucleus containing two protons and two neutrons). This reaction transmutes the Th nucleus into a nucleus with two fewer protons and two fewer neutrons, namely ^{228}Ra. Then the ^{228}Ra nucleus spontaneously emits a β-particle (an electron), which converts a neutron in the nucleus into a proton, raising the atomic number of the resultant nucleus by one with no change in atomic mass, yielding ^{228}Ac. This sequence of successive α and β decays continues from one element to another until the stable ^{208}Pb nucleus is produced (see Figure 1). There exist two other naturally occurring decay chains as well, one starting with ^{235}U (the actinium series) and one starting with ^{238}U (the uranium series). In addition to these three decay series, fourteen other radioactive **isotopes** exist in nature, ranging from ^{40}K to ^{190}Pt, which transmute by decay into stable elements.

isotope: form of an atom that differs by the number of neutrons in the nucleus

The idea of transmutation of elements in the natural decay chains did not accompany the discovery of radioactivity by Becquerel. However, Marie and Pierre Curie extended the investigations of Becquerel using a variety of

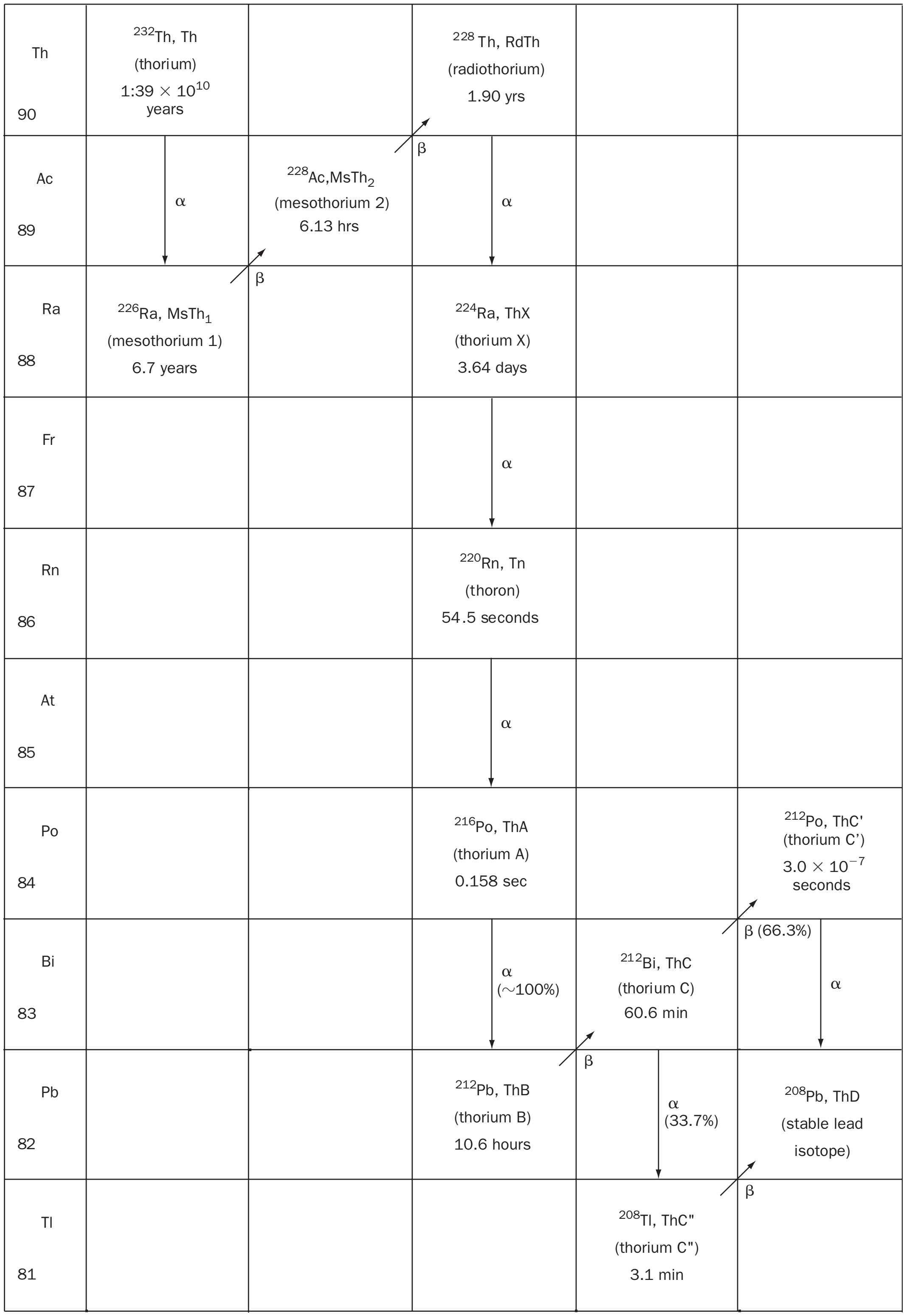

Th 90
^{232}Th, Th
(thorium)
1:39 × 10^{10} years
^{228} Th, RdTh
(radiothorium)
1.90 yrs
Ac 89
α
^{228}Ac,MsTh$_2$
(mesothorium 2)
6.13 hrs
β
α
Ra 88
β
^{226}Ra, MsTh$_1$
(mesothorium 1)
6.7 years
^{224}Ra, ThX
(thorium X)
3.64 days
Fr 87
α
Rn 86
^{220}Rn, Tn
(thoron)
54.5 seconds
At 85
α
Po 84
^{216}Po, ThA
(thorium A)
0.158 sec
^{212}Po, ThC'
(thorium C')
3.0 × 10^{-7} seconds
Bi 83
β (66.3%)
α (∼100%)
^{212}Bi, ThC
(thorium C)
60.6 min
α
Pb 82
β
^{212}Pb, ThB
(thorium B)
10.6 hours
α (33.7%)
^{208}Pb, ThD
(stable lead isotope)
Tl 81
β
^{208}Tl, ThC"
(thorium C")
3.1 min

Figure 1.

U minerals and found the radioactive properties to be *not* a function of the physical or chemical forms of the uranium, but properties of the element itself. Using chemical separation methods, they isolated two new radioactive substances associated with the U minerals in 1898 and named them polonium and radium. In 1902 Ernest Rutherford and Frederick Soddy explained the nature of the process occurring in the natural decay chains as the radioactive decays of U and Th to produce new substances by transmutation.

Lord Rutherford and his group of scientists were the first persons to produce and detect artificial nuclear transmutations in 1919. He bombarded nitrogen in the air with the α-particles emitted in the decay of ^{214}Po. The transmutation reaction involved the absorption of an α-particle by the ^{14}N nuclei to produce ^{17}O and a proton (a hydrogen nucleus). This reaction can be written as

$$^{14}\mathrm{N} + {}^{4}\mathrm{He} \rightarrow {}^{17}\mathrm{O} + {}^{1}\mathrm{H}$$

Lord Rutherford was able to detect and identify the protons produced in this nuclear reaction and thereby demonstrate the transmutation process.

Until 1934, only naturally occurring radioactive elements were available for study. However, in January of that year, Irene Curie (daughter of Marie Curie) and Frederic Joliot reported that boron and aluminum samples were made radioactive by bombarding them with α-particles from polonium to produce the two new radioactive products, ^{13}N and ^{30}P respectively. This discovery established the new fields of nuclear chemistry and radiochemistry and sparked their rapid growth.

With the development of nuclear reactors and charged particle accelerators (commonly referred to as "atom smashers") over the second half of the twentieth century, the transmutation of one element into another has become commonplace. In fact some two dozen synthetic elements with atomic numbers higher than naturally occurring uranium have been produced by nuclear transmutation reactions. Thus, in principle, it is possible to achieve the alchemist's dream of transmuting lead into gold, but the cost of production via nuclear transmutation reactions would far exceed the value of the gold. SEE ALSO Alchemy; Nuclear Chemistry; Nuclear Fission; Radioactivity; Transactinides.

Robert J. Silva

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Transport Protein

There are two different types of transport proteins: those that carry molecules to "distant" locations (within a cell or an organism), and those that serve as gateways, carrying molecules across otherwise impermeable membranes.

In order for vast numbers of multicellular organisms to exist, they must have a system for delivering oxygen to all their cells, especially those cells that are not in direct contact with the organism's external environment. Hemoglobin is an example of an oxygen-transport protein and is a part of these oxygen delivery systems.

A computer-generated representation of a molecule of the hemoglobin-carrier of oxygen in blood, a transport protein.

polypeptide: compound containing two or more amide units—C(O)NH—produced by the condensation of two or more amino acids

heme group: functional group formed by an iron atom interacting with a heterocyclic ligand called a porphyrin

A single human hemoglobin molecule consists of four **polypeptide** chains. Each of these chains contains a tightly bound prosthetic group called heme. A prosthetic group is a small organic molecule (non-amino acid) that is bound tightly to a protein. At the heart of each **heme group** is a tightly bound iron atom, to which oxygen binds. The function of hemoglobin is to bind oxygen in the oxygen-rich environment of the lungs, then to release that oxygen to oxygen-poor tissues elsewhere. The polypeptide chains are wrapped around the heme groups in such a way that the affinity between the iron and oxygen is strong enough for hemoglobin to bind oxygen in the lungs, but the resulting bond is weak enough such that hemoglobin will release the oxygen when it encounters organs or tissues that need oxygen. Hemoglobin also performs the complementary function of accepting carbon dioxide from the peripheral tissues and releasing it in the lungs.

glucose: common hexose monosaccharide; monomer of starch and cellulose; also called grape sugar, blood sugar, or dextrose

vitamins: organic molecules needed in small amounts for the normal function of the body; often used as part of an enzyme-catalyzed reaction

Cell membranes are impermeable to charged and polar molecules, meaning that these molecules cannot cross them spontaneously. Some transport proteins are intrinsic to cell membranes and facilitate the transport of polar molecules across the membranes. Each cell of the human body needs **glucose**, a very polar molecule, and human beings have five different glucose transport proteins (known as GLUT1 through GLUT5) that all serve a similar function: They carry glucose molecules across membranes and into cells. Without these transport proteins, the rate of glucose entry into cells would be very low indeed. Other membrane-linked transport proteins carry other molecules across membranes, including amino acids, ions, and **vitamins**. SEE ALSO PROTEINS.

Paul A. Craig

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Travers, Morris

ENGLISH CHEMIST
1872–1961

The discovery of a new chemical element is a rare event; therefore, it is amazing that, in the space of only forty-two days, Morris Travers was involved in the discovery of not one but three new elements—krypton, neon, and xenon.

Morris William Travers was born on January 24, 1872, in Kensington, London, England. His father was an eminent surgeon who was an early champion of antiseptic medicine. Young Morris was well schooled and showed an early interest in science. He entered University College, London, in 1889, and there came under the influence of Sir William Ramsay. Travers received his B.S. in 1893, and, like most of his contemporaries, he planned to specialize in organic chemistry. He began his studies in this field at the University of Nancy in France, but finding both the subject and his adviser disagreeable, he returned to University College, where he began work on his doctorate.

During this time, Ramsay was conducting the research that led to the discovery of argon in 1894 and then helium in 1895. He asked Travers to join him in identifying the properties of these new elements, and the young researcher never again returned to the study of organic chemistry. From 1895 until 1900 Travers worked with Ramsay to find the missing rare gases that the Periodic Table indicated should exist. The two isolated krypton in May 1898, and then a few days later, while examining a large volume of argon, they separated a small quantity of another new element, which they named neon. On further examination of the liquefied air residues from which they had isolated these new elements, they discovered yet another heavier gas, which was named xenon. Because of the chemical inertness of these gases, they were identified by passing an electric current through tubes containing the gases and measuring the characteristic frequencies at which they emitted light. Travers obtained his Ph.D. in 1898 and continued to work on cryogenic research at University College until 1903, when he accepted a position at University College in Bristol.

In 1906 Travers traveled to India to help found the Indian Institute of Science in Bangalore. He returned to England in 1915 and aided the World War I effort by applying his expertise to the production of scientific glassware and munitions. He remained in the chemical industry in various capacities until 1927, when he returned to Bristol as an honorary professor and research fellow. He retired in 1937 but remained active as a consultant and, in his eighties, wrote a vivid and erudite biography of Ramsay, his early mentor. He died on August 25, 1961, at his home in Stroud, Gloucestershire. SEE ALSO Krypton; Neon; Ramsay; William; Xenon.

Bartow Culp

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Triglycerides

Triglycerides are the most common storage form of fat in many organisms. They are neutral **lipid** molecules created via the **esterification** of three fatty acids to a single glycerol molecule. Triglycerides are an efficient storage

lipid: a nonpolar organic molecule; fatlike; one of a large variety of nonpolar hydrophobic (water-hating) molecules that are insoluble in water

esterification: chemical reaction in which esters (RCO_2R') are formed from alcohols (R_1OH) and carboxylic acids (RCO_2H)

hydrophobic: water repelling

medium because their highly **hydrophobic** nature allows them to be stored as part of droplets (in which they have little or no contact with water molecules).

synthesis: combination of starting materials to form a desired product

Triglycerides vary in molecular composition according to the identities of the fatty acids used in their **synthesis**. Fatty acids that have been esterified to the glycerol moiety of the triglyceride may be unsaturated (containing double bonds) or saturated (containing no double bonds). The number of double bonds in the fatty acids affects the melting temperature of the triglyceride. Saturated fats have higher melting points and are often solids at room temperature. Unsaturated fats have lower melting points and are often liquids at room temperature. Although all triglycerides are correctly identified as fats, triglycerides with melting points below room temperature are also known as oils. Animal triglycerides generally have more saturated fatty acyl groups than plant triglycerides. Beef triglycerides (lard) have a saturated to unsaturated fatty acyl group ratio of 50:50, whereas the ratio for olive oil is about 20:80. Hydrogenation (removal of the double bonds in the fatty acids) will convert an oil, such as vegetable oil, from a liquid to a solid.

adipose tissue: connective tissue in which fat is stored

In animals, triglycerides are either ingested as part of the diet or synthesized in the liver. Triglycerides are transported in blood as part of lipoprotein particles. Dietary triglycerides are transported as part of lipoprotein particles called chylomicrons. Triglycerides synthesized in the liver are transported as part of lipoprotein particles called very low density lipoproteins or VLDLs. Triglycerides are then removed from lipoprotein particles as they move through the circulatory system. Tissues either utilize this transported triglyceride immediately, or it is stored in **adipose tissue**.

hormonal signaling: collective processes by which hormones circulate in the blood stream to their target organs and trigger the desired responses

Triglyceride is stored within cells that make up adipose tissue (fat). Triglycerides are the most abundant form of stored potential fuel in the human body. A typical 70-kilogram (154-pound) man will have approximately 15 kilograms (33 pounds) of stored triglyceride, representing several months of stored fuel. When physiologic conditions necessitate the use of triglycerides stored in adipose tissue, a hormone or neurotransmitter signals their release. Exercise or stress triggers the release of the neurotransmitter norepinephrine from nerve terminals in the adipose tissue, thereby stimulating triglyceride release. Fasting also initiates the release of triglycerides. Insulin and glucagon, two hormones produced by the pancreas, control this release of triglycerides. During fasting, blood glucagon levels increase and insulin levels decrease. The combination of increased glucagon and decreased insulin levels in the blood is the hormonal signal that triggers the release of triglycerides from the adipose tissue. However, triglycerides do not exit adipose tissue intact. **Hormonal signaling** activates an enzyme called a lipase that hydrolyzes a triglyceride molecule into a glycerol molecule and three fatty acids. The glycerol and fatty acids are then transported within the circulatory system to tissues that will utilize them as fuel. Fatty acids are transported in the blood bound to the serum protein albumin, as their hydrophobic natures would otherwise make them insoluble in the blood. SEE ALSO Fats and Fatty Acids; Lipids.

Robert Noiva

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Tungsten

MELTING POINT: 3,422 ±15°C
BOILING POINT: 5,700 ±200°C
DENSITY: 19.3 g/cm^3
MOST COMMON IONS: WO_4^{2-}

74
W
TUNGSTEN
183.85 ±0.03

Tungsten is a metallic transition element in Period 6, Group 6 of the Periodic Table. It was first described in 1783 by Spanish brothers Juan Jose and Fausto de Elhuyar. They named the element *Wolfram* after a term used by the ancient tin miners in Saxony-Bohemia, describing a still unknown mineral. The name was later changed to tungsten, derived from the Swedish words *tung* and *sten* (meaning "heavy stone").

Tungsten has a silvery-white luster and is brittle at room temperature. At elevated temperatures (100°–500°C [212°–932°F]), it is transformed into the **ductile** state. Tungsten **metal** is stable in air only at moderate temperatures; all high-temperature applications are therefore limited to a protective atmosphere or vacuum.

ductile: property of a substance that permits it to be drawn into wires

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Thirty-five **isotopes** of tungsten are known; five of them are naturally occurring (180, 182, 183, 184, and 186). In nature, tungsten occurs only in a chemically combined state, mainly as tungstate. The most important tungsten minerals are: scheelite ($CaWO_4$), wolframite ($Fe,MnWO_4$), ferberite ($FeWO_4$), and huebnerite ($MnWO_4$). The average abundance in Earth's crust is 1.3 μg/g [1.3 ppm].

isotope: form of an atom that differs by the number of neutrons in the nucleus

Tungsten and tungsten **alloy** products are used in lighting (in the form of wires, coils, and coiled coils in incandescent lamps, and as electrodes in discharge lamps), electrical engineering (high-performance switches), electronics (integrated circuits), medical engineering (x-ray targets), sport equipment (golf club components), aviation and military components (tank ammunition), and steel technology (high-speed steels). Tungsten carbide (WC) forms the main constituent in cemented carbides (also known as hardmetals); these very hard and tough materials are used for metal cutting, machining of wood, plastics and composites, mining tools, construction and wear parts, and military components. Oxides are used as phosphors, pigments, catalysts (oil industry, **combustion** plants), and electrochromic devices (smart windows).

alloy: mixture of two or more elements, at least one of which is a metal

combustion: burning, the reaction with oxygen

Wolf-Dieter Schubert
Burghard Zeiler

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U

Uracil *See Nucleotide.*

Uranium

92
U
URANIUM
238.03

MELTING POINT: 1,408°C
BOILING POINT: 4,404°C
DENSITY: 19.04 g/cm^3
MOST COMMON IONS: U^{3+}, U^{4+}, UO_2^{+}, UO_2^{2+}

isotope: form of an atom that differs by the number of neutrons in the nucleus

equilibrium: condition in which two opposite reactions are occurring at the same speed, so that concentrations of products and reactants do not change

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Uranium is a very dense, highly reactive, metallic element that has the highest atomic mass of the naturally occurring elements. Natural uranium consists of two long-lived radioactive **isotopes**: ^{238}U (99.28%) and ^{235}U (0.72%). A very small amount of ^{234}U (0.005%) occurs in secular **equilibrium** with ^{238}U. Uranium was discovered in 1789 by Martin Klaproth, who named it after the planet Uranus (which had just been discovered). In 1841 Eugène Melchior Péligot prepared uranium **metal** and proved that Klaproth had actually isolated uranium dioxide.

Uranium is found in Earth's crust at an average concentration of about 2 ppm, and is more abundant than silver or mercury. The most common uranium-containing mineral is uraninite, a complex uranium oxide. Other uranium-containing minerals are autunite, a hydrated calcium uranium phosphate, and carnotite, a hydrated potassium uranium vanadate.

aqueous solution: homogenous mixture in which water is the solvent (primary component)

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

The most prevalent form of uranium in **aqueous solution** is the light yellow, fluorescent uranyl ion UO_2^{2+}. The U^{4+} cation (green in solution) can be obtained by strong reduction of U(VI), but readily oxidizes back to UO_2^{2+} in air. The pentavalent ion UO_2^{+} can be reversibly formed by reduction of UO_2^{2+}, but it readily disproportionates into U(IV) and U(VI). The trivalent U^{3+} can be formed by reduction of U(IV) but is unstable to **oxidation** in aqueous solution.

radioactive decay: process involving emission of a subatomic particle from a nucleus, typically accompanied by the emission of very short wavelength electromagnetic radiation

nuclear: having to do with the nucleus of an atom

fission: process of splitting an atom into smaller pieces

After the discovery of uranium radioactivity by Henri Becquerel in 1896, uranium ores were used primarily as a source of **radioactive decay** products such as ^{226}Ra. With the discovery of **nuclear fission** by Otto Hahn and Fritz Strassman in 1938, uranium became extremely important as a source of nuclear energy. Hahn and Strassman made the experimental discovery; Lise Meitner and Otto Frisch provided the theoretical explanation. Enrichment of the spontaneous fissioning isotope ^{235}U in uranium targets led to the development of the atomic bomb, and subsequently to the production of nuclear-generated electrical power. There are considerable amounts of uranium in nuclear waste throughout the world. SEE ALSO Actinium; Berkelium; Einsteinium; Fermium; Lawrencium; Mendelevium; Neptunium; Nobelium; Plutonium; Protactinium; Rutherfordium; Thorium.

W. Frank Kinard

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Urey, Harold

AMERICAN PHYSICAL CHEMIST
1893–1981

Harold Urey was a prolific scientist whose research interests included chemistry, astronomy, geology, and biology. Although he did important work on **isotope** applications and cosmochemistry, Urey is best remembered for his discovery of heavy hydrogen, or deuterium, for which he received the 1934 Nobel Prize in chemistry.

American chemist Harold Clayton Urey, recipient of the 1934 Nobel Prize in chemistry, “for his discovery of heavy hydrogen.”

isotope: form of an atom that differs by the number of neutrons in the nucleus

Urey was born in Walkerton, Indiana, on April 29, 1883. When he was six, his father died. His mother remarried and the family later moved to Montana. After graduating from high school in 1911, Urey taught in country schools in Indiana and Montana. In 1914 Urey entered the University of Montana and graduated three years later with a B.S. in biology and a minor in chemistry. During World War I he worked for a chemical company in Philadelphia, and after the war, Urey returned to the University of Montana as an instructor in chemistry. He enrolled in the chemistry department at the University of California at Berkeley in 1921 and only two years later received his Ph.D. in physical chemistry. After a year in Copenhagen, Denmark, Urey joined the chemistry faculty at Johns Hopkins University. He would later move to Columbia University, the University of Chicago, and finally the University of California at San Diego.

atomic spectrum: electromagnetic array resulting from excitement of a gaseous atom

In July 1931 Urey read a paper that proposed the existence of a stable isotope of hydrogen of mass 2, or heavy hydrogen. He decided to look for the isotope and designed an experimental plan with his lab assistant George Murphy. As a detection method, they chose to examine the lines in the **atomic spectrum** of hydrogen. Since the predicted natural abundance of the heavy hydrogen was only 0.05 percent, Urey hoped to detect the rare isotope by analyzing a sample of hydrogen enriched in heavy hydrogen prepared by Ferdinand G. Brickwedde, a physicist working at the National Bureau of Standards in Washington, D.C.

