INTERMOLECULAR ATTRACTIONS AND THE PROPERTIES OF LIQUIDS AND SOLIDS

11

Heated to high temperatures within the earth, lava bursts forth from a volcano's caldera on Hawaii. In addition to the lava, high temperatures and pressures inside the earth contribute to the formation of important minerals such as diamonds. The extreme properties of molten lava and diamond formation can be understood based on the principles in this chapter. *(Joanna McCarthy/Photographers Choice/Getty Images.)*

CHAPTER OUTLINE

THIS CHAPTER IN CONTEXT In the preceding chapter we studied the physical properties of gases, and we observed that all gases behave pretty much alike, regardless of their chemical composition. This is especially so at low pressures and high temperatures, which allows us to use one set of gas laws to describe the behavior of *any* gas. However, when we compare substances in their liquid or solid states (their *condensed states*), the situation is quite different. When a substance is a liquid or a solid, its particles are packed closely together and the forces between them, which we call *intermolecular forces*, are quite strong. Chemical composition and molecular structure play an important role in determining the strengths of such forces, and this causes different substances to behave quite differently from each other when they are liquids or solids.

In this chapter, we focus our attention on the properties of liquids and solids. We begin our study by looking at the basic differences among the states of matter in terms of both common observable properties and the way the states of matter differ at the molecular level. In this chapter we will also examine the different kinds and relative strengths of intermolecular forces. You will learn how they are related to molecular composition and structure, and how intermolecular forces influence a variety of familiar physical properties of liquids, such as boiling points and ease of evaporation. And by studying the energy changes associated with changes of states (for example, evaporation or condensation), you will become familiar with the forces that affect practical applications ranging from evaporative air-conditioning to weather prediction.

11.1 GASES, LIQUIDS, AND SOLIDS DIFFER BECAUSE INTERMOLECULAR FORCES DEPEND ON THE DISTANCES BETWEEN MOLECULES

There are differences among gases, liquids, and solids that are immediately obvious and familiar to everyone. For example, any gas will expand to fill whatever volume is available to it, even if it has to mix with other gases to do so. Liquids and solids, however, retain a constant volume when transferred from one container to another. A solid, such as an ice cube, also keeps its shape, but a liquid such as soda conforms to the shape of whatever bottle or glass we put it in.

In Chapter 10 you learned that gases are easily compressed. Liquids and solids, on the other hand, are nearly *incompressible*, which means their volumes change very little when they are subjected to high pressures. Properties such as the ones we've described can be understood in terms of the way the particles are distributed in the three states of matter, which is summarized in Figure 11.1.

Intermolecular forces depend on distance

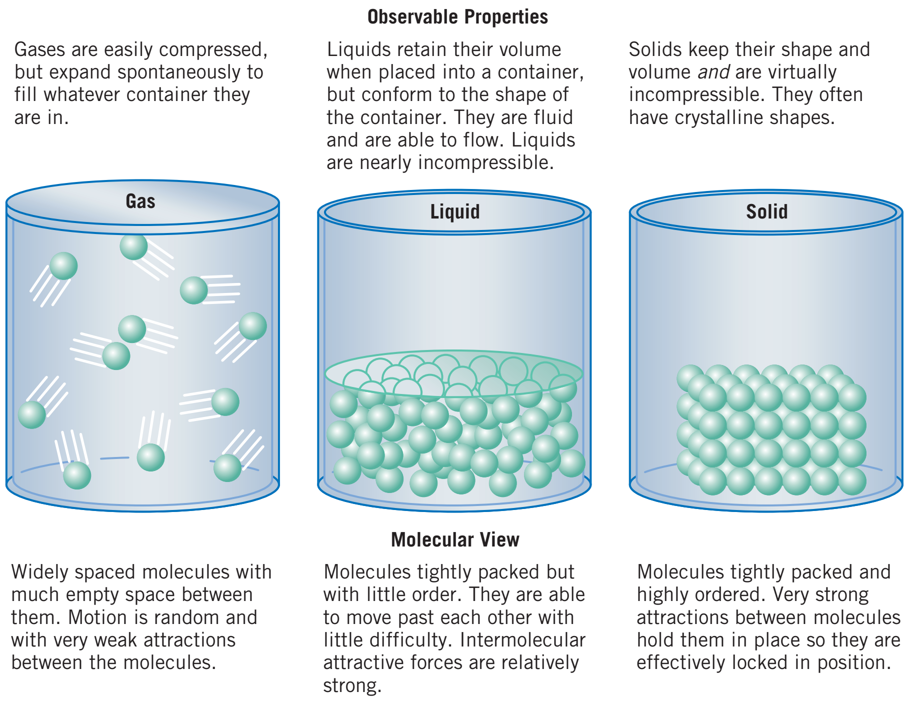
If you've ever played with magnets you know that their mutual attraction weakens rapidly as the distance between them increases. Intermolecular attractions are similarly affected by the distance between molecules, rapidly becoming weaker as the distance between the molecules increases.

In gases, the molecules are so far apart that intermolecular attractions are almost negligible, so differences between the attractive forces hardly matter. As a result, chemical composition has little effect on the properties of a gas. But in a liquid or a solid, the molecules are close together and the attractions are strong. Differences among these attractions caused by differences in chemical makeup are greatly amplified, so the properties of liquids and solids depend quite heavily on chemical composition.

▫ The closer two molecules are, the more strongly they attract each other.

11.2 INTERMOLECULAR ATTRACTIONS INVOLVE ELECTRICAL CHARGES

Inter*molecular forces** (the attractions *between* molecules) are always much weaker than the attractions between atoms *within* molecules (intra*molecular forces,** which are the *chemical bonds* that hold molecules together). In a molecule of HCl, for example,



Gases are easily compressed, but expand spontaneously to fill whatever container they are in.

Liquids retain their volume when placed into a container, but conform to the shape of the container. They are fluid and are able to flow. Liquids are nearly incompressible.

Solids keep their shape and volume *and* are virtually incompressible. They often have crystalline shapes.

Widely spaced molecules with much empty space between them. Motion is random and with very weak attractions between the molecules.

Molecules tightly packed but with little order. They are able to move past each other with little difficulty. Intermolecular attractive forces are relatively strong.

Molecules tightly packed and highly ordered. Very strong attractions between molecules hold them in place so they are effectively locked in position.

FIG. 11.1 **General properties of gases, liquids, and solids.** Properties can be understood in terms of how tightly the molecules are packed together and the strengths of the intermolecular attractions between them.

the H and Cl atoms are held very tightly to each other by a covalent bond, and it is the strength of this bond that affects the *chemical properties* of HCl. The strength of the chemical bond also keeps the molecule intact as it moves about. When a particular chlorine atom moves, the hydrogen atom bonded to it is forced to follow along (see Figure 11.2). Attractions between neighboring HCl molecules, in contrast, are much weaker. In fact, they are only about 4% as strong as the covalent bond in HCl. These weaker attractions are what determine the *physical properties* of liquid and solid HCl.

There are several kinds of intermolecular attractions, which are discussed in this section. They all have something in common; *they arise from attractions between opposite electrical charges.* Collectively, they are called **van der Waals forces,** after J. D. van der Waals who studied the nonideal behavior of real gases.

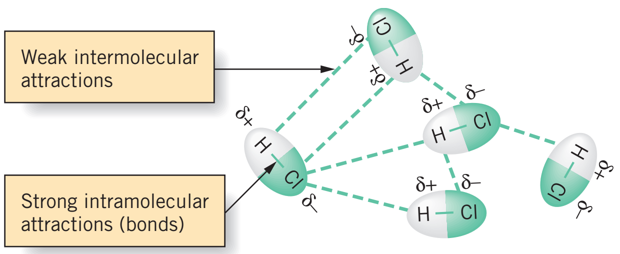
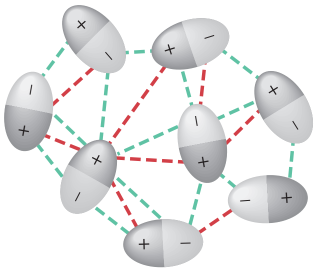


FIG. 11.2 **Attractions within and between hydrogen chloride molecules**. Strong *intramolecular* attractions (chemical bonds) exist between H and Cl atoms within HCl molecules. These attractions control the chemical properties of HCl. Weaker *intermolecular* attractions exist between neighboring HCl molecules. The intermolecular attractions control the physical properties of this substance.

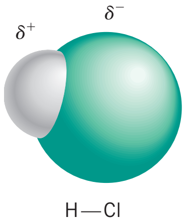


Attractions (– –) are greater than repulsions (– –), so the molecules feel a net attraction to each other.