While waiting for the enriched sample to arrive, Urey and Murphy analyzed a sample of regular hydrogen and were surprised to see evidence of heavy hydrogen (which Urey later called deuterium). Believing that it was an artifact of their detection method, Urey and Murphy decided to keep their results secret until they obtained further proof using the enriched sample. On Thanksgiving Day of 1931, Urey analyzed the sample of enriched hydrogen and observed the lines confirming the existence of deuterium. Urey received the 1934 Nobel Prize in chemistry for his discovery. He publicly acknowledged Brickwedde and Murphy's role by giving each of them one-quarter of the Nobel Prize money.

Since 1913 scientists had accepted the existence of isotopes, but conventional wisdom claimed that isotopes of a given element could not be differentiated or separated by a chemical process. Urey challenged and overturned this thinking in 1932 by showing that deuterium (D_2) could be concentrated in the form of deuterium oxide, or heavy water (D_2O), and then converted back into pure deuterium by electrolysis of the D_2O. Deuterium and deuterium oxide are convenient sources of deuterium-labeled compounds that today are used routinely in medicine and science.

After World War II Urey moved to the University of Chicago. While there, Urey perfected a method, also based on oxygen isotope ratios, that accurately measured the temperatures of ancient oceans.

Urey additionally developed an interest in the chemistry of the solar system. In his 1952 book, *The Planets*, he argued that what we needed to understand the origins of the solar system was a thorough understanding of the Moon. Urey's work on the chemical composition of meteorites set the stage for later studies that explained the origins of chemicals in stars.

Urey left Chicago in 1958 to become professor-at-large at the newly formed University of California at San Diego. He retired from that institute in 1970 and died in 1981. SEE ALSO HYDROGEN.

Thomas M. Zydowsky

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V

Valence Bond Theory

The valence bond (VB) theory of bonding was mainly developed by Walter Heitler and Fritz London in 1927, and later modified by Linus Pauling to take bond direction into account. The VB approach concentrates on forming bonds in localized orbitals between pairs of atoms, and hence retains the simple idea of Lewis structures and electron pairs. The wave function for the bonding electrons is described as the overlap of atomic orbitals. Thus, in the H_2 molecule, the spherical s orbitals of the two H atoms simply overlap, so that the electrons in the bond sense the nuclei of both atoms. This method also works well for simple molecules like H_2O, CH_4, and NH_3. First the appropriate hybrid orbitals are constructed on the central atom to give the correct molecular geometry (e.g., four sp^3 tetrahedral orbitals on the C atom in CH_4). The bonding picture is then constructed by simple overlap of the atomic orbitals, (e.g., one 1s orbital of a H atom with each sp^3 lobe of the C atom in CH_4 to give four C—H bonds).

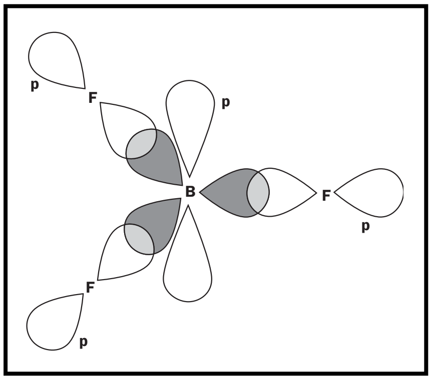
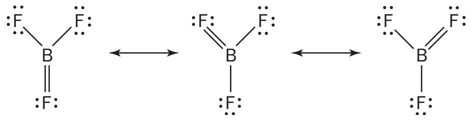


Figure 1. The bonding in the BF_3 molecule: Three sp^2 hybrid orbitals on the boron atom overlap a p orbital from each of the three fluorine atoms.

Bonding in BF_3

The electron configuration of the boron atom is $2s^22p^1$, with one unpaired electron. This electron is excited to the higher energy configuration $2s^12p^2$, with three unpaired electrons. These three orbitals are now hybridised to give three equivalent sp^2 hybrid orbitals, coplanar, and lying 120° apart, each containing one electron. These hybrid orbitals then overlap the half-filled p orbitals of the three fluorine atoms, thus forming three coplanar B—F electron-pair bonds. (See Figure 1.)

All seems well, except that the boron atom does not have an octet: One perpendicular 2p orbital remains empty. This orbital can accept electron density from the F atoms to a maximum of one electron pair. On average, each F atom donates one-third of an electron pair to the empty p orbital on boron. One model for BF_3 is a resonance hybrid of three structures, each having one double bond and two single bonds. The B—F bond is said to have a bond order of $1\frac{1}{3}$.



Some Shortcomings

The valence bond approach is especially useful in organic chemistry where so many molecules are built of tetrahedral C atoms, sp^3 hybridised. The concept of hybrids is intuitively very satisfying because they fit visually with our perceived picture of the shape of a molecule with its directed bonds between pairs of atoms. Unfortunately, the VB approach is not satisfactory for species like $CO_3^{=}$, NO_3^{-}, and benzene because the VB picture does not reflect the known chemical structure. A new concept of resonance hybrids must be introduced, and $CO_3^{=}$ must now be represented by a combination of three Lewis-octet structures. Worse still, the VB approach cannot easily give a satisfactory bonding picture for either of the important molecules O_2 or CO.

In cases where the VB approach does not work well, the molecular orbital (MO) method is often more successful. The situation is best summarized by using the strengths of the VB approach where they are appropriate, as in CH_4, and using the MO approach where it is best suited, as in O_2 and benzene. After all, each approach is an approximation, incomplete and imperfect. SEE ALSO BONDING; LEWIS STRUCTURES; MOLECULAR ORBITAL THEORY.

Michael Laing

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Vanadium

MELTING POINT: 1,910 ±10°C
BOILING POINT: 3,047°C
DENSITY: 6.11 g/cm^3
MOST COMMON IONS: V^{2+}, V^{3+}, VO^{+}, VO_2^{+}

23
V
VANADIUM
50.9415

Vanadium is a soft silver **metal** in group 5B of the Periodic Table. It was discovered in Mexican lead ore by Andreas Manuel del Rio in 1801. Because of the red color of its salts, he named it erythronium (the Greek word *erythro* means "red"). Upon challenge by H. V. Colett-Desotils, del Rio withdrew his claim. In 1830 the element was rediscovered by Nils Selfstöm in iron ore. Since the element is found in compounds of many different col-

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

ors, he named it "vanadium" after the Scandinavian goddess of beauty, Vanadis.

Vanadium is the nineteenth element in abundance (136 ppm) and the fifth most abundant transition element in Earth's crust. It is found in approximately sixty-five different minerals (such as roscoelite and vanadinite), phosphate rock, iron ores, and some crude oils as organic complexes. Since there are few concentrated deposits of vanadium compounds, it is obtained as a coproduct of refining. The element has two naturally occurring **isotopes**: ^{50}V (0.25%) and ^{51}V (99.75%).

isotope: form of an atom that differs by the number of neutrons in the nucleus

Although vanadium is an essential **trace element**, its exact role has not been determined. It is found in the blood of the ascidian seaworm. A related species has vanadium concentrations of up to 1.45 percent in its blood cells. The metal may play a role in the oxygen transport system.

trace element: element occurring only in a minute amount

Vanadium reacts with most nonmetals at high reaction temperatures (660°C; 1,220°F). The compounds of vanadium reflect the varied **oxidation** states possible for this element. Formal oxidation states of +5 to -1 have been found, with the +4 state being the most stable. The element has good corrosion resistance to alkali, acid, and salt water. For this reason it is used in rust resistant springs and high speed tools. Approximately 80 percent of the vanadium produced yearly is used as an additive to produce steel that has a resistance to wear. Vanadium oxide is used in ceramics and as a **catalyst**. SEE ALSO CORROSION; STEEL.

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

catalyst: substance that aids in a reaction while retaining its own chemical identity

Catherine H. Banks

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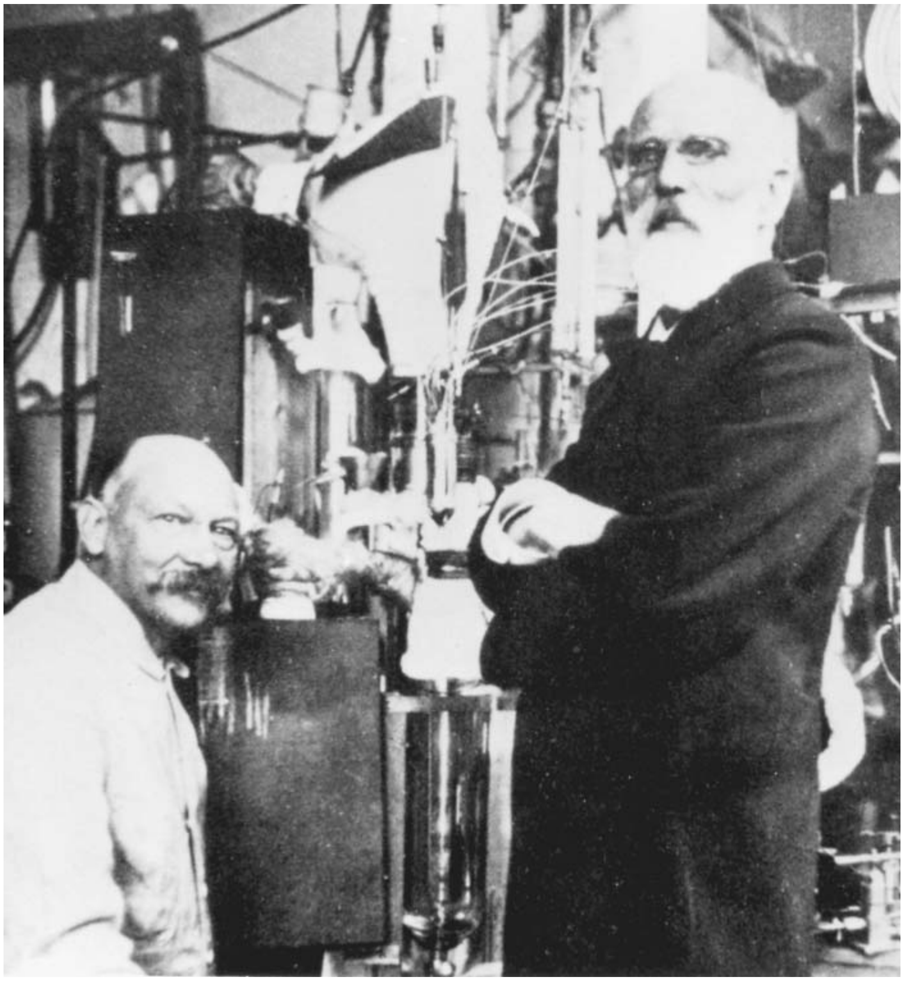
van der Waals, Johannes

DUTCH PHYSICIST
1837–1923

That atoms exist is a fact seemingly indisputable, but such was not always the case. In the early eighteenth century, when English chemist and physicist John Dalton made a case for his **atomic theory**, it was met with skepticism and spawned a vigorous debate that continued well into the twentieth century about whether or not atoms were real. Coming down squarely on the side of real atoms was van der Waals, the father of modern molecular science.

atomic theory: concept that asserts that matter is composed of tiny particles called atoms, the particular characteristics of which determine the type and form of matter

Johannes Diderik van der Waals was born in Leiden, the Netherlands, in 1837. The son of a carpenter, he was not afforded the advantages that some of his contemporaries enjoyed. Lacking knowledge of classical languages, he was barred from taking his academic examinations at the University of Leiden. Instead, he continued his studies in his spare time between



Dutch physicist Johannes Diderik van der Waals (right), recipient of the 1910 Nobel Prize in physics, "for his work on the equation of state for gases and liquids."

1862 and 1865, eventually obtaining teaching certificates in both mathematics and physics. In 1864 he was appointed as a teacher at a secondary school in Deventer. In 1866 he moved to the Hague, first as a teacher and then as a director of one of the secondary schools there.

When new legislation was introduced exempting science students from a classical education, van der Waals was finally allowed to sit for his university examinations. In 1873 he obtained his doctorate with a thesis titled, "On the Continuity of the Gas and Liquid State." His thesis proposed a correction to the **equation of state for ideal gases** that would allow the equation to be applied to real gases. That is, he proposed a modification of the formula $PV = nRT$ to account for the fact that atoms are real and that they interact.

equation of state for ideal gases: mathematical statement relating conditions of pressure, volume, absolute temperature, and amount of substance; PV = nRT

In his own words, his incentive to his life's work "came to me when, after my studies at university, I learned of a treatise by Clausius (1857) on the nature of the motion which we call heat. In this treatise . . . he showed how Boyle's law can very readily be derived on the assumption that a gas consists of material points which move at high velocity" (van der Waals, "The Equation of State of Gases and Liquids"). This treatise was a revelation, as it derived the ideal gas law from first principles and framed it in terms of atoms and molecules. Here was a theoretical rationalization for experimentally obtained data. But it also occurred to van der Waals that this treatise might not be complete. If the atoms of gases are in constant motion when a gas is dilute, then this must also be the case as the gas is compressed and, indeed, must still be the case down to maximum compression as the gas condenses to a liquid. This led to the idea of the continuity of matter and the notion that both the liquid and gaseous states can be described by a similar mathematical theory.

Further, van der Waals recognized that real gases take up volume and atoms do interact with one another. For the German mathematical physicist Rudolf Clausius to obtain his results, he had to ignore both of these factors. Van der Waals found experimentally derived constants that allowed him to modify the ideal gas law to take into account real atoms. His equation of state,

$$(P + a/V^2)(V - b) = RT$$

has subsequently been modified to include Avogadro's number, but it was critical to scientists' first steps in understanding atoms and molecules. *a* arises from considering interatomic forces (collectively called "van der Waals forces" in his honor), and *b* recognizes that atoms have a real volume—that they actually exist. SEE ALSO BOYLE, ROBERT; DALTON, JOHN.

Todd W. Whitcombe

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van Helmont, Johann Baptista

FLEMISH RELIGIOUS SCHOLAR, PHYSICIAN, AND CHEMIST
1579–1644

Johann Baptista van Helmont was a contemporary of the English philosopher Francis Bacon and the Italian astronomer Galileo Galilei. As with Galileo and his work, van Helmont's work in science brought him into conflict with religious authorities. He also spent about sixteen years under house arrest while an Inquisition court prosecuted its legal case against him. His use of chemistry to understand medicine made him a leading iatrochemist (physician-chemist, *iatro* being Greek for "physician") of his time.

philosopher's stone: the substance thought by the alchemists to have the power to transmute base metals into gold

Van Helmont was the first to use the term "gas" to describe an airlike substance that was distinct from ordinary atmospheric air. His approach to chemistry included both mysticism and the use of the new experimental philosophy (science). He believed in astrology and the **philosopher's stone**. His study of the written works of Paracelsus led to his criticism of established medical practice and his adoption of experimental testing. He tested Paracelsus's notion that all substance was made of "earth" by conducting his "willow tree experiment." In the experiment he weighed a pot that contained dry soil and a willow sapling cleansed of soil. After planting the sapling in the soil, he added no soil, and watered the sapling with pure rainwater

Flemish physician and chemist Johann van Helmont, the first person to distinguish gas from atmospheric air.

or distilled water (and not with mineral water or well water, which might contain dissolved earth). At the end of five years he removed the tree from the soil, weighed it, and weighed the dried pot of soil. The soil had lost nearly none of its weight, whereas the tree had gained a great deal of weight. Van Helmont concluded that a tree was not composed mostly of "earth," as avowed by Paracelsus, but was composed mostly of "water," somehow transformed into tree substance.

Van Helmont offered another experiment as a proof of the existence of vacuums. He positioned a lighted candle upright in a wide tray of water. He used a glass dome to enclose the candle, with the edge of the glass immersed in the water. The candle soon went out, and the level of the water enclosed by the glass rose. Van Helmont claimed there was something in the air that was annihilated by the fire. The water rose due to suction that had been created by a vacuum that resulted from the annihilation of a part of the air.

This description is essentially correct. The experiment would continue to be investigated by chemists for another 150 years, ultimately becoming a model experiment in the chemical revolution. SEE ALSO ALCHEMY; PARACELSUS; TRANSMUTATION.

David A. Bassett

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van't Hoff, Jacobus Hendricus

COFOUNDER OF MODERN STEREOCHEMISTRY AND PHYSICAL CHEMISTRY
1852–1911

Dutch chemist Jacobus Hendricus van't Hoff, recipient of the 1901 Nobel Prize in chemistry, "in recognition of the extraordinary services he has rendered by the discovery of the laws of chemical dynamics and osmotic pressure in solutions."

Jacobus Hendricus van't Hoff, born in Rotterdam, Netherlands, was in his youth, along with the French chemist Joseph Achille Le Bel, the cofounder of modern stereochemistry. He then became one of the fathers of modern physical chemistry. In 1901 he was awarded the first Nobel Prize in chemistry for his work on chemical dynamics and the osmotic pressure in solutions.

As is the case with many creative minds, van't Hoff's career initially encountered many roadblocks, mostly related to the ignorance of the scientific establishment. Unemployed for two years after receiving his doctorate, he eventually took a teaching job in physics at the veterinary school in Utrecht. Success finally came in 1877 when the newly founded University of Amsterdam offered him a lectureship; the next year he became a professor of chemistry at the same institute. Although his international reputation led to the formation of a new chemical laboratory at the Amsterdam school, which was completed in 1891, he moved to Berlin in 1896 as both a university professor and member of the prestigious Prussian Academy of Science.

isomer: molecules with identical compositions but different structural formulas

Shortly before he submitted an only average doctoral thesis in synthetic organic chemistry to the University of Utrecht, the twenty-two-year-old van't Hoff had printed and distributed a twelve-page pamphlet at his own expense that, although ignored for many years, essentially outlined the foundation of modern stereochemistry. Inspired by the earlier ideas of the German chemist Johannes Wislicenus to extend chemical structure theory from constitutional chemical formulas to representations in three-dimensional space, van't Hoff suggested a structural distinction between optical **isomers** that had been represented up until that time by the same formula. By screening known substances for optical activity (i.e., the rotation of the plane of polarized light), he found that all their constitutional formulas contained at least one carbon atom that combined with four different atomic groups. If the latter were placed at the corners of a tetrahedron in three-dimensional space, with the carbon atom at its center, there were exactly two possible tetrahedra with asymmetric carbon atoms, each being the mirror image of the other, that could account for the pairs of optical isomers. This structural theory was further supported by his observation that for every known chemical transformation where the optical activity of a reactant disappeared, there was no more asymmetric carbon atom in the structural representation of the reaction product. Independently and virtually simultaneously, Le Bel arrived at the same theory in Paris.

Due to his early interest in philosophy, particularly the ideas of French philosopher Auguste Comte, van't Hoff's chemical research strove for general and theoretical insight into chemistry and thus gradually shifted from organic to physical chemistry. In 1884 he published his well-known *Études de dynamique chimique* (Studies in chemical dynamics); it contained many important ideas on chemical kinetics and thermodynamics that confirm van't Hoff's status as a true pioneer in the field. Based on numerous measurements of organic reaction rates, he classified chemical reactions according to different orders and molecularities and formulated the temperature dependence of reaction rates, now known as the "Arrhenius equation." Following through on earlier ideas, he interpreted chemical equilibria as dynamic states where backward and forward reaction rates were equal, which he represented by a double arrow. He further formulated the temperature dependence of the **equilibrium** constant, known as the "van't Hoff isochore," and suggested what later came to be known as "Le Chatelier's principle." Most important, he established the foundation of chemical thermodynamics by expressing the relationship between what is now called the free energy of a reaction and its equilibrium constant.

equilibrium: condition in which two opposite reactions are occurring at the same speed, so that concentrations of products and reactants do not change

During the late 1880s van't Hoff turned the seemingly exotic phenomenon of osmotic pressure into a crucial part of the new physical chemistry of solutions. He discovered that the osmotic pressure π increased with the concentration of the solute, $c = n/V$, and the absolute temperature T according to the equation

$$\pi = \frac{nRT}{V}$$

which is equivalent to the ideal gas law if one replaces the osmotic pressure, π, with the gas pressure, p:

$$p = \frac{nRT}{V}$$

with R being the gas constant in both cases. The surprising correspondence between the two suggested that the osmotic pressure depended only on the number of solute molecules and not their chemical nature, like other so-called colligative properties such as vapor pressure lowering and freezing point depression. Van't Hoff did not simply advance all these phenomena on a common thermodynamic basis; he also successfully explained apparent anomalies with the Arrhenius theory of electrolytic dissociation.

In his later years, van't Hoff applied chemical thermodynamics to the formation of marine salt deposits, which made him one of the pioneers in the science of petrology. SEE ALSO THERMODYNAMICS.

Joachim Schummer

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Vasoconstrictors ***See Norepinephrine.***

Venom

It may be tempting to equate the concept of venom with poison, but to do so would be inaccurate. Many plants, for example, are poisonous but present no harm to humans because they have learned not to eat them. By contrast, one can be quite careful on a walk through the southwestern United States or Australian outback and still have an unfortunate accident involving the venom of a snake. In any given year, around 40,000 people die as a result of snakebites. To be more accurate with the definition of venom, therefore, it must be noted that venom is not just a poison, but one that is injected under the skin of the victim.

Snakes are not the only animals that use venom. Spiders, scorpions, bees, and wasps are also venomous animals. The specific venom used by these animals varies not only with its type (spider venom is different from bee venom, for example), but also within a species. Thus, some spiders are venomous but not actually a threat to adult humans, whereas the bite of other spiders is lethal unless treated with appropriate medicines.

The differences in venoms have important medical implications, but there are also similarities among many venoms. Most are rather complicated mixtures of chemicals, each of which plays some role in the action that the venom takes. Many involve some mechanism designed to immobilize the victim and are therefore targeted at nerve cells that control muscles.

Thus, snake venoms typically contain neurotoxins, but they also often include **enzymes** that promote various hydrolysis reactions. The neurotoxins carry out the task of immobilizing the victim by interrupting the ability

enzyme: protein that controls a reaction in a cell

The gila monster is a venemous animal. Venom is a poison injected under the skin.