FIG. 11.3 **Dipole–dipole attractions.** Attractions between polar molecules occur because the molecules tend to align themselves so that opposite charges are near each other and like charges are as far apart as possible. The alignment is not perfect because the molecules are constantly moving and colliding.

Dipole-dipole attractions

Polar molecules, such as HCl, have a partial positive charge at one end and a partial negative charge at the other. Because unlike charges attract, polar molecules tend to line up so the positive end of one dipole is near the negative end of another. Thermal energy (molecular kinetic energy), however, causes the molecules to collide and become disoriented, so the alignment isn't perfect. Nevertheless, there is still a net attraction between them (see Figure 11.3). We call this kind of intermolecular force a **dipole–dipole attraction.** Because collisions lead to substantial misalignment of the dipoles and because the attractions are only between partial charges, dipole–dipole forces are much weaker than covalent bonds, being only about 1–4% as strong. Dipole–dipole attractions fall off rapidly with distance, with the energy required to separate a pair of dipoles being proportional to $1/d^3$, where d is the distance between the dipoles.



Hydrogen bonds

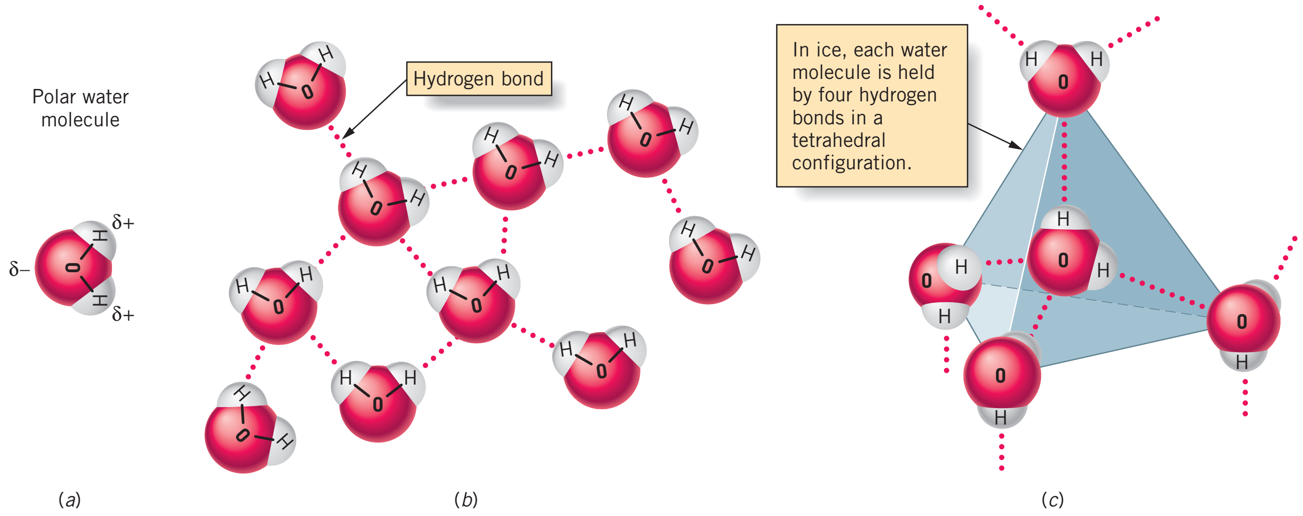
When hydrogen is covalently bonded to a very small, highly electronegative atom (principally, fluorine, oxygen, or nitrogen), a particularly strong type of dipole–dipole attraction occurs that's called **hydrogen bonding.** Hydrogen bonds are exceptionally strong because F—H, O—H, and N—H bonds are very polar, and because the partial charges can get quite close because they are concentrated on very small atoms. Typically, a hydrogen bond is about five to ten times stronger than other dipole–dipole attractions.

Hydrogen bonds in water and biological systems

Most substances become more dense when they change from a liquid to a solid. Not so with water. In liquid water, the molecules experience hydrogen bonds that continually break and re-form as the molecules move around (Figure 11.4*b*). As water begins to freeze, however, the molecules become locked in place, and each water molecule participates in four hydrogen bonds (Figure 11.4*c*). The resulting structure occupies a larger volume than the same amount of liquid water, so ice is less dense than the liquid. Because of this, ice cubes and icebergs float in the more dense liquid. The expansion of freezing water is capable of cracking a car's engine block, which is one reason we add antifreeze to a car's cooling system. Ice formation is also responsible for erosion, causing rocks to split where water has seeped into cracks. And in northern cities, freezing water breaks up pavement, creating potholes in the streets.

◻ A hydrogen bond is not a covalent bond. In water there are oxygen–hydrogen covalent bonds within H_2O molecules and hydrogen bonds between H_2O molecules.

Hydrogen bonding is especially important in biological systems because many molecules in our bodies contain N—H and O—H bonds. Examples are proteins and DNA. Proteins are made up mostly (in some cases, entirely) of long chains of amino acids, linked head to tail to form polypeptides.

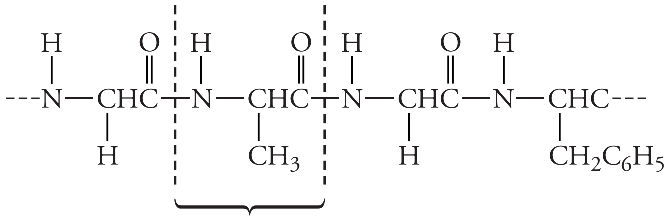


In ice, each water molecule is held by four hydrogen bonds in a tetrahedral configuration.

FIG. 11.4 **Hydrogen bonding in water.** (*a*) The polar water molecule. (*b*) Hydrogen bonding (dotted lines) produces strong attractions between water molecules in the liquid. (*c*) Hydrogen bonding between water molecules in ice, where each water molecule is held by four hydrogen bonds in a tetrahedral configuration.

Part of a polypeptide chain is shown below.

☐ Polypeptides are examples of *polymers*, which are large molecules made by linking together many smaller units called *monomers* (in this case, amino acids). An amino acid contains both a carboxyl group and an amine group, NH_2. An example is glycine, NH_2CH_2COOH.



$$\text{---}\overset{\text{H}}{\overset{|}{\text{N}}}\text{—}\underset{\underset{\text{H}}{|}}{\text{CH}}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—}\overset{\text{H}}{\overset{|}{\text{N}}}\text{—}\underset{\underset{\text{CH}_3}{|}}{\text{CH}}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—}\overset{\text{H}}{\overset{|}{\text{N}}}\text{—}\underset{\underset{\text{H}}{|}}{\text{CH}}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—}\overset{\text{H}}{\overset{|}{\text{N}}}\text{—}\underset{\underset{\text{CH}_2\text{C}_6\text{H}_5}{|}}{\text{CH}}\text{C---}$$