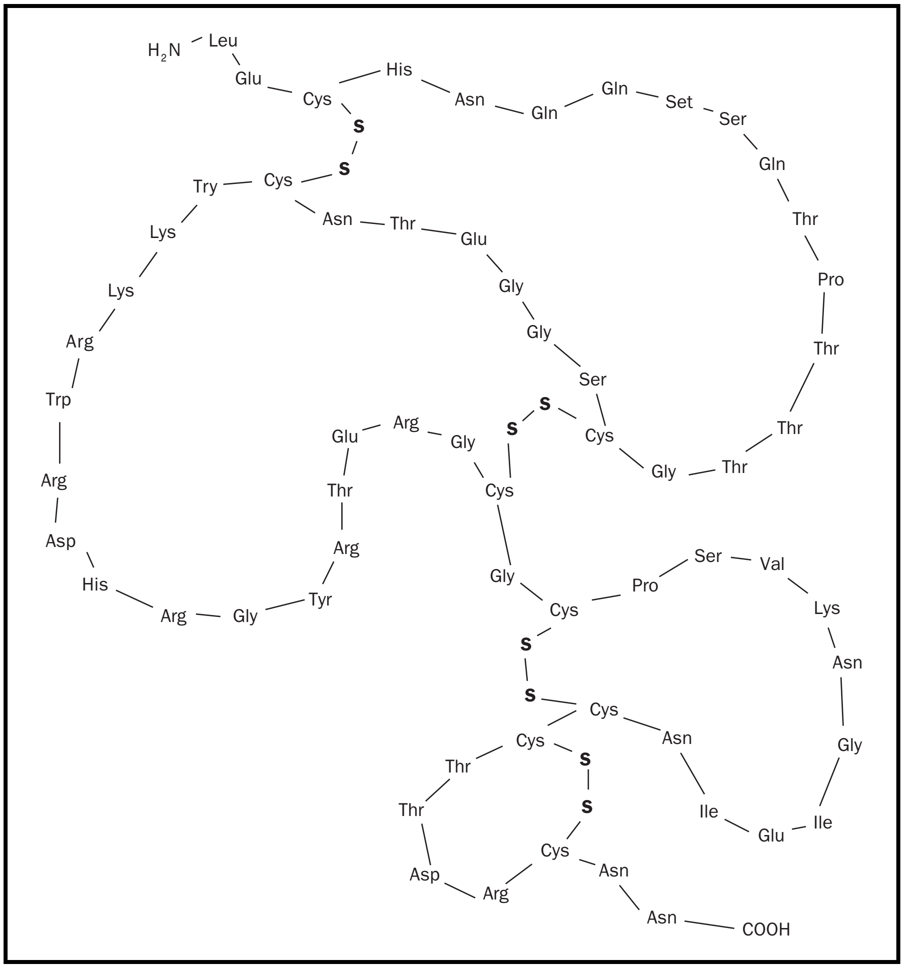

Figure 1. Primary structure of cobrotoxin.

of the nerve cells to stimulate muscle movement. Hydrolysis helps make the tissues of the victim easier for the snake to digest if it is eaten. These hydrolytic enzymes may include molecules capable of breaking down collagen and phospholipids as well as other enzymes.

For many who study the chemistry of venoms, the neurotoxins hold particular interest. One example would be the **polypeptide toxin cobrotoxin** that was isolated from the Formosan cobra and analyzed in 1965 by Chen-Chung Yang, a distinguished chair professor at Tsing Hua University in Taiwan. The primary structure of this neurotoxin is indicated in Figure 1, along with some components of its secondary structure. There are sixty-two residues in the primary structure and four di-sulfide bonds in the secondary structure. If even one of these di-sulfide bonds is somehow disrupted, the polypeptide is rendered nontoxic. This points to the fact that secondary structure is important even in small polypeptides, not only full-size proteins.

polypeptide: compound containing two or more amide units—C(O)NH—produced by the condensation of two or more amino acids

toxin: poisonous substance produced during bacterial growth

cobrotoxin: polypeptide toxin containing 62 residues that is found in the venom of cobras

The action of cobrotoxin arises from its ability to bind strongly to the **receptors** in postsynaptic neurons. In order for one nerve cell to signal a neighbor, it releases neurotransmitters that diffuse across a small gap called the synapse. The nerve on the other side of the synapse (the **postsynaptic neuron**) has proteins that are specifically geared to sense the presence of these neurotransmitters. If these receptors are blocked, the signal is not passed on, and the nerve cell function is disrupted. Cobrotoxin is able to

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

postsynaptic neuron: receptor nerve cell

acetylcholine: neurotransmitter with the chemical forumula $C_7H_{17}NO_3$; it assists in communication between nerve cells in the brain and central nervous system

disrupt a specific type of receptor that is sensitive to **acetylcholine**. Once this polypeptide binds to the receptor, it is not released, so the nerve cell loses its ability to signal and the muscles it is supposed to trigger do not function. If the muscle that stops working is the diaphragm, the animal will not be able to breathe and it essentially suffocates. Cobrotoxin is very toxic, with an LD_{50} of 65 nanograms per kilogram in mice. SEE ALSO GLOBULAR PROTEIN; NEUROTOXIN; PROTEINS; TOXICITY.

Thomas A. Holme

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Vitamins ***See Ascorbic Acid; Cholecalciferol; Retinol; Riboflavin; Thiamin.***

Volta, Alessandro

ITALIAN PHYSICIST
1745–1827

Until the late 1700s static electricity was the only known form of electricity. Alessandro Volta, born in Como, Italy, is best known for discovering current electricity and for developing the voltaic pile, which became an invaluable tool in electrochemistry.

Volta was interested in electricity early in his career. He published his first book on static electricity at the age of twenty-four. In 1775, Volta announced the discovery of the electrophorus, a new sort of instrument that could store static electricity. And in 1782, Volta invented another instrument, the condensing electroscope that was an extremely sensitive measuring device capable of detecting the existence of negative charge in water vapor and in the smoke of burning coals.

By this time, Volta was a professor at the University of Pavia in Italy, where he was to teach for forty years. He had a very good reputation among chemists and scientists throughout Europe. Among his correspondents was Luigi Galvani (1737–1798), a fellow Italian scientist. Galvani sent Volta a copy of a pamphlet he had written detailing his latest experiments in 1792. Galvani reported that when a partially dissected frog came into contact with two different **metals** that were grounded, its muscles flexed and legs twitched. He further reported that there was a relationship between the muscular **contraction** and the electrical stimulus, which he believed to be proof of the existence of "animal electricity."

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

contraction: the shortening and thickening of a functioning muscle or muscle fiber

Volta at first accepted Galvani's explanation of animal electricity as the reason for the frog's involuntary movements. But after carefully repeating Galvani's experiments, Volta became convinced that the contractions of the frog's legs did not result from animal electricity but were due to some external electricity caused by the two different metals in an arc coming into contact with the moist frog. He believed that the frog merely assumed the role of a simple and sensitive electroscope.

Italian physicist Alessandro Volta, who discovered current electricity.

In addition to repeating Galvani's experiments, Volta noticed some other effects involving dissimilar metals when they come into contact with moist substances. He found that if two different metals touched the tongue and were brought into contact, a bitter taste resulted. And when two metals touched the eye, contact between them created the sensation of light. After all these experiments, Volta was soon convinced that the metals not only served as conductors but also generated electricity when they were brought into contact.

By 1794 Volta had completely abandoned Galvani's theories of animal electricity. Instead, he advanced the notion of "metallic electricity" or, in modern terms, current electricity. Through further experimentation, he noticed that the electrical effects between select dissimilar substances became stronger the farther apart they were from one another in the following series: tin, lead, iron, copper, platinum, gold, silver, graphite, and charcoal. Volta also determined that an electrical force was generated when a metal was in contact with a fluid. By putting together these two findings, Volta created the first battery.

Volta found that a current was produced when two different metal disks such as silver and zinc were separated by a moist conductor, such as paper soaked in salt water, and brought into contact by a wire. By stacking a collection of silver-moist paper-zinc units, in effect forming a pile, Volta determined that the current intensified. If someone touched the top of such a "voltaic pile" (as this early battery was called) and put his or her other hand in a dish of salt water that was connected to the bottom metal disk by a strip of metal, that person would feel a continuous, if weak, shock.

potash: the compound potassium oxide, K_2O

Volta made his discovery of the current electricity–generating voltaic pile known to the scientific community by 1800. His invention gave rise to new fields of scientific inquiry, including electrochemistry, electromagnetism, and the modern applications of electricity. The first chemists to use the voltaic pile were William Nicholson and Anthony Carlisle, who built a pile and used it to decompose water. Humphry Davy (1778–1829) used the voltaic pile to decompose many substances, such as **potash** and soda. Davy was also able to isolate for the first time several elements, including calcium and magnesium, using the voltaic pile.

The voltaic pile also had applications in other fields of science. William Cruikshank discovered the process of electroplating while working with a voltaic pile. Davy constructed the first crude electric light with the pile in 1820. see also Davy, Humphry; Electrochemistry; Zinc.

Lydia S. Scratch

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Waksman, Selman Abraham

RUSSIAN MICROBIOLOGIST
1888–1973

streptomycin: antibiotic produced by soil bacteria of genus *Streptomyces*

Selman Waksman changed the course of medical history while investigating how soil microbes defended themselves against invaders. He and coworkers isolated twenty-two new defensive compounds produced by soil microbes and in the process discovered **streptomycin**, the first antibiotic effective against tuberculosis. For his discovery of streptomycin, Waksman received the 1952 Nobel Prize in physiology or medicine.

Selman Abraham Waksman was born on July 22, 1888, in Priluka, near Kiev, Russia (now the Ukraine). After graduating from the Fifth Gymnasium in Odessa, Russia, in 1910, Waksman immediately immigrated to the United States. In 1911 he enrolled at Rutgers University, where he received a B.S. in 1915 and an M.S. in 1916, both in agriculture. While at Rutgers, Waksman worked with Jacob G. Lipman, another Russian immigrant, whose primary research interest was soil microbiology. After receiving his Ph.D. in biochemistry from the University of California, Berkeley, in 1918, Waks-

American biochemist Selman Waksman, recipient of the 1952 Nobel Prize in physiology or medicine for his discovery of streptomycin.

man returned to New Jersey to begin work as a microbiologist and as a part-time instructor at Rutgers. He was appointed professor of soil microbiology at Rutgers in 1930, a position he held until his retirement in 1958. He also established a lab to study marine microbiology at the Woods Hole Oceanographic Institute in Woods Hole, Massachusetts, in 1931.

Although Waksman was involved in many areas of soil microbiology, it was his interest and expertise in the life-and-death struggles between soil microbes that eventually led to a cure for tuberculosis. In 1932 the American National Association against Tuberculosis asked Waksman to investigate earlier reports that the tubercle bacillus, or the bacteria that cause tuberculosis, was rapidly destroyed in soil. Waksman confirmed those reports and concluded that the tubercle bacillus was probably killed by other bacteria present in the soil. He proposed that the soil bacteria defended themselves by producing an unknown substance that destroyed the tubercle bacillus. He also coined the term “antibiotic” for substances produced by one microorganism that suppress the growth of another.

screen: process of comparing multiple reagents simultaneously to provide information on reaction of one reagent with another

Waksman and his collaborators grew a batch of a soil microorganism called *Actinomyces griseus* and isolated their first antibiotic from the brew in 1940. They called it actinomycin, after the species of microorganism from which it was isolated. In 1942 they isolated streptothricin. Like actinomycin, it was too toxic to use in humans, but unlike actinomycin, it destroyed the tubercle bacillus. Encouraged by these discoveries, Waksman continued to test, or **screen**, other soil microbes for their ability to produce antibiotics with activity against the bacteria that caused tuberculosis (now known as *Mycobacterium tuberculosis*).

Waksman and his colleagues screened more than 10,000 different soil microbes before they isolated streptomycin in 1943. Streptomycin was what they were looking for: It destroyed the tubercle bacillus and was safe enough to test in humans. Subsequent clinical trials proved that streptomycin cured several types of tuberculosis and that it was safe enough to prescribe for a variety of gram-negative bacterial infections. Even after sixty years, streptomycin continues to be used in the battle against tuberculosis and other life-threatening infections.

Waksman died on August 16, 1973, and is buried in a churchyard in Woods Hole, Massachusetts. SEE ALSO ANTIOBIOTICS.

Thomas M. Zydowsky

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Water

If a person knows nothing else about chemistry, he or she will likely know that water is H_2O. The chemical formula for water is common knowledge, used in advertisements, elementary school science classes, and casual conversation. But more than just a conversation piece, the formula H_2O can tell a chemist a great deal of information.

For starters, H_2O indicates that water is composed of two hydrogen atoms and one oxygen atom. That this is so can be demonstrated using very simple apparatus—a couple of pieces of wire, a battery, and some tap water. Electrolysis—the decomposition of water molecules with electricity—will result when the wires are connected to the ends of the battery and the other ends are immersed in the water with a small gap between them. One electrode releases bubbles of pure oxygen and the other pure hydrogen. Measuring the volume of gases released reveals that twice as much hydrogen is produced as oxygen. Twice as much gas means two hydrogen atoms for every one oxygen atom. Of course, this is our modern understanding of water. When these experiments were first tried, around 1800, an explanation for the results was not available. But the experiments did force scientists to think about the nature of water.

From our modern understanding of both the formula of water and the Periodic Table, we also know that the hydrogen atoms in water are bound to the oxygen. That is, water is "HOH" and not "HHO." We know that atoms can form either covalent or ionic bonds to give molecules. In water, the interaction of hydrogen and oxygen is a polar covalent bond, meaning that the two elements share a pair of electrons and that each atom contributes one of the electrons in the pair. Since hydrogen is the first element of the Periodic Table, it has only one electron and can form just one covalent bonding interaction. In the case of water, hydrogen bonds by sharing its electron with the oxygen. If hydrogen shared its electron with the other hydrogen atom in this instance, there would be no electron available to interact with the oxygen. Indeed, hydrogen gas, H_2, results when two hydrogen atoms form a covalent bond, and hydrogen gas is very different from water.

A molecular graphic of water molecules evaporating from a solution.

In a pure (nonpolar) covalent bond, both atoms have possession of the electron pair exactly the same amount of time. In a polar covalent bond, there is unequal sharing that results from an inequity in the distribution of the electrons due to the effective nuclear charge on the atoms. This polarization of the O-H interaction is critical to explaining all of the properties of water. It results in water having a dipole with the hydrogens having a slight positive charge and the oxygen having a slight negative charge. (More precisely, the advanced explanation is that the molecular orbital that describes the oxygen-hydrogen interaction has more oxygen character, resulting in a skewed electron distribution.)

If we consider oxygen's position in the Periodic Table, we know that it starts with six valence electrons, and since it has two bonds with hydrogen, two of its electrons are involved in bonding pairs. This means that the oxygen has four electrons remaining. These electrons are organized into two "non-bonding" pairs. That is, the oxygen of water has four pairs of electrons around it—two that are interacting in polar covalent bonds with hydrogen and two that are not interacting when water is in the gaseous state. Four electron pairs means that the atoms adopt a tetrahedral arrangement with the two hydrogens occupying two corners and the electron pairs occupying the other two.

In a perfect tetrahedron, the angle between the hydrogens would be 109.5°, but because the lone pairs occupy a little more space, the experimentally measured angle in water is actually 104.5°.

The presence of two lone pairs plays a very important role in "hydrogen bonding," which is one of the most critical properties of water. The positively charged hydrogen of one water molecule can be attracted to the lone pair of an adjacent molecule, resulting in a weak hydrogen bonding interaction. This bonding is much weaker than the polar covalent bond that holds a water molecule together, but it is a substantial inter-molecular interaction resulting in two water molecules being attracted to one another. Water forms an extended network of hydrogen bonding interactions, with each water molecule capable of both creating and accepting two hydrogen bonds. As a result each and every water molecule in the liquid or solid state is surrounded by four hydrogen bonded neighbors. The presence of hydrogen bonding interactions means:

- that water has an anomalously high melting and boiling point;
- that solid water or ice is less dense than liquid; and
- that water has a high surface tension.

Melting and Boiling Point of Water

Phase changes in matter result because of a change in the translational motion of molecules. A solid is a solid because its molecules are stuck in place. In a liquid, molecules can move past one another but are still closely associated. In a gas, molecules move independent of one another and only occasionally collide. It would make sense then that lighter molecules would shift from a solid to a liquid to a gas at lower temperatures than heavy molecules because they require less energy to get moving. Consider the molecular substances in Table 1.

Hydrogen gas, being the lightest and smallest molecule in the list, has the lowest melting point (−259°C or 14.15 K or −434°F) and boiling point (−253°C or 20.15 K or −423°F). Similarly, of the second row compounds with hydrogen, methane (CH_4) has the lowest melting and boiling points. However, water does not follow this trend. Its melting point is 0°C or 32°F. Its boiling point is 100°C or 212°F. Compared to the other molecules around it or its heavier cousin, hydrogen sulphide (H_2S), water has melting and boiling points that are anomalously high. This is due to the fact that the hydrogen bonds between water molecules must be broken for a phase transition to occur. The extra energy required results in more heat being necessary and a higher temperature.

Density of Ice

Hydrogen bonding interactions between water molecules hold the molecules in place in the solid state. The O-H···O interaction spaces all of the water molecules in an orderly array, much like students sitting in rows of desks. This spacing provides an open structure. When water is in the liquid state, the water molecules hold on to each other through hydrogen bonding interactions, but individual molecules can occupy the space between rows. The result is that at a molecular level, more liquid water molecules can occupy a given volume than when water is in the solid state. More students will fit in a classroom if they are allowed to stand than if they are arranged in nice neat rows. More molecules or more mass in a given volume means a higher density.

PHASE CHANGES FOR SOME COMMON MOLECULAR SUBSTANCES

Substance	Molecular Weight (g/mol)	Melting Point °C	Boiling Point °C
H_2	2.016	−259	−253
N_2	28.01	−210	−196
O_2	32.00	−218	−183
CH_4	16.04	−182	−162
NH_3	17.03	−78	−33
H_2O	18.02	0	100
HF	20.01	−93	20
H_2S	34.08	−86	−60

SOURCE: Adapted from Jones, Loretta, and Atkins, Peter (1999). *Chemistry: Molecules, Matter, and Change.* New York: W. H. Freeman.

Table 1.

The decrease in density between water and ice has a number of important implications for the world around us. Ice floats because it is less dense than liquid water. This is not true of any other liquid/solid equilibrium. Solid methane sinks in liquid methane and solid ammonia sinks in liquid ammonia. Floating ice means that ponds and lakes freeze from the top down, allowing fish and other biota to live protected from the cold weather of winter. If water froze from the bottom up, life as we know it would not have evolved on Earth.

Surface Tension

Surface tension is a bulk property of matter and results in liquid water trying to contract to the smallest possible surface area for a given volume. Surface tension explains why water beads up on the surface of a freshly waxed car and droplets of water in a fog are spherical. The sphere is the shape with the minimum area for a given volume. Surface tension results because of the asymmetry of forces at the surface of liquid water. Water molecules at the surface are missing their hydrogen bonding interactions on one side. They are being “tugged” back into the bulk of solution.

Of course, occasionally water molecules have sufficient energy to leave the surface, resulting in evaporation. Conversely, sometimes water molecules in the gaseous state strike the surface of a drop of water and have insufficient energy to leave again. The result is condensation. The competing rates of evaporation and condensation lead to the formation of clouds and fog, to cloudy mirrors after a shower and iced-up windows on a winter’s day.

Surface tension is also critical to capillary action. A surface that is covered in suitable molecules or functional groups, such as a glass surface or the cellulose of paper, will interact with water molecules and can actually draw the molecules out of the bulk. In this case, the interaction with the surface is stronger than the hydrogen bonding interaction between adjacent water molecules. As a result, water will creep up a glass tube or adsorb into paper. The latter is critically important in mopping up a spill or mess.

Universal Solvent

Water is often called the “universal solvent,” as it is capable of dissolving a wide range of compounds—from sugars to salt, from DNA to hydrogen. Again, hydrogen bonding interactions play a role. For example, sugar dissolves because of the hydrogen bonding interactions between the hydroxyl groups on the sugar molecules (-OH groups) and the water molecules. But of equal importance to the dissolution of substances in water is water’s capacity to act as a dipole. Water’s negatively charged oxygen binds to sodium ions in salt while the positively charged hydrogens interact with the chloride ions. The result is that sodium chloride or table salt dissolves into ionic species that are more energetically stable with the sodium and chloride ions surrounded by water.

The ability of water to dissolve a wide variety of substances makes it the ideal medium for living organisms. Water’s great solvency is also the reason that water pollution is so pervasive. Almost any substance will dissolve in water, including pesticides, herbicides, industrial waste, household byproducts, and a wide variety of other potentially harmful compounds. Indeed, we rely on the dissolving properties of water to get our clothes clean.

Table 2. Most of the water we use is obtained from rivers and ground water.

Water Source	Water Volume (cubic miles)	Mass (kg)	Percent of Total Water
Oceans	317,000,000	1.335×10^{21}	97.24%
Icecaps, glaciers	7,000,000	2.949×10^{19}	2.14%
Ground water	2,000,000	8.424×10^{18}	0.61%
Fresh-water lakes	30,000	1.264×10^{17}	0.009%
Saline lakes and inland seas	25,000	1.053×10^{17}	0.008%
Soil moisture	16,000	6.740×10^{16}	0.005%
Atmosphere	3,100	1.306×10^{16}	0.001%
Rivers and streams	300	$1{,}264 \times 10^{15}$	0.0001%

SOURCE: Adapted from the U.S. Geological Survey at http://ga.water.usgs.gov/edu/waterdistribution.html.

But the dirt and grime from our clothes must end up somewhere, and that somewhere is in the water that we discharge from our homes. The Law of Conservation of Matter says that matter can be neither created nor destroyed. The atoms and molecules that we dissolve into the water in our washing machines are only being removed to another location.

Dealing with the pollution of water is a huge task, and for too long the philosophy was "the solution to pollution is dilution." Dilution is no longer an acceptable approach, as it just shifts the problem instead of addressing it. Significant effort is being spent in both addressing the real problems of water pollution and in ensuring that we have access to clean water sources. There are many techniques for purifying water, with distillation providing the cleanest and purest water. Unfortunately, distillation requires a lot of energy as it is difficult to overcome the hydrogen bonds between water molecules. Distillation also leaves behind the polluting material, which must be disposed of in a manner that does not allow it to come in contact with water and thus simply dissolve again. The difficulties of maintaining clean water is one of the major challenges facing us in the twenty-first century. For without water, life as we know it would not exist. It is because of the shape and the interactions of that very simple molecule, H_2O, that water is the most essential of all chemical compounds. SEE ALSO Green Chemistry; Molecular Geometry; Valence Bond Theory; Water Pollution; Water Quality.

Todd W. Whitcombe

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Water Pollution

Water pollution occurs when undesirable foreign substances are introduced into natural water. The substances may be chemical or biological in nature. Common pollutants include human or animal waste; disease-producing organisms; radioactive materials; toxic **metals** such as lead or mercury; agricultural chemicals such as pesticides, herbicides, or fertilizers; **acid rain**; and high-temperature water discharged from power plants, often called "thermal pollution." Pollutants in water are dangerous for human or animal consumption and harm crops. High temperatures may cause algae to grow rapidly, rendering water unfit for consumption.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

acid rain: precipitation that has a pH lower than 5.6; term coined by R. A. Smith during the 1870s

Point sources of pollution, such as an oil leak from a pipeline or chemical waste from a factory, can often be controlled. Nonpoint sources, such as runoff sediment and nitrate-rich water from feedlots represent larger amounts of pollution and are difficult to identify and remedy. Pollution from nonpoint sources may pass into streams or aquifers, covering a wide area.

Although water has been identified on several planets, none has as much water as Earth, of which 70 percent is covered with water. Approximately 97.4 percent of the water on Earth is found in oceans and is too salty for human consumption. An additional 2.6 percent is freshwater found in underground bodies of water called aquifers or frozen in glaciers or polar ice caps. Less than 0.02 percent of Earth's water is present in lakes, rivers, or the atmosphere.

In a few places, water is pure enough to drink directly from wells or springs, but increasingly water must be treated to remove dangerous contaminants, and substances such as chlorine, chloramines, or ozone must be added to kill harmful bacteria.