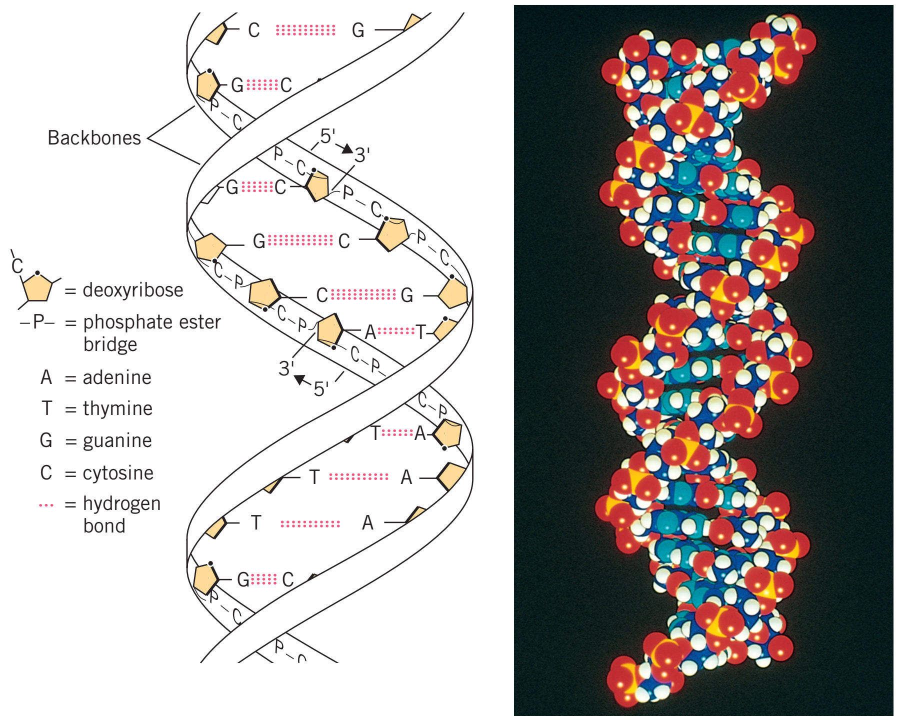
One amino acid segment of a polypeptide

Hydrogen bonding between N—H units in one part of the chain and polar C═O groups in another part help determine the shape of the protein, which greatly influences its biological function. Hydrogen bonding is also responsible for the double helix structure of DNA, which carries our genetic information. This structure is illustrated in Figure 11.5.

London forces

Even nonpolar substances experience intermolecular attractions, as evidenced by the ability of the noble gases and nonpolar molecules such as Cl_2 and CH_4 to condense to liquids, and then crystallize into solids, when cooled to very low temperatures. In such liquids or solids attractions between their particles must exist to cause them to cling together.

In 1930 Fritz London, a German physicist, explained how the particles in even nonpolar substances can experience intermolecular attractions. He noted that in any atom or molecule the electrons are constantly moving. If we could examine such motions in two neighboring particles, we would find that the movement of electrons in one influences the movement of electrons in the other. Because electrons repel each other, as an electron of one particle gets near the other particle, electrons on the second particle are pushed away. This happens continually as the electrons move around, so to some extent, the electron density in both particles flickers back and forth in a synchronous fashion. This is illustrated in Figure 11.6, which depicts a series of instantaneous views of the electron density. Notice that *at any given moment the electron density of a particle can be unsymmetrical,* with more negative charge on one side than on the other. For that particular instant, the particle is a dipole, and we call it a momentary dipole or **instantaneous dipole.**



(*a*) (*b*)

FIG. 11.5 Hydrogen bonding holds the DNA double helix together. (*a*) A schematic drawing in which the hydrogen bonds between the two strands are indicated by dotted lines. The legend to the left of the structure describes the various components of the DNA molecule. (*b*) Phosphorous atoms are shown in blue and they help us trace the DNA "backbone" in this short section of the double helix. *(Nelson Max/Peter Arnold, Inc.)*

As an instantaneous dipole forms in one particle, it causes the electron density in its neighbor to become unsymmetrical, too. As a result, this second particle also becomes a dipole. We call it an **induced dipole** because it is caused by, or *induced* by, the formation of the first dipole. Because of the way the dipoles are formed, they always have the positive end of one near the negative end of the other, so there is a dipole–dipole attraction between them. It is a very short-lived attraction, however, because the electrons keep moving; the dipoles vanish as quickly as they form. But, in another moment, the dipoles will reappear in a different orientation and there will be another brief dipole–dipole attraction. In this way the short-lived dipoles cause momentary tugs between the particles. When averaged over a period of time, there is a net, overall attraction. It tends to be relatively weak, however, because the attractive forces are only "turned on" part of the time.

The momentary dipole–dipole attractions that we've just discussed are called *instantaneous dipole–induced dipole attractions*, to distinguish them from the kind of permanent dipole–dipole attractions that exist without interruption in polar substances like HCl. They are also called **London dispersion forces** (or simply **London forces** or **dispersion forces**).

London forces exist between all molecules and ions. Although they are the only kind of attraction possible between nonpolar molecules, London forces also contribute significantly to the total intermolecular attraction between polar molecules, where they are present in addition to the regular dipole–dipole attractions. London forces even occur between oppositely charged ions, but their effects are relatively weak compared to ionic attractions. London forces contribute little to the net overall attractions between ions and are often ignored.

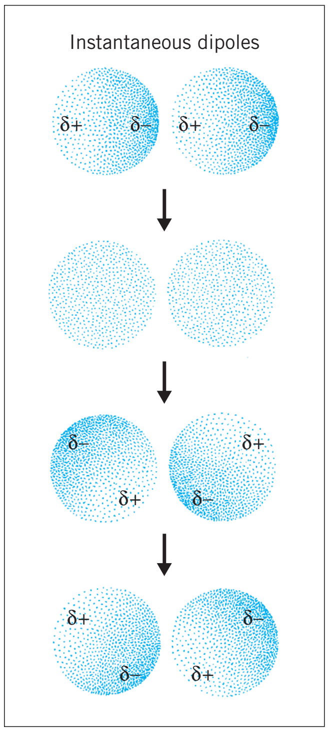
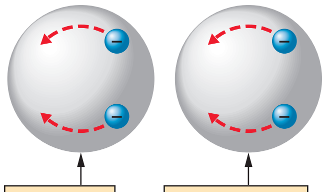


FIG. 11.6 Instantaneous "frozen" views of the electron density in two neighboring particles. Attractions occur between the instantaneous dipoles while they exist.



Electrons in the atom on the left move to the left ...

... when electrons in the atom on the right also move to the left.

The strengths of London forces

To compare the strengths of intermolecular attractions, a property we can use is boiling point. As we will explain in more detail later in this chapter, the higher the boiling point, the stronger are the attractions between molecules in the liquid.

TABLE 11.1 **Boiling Points of the Halogens and Noble Gases**

Group VIIA	Boiling Point (°C)	Group VIIIA	Boiling Point (°C)
F_2	−188.1	He	−268.6
Cl_2	−34.6	Ne	−245.9
Br_2	58.8	Ar	−185.7
I_2	184.4	Kr	−152.3
		Xe	−107.1
		Rn	−61.8

☐ London forces decrease very rapidly as the distance between particles increases. The energy required to separate particles held by London forces varies as $1/d^6$, where d is the distance between the particles.

The strengths of London forces are found to depend chiefly on three factors. One is the **polarizability** of the electron cloud of a particle, which is a measure of the ease with which the electron cloud is distorted, and thus is a measure of the ease with which the instantaneous and induced dipoles can form. In general, *as the volume of the electron cloud increases, its polarizability also increases.* When an electron cloud is large, the outer electrons are generally not held very tightly by the nucleus (or nuclei, if the particle is a molecule). This causes the electron cloud to be "mushy" and rather easily deformed, so instantaneous dipoles and induced dipoles form without much difficulty (see Figure 11.7). As a result, particles with large electron clouds experience stronger London forces than do similar particles with small electron clouds.

The effects of size can be seen if we compare the boiling points of the halogens and the noble gases (see Table 11.1). As the atoms become larger, the boiling points increase, reflecting increasingly stronger intermolecular attractions (stronger London forces).

A second factor that affects the strengths of London forces is the number of atoms in a molecule. For molecules containing the same elements, London forces increase with the number of atoms, as illustrated by the hydrocarbons (see Table 11.2). As the number of atoms increases, there are more places along their lengths where instantaneous dipoles can develop and lead to London attractions (Figure 11.8). Even if the strength of attraction at each location is about the same, the *total* attraction experienced between the longer molecules is greater.[1]

The third factor that affects the strengths of London forces is molecular shape. Even with molecules that have the same number of the same kinds of atoms, those that have compact shapes experience weaker London forces than long, chainlike molecules (Figure 11.9). Presumably, because of the compact shape of the $(CH_3)_4C$ molecule, the individual hydrogens on neighboring molecules cannot interact with each other as effectively as those on the chainlike molecule.

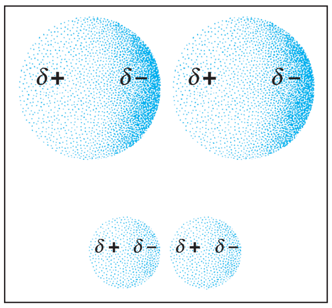


FIG. 11.7 **Effect of molecular size on the strengths of London dispersion forces.** A large electron cloud is more easily deformed than a small one, so in a large molecule the charges on opposite ends of an instantaneous dipole are larger than in a small molecule. Large molecules therefore experience stronger London forces than small molecules.

TABLE 11.2 **Boiling Points of Some Hydrocarbons**[a]

Molecular Formula	Boiling Point at 1 atm (°C)
CH_4	−161.5
C_2H_6	−88.6
C_3H_8	−42.1
C_4H_{10}	−0.5
C_5H_{12}	36.1
C_6H_{14}	68.7
⋮	⋮
$C_{10}H_{22}$	174.1
⋮	⋮
$C_{22}H_{46}$	327

[a] The molecules of each hydrocarbon in this table have carbon chains of the type C—C—C—C—etc.; that is, one carbon follows another.

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[1] The effect of large numbers of atoms on the total strengths of London forces can be compared to the bond between loop and hook layers of the familiar product Velcro. Each loop-to-hook attachment is not very strong, but when large numbers of them are involved, the overall bond between Velcro layers is quite strong.