Pollutants in water are commonly measured and reported as parts per million (ppm) or parts per billion (ppb). A solution that contains 2 grams (0.071 ounces) of lead in 1 million grams (2,205 pounds) of water (1,000 liters, or 264.2 gallons) is a 2 ppm solution. A 1 ppb solution of calcium contains 1 gram (0.036 ounces) of calcium in 1 billion grams (2,205,000 pounds) of water. A concentration of 1 ppm is the same as 1 milligram (3.6×10^{-5} ounces) per liter.

While it is impractical to remove all impurities from water, the Safe Drinking Water Act, passed by the U.S. Congress in 1974, gives the Environmental Protection Agency (EPA) the authority to set limits for harmful contaminants in water. For each substance, the EPA establishes Maximum Contaminant Level Goals (MCLGs), levels at which the substance can be consumed over a long period of time with no known adverse effects. This level is defined as the amount of impurity that could be present in two liters of water drunk by a person weighing 70 kilograms (154 pounds), each day for seventy years, without ill effects. In addition, the EPA sets Maximum Contaminant Levels (MCLs) of substances for exposure at any single time. A single exposure to concentrations of pollutants below the MCL is considered to be harmless. The MCLG of lead is 0; continuous exposure to lead in any concentration is considered hazardous. The MCL of lead is 0.015 ppm. Both the MCLG and MCL of mercury are set at 0.002 ppm.

Specialized analytical equipment allows technicians to monitor pollutants. In the field, pH meters are used to measure acidity and turbidometers measure the presence of suspended solids. Samples taken to laboratories are analyzed by gas **chromatography** to determine the presence of organic

chromatography: the separation of the components of a mixture in one phase (the mobile phase) by passing it through another phase (the stationary phase) making use of the extent to which the components are absorbed by the stationary phase

These fish were killed as a result of living in polluted water.

spectroscopy: use of electromagnetic radiation to analyze the chemical composition of materials

heavy metal: by convention, a metal with a density greater than 5 g/cm^3; 70 elements are thus classified as heavy metals

Industrial Revolution: widespread replacement of hand tools by power-driven machines, beginning about 1750 (especially in England)

compounds such as vinyl chloride, by emission **spectroscopy** to detect **heavy metals**, and by high performance liquid chromatography (HPLC) to detect pesticide residues. Such instruments are capable of detecting as little as one part per trillion of pollutants in water.

For much of history, humans used waterways and bodies of water as waste dumps. When the human population was low, fewer people were exposed to the effects of pollution, and the sources were fewer and produced less pollution. During the **Industrial Revolution** of the nineteenth century, water pollution was recognized as a danger to public health.

Even early settlers were concerned with water quality. Two hundred years before laws were written to protect consumers from lead poisoning, Benjamin Franklin wrote of a family that suffered gastrointestinal pains after drinking water collected from their lead roof. During the trek west, members of wagon trains avoided drinking from stagnant pools, some of which contained large amounts of alkali.

As populations and production grew, industrial and household refuse accumulated, and it became clear that many discarded materials did not simply disappear, but were spread through the water table, absorbed by lower forms of life and passed up the food chain, causing deaths, birth defects, and mental problems. Now, many beaches are closed occasionally or permanently due to pollution, and at a time when populations of fish have decreased, many areas are unsafe for fishing. Water pollution represents an especially dangerous problem in developing nations, which have high populations and manufacturing facilities that do not meet safety standards.

The most dangerous forms of water pollutants include sewage, which frequently contains dangerous pathogenic organisms; oil and hydrocarbons;

heavy metals; radioactive substances; pesticides and herbicides; and corrosive substances such as acids and bases.

In developed countries, few direct sources of water pollution should exist, but homeowners still discharge motor oil, antifreeze, pet waste, and paint into storm sewers, and small manufacturers sometimes ignore proper disposal procedures. In developing countries, businesses and households often discharge wastes directly into streams or ponds that are also used for water supplies. Many sources contaminate water supplies indirectly. Indirect sources of pollution include runoff of waste from feedlots or runoff of agricultural chemicals from farmlands; leaking oil from pipelines, wells, or platforms; and large amounts of sediment from streets and parking lots.

Most industrial operations are required to treat wastewater before discharging it into rivers. Wastes from feedlots are collected in lagoons, settled, collected, and used for fertilizer. Heavy metals and organic compounds from industry are often reclaimed from wastewater and recycled, decreasing manufacturing costs. Sewage from homes undergoes at least two stages of treatment. Primary treatment consists of sedimentation and dyeing of solids, which may be used as fertilizer. Secondary treatment consists of aeration of the remaining liquid, through a process of stirring, trickling over filters, and spraying; aerobic bacteria oxidize much of the remaining organic matter. Tertiary treatment, using antibacterial agents such as chlorine or ozone, may be used to produce effluent water that is safe for further use. SEE ALSO NEUROTOXINS; TOXICITY; WATER; WATER QUALITY.

Dan M. Sullivan

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Water Quality

Next to a supply of air, nothing is so essential to life as a supply of high-quality water. We drink it, cook our food in it, use it as a source of energy, and lift a hundred pounds or so of it each time we stand up. Water carries nutrients in and removes waste materials from our bodies. Contaminated water also spreads numerous diseases.

We judge the quality of water by taste, smell, color, and lack of pathogenic organisms or harmful contaminants. Often bad taste, odor, or color indicates contamination. Most of the water we drink has been treated to remove harmful substances and has had chlorine, ozone, or chloramines added to kill bacteria. Ordinary water contains dissolved gases such as oxygen, nitrogen, carbon dioxide, and other atmospheric components, as well as harmless minerals.

Pollutants are usually present at very low concentrations, commonly measured and reported as parts per million (ppm) or parts per billion (ppb). A solution containing 2 grams (0.071 ounces) of lead in 1 million grams of water (1,000 liters, or 264.2 gallons) is a 2 ppm solution of lead in water. A

1 ppb solution of calcium in water contains 1 gram (0.036 ounces) of calcium in 1 billion grams (2,205,000 pounds) of water. A concentration of 1 ppm is the same as 1 milligram (3.6×10^{-5} ounces) per liter.

It would be impractical and expensive to remove all impurities from water. The Safe Drinking Water Act of 1974 gives the Environmental Protection Agency (EPA) authority to set limits for dangerous contaminants. For each substance, the EPA sets Maximum Contaminant Level Goals (MCLGs), levels at which the substance could be consumed over a long period of time with no known adverse effects. The MCLG is the amount of contaminant that can safely be present in two liters of water drunk each day for seventy years by a person weighing 70 kilograms (154 pounds). In addition, the EPA sets Maximum Contaminant Levels (MCLs), the maximum permissible level of a contaminant in drinking water.

Removing all pollutants from water would be difficult and expensive, but concentrations below the MCL and MCLG are considered harmless. Lead damages kidneys, and chronic exposure to even tiny amounts may cause damage to the nervous system. The MCLG of lead is 0; the EPA maintains that no amount of lead should be consumed for an extended time. The MCL of lead is 0.015 ppm, but consumption of even low levels of lead in water is not recommended. Both the MCLG and MCL of mercury are set at 0.002 ppm.

Technicians use specialized analytical equipment to monitor pollutants. In the field, pH meters are used to measure acidity; very acidic or basic water may be corrosive. Turbidometers measure suspended solids, which may be harmless but often carry or hide pathogenic organisms. In laboratories, samples are subjected to gas **chromatography** to determine the presence of organic compounds such as vinyl chloride, high pressure liquid chromatographs measure pesticide traces, and absorption and emission **spectroscopy** are used to detect **heavy metals**. Such instruments are capable of detecting as little as one part per trillion of pollutants.

chromatography: the separation of the components of a mixture in one phase (the mobile phase) by passing it through another phase (the stationary phase) making use of the extent to which the components are absorbed by the stationary phase

spectroscopy: use of electromagnetic radiation to analyze the chemical composition of materials

heavy metal: by convention, a metal with a density greater than 5 g/cm^3; 70 elements are thus classified as heavy metals

Biological tests are also commonly performed on drinking water. Biochemical oxidative demand (BOD) is a measure of the concentration of biodegradable organic matter. While coliform bacteria such as *Eschericia coli* are seldom dangerous themselves, they act as indicator bacteria. Water containing coliforms is likely to contain other, more dangerous pathogens.

The acceptable level of pollutants depends on the use intended. We need not flush toilets or water lawns with water pure enough to drink. River water commonly contains traces of animal wastes that are acceptable for irrigation but must be removed before human consumption. Ocean water too salty for consumption can be used for industrial cooling and may be purified by distillation or reverse osmosis to render it suitable for drinking.

Common pollutants include traces of human or animal waste; disease organisms; radioactive materials; toxic **metals** such as lead or mercury; agricultural chemicals such as pesticides, herbicides, or fertilizers; and high-temperature water discharged from industrial plants. Polluted water may be dangerous to drink, may harm crops, and may cause eutrophication.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Metals such as lead, cadmium, chromium, and mercury are toxic even at low concentrations (the MCL for cadmium is 0.005 ppm). Aquatic microorganisms often concentrate toxic materials from soil or water and may

Newly treated water in the Orange County Water Treatment Works, Florida.

convert inorganic substances such as mercury to organic forms such as methylmercury. These organisms may be consumed by fish, which in turn are eaten by animals higher on the food chain, and eventually the toxic materials can find their way into human diets. Organic mercury is sometimes absorbed by the central nervous system. Mercurial wastes discharged into the bay at Minimata, Japan, resulted in birth defects and **neurological** disorders among many children. Even small amounts of lead or mercury may be converted by aquatic microorganisms into toxic organic mercury compounds such as methyl- or dimethylmercury, which, acting as neurotoxins, may be passed up the food chain, eventually causing damage to the central nervous system of humans.

neurologic: of or pertaining to the nervous system

Lead and copper ions in water pose health risks and contribute to the corrosion of pipes and fittings, as does water that is at a high or low pH. Lead solder was banned from pipes in 1986, but much old plumbing still contains a mixture of 50 percent lead and 50 percent tin solder in joints. In plumbing systems having pipes and fittings of two different metals, corrosion may lead to the failure of joints.

Hot water discharged by industries, such as at power plants, and nitrates and phosphates from feedlot runoff cause algae to grow rapidly, rendering water unfit for consumption by humans or farm animals. High-BOD organic matter in sewage, feedlot runoff, or excess fertilizer from farm fields accumulates in ponds and lakes. Oxidative processes then consume so much oxygen that fish and aquatic plants die.

Organic contaminants such as vinyl chloride or hydrocarbons, hormones from animal feed, and pesticides and herbicides often find their way into streams or aquifers. From these sources, the contaminants may make their way into water supplies.

Hard water contains metallic ions, such as magnesium or calcium ions, that interact with soap to form insoluble films or scum. Hardness is not hazardous to health but may form scale in boilers and clog water pipes. Excess calcium and magnesium can be removed by ion exchange water softeners. SEE ALSO GREEN CHEMISTRY; NEUROTOXINS; TOXICITY; WATER; WATER POLLUTION.

Dan M. Sullivan

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Watson, James Dewey

AMERICAN BIOCHEMIST
1928–

The American biochemist James Dewey Watson was a discoverer of the double-**helical** structure of the deoxyribonucleic acid molecule.

helical: in the form of a helix—a spiral or coil, such as a corkscrew

James D. Watson was born April 6, 1928, in Chicago, Illinois. At age fifteen he entered the University of Chicago. He graduated in 1947 and went on to pursue graduate study in the biological sciences at Indiana University. There he came under the influence of some distinguished scientists, including Nobel laureate Hermann J. Muller, who were instrumental in shifting his interests from natural history toward genetics and biochemistry. In 1950 Watson successfully completed his doctoral research project on the effect of x rays upon the multiplication of **bacteriophages**.

bacteriophages: viruses that attack bacterial cells

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

Watson spent 1950 and 1951 as a National Research Council fellow in Copenhagen doing postdoctoral work with biochemist Herman Kalckar. Watson had hoped to learn more about the biochemistry of the genetic material deoxyribonucleic acid (**DNA**). These studies proved unproductive. It was not until the spring of 1951, when he heard the English biophysicist

Maurice Wilkins speak in Naples on the structure of the DNA molecule, that Watson enthusiastically turned his full attention to the DNA problem.

Watson's next research post at Cavendish Laboratory, Cambridge, England, brought him into contact with the physicist turned biologist Francis Crick. Together they shared an interest in DNA. Thus began the partnership between Watson and Crick that resulted in their joint proposal of the double-helical model of the DNA in 1953. Watson, Crick, and Wilkins shared the 1962 Nobel Prize in physiology or medicine for their DNA studies.

The structure of the giant and complex DNA molecule reveals the physical and chemical basis of heredity. Watson and Crick were convinced that the molecular subunits which made up DNA were arranged in a relatively simple pattern that could be discovered by them. Their mode of operation stressed the conception and construction of large-scale models that would account for the known chemical and physical properties of DNA. To this model-building endeavor Watson contributed the double-helical structure, along with other fruitful, intuitive suggestions, while Crick provided the necessary mathematical and theoretical knowledge. After their work on DNA was completed, Watson and Crick collaborated again in 1957, this time in clarifying the structure of viruses.

American biochemist James Dewey Watson, corecipient, with Francis Harry Compton Crick and Maurice Hugh Frederick Wilkins, of the 1962 Nobel Prize in physiology or medicine, "for their discoveries concerning the molecular structure of nucleic acids and its significance for information transfer in living material."

After a two-year stay at the California Institute of Technology, Watson accepted a position as professor of biology at Harvard University in 1956 and remained on the faculty until 1976. In 1968 he became the director of the Cold Spring Biological Laboratories but retained his research and teaching position at Harvard. That same year he published The Double Helix, revealing the human story behind the discovery of the DNA structure, including the rivalries and deceits that were practiced by all.

In l989 Watson was appointed the director of the Human Genome Project of the National Institutes of Health. He resigned in 1992 in protest over policy differences in the operation of this massive project. He continued to speak out on various issues concerning scientific research and upheld his strong presence concerning federal policies in supporting research. In addition to sharing the Nobel Prize, Watson received numerous honorary degrees from institutions, including one from the University of Chicago (1961) when Watson was still in his early thirties. He was also awarded the Presidential Medal of Freedom in 1977 by President Jimmy Carter. On July 4, 2000, Watson and Crick were awarded the Philadelphia Liberty Medal. The Liberty Medal was established in 1988 to honor individuals or organizations whose actions represent the founding principles of the United States.

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FRANCIS CRICK (1916–)

Starting in his childhood in England, Francis Crick developed a fascination with science. After his collaborative work on DNA with James Watson, for which the two received a Nobel Prize, Crick unraveled the mystery of how DNA bases code for the primary sequence of a protein, and in 1957 he introduced its central dogma. Since 1976 Crick has been studying the functions of the human brain.

—Valerie Borek

Weizmann, Chaim

RUSSIAN-BORN BRITISH CHEMIST, PRESIDENT OF ISRAEL
1874–1952

One of the few who have achieved success in two disparate fields, chemist and statesman Chaim Weizmann was born on November 17, 1874, in the small town of Motol, Russia—part of what was known as the Pale of Settlement, an area where Jewish families were allowed to live. Beginning at age four he attended a religious school in which classes were conducted in Yiddish. (He did not learn Russian until he was eleven.) In 1885 he migrated to Pinsk to attend a Russian high school, where he studied chemistry and devoted much of his spare time to Zionist activities. He later became president of the World Zionist Organization (from 1921), president of the Hebrew University in Palestine (from 1932), and the first president, a largely ceremonial position, of the new State of Israel (from its establishment in 1948 until his death).

After university studies in Germany and Switzerland (he earned a Ph.D. in 1899 for research on dyestuffs), he taught as a privatdocent (unsalaried lecturer) at the University of Geneva. He subsequently carried out basic and applied research at the University of Manchester in England. His academic research was supplemented by industrial research. In 1904 he was awarded the first of his 110 patents. He became a British citizen in 1910.

glucose: common hexose monosaccharide; monomer of starch and cellulose; also called grape sugar, blood sugar, or dextrose

During World War I, a search for synthetic rubber in England led to Weizmann's classic work on the fermentation of **glucose**, a sugar containing six carbon atoms, as a source of acetone (1915), urgently needed by the British government for the manufacture of cordite (smokeless powder). Weizmann's use of a fermenting agent to produce acetone followed his discovery of the acid-resistant microorganism *Clostridium acetobutylicum*; this method of acetone production became known as the Weizmann process. At the request of Winston Churchill, then first lord of the admiralty, the Weizmann process was put into operation on an enormous scale in England, Canada, and the United States. The rapid wartime expansion of this process (from a laboratory to an industrial scale) was not only unique among microbiological processes used in industry, but was also the forerunner of the rapid expansion of penicillin production during World War II, as well as of the breadth of operations of many of today's biotechnological processes.

Weizmann knew that his fermentation process yielded chemical compounds containing three and four carbon atoms and predicted that the same process could produce the substances on which modern petrochemical industries are based. He often enunciated the need for countries (especially those poor in natural oil) to replace a petroleum-based chemical industry with one based on fermentation.

The Balfour Declaration (1917), the first formal international recognition of Zionism, was, to some extent, a culmination of Weizmann's scientific and political efforts. His fermentation process, which contributed to the Allies' victory in World War I, was not a direct cause of the declaration but was certainly an indirect one.

During the two decades following World War I, politics replaced chemistry as Weizmann's main pursuit. However, he did pursue scientific research, alongside his political activities, until the end of his life. In his later years (and while president of Israel), he worked at the Weizmann Institute of Science in Rehovot, Israel, where he died on November 9, 1952. In Israel his grave is a place of national pilgrimage. SEE ALSO Starch.

George B. Kauffman

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Werner, Alfred

FRENCH-BORN SWISS CHEMIST
1866–1919

Alfred Werner, the founder of **coordination chemistry**, was born on December 12, 1866, in Mulhouse, Alsace, France (in 1870 annexed to Germany). He was the fourth and last child of Jean-Adam Werner, a foundry worker and locksmith, and his second wife, Salomé Jeanette Tesché, the dominant figure in the Werner household and a member of the wealthy Tesché family. Although most of Werner's articles were published in the German language and in German journals, his cultural and political sympathies remained with France. The spirit of rebellion and resistance to authority that characterized his childhood and adolescence may have contributed to the development of his revolutionary coordination theory.

Swiss chemist Alfred Werner, recipient of the 1913 Nobel Prize in chemistry, "in recognition of his work on the linkage of atoms in molecules by which he has thrown new light on earlier investigations and opened up new fields of research especially in inorganic chemistry."

coordination chemistry: chemistry involving complexes of metal ions surrounded by covalently bonded ligands

Werner attended the École Libre des Frères (1872–1878), and then the École Professionelle (1878–1885), a technical school where he studied chemistry. During his compulsory year of military service in the German army (1885–1886), he audited chemistry lectures at the Technische Hochschule (Technical University) in Karlsruhe. He then attended the Eidgenössisches Polytechnikum, now the Eidgenössische Technische Hochschule (Federal Polytechnic University), in Zurich, Switzerland, from which he received a degree in technical chemistry in 1889. He received his Ph.D. from the University of Zurich in 1890.

Between 1890 and 1893, Werner produced the three most important theoretical papers of his career. His doctoral dissertation (1890, cowritten with his teacher Arthur Hantzsch), a true classic of science writing on the topic of stereochemistry, extended Joseph Achille Le Bel and Jacobus Henricus van't Hoff's concept of the tetrahedral carbon compound (1874) to the nitrogen compound. It explained many puzzling paradoxes of geometrically isomeric, trivalent nitrogen compounds and placed nitrogen compound stereochemistry on a firm theoretical basis.

Werner's second theoretical paper (1891)—his Habilitationsschrift (an original article that was a requirement for teaching at a university)—took a stand against August Kekulé, the supreme architect of structural organic chemistry: It replaced Kekulé's focus on rigidly directed valences with a more flexible theory that viewed affinity as a somewhat cloudlike, attractive force emanating from the center of an atom and acting equally in all directions. During the winter of 1891–1892 Werner worked on thermochemical studies at the Collège de France in Paris with Marcellin Berthelot, but then returned to Zurich to become a privatdocent (unsalaried lecturer) at the Polytechnikum.

In 1893, at age twenty-six, Werner was appointed associate professor at the University of Zurich, largely owing to the almost overnight fame that resulted from his third article—the one that set forth his revolutionary, controversial coordination theory (which had occurred to him in a dream). Although his knowledge of inorganic chemistry was limited, he awoke at 2 A.M. with the solution of a long-standing puzzle centered on what were then called "molecular compounds." An enthralling lecturer and gifted researcher, he was promoted to full professor in 1895.

Werner discarded Kekulé's distinction between **"valence"** compounds, which are eminently explainable using classical valence theory, and "molecular compounds," which are not. Werner proposed a new approach in which the configurations of some compounds—**metal**-ammines (now sometimes called "Werner complexes"), double salts, and metal salt hydrates—were logical consequences of their coordination numbers (a new concept) and two types of valence, primary and secondary. For compounds having coordination number six he postulated an **octahedral** configuration; for those having coordination number four he proposed a square planar or tetrahedral configuration.

valence: combining capacity

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

octahedral: relating to a geometric arrangement of six ligands equally distributed around a Lewis acid; literally, eight faces

Werner's "ionogenic and nonionogenic" bonding concepts predated the currently used models of electrostatic and covalent bonding by a full generation. His ideas encompassed almost the entire field of inorganic chemistry and even found application in organic chemistry, analytical chemistry, and physical chemistry, as well as in biochemistry, geochemistry, and mineralogy. He was one of the first scientists to recognize that stereochemistry was not limited to organic chemistry, but is a general phenomenon. His coordination theory exercised an influence over inorganic chemistry comparable to that of the ideas of Kekulé, Archibald Scott Couper, Le Bel, and van't Hoff over organic chemistry.

Although today it is known that electronic configuration is the underlying basis for chemical periodicity and the periodic system, Werner (in 1905), relying only on intuition, his vast knowledge of chemistry, and his recognition of analogies among elements, devised a "long form" of the Periodic Table, in which the **lanthanide** elements (inner transition elements or **"rare earths,"** having atomic numbers 58 through 71), occupied a separate place in the table—a characteristic of all modern tables.

lanthanides: a family of elements (atomic number 57 through 70) from lanthanum to lutetium having from 1 to 14 4f electrons

rare earth elements: older name for the lanthanide series of elements, from lanthanum to lutetium

In 1913 Werner became the first Swiss chemist to win the Nobel Prize in chemistry, the prize given "in recognition of his work on the linkage of atoms in molecules, by which he has thrown fresh light on old problems and opened new fields of research, particularly in inorganic chemistry."

Shortly thereafter, his health was declining. He died in a Zurich psychiatric hospital, on November 15, 1919. He was not only the founder of modern inorganic stereochemistry, but also one of the most brilliantly innovative chemists of all time. SEE ALSO Coordination Compounds.