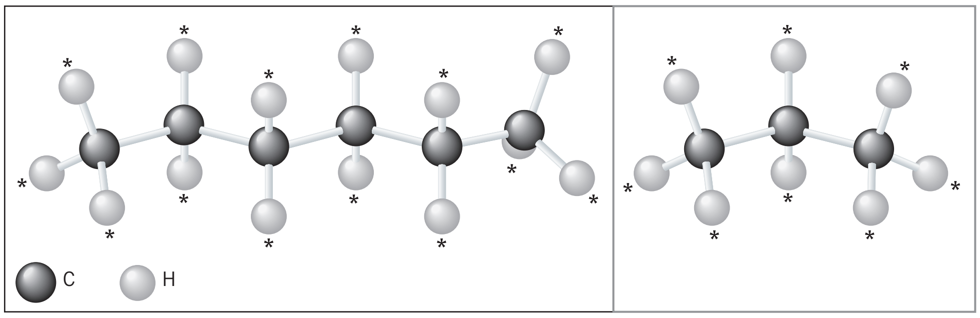
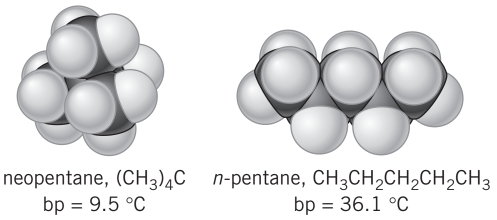


FIG. 11.8 **The number of atoms in a molecule affects London forces.** The C_6H_{14} molecule, left, has more sites (indicated by asterisks, *) along its chain where it can be attracted to other molecules nearby than does the shorter C_3H_8 molecule, right. As a result, the boiling point of C_6H_{14} (hexane, 68.7 °C) is higher than that of C_3H_8 (propane, −42.1 °C).


neopentane, $(CH_3)_4C$
bp = 9.5 °C

n-pentane, $CH_3CH_2CH_2CH_2CH_3$
bp = 36.1 °C

FIG. 11.9 **Molecular shape affects the strengths of London forces.** Shown are two molecules with the formula C_5H_{12}. Not all hydrogen atoms can be seen in these space-filling models. The neopentane molecule, $(CH_3)_4C$, has a more compact shape than the *n*-pentane molecule, $CH_3CH_2CH_2CH_2CH_3$. In the more compact structure, the H atoms cannot interact with those on neighboring molecules as well as the H atoms in the long chainlike structure, so overall the intermolecular attractions are weaker between the more compact molecules

Ion–dipole and ion–induced dipole forces of attraction

In addition to the attractions that exist between neutral molecules, which we discussed above, there are also forces that arise when ions interact with molecules. For example, ions are able to attract the charged ends of polar molecules to give **ion–dipole attractions.** This occurs in water, for example, when ionic compounds dissolve to give hydrated ions. Cations become surrounded by water molecules that are oriented with the negative ends of their dipoles pointing toward the cation. Similarly, anions attract the positive ends of water dipoles. This is illustrated in Figure 11.10. These same interactions can persist into the solid state as well. For example, aluminum chloride crystallizes from water as a hydrate with the formula $AlCl_3{\cdot}6H_2O$. In it the Al^{3+} ion is surrounded by water molecules at the vertices of an octahedron, as illustrated in Figure 11.11. They are held there by ion–dipole attractions.

Ions are also capable of distorting nearby electron clouds, thereby creating dipoles in neighboring particles (like molecules of a solvent, or even other ions). This leads to **ion–induced dipole** attractions, which can be quite strong because the charge on the ion doesn't flicker on and off like the instantaneous charges responsible for ordinary London dispersion forces.