George B. Kauffman

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Willstätter, Richard Martin

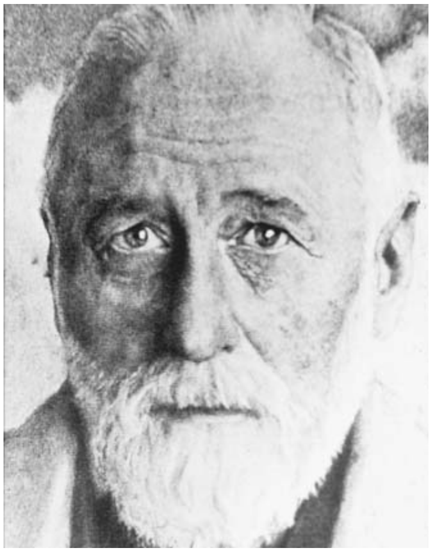
GERMAN CHEMIST
1872–1942

chromatography: the separation of the components of a mixture in one phase (the mobile phase) by passing in through another phase (the stationary phase) making use of the extent to which the components are absorbed by the stationary phase

chlorophyll: active molecules in plants undergoing photosynthesis

As a boy, Willstätter proved to be a gifted student and tried to attend the best schools in Germany. But since he was a Jew, he was denied admission and was forced to attend public school. After graduation he entered the University of Munich, where he established himself in the scientific community.

He studied the structure of cocaine, the subject of his 1894 doctoral thesis, and analyzed and synthesized such similar plant extracts as *atropine* and *tropine*. One of his teachers greatly disapproved of this line of work, and Willstätter soon turned his attention to quinone chemicals, which are the basis for many dyes, including aniline black. After spending several years as a research assistant in Germany, Willstätter joined the teaching staff of the University of Zurich as a professor in 1905. He became intrigued by chlorophyll and other pigments because of their extreme complexity and their intimate role in plant and animal life. To study these pigments, Willstätter revived the technique of **chromatography**, which had been introduced by Mikhail Tsvett (1872–1920) in 1906.



German chemist Richard Martin Willstätter, recipient of the 1915 Nobel Prize in chemistry, "for his researches on plant pigments, especially chlorophyll."

Before Willstätter began studying **chlorophyll**, scientists thought that each different shade of green in plants was created by a unique chlorophyll molecule. Working with the dried leaves from more than two hundred plants, Willstätter showed that there are two major types of chlorophyll found in land plants—the blue-green, or *a type*, and the yellow-green, or *b type*. Willstätter also discovered a similarity between chlorophyll and hemoglobin—the red pigment that carries oxygen through blood. Both chlorophyll and hemoglobin contain a ring-like structure surrounding a single atom, but chlorophyll contains a magnesium atom, while the hemoglobin molecule holds an atom of iron. This discovery was the first clue to magnesium's importance as a plant nutrient. Since then, agricultural fertilizers for magnesium-deficient soils have greatly increased crop yields. Willstätter also studied the chemistry of nongreen plant pigments, which give flowers and fruits their bright colors. As a result of Willstätter's research on plant pigments, he was awarded the Nobel Prize in chemistry in 1915.

In 1911 Willstätter had returned to Germany where his work was interrupted by World War I. His friend Fritz Haber (1868–1934) convinced him to help design an effective gas mask for German troops. In 1916 he succeeded his mentor Adolf von Baeyer as chemistry professor at the University of Munich, where he became interested in **enzymes**, a class of biological **catalysts**. Although he succeeded in obtaining pure enzyme samples, he tried to prove, incorrectly, that enzymes were not proteins.

enzyme: protein that controls the reaction in a cell

catalyst: substance that aids in a reaction while retaining its own chemical identity

In 1925 prejudice again interfered with Willstätter's career. When his university rejected a qualified Jewish scientist for a professorship, Willstätter resigned in protest. Willstätter was offered many industrial and university positions outside of Germany, but he preferred to live in Germany. He was forced into hiding when the Nazis targeted him for arrest. He was caught when he tried to escape to Switzerland, but was turned over to the Swiss authorities. Willstätter died in Switzerland in 1942.

Wöhler, Friedrich

GERMAN CHEMIST
1800–1882

German chemist Friedrich Wöhler, who isolated the element aluminum.

Friedrich Wöhler was born on July 31, 1800, at Eschersheim, near Frankfurt-am-Main, Hesse. The son of a veterinary surgeon, young Wöhler attended public schools in Frankfurt and passed exams qualifying him for admission to a university in 1820. During his earlier school years Wöhler had acquired an all-consuming interest in practical chemistry and mineralogy. He chose to study medicine at Heidelberg University and obtained an M.D. degree from that institution in 1823.

As a student at Heidelberg Wöhler attended the chemistry lectures of Leopold Gmelin, and the experience prompted Wöhler to choose chemistry over medicine. On the advice of Gmelin, Wöhler spent a year at the laboratory of Jöns Jakob Berzelius in Stockholm, where he honed his experimenter's skills. Wöhler developed a lifelong friendship with Berzelius and acted as the translator into German of Berzelius's influential *Textbook of Chemistry* (1808–1818, published in six parts over ten years) as well as of his annual reports of new developments in chemistry. Wöhler himself was a prolific writer of textbooks; his organic and inorganic chemistry texts went through thirteen and fifteen editions, respectively, in his lifetime.

Returning to Germany in 1825 Wöhler held positions in technical schools in Berlin and Kassel. In 1832 he was offered the professorship of chemistry of the medical faculty at the University of Göttingen, where he stayed until his death (on September 23, 1882). Wöhler is best known for his **synthesis** of urea and the isolation of aluminum. He is also known

synthesis: combination of starting materials to form a desired product

for his important studies of the elements boron, silicon, beryllium, and titanium.

Wöhler's synthesis of urea was the result of experiments begun in 1823, in which he investigated the salts of cyanic acid, known as cyanates. In 1824 Wöhler showed that the empirical formula of silver cyanate was AgNCO. Justus von Liebig, who had studied the compound silver fulminate, had come up with the same formula for an entirely different compound. (These two compounds were structural **isomers**.) Isomerism was a novel idea at that time, as it was believed that each compound had a unique formula: No two compounds could have the same formula. (Berzelius had first described the phenomenon of isomerism in 1831.)

isomer: molecules with identical compositions but different structural formulas

In 1828 Wöhler attempted to synthesize ammonium cyanate via the treatment of silver cyanate with aqueous ammonium chloride. The reaction produced a white crystalline solid that did not possess the properties of ammonium cyanate. Wöhler then attempted to synthesize ammonium cyanate using lead cyanate and ammonium hydroxide. This produced the same white powder, but with fewer contaminants so that it could be analyzed. Upon analysis this white powder proved to have the composition and properties of urea, a compound that had been isolated from urine.

$$Pb(OCN)_2 + 2\ NH_3 + H_2O \rightarrow PbO + NH_4OCN \rightarrow H_2NCONH_2$$

Wöhler recognized in the urea he had synthesized the phenomenon of isomerism, and, incidentally, that he had prepared an organic compound outside a living system. At that time it was believed that all organic (carbon-based) compounds could be made within living organisms only. Vitalism was a theory that developed as a reaction to mechanistic explanations of physical phenomena, which were viewed as a threat to belief in the unique nature of life. It held that living processes could not be understood according to totally mechanistic models, and that it was a material invisible force in organisms that made life possible. August W. von Hofmann, in his obituary notice for Wöhler, alleged that it was Wöhler's synthesis of urea that led to the demise of the theory of vitalism.

Wöhler's other major achievement was his isolation of the element aluminum in 1827. Attempts by chemists Humphry Davy and Berzelius to prepare aluminum from alumina (Al_2O_3) via electrolytic decomposition had all failed. Wöhler employed a chemical approach that included the reduction of anhydrous aluminum chloride by potassium **amalgam**, followed by treatment with water. It produced a gray powder that Wöhler was able to identify as the element aluminum.

amalgam: metallic alloy of mercury and one or more metals

$$3K + AlCl_3 \rightarrow Al + 3KCl$$

SEE ALSO ALUMINUM; BERZELIUS, JÖNS JAKOB.

Martin D. Saltzman

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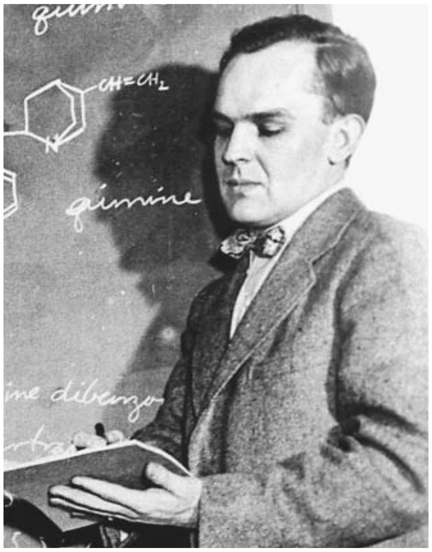
Woodward, Robert Burns

AMERICAN CHEMIST
1917–1979



American chemist Robert Woodward, recipient of the 1965 Nobel Prize in chemistry, "for his outstanding achievements in the art of organic synthesis."

Robert Burns Woodward is generally recognized as the leading organic chemist of the twentieth century. He and his coworkers determined the structures of biologically active natural products, developed theoretical rules for predicting the outcomes of organic reactions, and synthesized some of the most complex molecules known to humans. In 1965 Woodward received the Nobel Prize in chemistry for his "outstanding achievements in the art of organic synthesis."

Woodward was born on April 10, 1917, in Boston, Massachusetts. His father, Arthur Woodward, died of influenza eighteen months later. His mother, Margaret Burns Woodward, remarried, and the family eventually settled in Quincy, Massachusetts. Young Woodward fell in love with chemistry while doing experiments with his boyhood pals in Quincy: He ate, drank, and slept chemistry and dreamed up ways to synthesize the antimalarial drug quinine.

At age sixteen Woodward entered the Massachusetts Institute of Technology (MIT) and raced through their chemistry studies in record time: It took him three years to get his B.S. degree (in 1936), and only one to get his Ph.D. (in 1937). After a summer stint at the University of Illinois, Woodward joined the chemistry department at Harvard University, where, for the next forty-two years, he urged chemists worldwide to accept the creative challenges that organic synthesis had introduced.

Woodward was always attracted to molecules with novel structures or interesting biological activities. He attacked the synthesis of steroids during his years at MIT, and with American chemist Bill Doering in 1944, he published the paper that described the fulfillment of his boyhood dreams: the synthesis of quinine. What Woodward and Doering actually reported was the twenty-step synthesis of a quinotoxine, a molecule whose conversion into quinine had been reported by the German chemist Paul Rabe in 1918. Rabe's reported synthesis of quinine was later discredited, but that in no way diminished the impact of Woodward's beautifully planned synthesis of quinotoxine.

After quinine, Woodward and his coworkers synthesized a series of increasingly complex natural products, such as **reserpine**, **lysergic acid**, **chlorophyll**, **cephalosporin C**, **vitamin B$_{12}$**, and **erythromycin**. Each synthesis had its own unique set of challenges, but Woodward's insistence on careful planning, great attention to detail, and observation shines through in all of them. He took full advantage of the latest advances in organic stereochemistry and reaction mechanisms and pushed for the use of **spectroscopic** and analytical tools to determine the structures of reaction products. Woodward used the same approach to determine the structures of natural (plant- or animal-derived) and synthetic products. During World War II he was asked to join the team of scientists that was investigating the miracle antibiotic penicillin. In characteristic Woodward fashion, he summarized all of the available chemical and spectroscopic data and was the first to propose the β-lactam structure for penicillin. After penicillin came strychnine, tetracycline, and, with its unprecedented iron-sandwich structure, ferrocene.

reserpine: one of a group of alkaloids found naturally in the shrub *Rarewolfia serpentina*; has been used for centuries to treat hypertension, insomnia, and mental disorders; more recently it has been used to reduce blood pressure

lysergic acid: one of the Ergot series of alkaloids, which constrict blood vessels so that the victim develops burning sensations in the limbs, gangrene, and, ultimately, convulsions; the diethylamide of this substance (LSD) induces visual perception disorders, delusion

chlorophyll: active molecules in plants undergoing photosynthesis

cephalosporin C: family of antibiotics obtained from a fungus acting in a manner similar to penicillin

vitamin B$_{12}$: also known as cyanocobalamin; a complex red crystalline compound containing cyanide and cobalt and occurring in the liver; lack of it in the tissues leads to pernicious anaemia.

erythromycin: antibiotic used to treat infections

spectroscopy: use of electromagnetic radiation to analyze the chemical composition of materials

Woodward saw organic synthesis as a way to advance science and to solve practical problems. One need only look to his vitamin B_{12} work to illustrate this. A reaction that Woodward had planned to use as part of the early stages of the synthesis of vitamin B_{12} gave a product with unexpected stereochemistry, leading the perplexed Woodward to look for similar reactions in the organic literature. He found them, and with Roald Hoffmann, a theoretical chemist at Harvard, formulated what are now known as the Woodward-Hoffmann rules for the conservation of orbital symmetry. These rules explained the outcomes of a series of seemingly unrelated chemical reactions and correctly predicted the outcomes of many others. For his contributions to the orbital symmetry rules, Hoffmann shared the 1981 Nobel Prize in chemistry with Kenichi Fukui of Japan, who had reached similar conclusions independently. Woodward died before the 1981 Nobel Prize was awarded, and had he lived longer, he certainly would have received his second Nobel Prize.

Woodward also recognized in the drive of scientists to synthesize molecules something that spoke to the spirit of people. According to Woodward: "The structure known, but not yet accessible by synthesis, is to the chemist what the unclimbed mountain, the uncharted sea, the untilled field, the unreached planet, are to other men" (Woodward, p. 63).

Woodward died from a heart attack on July 8, 1979, but not before teaching generations of chemists the fine art of organic synthesis. SEE ALSO CHEMICAL REACTIONS; ORGANIC CHEMISTRY; PENICILLIN; SYNTHESIS, CHEMICAL.

Thomas M. Zydowsky

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X

Xenon

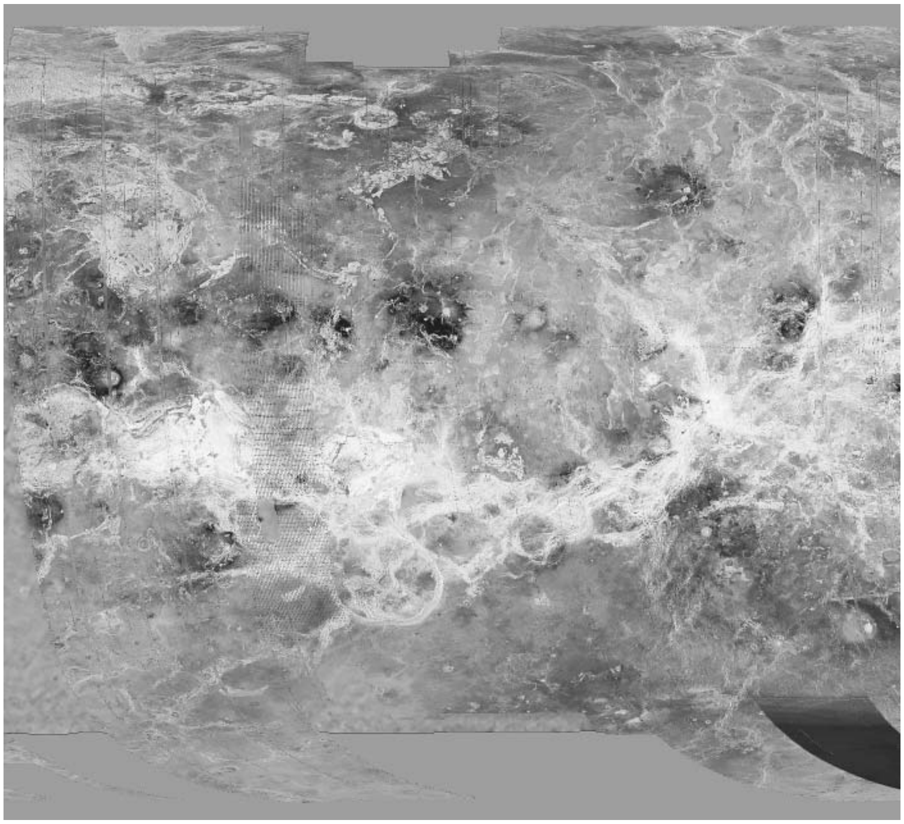
MELTING POINT: **−111.79°C**
BOILING POINT: **−108.12°C**
DENSITY: **No data available**
MOST COMMON IONS: **$HXeO_4^-$, $HXeO_6^{3-}$**

54
Xe
XENON
131.293

Xenon (its name derived from the Greek word *xenos*, meaning "strange"), is the heaviest of the **noble gases**. Discovered in 1898 in London by Sir William Ramsay and Morris Travers while engaged in their investigations of liquid air, xenon accounts for less than 1 ppm of the volume of Earth's atmosphere. It is present in the Sun and in the atmospheres of Mars, Venus, and Mercury.

At room temperature xenon is a colorless, odorless gas. Upon freezing it forms a crystal with a face-centered cubic structure. The chief application of xenon gas is its use in various kinds of lamps. In an electric discharge

noble gas: element characterized by inert nature; located in the rightmost column in the Periodic Table



The gas xenon is present in the atmosphere of Venus.

tube it produces a blue glow. Liquid xenon is used in some particle detectors that are used in space-based research.

nucleosynthesis: creation of heavier elements from lighter elements via fusion reactions in stars

radioactive decay: process involving the emission of a subatomic particle from a nucleus, typically accompanied by the emission of very short wavelength electromagnetic radiation

fission: process of splitting an atom into smaller pieces

isotope: form of an atom that differs by the number of neutrons in the nucleus

Unlike the lighter noble gases, xenon is not produced by **nucleosynthesis** within stars. It is made during supernova explosions. It is also formed on Earth through **radioactive decay** (e.g., of iodine-135) and in **fission** reactions, and it is sometimes found in gases emitted from mineral springs. It has nine stable **isotopes**, of which xenon-129 and xenon-132 are the most abundant (26.4% and 26.9%, respectively).

Also, unlike the lighter noble gases, which are inert, xenon is able to form compounds, mostly with oxygen and fluorine. SEE ALSO NOBLE GASES.

Richard Mowat

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Yalow, Rosalyn Sussman

AMERICAN PHYSICIST AND MEDICAL RESEARCHER
1921–

Rosalyn Sussman Yalow was awarded the Nobel Prize in physiology or medicine in 1977 for her pioneering work in developing the technique known as radioimmunoassay (RIA), a method first applied to the measurement of concentrations in blood of the hormone insulin. Subsequently the use of RIA was extended to include the detection and quantification of a wide range of substances of biological interest, including other hormones, serum proteins, enzymes, viruses, and tumor antigens.

Born on July 19, 1921, in the Bronx, New York, Rosalyn Sussman studied physics and chemistry at New York's Hunter College, graduating in 1941. She was awarded a Ph.D. in **nuclear** physics by the University of Illinois in 1945. Two years earlier she had married fellow physics student Aaron Yalow. For a time in the mid-1940s Rosalyn Yalow worked at the Federal Communications Laboratory in New York, but then returned to Hunter College to teach physics. Her work in medical physics began in 1947 at the Veterans Administration (VA) Hospital in the Bronx, which was then in the process of establishing a radioisotope service.

nuclear: having to do with the nucleus of an atom

American physicist and medical researcher Rosalyn Yalow, corecipient of the 1977 Nobel Prize in physiology or medicine, "for the development of radioimmunoassays of peptide hormones."

metabolism: all of the biochemical processes that take place within living organisms; comprises processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those that break down complex food molecules, thus liberating energy (catabolism)

antibody: protein molecule that recognizes external agents in the body and binds to them as part of the immune response of the body

After designing and building much of the equipment she would need to detect and quantify minute amounts of radioactive substances, Yalow devised studies in the early 1950s that used a radioactive isotope of iodine to investigate a number of physiological processes, including the **metabolism** of proteins. Similar studies monitored changes in insulin levels following the intravenous administration of foreign insulin in both diabetic and nondiabetic patients. The unexpected finding that radiolabeled insulin disappeared more slowly in patients who had received prior insulin injections led Yalow and her colleague Solomon Berson to postulate that the presence of the foreign insulin triggered **antibody** production. They further concluded that the binding of the radiolabeled insulin to these antibodies caused it to be cleared more slowly from the plasma. Yalow and Berson understood that the binding of labeled insulin to a fixed concentration of antibody depends quantitatively on the amount of insulin present. This led directly to their realization that RIA could be used to measure concentrations of the body's own insulin; insulin levels were not easily determined before the advent of RIA in 1959. Although slow to be adopted by others in the field, the technique was further developed by Yalow and Berson such that it could be used to measure concentrations of substances in body tissues and fluids in even infinitesimal concentrations. RIA is now used to identify hypothyroidism in newborn infants. It is also used in blood bank screening, for cancer detection, for the measurement of neurotransmitters, and in forensic chemistry.

Yalow received many honorary doctorates and awards in addition to her 1977 Nobel Prize (which she shared with Andrew Schally and Robert Guillemin). She was the first woman to receive the Albert Lasker Prize for Basic Medical Research (1976). She has served on several national committees, among them the President's Study Group on Careers for Women. Particularly interested in early science education, she frequently visits junior high and high schools. A strong supporter of nuclear medicine and a defender of nuclear power generation, she works to increase public awareness of the major benefits of these technologies. SEE ALSO Insulin; Nuclear Medicine.

Mary R. S. Creese

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70
Yb
YTTERBIUM
173.04

Ytterbium

MELTING POINT: **824°C**
BOILING POINT: **1,196°C**
DENSITY: **6.98 g/cm^3**
MOST COMMON IONS: **Yb(III)**

Ytterbium was discovered by the Swiss chemist Jean Charles Galissard de Marignac in 1878 and named after the town of Ytterby, in Sweden (the site of the discovery of the ore with which de Marignac worked). Its primary source is xenotime and monazite ores, which are mixtures of rare earth orthophosphates. In the earth, ytterbium is more abundant than tin. Ytterbium has been found in meteorites, in lunar rock samples, and to a small extent in the oceans.

At room temperature the element is a silvery **metal**. Its ground state electronic configuration is Xe $6s^24f^{14}$. Ytterbium has many stable **isotopes**: ^{168}Yb, from ^{170}Yb through ^{174}Yb, and ^{176}Yb. Unstable synthetic isotopes have been produced: from ^{151}Yb through ^{167}Yb, as well as ^{169}Yb and ^{175}Yb. Yb(III) compounds, as solids and in solution, are colorless.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

isotope: form of an atom that differs by the number of neutrons in the nucleus

Ytterbium has no known biological function or toxicity. The metal has been used to improve the strength and mechanical properties of stainless steel. Ytterbium also finds use in fiber amplifiers and fiber optic technologies. Its single absorption band in the infrared at 985 nanometers (3.88×10^{-5} inches) has made it useful in silicon photocells that convert radiant energy directly into electrical energy. In the laboratory, chemists usually start with Yb_2O_3 to make other compounds.

Herbert B. Silber

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Yttrium

MELTING POINT: 1,522°C
BOILING POINT: 3,338°C
DENSITY: 4.469 g/cm^3
MOST COMMON IONS: Y^{3+}

39
Y
YTTRIUM
88.90585

Carl Axel Arrhenius found in 1787 in a quarry near Ytterby, Sweden, a new mineral, which he named ytterbite, and made a summary analysis of it. Further, the Finnish chemist Johan Gadolin isolated in 1794 from this mineral an impure new oxide that he named ytterbia. Friedrich Wöhler partly purified the metal yttrium in 1828, whereas Carl Gustaf Mosander separated the oxides of yttrium, erbium and terbium in 1843 from a mixture of yttria oxide.

Yttrium is trivalent and has an effective ionic radius of 0.900 angstroms. At room temperature the metal structure is hexagonal, close packed, and **diamagnetic**. The metal yttrium has a silver-metallic luster and is relatively stable in air.

One stable **isotope** ^{89}Y and thirty-seven unstable isotopes and **isomers** have been characterized. All four halides of yttrium are known and are commonly prepared by dissolving the oxide in corresponding acids.

diamagnetic: property of a substance that causes it to be repelled by a magnetic field

isotope: form of an atom that differs by the number of neutrons in the nucleus

isomer: molecules with identical compositions but different structural formulas

Main yttrium minerals are bastnäsite, kainosite, xerosime, and zinnwaldite. It is estimated that the upper continental crust contains yttrium at a concentration of 20.7 milligrams (0.00073 ounces) per kilogram and seawater contains a total amount of 1,569,000,000 kilograms (1,730,000 tons).

The Porifera *Melythoea* and the tree *Carya* sp. are considered accumulator organisms. Yttrium accumulates in bone and teeth, a phenomenon that is explained by its ability to bind to phosphorus-containing compounds, and to polysaccharides. Nucleic acids have high affinities for yttrium, which binds to phosphate at a ratio of 1:3. Yttrium has stimulatory effects on some fungi and other lower organisms. It is believed that yttrium binds to the surface of cells, without penetrating the cell membrane.

Chaim T. Horovitz

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Yukawa, Hideki

JAPANESE PHYSICIST
1907–1981

Hideki Ogawa (he changed his surname upon marrying Sumi Yukawa) was born on January 23, 1907, in Tokyo. A year thereafter his family moved to Kyoto, where he was raised and attended school. The fifth of seven children of Takuji and Koyuki Ogawa, Hideki came from a family of scholars. Although not inclined to science as he grew up, Hideki happened upon some books on modern physics while in high school and soon found quantum mechanics (which was still a rapidly developing field at the time) very intriguing. As a result of that interest, he entered Kyoto University to study physics in 1926. He received his M.S. from that institution in 1929 and a Ph.D. from Osaka University in 1938.

nuclear: having to do with the nucleus of an atom

In the 1930s the English physicist James Chadwick had discovered the neutron, and scientists were struggling to determine how protons and neutrons interacted inside a nucleus. A theory known as quantum electrodynamics explains electricity and magnetism by assuming that the force is caused by the interaction of photons with charged particles. Scientists tried to create a similar theory of **nuclear** forces based on the interaction of protons and neutrons with some particle analogous to photons. Yukawa developed a theory for the interaction of massive force carriers, the so-called Yukawa potential, and predicted that, since the nuclear force only acts over distances of 10^{-15} meters (3.281×10^{-14} feet), these unknown force carriers should have a mass about two hundred times as heavy as an electron. Yukawa published his theory in 1935, but since such a particle was unknown at the time, his results were largely ignored.

Japanese physicist Hideki Yukawa, recipient of the 1949 Nobel Prize in physics, "for his prediction of the existence of mesons on the basis of theoretical work on nuclear forces."

This situation changed in 1937 when a new particle was discovered in a cosmic-ray experiment. It had the correct mass, and Yukawa's theory was thought to be vindicated as a consequence. However, the details of the theory did not correspond with the measured properties of this particle. In a confusing cosmic coincidence, it turned out that particle was a muon (a heavier electronlike particle), and it was not until 1947 that the pion (as the force carrier came to be known) was discovered. Finally, all the pieces of the theory of nuclear force fell into place, and in 1949 Yukawa received the Nobel Prize in physics.

Yukawa had left Osaka in 1948 to work in the United States. However, in 1953 he returned home to Kyoto to become director of a new interuniversity research institute housed in an academic building named for him. He retired from this position in 1970 and died in Kyoto on September 8, 1981. SEE ALSO CHADWICK, JAMES.

Michael J. Fosmire

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Zeolites

Zeolites are a large group of natural and synthetic hydrated aluminum silicates. They are characterized by complex three-dimensional structures with large, cagelike cavities that can accommodate sodium, calcium, or other cations (positively charged atoms or atomic clusters); water molecules; and even small organic molecules. Ions and molecules in the cages can be removed or exchanged without destroying the aluminosilicate framework. Zeolites find wide use as ion-exchange agents, catalysts, and molecular filters in a range of industrial processes. The word "zeolite" comes from the Greek for "boiling stone," because of the early observation that zeolites release water when heated. As their compositions are not fixed, they are examples of nonstoichiometric compounds.

The Structures of Zeolites

The atomic structures of zeolites are based on three-dimensional frameworks of silica and alumina tetrahedra, that is, silicon or aluminum ions surrounded by four oxygen ions in a tetrahedral configuration. Each oxygen is bonded to two adjacent silicon or aluminum ions, linking them together. Clusters of tetrahedra form boxlike polyhedral units that are further linked to build up the entire framework. In different zeolites the polyhedral units may be equidimensional, sheetlike, or chainlike. The aluminosilicate framework of a zeolite has a negative charge, which is balanced by the cations housed in the cagelike cavities. Zeolites have much more open, less dense structures than other silicates; between 20 and 50 percent of the volume of a zeolite structure is voids. Silicates such as zeolites that have three-dimensional frameworks of tetrahedra are termed tectosilicates. Besides the zeolites, other tectosilicates include quartz and feldspars.

Natural Zeolites

There are about forty-five natural zeolites. They form in a number of relatively low temperature geologic environments. Gas pockets in basalt and other volcanic rocks may contain dramatic crystal groups of zeolites. Economically more important are the fine-grained zeolites such as clinoptilolite $(Na, K)AlSi_5O_{12} \cdot 3H_2O$ formed by the alteration of fine-grained volcanic deposits by underground water. These are mined in the western United States and Mexico. Zeolites also form in alkaline desert lake sediments, in alkaline soils in deserts, and in marine sediments. Zeolites occur in low-temperature metamorphic rocks in geologically young regions of mountain building, such as South Island, New Zealand.

Synthetic Zeolites

synthesis: combination of starting materials to form a desired product

Although some natural zeolites occur in large amounts, they offer only a limited range of atomic structures and properties. Synthetic zeolites have a wider range of properties and larger cavities than their natural counterparts. They were first produced in the 1950s. Today more than 100 different zeolites have been made, and the annual production of synthetic zeolites exceeds 12,000 tons. Zeolites are manufactured in a number of ways; one important technique involves mixing sodium, aluminum, and silica chemicals with steam to create a gel (an amorphous, noncrystalline, water-rich solid). The gel is aged, then heated to about 90°C (194°F). Another technique uses kaolin clay that has been heated in a furnace until it begins to melt, then chilled and ground to powder. This powder is mixed with sodium salts and water, aged, and heated. In all the **synthesis** methods, the zeolite produced depends on the compositions of the starting materials and the conditions of reaction, including acidity, temperature, and water pressure.

Uses of Zeolites

catalysis: the action or effect of a substance in increasing the rate of a reaction without itself being converted

brine: water containing a large amount of salts, especially sodium chloride (NaCl)

The uses of zeolites derive from their special properties: They can interact with water to absorb or release ions (ion exchange); they can selectively absorb ions that fit the cavities in their structures (molecular sieves); they can hold large molecules and help them break into smaller pieces (**catalytic** cracking). Zeolites are used as water softeners, to remove calcium ions, which react with soap to form scum. The water is filtered through a sodium-bearing zeolite, which absorbs the calcium and releases sodium ions into the water. When the zeolite can absorb no more calcium, it may be recharged by flushing it with **brine** (a saturated sodium chloride solution), which forces out the calcium ions and replaces them with sodium. At the Hanford Nuclear Facility in Richland, Washington, radioactive strontium-90 (Sr^{90}) and cesium-137 (Cs^{137}) have been removed from radioactive waste solutions by passing them through tanks packed with the natural zeolite clinoptilolite. Zeolites have also been used to clean radioactive wastes from the Three Mile Island nuclear power plant site and elsewhere. In addition, clinoptilolite is used to clean ammonium ions (NH_4^+) from sewage and agricultural wastewater.

acid rain: precipitation that has a pH lower than 5.6; term coined by R. A. Smith during the 1870s

Sulfur dioxide (SO_2) is a pollutant produced by burning high-sulfur coal. It is a major cause of **acid rain**. Natural zeolites are the most effective filters yet found for absorbing sulfur dioxide from waste gases. As efforts to improve air quality continue, zeolites can be used to help purify the gases from power plants that burn high-sulfur coal from the Ohio River Valley and other regions.

Industrial applications make use of synthetic zeolites of high purity, which have larger cavities than the natural zeolites. These larger cavities enable synthetic zeolites to absorb or hold molecules that the natural zeolites do not. Some zeolites are used as molecular sieves to remove water and nitrogen impurities from natural gas. Because of their ability to interact with organic molecules, zeolites are important in refining and purifying natural gas and petroleum chemicals. The zeolites are not affected by these processes, so they are acting as catalysts. Zeolites are used to help break down large organic molecules found in petroleum into the smaller molecules that make up gasoline, a process called catalytic cracking. Zeolites are also used in hydrogenating vegetable oils and in many other industrial processes involving organic compounds. SEE ALSO GREEN CHEMISTRY; PETROLEUM; STOICHIOMETRY.

Peter B. Leavens

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Zinc

MELTING POINT: 419°C
BOILING POINT: 907°C
DENSITY: 7.14 g/cm^3
MOST COMMON IONS: Zn^{2+}

30
Zn
ZINC
65.39

Like many **transition metals**, zinc has been known in impure form since ancient times. Brass (copper and zinc) coins were used by Egyptians and Palestinians as early as 1400 B.C.E. The first purification of zinc probably occurred during India in the thirteenth century C.E. Although the origin of the name is unknown, it has been suggested that it derives from the German word *Zincke*, meaning "spike" or "tooth."

transition metals: elements with valence electrons in d-sublevels; frequently characterized as metals having the ability to form more than one cation

Zinc is a **trace element** (with an abundance of 0.0076%) in Earth's crust. Like the other elements in its family, zinc is found predominantly as a sulfide compound (ZnS). Pure zinc is a silver-white solid at room temperature. Like other **metals**, zinc conducts electricity and can be formed into wires or sheets. Some properties of zinc are quite different from those of the other transition metals—namely, its relatively low melting point, boiling point, and density. These different properties are attributed to zinc's full outermost **subshell** of electrons, which also causes it to be relatively unreactive.

trace element: element occurring only in a minute amount

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

subshell: electron energy sublevel, of which there are four: s, p, d, and f

Due to the low reactivity of zinc, its most common use is in anticorrosion coatings. Zinc is also often used to form **alloys**, including brass and commercial bronze. Pennies minted after 1983 are made of a core of zinc surrounded by copper. Historically, zinc was used by Alessandro Volta in 1800 to produce

alloy: mixture of two or more elements, at least one of which is a metal

cofactor: inorganic component that combines with an apoenzyme to form a complete functioning enzyme

glucose: common hexose monosaccharide; monomer of starch and cellulose; also called grape sugar, blood sugar, or dextrose

the first battery. Zinc ions, due to their low reactivity, are important biologically. In animals zinc is the most abundant metallic **cofactor**; it is used by insulin in the regulation of **glucose** consumption and by hydrolytic enzymes. An adult human body contains 2 to 3 grams (0.071–0.106 ounces) of zinc. SEE ALSO COFACTORS; VOLTA, ALESSANDRO.

Thomas B. Rauchfuss
Amanda Lawrence

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40
Zr
ZIRCONIUM
91.224

Zirconium

MELTING POINT: **185°C**
BOILING POINT: **4,375°C**
DENSITY: **6.4 g/cm^3**
MOST COMMON IONS: **Zr^{4+}**

Zirconium was discovered by the German chemist Martin H. Klaproth in 1789. The principal ore of zirconium is zircon, which is widely distributed in nature as beach sands, particularly in Australia and India. Zirconium is the nineteenth most abundant element in the earth's crust (at approximately 0.03%). Zircon is a silicate of formula $ZrSiO_4$ and occurs as the gemstones hyacinth and zirconite. Synthetic gemstones are prepared from zircon and from the oxide ZrO_2. Zirconium **metal** is difficult to produce. Its production requires treatment of the **tetrachloride** $ZrCl_4$ with magnesium metal. Zirconium metal is silvery-gray, **ductile**, and malleable.

Zirconium's major use is as **cladding** for **nuclear** reactors. It is ideal for this use, as it has a limited ability to capture neutrons, strength at elevated temperatures, considerable corrosion resistance, and satisfactory neutron damage resistance. Almost all ores of zirconium contain about 2 percent of zirconium's sister element, hafnium (Hf). Hafnium readily absorbs neutrons and therefore must be completely separated and removed from zirconium before either element can be used in nuclear reactors. A major task of the **Manhattan Project** was the separation of hafnium from zirconium. The elements are the two most chemically similar in the Periodic Table. The recovered hafnium metal is used to make the control rods of nuclear reactors, as the metal readily absorbs neutrons.

Zirconium oxide, or zirconia, occurs as the mineral baddeleyite, but zirconium oxide is obtained commercially mainly via its recovery from zircon. Zircon is treated with molten sodium hydroxide to dissolve the silica. Zirconia is used as a ceramic, but it must be **doped** with about 10 percent CaO or Y_2O_3 to stabilize it in its face-centered cubic form. Zirconia is **monoclinic**, meaning that it has one oblique intersection of crystallographic axes, but it undergoes a **phase** change at about 1,100°C (2,012°F), its crystal structure becoming tetragonal, and above 2,300°C (4,172°F) it becomes cubic. To

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

tetrachloride: term that implies a molecule has four chlorine atoms present

ductile: property of a substance that permits it to be drawn into wires

cladding: protective material surrounding a second material, which is frequently tubes filled with uranium dioxide pellets in a nuclear reactor

nuclear: having to do with the nucleus of an atom

Manhattan Project: government project dedicated to creation of an atomic weapon; directed by General Leslie Groves

dope: to add a controlled amount of an impurity to a very pure sample of a substance, which can radically change the properties of a substance

monoclinic: one of several arrangements of atoms found in crystalline solids; characterized by a unit cell of three axes each of a differing length; two axes are mutually perpendicular while the third is at an oblique angle

phase: homogeneous state of matter

Zirconium is found in beach sand, such as on this beach in Australia.

prevent expansion and shrinkage across the 1,100°C phase change (which produces cracking), the stabilized form of zirconia is used, as it does not change phase until very high temperatures are reached. Stabilized zirconia is used to regulate the air-fuel mixtures in automobiles, as it is an **oxide ion conductor**. It generates an electric potential based on the amount of oxygen in the fuel and can adjust the mixture by electrical control of valves to ensure proper fuel burning.

The most important soluble compound of zirconium is zirconyl chloride, $ZrOCl_2{\cdot}8H_2O$, but this compound does not contain the zirconyl ion ZrO^{2+}. It is a tetramer of composition $[Zr(OH)_2{\cdot}4H_2O]_4^{8+}$, prone to polymerize to larger species as pH increases, forming hydrous zirconia, $ZrO_x(OH)_y{\cdot}nH_2O$. Other important soluble salts are the sulfate, $Zr(SO_4)_2{\cdot}4H_2O$, and the nitrate, $Zr(NO_3)_4{\cdot}5H_2O$, isolated from strongly acidic solutions. Both zirconium and titanium form **organometallic compounds** that are important catalysts in the conversion of ethylene to polyethylene. SEE ALSO HAFNIUM; NUCLEAR CHEMISTRY; MANHATTAN PROJECT; ORGANOMETALLIC COMPOUNDS.

Abraham Clearfield

oxide ion conductor: series of oxides of various compounds in perovskite structure—especially of interest in high-temperature fuel cells

organometallic compound: compound containing both a metal (transition) and one or more organic moieties

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Zsigmondy, Richard Adolf

AUSTRIAN CHEMIST
1865–1929

Richard Zsigmondy received the 1925 Nobel Prize in chemistry for his elucidation of the nature of colloidal suspensions. With Henry Siedentopf (1872–1940), he invented, used, and promoted the ultramicroscope. Zsigmondy and others used ultramicroscopic studies of colloidal suspensions to convince influential skeptics that molecules are real and that matter is discontinuous at the molecular level.

Austrian chemist Richard Adolf Zsigmondy, recipient of the 1925 Nobel Prize in chemistry, "for his demonstration of the heterogeneous nature of colloid solutions and for the methods he used, which have since become fundamental in modern colloid chemistry."

Zsigmondy was born in Vienna, Austria, the fourth child of Irma von Szakmáry and Adolf Zsigmondy. Both parents encouraged chemical and physical experiments at home for their children. Young Zsigmondy studied chemistry in Vienna and Munich. Between 1883 and 1887 he worked at a glass factory in Bohemia, investigating luster and color in glasses. The University of Erlangen awarded him a doctorate degree in 1889. From 1890 to 1892 he worked in Berlin with August Kundt (1839–1894), studying the phenomenon of colors appearing on porcelain when suspensions of colloidal gold were applied before firing.

Beginning in 1893, Zsigmondy taught chemical technology and at the same time continued his own research on colloidal gold at the Technische Hochshule in Graz. He formed associations with glassmakers at the Schott Glass Company in Jena. The Schott Glass Company was famous for its making of glass scientific apparatus, including optical instruments. Zsigmondy left Graz in 1897 and became part of the Schott laboratory, where he conducted systematic investigations of colored glasses as colloidal systems.

Zsigmondy needed new types of optical instruments for his experiments. At the Schott laboratory, he had a hand in designing and constructing such instrumentation. Siedentopf joined the laboratory in 1899, and there he and Zsigmondy created the ultramicroscope. The Carl Zeiss Company, also in Jena, manufactured and sold the instruments.

perpendicular: condition in which two lines (or linear entities like chemical bonds) intersect at a 90-degree angle

aqueous solution: homogenous mixture in which water is the solvent (primary component)

formaldehyde: name given to the simplest aldehyde HC(O)H, incorporating the –C(O)H functional group

Just as individual dust particles suspended in air can be seen and counted in a beam of sunlight, so individual colloidal particles can be seen and counted when a sample is illuminated in an ultramicroscope. In each case, the best viewing direction is **perpendicular** to the direction of illumination. Zsigmondy used **aqueous solutions** of colloidal gold as model systems. He prepared colloidal gold by reducing solutions of gold chloride with **formaldehyde**. Knowing the mass of gold in a known volume of solution and using the ultramicroscope to count the number of colloidal particles in that volume, he determined the molecular weight of the gold colloid.

Zsigmondy extended his observations to a wide range of important colloids—proteins, soaps, dyestuffs, clays, and polysaccharides. He was an influential leader in colloid physical chemistry throughout the first quarter of the twentieth century. SEE ALSO COLLOIDS; DYES; PROTEINS; SOAP.

George Fleck

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Zwitterions

Zwitterions (the word is derived from the German for "hybrid ion") are ions that are electrically neutral overall but contain nonadjacent regions of positive and negative charges; they are sometimes referred to as "dipolar ions." The best-known examples of zwitterions are the free amino acids found in cells.

An examination of the general structure of an amino acid reveals that there are two parts, or groups, of the molecule that can function as an acid/base pair, the –COOH and $-NH_2$ groups. At pH values near neutrality, a protein transfer reaction takes place that results in the –COOH becoming $-COO^-$ and the $-NH_2$ becoming $-NH_3^+$. A large favorable (stabilizing) **electrostatic interaction** now develops between these two parts of the molecule. This interaction is favorable enough to shift the **equilibrium** constant for the proton transfer reaction toward the formation of the charged species, by a factor of between 10- and 50-fold. In addition to the favorable electrostatic interaction between the charged regions, these same charged regions have very favorable electrostatic interactions with surrounding water molecules. Water molecules solvate these regions of the amino acid in a manner very similar to their solvation of cations and **anions**.

electrostatic interaction: force that arises between electrically charged particles or regions of particles

equilibrium: condition in which two opposite reactions are occurring at the same speed, so that concentrations of products and reactants do not change

anion: negatively charged chemical unit, like Cl^-, CO_3^{2-}, or NO^{3-}

The physical properties of crystalline amino acids are consistent with their existence as zwitterions. Their melting points are relatively high, often above 200ºC (392°F), and they are far more soluble in water than in **nonpolar** solvents such as ether or chloroform. Measured dipole moments for crystalline amino acids are fairly large, reflecting the significant degree of charge separation. SEE ALSO Amino Acid.

nonpolar: molecule, or portion of a molecule, that does not have a permanent, electric dipole

Matthew A. Fisher

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Volume 1

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Volume 2

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Volume 3

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Chinch Gryniewicz. Ecoscene/Corbis. Reproduced by permission; p. 89: Matrix of diamond, photograph. U. S. National Aeronautics and Space Administration (NASA); p. 104: Chaney, Michael wearing special 3-D glasses to view a computer model of Fluoxetine, or Prozac. Lilly Research Labs, Indianapolis, February 22, 1994, photograph. Corbis. Reproduced by permission; p. 115: Three-dimensional computer model of a protein molecule of matrix porin found in the E. Coli bacteria, photograph. © Corbis. Reproduced by permission; p. 118: Two models which represent the arrangement of atoms in a chemical molecule, illustration. Tek Image/Science Photo Library. Photo Researcher, Inc. Reproduced by permission; p. 122: Moseley, Henry, photograph. Photo Researchers, Inc. Reproduced by permission; p. 124: Six-legged frog, photograph. JLM Visuals. Reproduced by permission; p. 130: Coffee shop sign at the Pike Place Public Market, Seattle, Washington, ca. 1990, photograph by Stuart Westmorland. CORBIS/Stuart Westmorland. Reproduced by permission; p. 132: Professor Walther Nernst of Berlin University, Nobel Prize winner for physics, in his laboratory, photograph. © Bettmann/Corbis. Reproduced by permission; p. 137: Diagram showing transmitting and receiving neurons and the role of serotonin in communication between one neuron and the next, illustration by Frank Forney; p. 143: Photovoltaic cell powered desalination system, Saudi Arabia, photograph. Mobil Solar Energy Corporation/Phototake NYC. Reproduced by permission; p. 144: Newton, Sir Isaac (oval frame, allegorical elements surrounding), engraving. The Library of Congress; p. 153: Hand pouring liquid nitrogen into beaker, photograph. © David Taylor/Photo Researchers. Reproduced by permission; p. 155: Nobel, Alfred (wearing suit, checked bow tie), drawing. The Library of Congress; p. 158: Scientist from University of California—Berkley studying helium gas being released from a hot spring in Yellowstone National Park, photograph. © James L. Amos/Corbis. Reproduced by permission; p. 168: Lasers focus on a small pellet of fuel in attempt to create nuclear fusion reaction, photograph. © Roger Ressmeyer/Corbis. Reproduced by permission; p. 169: Seaborg, Glenn, photograph by Lawrence Berkeley. Photo Researchers, Inc. Reproduced by permission; p. 172: Nuclear reactors, interior of the containment building, photograph by Mark Marten. Photo Researchers, Inc. Reproduced by permission; p. 174: Nuclear fusion, computer simulation, photograph by Jens Konopka and Henning Weber. Photo Researchers, Inc. Reproduced by permission; p. 178: Magnetic Resonance Imaging System (room with equipment and viewing machine), photograph by Mason Morfit. FPG International Corp. Reproduced by permission; p. 181: Colored positron emission tomography (PET) scans comparing the brain of a depressed person (top) with the brain of a healthy person, illustration. © Photo Researchers, Inc. Reproduced by permission; p. 192: Oppenheimer, Dr. J. Robert, atomic physicist and head of the Manhattan Project, photograph. National Archives and Records Administration; p. 209: Ostwald, Friedrich Wilhelm, portrait. The Library of Congress; p. 211: Doctor communicating with a patient lying in a pressure chamber and undergoing hyperbaric oxygen therapy, photograph by James King-Holmes/Science Photo Library. Reproduced by permission; p. 214: Woodcut from “Works”, of Paracelsus ca. 1580 edition, of Mercury in its alchemical form as Azoth, photograph. Fortean Picture Library. Reproduced by permission; p. 218: © Kevin Fleming/Corbis. Reproduced by permission; p. 220: Pasteur, Louis, photograph. Hulton-Deutsch Collection/Corbis. Reproduced by permission; p. 222: Pauli, Wolfgang, photograph by Zurich Bettina. Courtesy of CERN-European Organization for Nuclear Research. Reproduced by permission; p. 223: Pauling, Linus, proponent of heavy vitamin C use, tossing an orange, photograph. © Roger Ressmeyer/Corbis. Reproduced by permission; p. 225: Penicillin, photograph by Andrew McClenaghan, photograph. Photo Researchers, Inc. Reproduced by permission; p. 229: Early Periodic Table, portrait. The Library of Congress; p. 234: Worker in

protective photograph by Ed Young. Corbis. Reproduced by permission; p. 238: Smith, Billy, Drilling Foreman, seated at Drake Well, photograph. AP/Wide World. Reproduced by permission; p. 241: Man in red hardhat standing on bluish oil refinery equipment, yellow flames from burning natural gas at top right, photograph. © Lowell Georgia/Corbis. Reproduced by permission; p. 249: The first known photograph of a courtyard outside Niepce's room, photograph. The Bettmann Archive/Corbis. Reproduced by permission; p. 256: Hot water vaporizing as it is thrown into air during minus 35-degree Fahrenheit temperature, Boundary Waters Canoe Area Wilderness, Minnesota, USA, photograph © Layne Kennedy/Corbis. Reproduced by permission; p. 258: X-ray diffraction crystallography, photograph by James King-Holmes. OCMS/Science Photo Library/ Photo Researchers, Inc. Reproduced by permission; p. 259: Several open cans of paint in an assortment of colors, photograph by Matthias Kulka. Corbis. Reproduced by permission; p. 262: Planck, Max, photograph. © Bettmann/Corbis. Reproduced by permission.

Volume 4

p. 5: Travolta, John, with Karen Lynn Gorney in a scene from "Saturday Night Fever," photograph. The Kobal Collection. Reproduced by permission; p. 12: Ghost crab walking among a sandy shoreline, photograph. Sapelo Island National Estuarine Research Reserve. Reproduced by permission; p. 30: Priestley, Joseph, engraving. International Portrait Gallery; p. 38: Scientist adjusts equipment used in fast protein liquid chromatography, photograph. Photo Researchers, Inc. Reproduced by permission; p. 50: Spectrum of electromagnetic radiation, (chart) illustrations by Robert L. Wolke. Reproduced by permission; p. 52: Radioactive emission of alpha particles from radium, yellow sunburst, dark blue background, photograph. Photo Researchers, Inc. Reproduced by permission; p. 58: International mobile radiological radiologists measuring soil radioactivity levels near Ukraine's Chernobyl Nuclear Plant, wearing protective clothing, from International Mobile Radiological Laboratories, near Chernobyl, Ukraine, photograph. © Reuters NewsMedia Inc./Corbis. Reproduced by permission; p. 60: Radon test kit and carbon monoxide detector, photograph by Robert J. Huffman.
Field Mark Publications. Reproduced by permission; p. 63: Ramsay, William, portrait. The Library of Congress; p. 65: Reaction rate, illustration. GALE Group. Studio: EIG; p. 74: Bragg, Kevin, photograph. © James A. Sugar/Corbis. Reproduced by permission; p. 80: Open electric oven showing the glowing red heating element, photograph by Robert J. Huffman. FieldMark Publications. Reproduced by permission; p. 86: Robinson, Robert, portrait. The Library of Congress; p. 89: Captured German V-2 rocket cuts through the clouds during experiment, 1947, photograph. AP/Wide World Photos. Reproduced by permission; p. 90: Full-scale operational model of the Mars Viking Lander, photograph by Lowell Georgia/Corbis. Reproduced by permission; p. 97: Rubidium, photograph. © Russ Lappa/Science Source, National Audubon Society Collection/Photo Researchers, Inc. Reproduced by permission; p. 99: Rutherford, Ernest, Walton (left to right), Ernest Rutherford, and J.D. Cockcroft, standing together outside, photograph. © Hulton-Deutsch Collection/Corbis; p. 103: Large pile of salt at a salt mine, October 29, 1996, Upington, South Africa, photograph. © Charles O'Rear/Corbis; p. 106: Sanger, Frederick looking up at model of DNA molecule, photograph. © Bettmann/Corbis. Reproduced by Corbis Corporation; p. 108: Scheele, Carl Wilhelm, portrait. The Library of Congress; p. 110: Schrodinger, Professor Erwin of Magdalen College, Oxford, winner of the 1933 Nobel Prize in Physics along with Professor P.H.M. Dirac of Cambridge University, England, November 18, 1933, photograph. © Bettmann/Corbis. Reproduced by permission; p. 111: Seaborg, Glenn T., photograph. © Roger Ressmeyer/Corbis. Reproduced by permission; p. 115: Seibert, Florence, photograph. AP/Wide World Photos. Reproduced by permission; p. 116: Dish of selenium, photograph. © Rich

Treptow, National Audubon Society Collection/Photo Researchers, Inc. Reproduced by permission; p. 117: Person holding a conventional tub amplifier, photograph. © Bettmann/Corbis. Reproduced by permission; p. 120: Micro wires, silicon chip, photograph by Andrew Syred. The National Audubon Society Collection/ Photo Researchers, Inc. Reproduced by permission; p. 122: Worker testing silicon wafers at the Matsushita Semiconductor plant in Puyallup, Washington, c. 1994, photograph. © Kevin R. Morris/Corbis. Reproduced by permission; p. 131: Soddy, Frederick, drawing. The Library of Congress; p. 132: Sodium acetate hot pack reacting, photograph by Charles D. Winters. Photo Researchers, Inc. Reproduced by permission; p. 149: Solution of water and oil, droplets are exposed to polarized light, magnification, photograph by David Spears. © Science Pictures Limited/Corbis; p. 154: Electron spectroscopy, chemical analysis, photograph by Joseph Nettis. Photo Researchers, Inc. Reproduced by permission; p. 157: Stanley, Wendell Meredith, photograph. The Library of Congress; p. 159: Staudinger, Hermann, portrait. The Library of Congress; p. 161: Steel worker sampling molten metal, photograph by John Olson. Stock Market. Reproduced by permission; p. 164: Steel Bridge, Portland, Oregon, photograph by James Blank. © James Blank. Reproduced by permission; p. 167: Hand holding 50 mg bottle of the injectable anabolic steroid Durabolin, photograph. Custom Medical Stock Photo. Reproduced by permission; p. 169: Razor blade cutting powder form of the drug Speed into lines for snorting, photograph. Science Photo Library. Reproduced by permission; p. 174: Germinating garden pea Pisum Sativum, showing embryonic root growing downward, macrophotograph, photograph. © J. Burgess/Photo Researchers. Reproduced by permission; p. 176: Rayleigh, 3rd Baron (John W. Strut, III), drawing. The Library of Congress; p. 179: Vat of sulfur, photograph by Farrell Grehan. Corbis. Reproduced by permission; p. 180: Sumner, James B., portrait. The Library of Congress; p. 182: Meissner effect, cube floating above a superconductor, photograph by Yoav Levy. Phototake NYC. Reproduced by permission; p. 187: Scanning tunneling microscope image of sulfur atoms on rhodium surface, photograph by Dr. James Batteas. National Institute of Standards and Technology; p. 187: Topographic image of a reconstructed silicon surface showing outermost atomic positions, photograph of Dr. James Batteas. National Institute of Standards and Technology. Reproduced by permission; p. 189: Infrared near-field scanning optical microscope (NSOM) image of blended polystyrene/polyethylacrylate film on silicon, photograph by f Dr. Chris Michaels and Dr. Stephan Stranick, National Institute of Standards and Technology. Reproduced by permission; p. 189: Nanowriting of a mercaptbenzoic acid layer into a background layer of dodecanethiol using nanografting, photograph by Dr. Jayne Gerano, National Institute of Standards and Technology. Reproduced by permission; p. 191: Tractor riding past wind generators, photograph. © AP/Wide World Photos. Reproduced by permission; p. 192: Cutaway of the ITER tokamak device, photograph. Photo Researchers, Inc. Reproduced by permission; p. 193: Svedberg, Theodor, portrait. The Library of Congress; p. 195: Synge, Richard L.M., photograph. The Library of Congress; p. 198: Organic chemist synthesizing chemotherapy agent, photograph by Geoff Tompkinson. Photo Researchers, Inc. Reproduced by permission; p. 200: Szent-Gyorgyi, Dr. Albert, Nobel Prize winner, discoverer of Vitamin C and bioflavinoids, photograph. © Bettmann/CORBIS. Reproduced by permission; p. 205: Photocopier in office, photograph by Robert J. Huffman. FieldMark Publications. Reproduced by permission; p. 207: © Royalty-Free/Corbis. Reproduced by permission; p. 209: Yendell, Thomas, a Thalidomide baby, picks up a toy with his feet, photograph. AP/Wide World Photos. Reproduced by permission; p. 215: Thallium heart scan, photograph by Peter Berndt, M.D. Custom Medical Stock Photo. Reproduced by permission; p. 226: Thomson, Sir Joseph John, photograph. UPI/Corbis-Bettmann.

Reproduced by permission; p. 227: Man, writing, being flanked by two other men watching. AP/Wide World Photos. Reproduced by permission; p. 228: Army medic, taking an x-ray of a fellow soldier simulating an injury, photograph. © Bettmann/Corbis. Reproduced by permission; p. 236: Stanford Linear Accelerator Center, photograph by David Parler. National Audubon Society Collection/Photo Researchers Inc. Reproduced by permission; p. 241: Alchemist (seated left wearing eyeglasses) and his assistants, engraving. The Granger Collection, New York. Reproduced by permission; p. 244: Computer generated graphic of a molecule of hemoglobin-carrier of oxygen in the blood, photograph. © Science Photo Library. Photo Researchers. Reproduced by permission; p. 249: Urey, Harold, photograph. The Library of Congress; p. 253: Van Der Waals, Johannes Diderik, photograph. Science Photo Library. Photo Researchers, Inc. Reproduced by permission; p. 255: Helmont, Jan (Baptise) Van (standing), print; p. 256: Hoff, Jacobus Henricus vant, photograph. Photo Researchers, Inc. Reproduced by permission; p. 258: Banded gila monster, photograph by Renee Lynn. The National Audubon Society Collection/Photo Researchers, Inc. Reproduced by permission; p. 261: Allesandro Volta, standing, body turned slightly to his left, painting. UPI/Corbis-Bettmann. Reproduced by permission; p. 263: Waksman, Selman A.(in laboratory), photograph. The Library of Congress.; p. 265: Molecular graphic of water molecules evaporating from a solution, photograph. © K. Eward/Photo Researchers. Reproduced by permission; p. 270: Dead fish, killed from water pollution, photograph. © U.S. Fish & Wildlife Service; p. 273: Newly treated water in the Orange County Water Treatment Works, Florida, photograph by Alan Towse. © Ecoscene/CORBIS. Reproduced by permission; p. 275: Watson, Dr. James Dewey, with DNA model, 1962, photograph. UPI/Corbis-Bettmann. Reproduced by permission; p. 277: Werner, Alfred, portrait. The Library of Congress; p. 279: Willstatter, Richard, photograph. Photo Researchers, Inc. Reproduced by permission; p. 280: Wohler, Friedrich, portrait. The Library of Congress; p. 282: Woodward, Robert Burns (standing with unknown man, viewing book), photograph. The Library of Congress; p. 284: Cylindrical map of the eastern half of the surface of Venus, as viewed from the spacecraft Magellan, photograph. NASA/JPL/CALTECH. Reproduced by permission; p. 285: Yalow, Rosalyn, 1978, photograph. Corbis-Bettmann. Reproduced by permission; p. 288: Yukawa, Hideki (holding chalk, pointing to writing on board), photograph. The Library of Congress; p. 293: Kangaroo on the beach in Australia, photograph. © Australian Picture Library/Corbis. Reproduced by permission; p. 294: Zsigmondy, Richard, portrait. The Library of Congress.

Glossary

acetylcholine: neurotransmitter with the chemical formula $C_7H_{17}NO_3$; it assists in communication between nerve cells in the brain and central nervous system

acid rain: precipitation that has a pH lower than 5.6; term coined by R. A. Smith during the 1870s

activation analysis: technique that identifies elements present in a sample by inducing radioactivity through absorbtion of neutrons

adenine: one of the purine bases found in nucleic acids, $C_5H_5N_5$

adenosine triphosphate (ATP): molecule formed by the condensation of adenine, ribose, and triphosphoric acid, HOP(O)OH–O–(O)OH–OP(O)OH–OH; it is a key compound in the mediation of energy in both plants and animals

adrenalin: chemical secreted in the body in response to stress

alchemy: medieval chemical philosophy having among its asserted aims the transmutation of base metals into gold

aldehyde: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the RC(O)H functional group

aliphatic: having carbon atoms in an open chain structure (as an alkane)

aliquot: specific volume of a liquid used in analysis

alkaloid: alkaline nitrogen-based compound extracted from plants

alloy: mixture of two or more elements, at least one of which is a metal

α subunit: subunit that exists in proteins that are composed of several chains of amino acids, the first unit in the "counting" of the units

α-particle: subatomic particle with 2+ charge and mass of 4; a He nucleus

amalgam: metallic alloy of mercury and one or more metals

amine functional group: group in which nitrogen is bound to carbon in an organic molecule in which two other groups or hydrogen atoms are bound to nitrogen; major component of amino acids

amino acid residue: in a protein, which is a polymer composed of many amino acids, that portion of the amino acid that remains to become part of the protein

amino acid sequence: twenty of the more than five hundred amino acids that are known to occur in nature are incorporated into a variety of proteins that are required for life processes; the sequence or order of the amino acids present determines the nature of the protein

amphetamine: class of compounds used to stimulate the central nervous system

anabolism: metabolic process involving building of complex substances from simpler ones, using energy

analgesic: compound that relieves pain, e.g., aspirin

androgen: group of steroids that act as male sex hormones

angiotensin: chemical that causes a narrowing of blood vessels

anhydrous compound: compound with no water associated with it

anion: negatively charged chemical unit, like Cl−, CO_{32}−, or NO_3−

anthcyanin: antioxidant flavanoid that makes raspberries red and blueberries blue

antibody: protein molecule that recognizes external agents in the body and binds to them as part of the immune response of the body

anticoagulant: molecule that helps prevent the clotting of blood cells

antiscorbutic: substance that has an effect on scurvy

apoenzyme: the protein part of an enzyme that requires a covalently bound coenzyme (a low molecular weight organic compound) or a cofactor (such as a metal ion) for activity

aqueous solution: homogenous mixture in which water is the solvent (primary component)

aromatic: having a double-bonded carbon ring (typified by benzene)

asparagine residue: amino acid asparagine unit as it occurs in a polypeptide chain

atomic mass units: unit used to measure atomic mass; 1/12 of the mass of a carbon-12 atom

atomic number: the number of protons in an atomic nucleus, expressed in terms of electric charge; it is usually denoted by the symbol Z

atomic orbital: mathematical description of the probability of finding an electron around an atom

atomic spectrum: electromagnetic array resulting from excitement of a gaseous atom

atomic theory: concept that asserts that matter is composed of tiny particles called atoms

atomic weight: weight of a single atom of an element in atomic mass units (amu)

attraction: force that brings two bodies together, such as two oppositely charged bodies

axial bond: covalent bond pointing along a molecular axis

azo dye: synthetic organic dye containing a –N=N– group

bacteriophage multiplication: process by which immune system cells responsible for battling bacterial infections reproduce

basal metabolism: the process by which the energy to carry out involuntary, life-sustaining processes is generated.

β subunit: subunit that exists when two or more polypeptide chains associate to form a complex functional protein, the chains are referred to as "subunits"; these subunits are often identified as α, β, etc.

biological stain: dye used to provide contrast among and between cellular moieties

biomass: collection of living matter

biosynthesis: formation of a chemical substance by a living organism

boat conformation: the arrangement of carbon atoms in cyclohexane, C_6H_{12}. In which the spatial placement of the carbon atoms resembles a boat with a bow and a stern

brine: water containing a large amount of salts, especially sodium chloride (NaCl)

Brownian motion: random motion of small particles, such as dust or smoke particles, suspended in a gas or liquid; it is caused by collisions of the particle with gas or solvent molecules which transfer momentum to the particle and cause it to move

calc: calcium carbonate

calcine: to heat or roast to produce an oxide (e.g., CaO from calcite)

capacitor plate: one of several conducting plates, or foils, in a capacitor, separated by thin layers of dielectric constant, an insulating material

carboxylate: structure incorporating the –COO– group

carboxyl group: an organic functional group, –C(O), found in aldehydes, ketones, and carboxyl acids.

carboxylic acid: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the $-CO_2H$ functional group

catabolism: metabolic process involving breakdown of a molecule into smaller ones resulting in a release of energy

catalysis: the action or effect of a substance in increasing the rate of a reaction without itself being converted

catalyst: substance that aids in a reaction while retaining its own chemical identity

catalytic conversion: catalytic oxidation of carbon monoxide and hydrocarbons in automotive exhaust gas to carbon dioxide and water

cell culture: artificially maintained population of cells, grown in a nutrient medium and reproducing by asexual division

cephalosporin C: family of antibiotics obtained from a fungus acting in a manner similar to penicillin

chain of custody: sequence of possession through which evidentiary materials are processed

chair conformation: arrangement of atoms in a cycle structure (usually a six-membered ring) that appears to be arranged like a chair (as opposed to the other conformation which is described as a “boat”)

chemical-gated: of a membrane protein whose action to open a pore in the membrane occurs only after a substrate has been binded to the protein or a cofactor

chlorofluorocarbon (CFC): compound containing carbon, chlorine, and fluorine atoms that remove ozone in the upper atmosphere

chlorophyll: active molecules in plants undergoing photosynthesis

chromatography: the separation of the components of a mixture in one phase (the mobile phase) by passing in through another phase (the stationary phase) making use of the extent to which the components are absorbed by the stationary phase

chromophore: part of the molecule that yields characteristic colors

cladding: protective material surrounding a second material, which is frequently tubes filled with uranium dioxide pellets in a nuclear reactor

cleave: split

cobrotoxin: polypeptide toxin containing sixty-two residues that is found in the venom of cobras

code: mechanism to convey information on genes and genetic sequence

cofactor: inorganic component that combines with an apoenzyme to form a complete functioning enzyme

coherent mass: mass of particles that stick together

color fastness: condition characterized by retention of colored moieties from a base material

combustion: burning, the reaction with oxygen

competitive inhibitor: species or substance that slows or stops a chemical reaction

complementarity: basis for copying the genetic information, where each nucleotide base has a complementary partner with which it forms a base-pair

congener: an element or compound belonging to the same class

constitutional isomer: form of a substance that differs by the arrangement of atoms along a molecular backbone

contact activity: process involving the touching of different surfaces

contraction: the shortening of a normal trend of a quantity

coordinate covalent bond: covalent bond in which both of the shared electrons originate on only one of the bonding atoms

coordination chemistry: chemistry involving complexes of metal ions surrounded by covalently bonded ligands

corrosive gas: gas that causes chemical deterioration

covalent bond: bond formed between two atoms that mutually share a pair of electrons

crystal lattice: three-dimensional structure of a crystaline solid

crystallization: process of producing crystals of a substance when a saturated solution in an appropriate solvent is either cooled or some solvent removed by evaporation

culture: living material developed in prepared nutrient media

cyanobacterium: eubacterium sometimes called “the blue-green alga”; it contains chlorophyll (the pigment most abundant in plants), has very strong cell walls, and is capable of photosynthesis

cyclopentadienyl ring: five-membered carbon ring containing two C–C double bonds; formula C_5H_6

cysteine residue: sulfhydryl-containing cysteine unit in a protein molecule

cytosine: heterocyclic, pyrimidine, amine base found in DNA

dedifferentiation: the opposite of the biological process of differentiation by which a relatively unspecialized cell undergoes a progressive change to a more specialized form or function

degradative: relating to or tending to cause decomposition

degrade: to decompose or reduce the complexity of a chemical

delocalized: of a type of electron that can be shared by more than one orbital or atom

denitrification: process of removing nitrogen

density-functional theory: quantum mechanical method to determine ground states

depolarization: process of decreasing the separation of charge in nerve cells; the opposite of hyperpolarization

deterministic: related to the assumption that all events are based on natural laws

deuteron: nucleus containing one proton and one neutron, as is found in the isotope deuterium

dialcohol: organic molecule containing two covalently-bonded –OH groups

diamagnetic: property of a substance that causes it to be repelled by a magnetic field

diamine: compound, the molecules of which incorporate two amino groups ($-NH_2$) in their structure, such as 1,2 diamino ethane (sometimes called ethylenediamine) and the three diamine benzene compounds

dibasic acid: acidic substance that incorporates two or more acidic hydrogen atoms in one molecule, such as sulfuric (H_2SO_4) and phosphoric (H_3PO_4) acids

dihydroxy compound: compound with molecules that incorporate two hydroxyl groups (–OH) in their structure, such as 1,2 dihydroxy ethane (sometimes called glycol) and the three dihydroxy benzene compounds

directing effect: ability of a functional group to influence the site of chemical reaction, such as substitution, for a molecule

discharge display tube: glass tube containing gas at low pressure through which a beam of electrons is passed

disperse system: two-phase system in which one phase, the disperse phase, is distributed in the second phase, the dispersion medium

disulfide bond: bond in a complex substance that involves two bonding sulfur atoms, –S–S–

disulfide bridge: covalent –S–S– linkage that provides cross-links in protein molecules

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

dope: to add a controlled amount of an impurity to a very pure sample of a substance, which can radically change the properties of a substance

drug resistance: ability to prevent the action of a particular chemical substance

ductile: property of a substance that permits it to be drawn into wires

Eighteen Electron Rule: rule noting that coordination complexes with eighteen electrons are stable; electrons from both metal species and ligand donor species are counted

electrolyte solution: a liquid mixture containing dissolved ions

electron correlation error: quantum mechanical method for studying atoms, ions, or molecules

electronegative: capable of attracting electrons

electrophoresis: migration of charged particles under the influence of an electric field, usually in solution; cations, the positively charged species, will move toward the negative pole and anions, the negatively charged species, will move toward the positive pole

electrostatic interaction: force that arises between electrically charged particles or regions of particles

elemental analysis: determination of the percent of each atom in a specific molecule

emulsifier: substance that stabilizes the formation of an emulsion—normally it contains molecules with both polar and non-polar functional groups

emulsion: immiscible two-phase mixture in which one phase is dispersed (as small droplets) in the other phase

enantiomorphic shape: mixture of molecules with the same molecular formulas but different optical characteristics

endohedral: descriptive term for a point within a three-dimensional figure

endoplasmic reticulum: internal membrane system that forms a net-like array of channels and interconnections of organelles within the cytoplasm of eukaryotic cells

Equation of State for Ideal Gases: mathematical statement relating conditions of pressure, volume, absolute temperature, and amount of substance; $PV = nRT$

equatorial bond: covalent bond perpendicular to a molecular axis

equilibrium: condition in which two opposite reactions are occurring at the same speed, so that concentrations of products and reactants do not change

erythromycin: antibiotic used to treat infections

ester: organic species containing a carbon atom attached to three moieties: an O via a double bond, an O attached to another carbon atom or chain, and an H atom or C chain; the R(C=O)OR functional group

esterification: chemical reaction in which esters (RCO_2R_1) are formed from alcohols (R_1OH) and carboxylic acids (RCO_2R')

estrogen: female sex hormone

eukaryotic cell: cell characterized by membrane-bound organelles, most notably the nucleus, and that possesses chromosomes whose DNA is associated with proteins

excitatory: phenomenon causing cells to become active

excitatory neurotransmitter: molecule that stimulates postsynaptic neurons to transmit impulses

exclusion principle: principle that states that no two electrons can have the same four quantum numbers

excrete: to eliminate or discharge from a living entity

expressed: made to appear; in biochemistry—copied

extracellular matrix: entity surrounding mammalian tissue cells, also called connective tissue; composed of structural proteins, specialized proteins, and proteoglycans

face centered cubic structure: close-packed crystal structure having a cubic unit cell with atoms at the center of each of its six faces

feedstock: mixture of raw materials necessary to carry out chemical reactions

Fermi conduction level: vacant or partially occupied electronic energy level resulting from an array of a large number of atoms in which electrons can freely move

ferric: older name for iron in the +3 oxidation state

ferrous: older name for iron in the +2 oxidation state

fibril: slender fiber or filament

fission: process of splitting of an atom into smaller pieces

fissionable: of or pertaining to unstable nuclei that decay to produce smaller nuclei

5′ end: situation in nucleic acids in which the phosphate group is attached at the fifth carbon atom from where the base is attached

folic acid: pteroylglutamic acid; one of the B complex vitamins

formaldehyde: name given to the simplest aldehyde HC(O)H, incorporating the –C(O)H functional group

fractional distillation: separation of liquid mixtures by collecting separately the distillates at certain temperatures

fulcrum: prop or support to an item as in a lever

functional group: portion of a compound with characteristic atoms acting as a group

galactose: six-carbon sugar

galvanic: relating to direct current electricity, especially when produced chemically

galvanometer: instrument used to detect and measure the strength of an electric current

gas density: weight in grams of a liter of gas

glucocorticoid: class of hormones that promotes the breakdown of proteins to make amino acids available for gluconeogenesis; this elevates the blood sugar level and leads to glycogen synthesis in the liver

glucose: common hexose monosaccharide; monomer of starch and cellulose; also called grape sugar, blood sugar, or dextrose

golgi apparatus: collection of flattened stacks of membranes in the cytoplasm of eukaryotic cells that function in the collection, packaging, and distribution of molecules synthesized in the cell

gram negative: bacteria that do not retain their color when exposed to basic dyes such as crystal violet and then exposed to organic solvents; named after Danish bacteriologist Hans Christian Joachim Gram

gram positive: bacteria that retain their color when exposed to basic dyes such as crystal violet and then exposed to organic solvents; named after Danish bacteriologist Hans Christian Joachim Gram

Gray: unit of radiation dose per second; 1 Gray = 1 J/kg

greenhouse effect: presence of carbon dioxide in the atmosphere prevents heat from escaping, thereby raising Earth's temperature

Griess reagent: solution of sulfanilic acid and a-naphthylamine in acetic acid; reagent for nitrites

guanine: heterocyclic, purine, amine base found in DNA

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

heavy metal: by convention, a metal with a density greater than 5 g/cm^3; 70 elements are thus classified as heavy metals

helix: in the shape of a spiral or coil, such as a corkscrew

heme group: functional group formed by an iron atom interacting with a heterocyclic ligand called a porphyrin

hemiacetal: relating to organic compounds formed from an alcohol and a carbonyl-containing molecule

hemlock: poisonous herb of the genus Conium

Hippocrates: Greek physician of fifth century B.C.E. known as the "father of medicine"

homogeneous: relating to a mixture of the same materials

homogeneous solution: mixture of molecules that forms a single phase (solid, liquid, or gas)

hormonal signaling: collective processes by which hormones circulate in the blood stream to their target organs and trigger the desired responses

hydrogen bonding: intermolecular force between the H of an N–H, O–H or F–H bond and a lone pair on O, N or F of an adjacent molecule

hydrolyze: to react with water

hydrophilic: having an affinity with water

hydrophobic: water repelling

hyperbolic relationship: a geometric system in which two or more lines can be drawn through any point in a plane and not intersect a given line in that plane

hyperpolarization: process of causing an increase in charge separation in nerve cells; opposite of depolarization

hypertension: condition in which blood pressure is abnormally high

Ibn Sina: given name of an Islamic scientist known in the West as Avicenna (979–1037); reputed to be the author of more than 100 books that were Europe's most important medical texts from the 12th century until the 16th century

inert: incapable of reacting with another substance

inhibitory: preventing an action that would normally occur

integro-differential: complex mathematical model used to calculate a phase transition

interface tension: contractile force at the junction of two liquids

intermediate: molecule, often short-lived, that occurs while a chemical reaction progresses but is not present when the reaction is complete

intermolecular force: force that arises between molecules, generally it is at least one order of magnitude weaker than the chemical bonding force

internuclear: distance between two nuclei

intestinal epithelium: layer of cells in the intestines that allows the passage of water and solutes

intramolecular force: force that arises within molecules—essentially the force associated with chemical bonds

invertebrate: category of animal that has no internal skeleton

in vitro: Latin, meaning "in glass" and applied to experiments done under artificial conditions, that is, in a test tube

in vivo: Latin, meaning "in life" and applied to experiments conducted in a living cell or organism

ion exchange chromatography: form of liquid-solid chromatography based on the reversible formation of bonds between the fixed ions bound to an insoluble matrix of an ion exchanger and mobile counter ions present in the liquid phase passing over the insoluble matrix

ionization: dissociation of a molecule into ions carrying + or − charges

isolate: part of a reaction mixture that is separated and contains the material of interest

isomer: molecules with identical compositions but different structural formulas

isoprene: common name for 2-methyl-1,3butadiene, the monomer of the natural rubber polymer

isostructural: relating to an arrangement of atomic constituents that is geometrically the same although different atoms are present

isotope: form of an atom that differs by the number of neutrons in the nucleus

ketone: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the RC(O)R functional group

kinetic theory: theory of molecular motion

Kohlrausch drum: rotating cylinder used to mount a variable resistance slide wire for a polarograph

lanthanides: a family of elements (atomic number 57 through 70) from lanthanum to lutetium having from 1 to 14 4f electrons

lattice: systematic geometrical arrangement of atomic-sized units that describe the structure of a solid

ligand: molecule or ion capable of donating one or more electron pairs to a Lewis acid

lipid: a nonpolar organic molecule; fatlike; one of a large variety of nonpolar hydrophobic (water-hating) molecules that are insoluble in water

lipophilic: a molecule that tends to congregate in solution with lipids—it will be a nonpolar molecule or the nonpolar portion of a molecule

liposome: sac formed from one or more lipid layers that can be used for drug transport to cells in the body

liquefaction: process of changing to a liquid form

locomotor: able to move from place to place

Lucretius: Roman poet of first century B.C.E., also known as Titus Carus; author of *De Rerum Natura*

lysergic acid: one of the Ergot series of alkaloids, which constrict blood vessels so that the victim develops burning sensations in the limbs, gangrene, and, ultimately, convulsions; the diethylamide of this substance (LSD) induces visual perception disorders, delusion

lysis: breakdown of cells; also the favorable termination of a disease

macrolide: substance with a large ring lactone structure

macronutrient: one of a number of substances, needed in relatively large amounts, that provide nourishment for living organisms

macroscopic phenomena: events observed with human vision unassisted by instrumentation

mammalian toxicity: poisonous effect on humans and other mammals

Manhattan Project: government project dedicated to creation of an atomic weapon; directed by General Leslie Groves

manifold of ensemble states: a set of quantum states that meet the specific requirements (such as total energy) being considered in a calculation

mechanical energy: energy of an object due to its position or motion

mediate: to act as an intermediary agent

melting point: temperature at which a substance in the solid state undergoes a phase change to the liquid state

mentorship: the process by which a wise and trusted teacher guides a novice in the development of his/her abilities

metabolism: the complete range of biochemical processes that take place within living organisms; comprises processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those that break down complex food molecules, thus liberating energy (catabolism)

metabolites: products of biological activity that are important in metabolism

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

metal cation: positively charged ion resulting from the loss of one or more valence electrons

metalloenzyme: a protein enzyme that contains at least one metal atom, often in an active site of the protein

metalloid: elements that exhibit properties that are between those of metals and nonmetals; generally considered to include boron, silicon, germanium, arsensic, antimony, tellurium, and polonium

metallothionein: class of low molecular weight proteins and polypeptides with very high metal and sulfur content; thought to play a role in concentration and flow of essential elements, e.g., Cu and Zn, and in ameliorating the influence of toxic elements, e.g., Hg and Cd, in the body

metallurgy: the science and technology of metals

microchemistry: chemical investigation carried out on a microscopic level

microcrystalline: relating to the structure of crystals of very small size, typically a micron (μm) in dimension

micromolar: relating to a solution of a substance that is in the concentration range of micromoles per liter, or 10^{-6} moles per liter

mitochondrial matrix: soluble phase inside the inner mitochondrial membrane containing most of its enzymes

mitosis: process by which cells divide, particularly the division of the cell nucleus

molecular identity: “fingerprint” of a molecule describing the structure

monoclinic: one of several arrangements of atoms found in crystalline solids; characterized by a unit cell of three axes each of a differing length; two axes are mutually perpendicular while the third is at an oblique angle

monodentate: capable of donating one electron pair; literally, one-toothed

monosaccharide: one class of the natural products called carbohydrates with the general formula $C_x(H_2O)_y$; monosaccharides have a weak sweet taste, are readily soluble in water, and are called sugars

mordant dye: dye substance containing an acidic moiety, e.g., a carboxyl group, which binds metallic compounds, forming insoluble colored compounds

natural philosophy: study of nature and the physical universe

nesosilicate: any silicate in which the SiO_4 tetrahedra are not interlinked

net charge: total overall charge

neurologic: of or pertaining to the nervous system

neuropathy: degenerative state of the nerves or nervous system

neuropeptide: neurotransmitter released into the blood stream via nerve cells

neutron activation analysis: method for detecting traces of elements by bombardment with high-flux neutrons and then measuring the decay rate of the radioactive products

Newtonian: based on the physics of Isaac Newton

nicotine adenine dinucleotide (NAD): one compound of a group of coenzymes found in hydrogen-transferring enzymes

nitric oxide: compound, NO, which is involved in many biological processes; the drug Viagra enhances NO-stimulation of pathways to counteract impotence; may be involved in killing tumors

nitrotoluic acid: benzoic acid molecule with methyl and nitro groups attached

noble gas: element characterized by inert nature; located in the rightmost column in the Periodic Table

noncovalent: having a structure in which atoms are not held together by sharing pairs of electrons

noncovalent aggregation: non-specific interaction leading to the association of molecules

nonpolar: molecule, or portion of a molecule, that does not have a permanent, electric dipole

nuclear: (a) having to do with the nucleus of an atom; (b) having to do with the nucleus of a cell

nucleosynthesis: creation of heavier elements from lighter elements via fusion reactions in stars

octahedral: relating to a geometric arrangement of six ligands equally distributed around a Lewis acid; literally, eight faces

odd chain fatty acid: long chain carboxylic acid with an odd number of carbon atoms

oligomeric chain: chain that contains a few repeating units of a growing polymeric species

opioid: naturally produced opium-like substance found in the brain

optically active: capable of rotating the plane of plane-polarized light

organoleptic: effect of a substance on the five senses

organometallic compound: compound containing both a metal (transition) and one or more organic moieties

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

oxidation state zero: condition characterized by an atom having neither lost nor gained electrons

oxidation–reduction reaction: reaction, sometimes called redox, that involves the movement of electrons between reactants to form products

oxide ion conductor: series of oxides of various compounds in perovskite structure—especially of interest in high-temperature fuel cells

parabolic curve: planar curve each point of which is equidistant from a straight line (axis)

paraffin: saturated aliphatic hydrocarbon (alkane), or hydrocarbon wax

partial pressure: portion of a total pressure of a gas mixture contributed by a single type of gas in the sample

passive diffusion: mechanism of transporting solutes across membranes

pasteurization: process of heating foods such as milk to destroy bacteria

peerage: a body of peers; dignitaries of equal standing

perpendicular: condition in which two lines (or linear entities like chemical bonds) intersect at a 90-degree angle

pH effect: effect caused by a change in the concentration of hydrogen ions

phase: homogenous state of matter

phenol: common name for hydroxybenzene (C_6H_5OH)

phosphorylation: the addition of phosphates into biological molecules

photodiode assembly: grouping of electronic devices which includes a photodiode—a photodetector; useful in medical diagnostics, bar code readers, and guidance systems

photon: a quantum of electromagnetic energy

photosynthesis: process by which plants convert carbon dioxide and water to glucose

physostigmine: alkaloid derived from the leaves of the Calabar bean, formula $C_{15}H_{12}N_3O_2$; salts used for anticholinesterase activity

pilot plant: intermediate stage of testing for chemical process, between bench-top and production scale

planar complex: arrangement of atoms in which all atoms lie within a common two-dimensional plane

plane polorized light: electromagnetic radiation (light) in which the electric (or magnetic) vectors are all vibrating in the same plane

platelet: smallest noncellular component of human blood

pneumatic chemist: early chemist who studied primarily the properties of gases

polynucleotide synthesis: formation of DNA or RNA

polypeptide: compound containing two or more amide units—C(O)NH—produced by the condensation of two or more amino acids

porphyrin: common type of heterocyclic ligand that has four five-member rings with a nitrogen, all of which lie in a plane; nitrogen atom lone pairs are available for coordinate covelent bonds

postsynaptic neuron: receptor nerve cell

potash: the compound potassium oxide, K_2O

precipitation: process of separating a solid substance out of a solution

precursor molecule: molecule that is the chosen starting point for the preparation of another molecule; a starting molecule in a chemical synthesis; a reactant molecule

primary electrochemical cell: voltaic cell based on an irreversible chemical reaction

principal oxidation state: oxidation state that is most important

prism: triangular-shaped material made from quartz or glass used to diffract light

prodrug: precursor of a drug that is converted into an active form by a metabolic process

progesterone: steroid found in the female reproductive system; formula $C_{21}H_{30}O_2$

prokaryotic: relating to very simple cells of the type found in bacteria

propagating: reproducing; disseminating; increasing; extending

protecting group: substance added to a functional group of a molecule preventing further reaction until the substance is removed by subsequent reactions

proximate percent: nearest percent of a population (e.g. people, substances)

purine base: one of two types of nitrogen bases found in nucleic acids

putative: commonly believed or hypothesized

pyramidal: relating to a geometric arrangement of four electron-donating groups at the four vertices of a pyramid

pyrimidine base: one of two types of nitrogen bases found in nucleic acids

pyruvate: anion of pyruvic acid produced by the reaction of oxygen with lactic acid after strenuous exercise

quantum: smallest amount of a physical quantity that can exist independently, especially a discrete amount of electromagnetic energy

quantum mechanical: theoretical model to describe atoms and molecules by wave functions

quantum physics: physics based on the fact that the energy of an electron is equal to its frequency times Planck's constant

radioactive decay: process involving emission of subatomic particles from a nucleus, typically accompanied by emission of very short wavelength electromagnetic radiation

radioelement: a radioactive element; one in which the nucleus spontaneously decomposes (decays) producing α (alpha) and β (beta) particles and γ (gamma) rays

rare earth elements: older name for the lanthanide series of elements, from lanthanum to lutetium

rate-limiting step: slowest step in a complex reaction; it determines the rate of the overall reaction; sometimes called the rate-determining step

reagent: chemical used to cause a specific chemical reaction

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

reducing agent: substance that causes reduction, a process during which electrons are lost (or hydrogen atoms gained)

reducing potential: stored energy capable of making a chemical reduction occur

relativistic calculation: quantum mechanical model that includes the effects of relativity, particularly for core electrons

repulsive force: force that repels two bodies; charges of the same sign repel each other

reserpine: one of a group of alkaloids found naturally in the shrub *Rarewolfia serpentina*; has been used for centuries to treat hypertension, insomnia, and mental disorders; more recently it has been used to reduce blood pressure

retardation: to slow down a chemical reaction

retrosynthetic analysis: method of analyzing chemical reactions that starts with the product and works backward to determine the initial reactants

reverberator furnace: furnace or kiln used in smelting that heats material indirectly by deflecting a nearby flame downward from the roof

ribosome: large complex of proteins used to convert amino acids into proteins

RNA: ribonucleic acid, a natural polymer used to translate genetic information in the nucleus into a template for the construction of proteins

RNA polymerase: enzyme used to make RNA using DNA as a template

rough endoplasmic reticulum: regions of endoplasmic reticulum the outer surfaces of which are heavily studded with ribosomes, which make proteins for activities within membrane-bounded organelles

Royal Society: The U.K. National Academy of Science, founded in 1660

rutile: common name of TiO_2; also a common structural type for compounds with the general composition AB_2

saltpeter: potassium nitrate; chile saltpeter is sodium nitrate

screen: process of comparing multiple reagents simultaneously to provide information on reaction of one reagent with another

seed germination: beginning of the process by which a seed produces a new plant

selenium toxicity: condition created by intake of excess selenium (Se) from plants or seleniferous water; acute and chronic toxicity are known

semisynthetic: produced by synthesis from natural starting materials

serology: the study of serum and reactions taking place within it

sigma plus pi bonding: formation of a double bond within a molecule or ion

single Slater determinant: wave function used to describe atoms and molecules

size of the basis set: number of relatively simple mathematical functions (called the basis set) used to represent a more complicated mathematical function such as an atomic orbital

smelting: process by which ores are reduced in the production of metals

Socrates: Greek philosopher, c.470–399 B.C.E.

somatic cell: cells of the body with the exception of germ cells

spectral line: line in a spectrum representing radiation of a single wavelength

spectroscopy: use of electromagnetic radiation to analyze the chemical composition of materials

spinel: name given to a group of minerals that are double oxides of divalent and trivalent metals, for example, $MgO \cdot Al_2O_3$ or $MgAl_2O_4$; this mineral is called spinel; also a structural type

stacking interactions: one type of interaction that affects conformation of double-stranded DNA; caused by van der Waals forces

stereospecific: yielding one product when reacted with a given compound but the opposite product when reacted with its stereoisomer

steric repulsion: repulsive force that exists when two atoms or groups get too close together

sterol: steroid containing an alcohol group; derived from plants or animals; e.g., cholesterol

stigmasterol: sterol found in soybeans, $C_{29}H_{48}O$

stratosphere: layer of the atmosphere where ozone is found; starts about 6.2 mi (10 km) above ground

streptomycin: antibiotic produced by soil bacteria of genus *Streptomyces*

subcritical: mass of nuclear materials below the amount necessary to cause a chain reaction

subshell: electron energy sublevel, of which there are four: *s*, *p*, *d*, and *f*

sulfonamides: first of a series of drugs used for the prevention and cure of bacterial infections in humans; sulfanomides are amides of sulfuric acids and contain the $–SO_2NRR_1$ group

super-heavy elements: elements of atomic number greater than 103

superhelix: helical-shaped molecule synthesized by another helical-shaped molecule

surfactants: surface-active agents that lower the surface tension of water; e.g., detergents, wetting agents

synaptic cleft: tiny space between the terminal button of one neuron and the dendrite or soma of another

synthesis: combination of starting materials to form a desired product

synthon: in retrosynthesis, molecules are broken into characteristic sections called synthons

tetrachloride: term that implies a molecule has four chlorine atoms present

tetravalent oxidation state: bonding state of an atom that can form four bonds

theoretical physics: branch of physics dealing with the theories and concepts of matter, especially at the atomic and subatomic levels

3′ end: situation in nucleic acids in which the phosphate group is attached at the third carbon atom from where the base is attached

thykaloid membrane: part of a plant that absorbs light and passes the energy on to where it is needed

thymine: one of the four bases that make up a DNA molecule

toluic acids: methylbenzoic acids

torsion balance: instrument used to measure small forces (weights), based upon the resistance of a wire to be twisted

toxicology: division of pharmacology dealing with poisons, their identification, detection, effects on the body, and remedies

toxin: poisonous substance produced during bacterial growth

trace element: element occurring only in a minute amount

transcription: enzyme-catalyzed assembly of an RNA molecule complementary to a strand of DNA

transition metal complex: species formed when a transition metal reacts with ions or molecules, including water

transition metals: elements with valence electrons in d-sublevels; frequently characterized as metals having the ability to form more than one cation

translational process: transfer of information from codon on mRNA to anticodon on tRNA; used in protein synthesis

trigonal bipyramidal: geometric arrangement of five ligands around a central Lewis acid, with ligands occupying the vertices of two trigonal pyramids that share a common face; three ligands share an equatorial plane with the central atom, two ligands occupy an axial position

tropocollagen: fibers, or fibrils, consisting of three polypeptide sequences arranged in a helix

tyrosine: one of the common amino acids

ultraviolet radiation: portion of the electromagnetic spectrum with wavelengths shorter than visible but longer than x rays

uracil: heterocyclic, pyrimidine, amine base found in RNA

valence: combining capacity

vertabrates: animals that have a skeleton

vesicle: small compartment in a cell that contains a minimum of one lipid bilayer

vitamins: organic molecules needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

vitriol: sulfate of a metal; there are blue (Cu), white (Zn), green (Fe), and rose (Co) vitriols

volatile: low boiling, readily vaporized

voltage: potential difference expressed in volts

vulcanized rubber: chemical process of mixing rubber with other materials like sulfur; it strengthens rubber so it can be used under hot or cold conditions; discovered by Charles Goodyear

wetting agent: molecule that, when added to a liquid, facillitates the spread of the liquid across a surface

zoology: branch of biology concerned with the animal kingdom

zwitterion: molecule that simultaneously contains a positive and a negative charge

Index

The number preceding the colon indicates the volume number; the number after the colon indicates the page number. Page numbers in ***boldface type*** indicate article titles; those in *italic type* indicate illustrations. The letter *t* indicates a table.