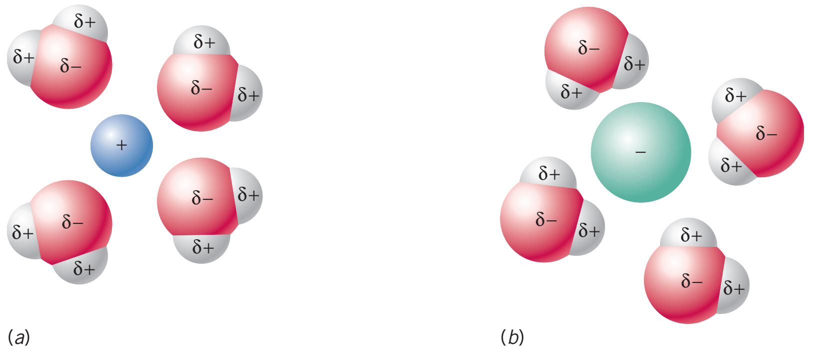


FIG. 11.10 **Ion–dipole attractions.** Here we see the attractions between water molecules and positive and negative ions. (*a*) The negative ends of water dipoles surround a cation and are attracted to the ion. (*b*) The positive ends of water molecules surround an anion, which gives a net attraction.

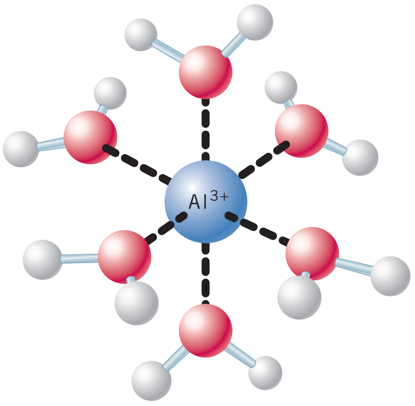


FIG. 11.11 **Ion–dipole attractions hold water molecules in a hydrate.** Water molecules are arranged at the vertices of an octahedron around an aluminum ion in $AlCl_3{\cdot}6H_2O$.

TOOLS

Intermolecular attractions: Hydrogen bonding, dipole–dipole forces, and London forces

TABLE 11.3 Summary of Intermolecular Attractions

Intermolecular Attraction	Types of Substances That Exhibit Attraction	Strength Relative to a Covalent Bond
Dipole–dipole attractions	Occurs between molecules that have permanent dipoles (i.e., polar molecules)	1–5%
Hydrogen bonding	Occurs when molecules contain N—H and O—H bonds	5–10%
London dispersion forces	All atoms, molecules, and ions experience these kinds of attractions. They are present in all substances.	Depends on sizes and shapes of molecules. For large molecules, the cumulative effect of many weak attractions can lead to a large net attraction.
Ion–dipole attractions	Occurs when ions interact with polar molecules	~10%; depends on ion charge and polarity of molecule
Ion–induced dipole attractions	Occurs when an ion creates a dipole in a neighboring particle, which may be a molecule or another ion	Variable, depends on the charge on the ion and the polarizability of its neighbor

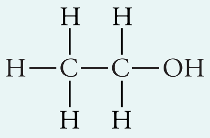
Estimating the effects of intermolecular forces

In this section we have described a number of different types of intermolecular attractive forces and the kinds of substances in which they occur (see the summary in Table 11.3). With this knowledge, you should now be able to make some estimate of the nature and relative strengths of intermolecular attractions if you know the molecular structure of a substance. This will enable you to understand and sometimes predict how the physical properties of different substances compare. For example, we've already mentioned that boiling point is a property that depends on the strengths of intermolecular attractions. By being able to compare intermolecular forces in different substances, we can sometimes predict how their boiling points compare. This is illustrated in Example 11.1.

EXAMPLE 11.1

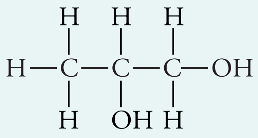
Using Relative Attractive Forces to Predict Properties

Below are structural formulas of ethanol (ethyl alcohol) and propylene glycol (a compound used as a nontoxic antifreeze). Which of these compounds would be expected to have the higher boiling point?



$$\begin{array}{ccccccc} & & \mathrm{H} & & \mathrm{H} & & \\ & & | & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{OH} \\ & & | & & | & & \\ & & \mathrm{H} & & \mathrm{H} & & \end{array}$$

ethanol



$$\begin{array}{ccccccccc} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \\ & & | & & | & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{OH} \\ & & | & & | & & | & & \\ & & \mathrm{H} & & \mathrm{OH} & & \mathrm{H} & & \end{array}$$

propylene glycol

ANALYSIS: We know that boiling points are related to the strengths of intermolecular attractions—the stronger the attractions, the higher the boiling point. Therefore, if we can determine which compound has the stronger intermolecular attractions, we can answer the question. Let's decide which kinds of attractions are present and then try to determine their relative strengths.

SOLUTION: We know that both substances will experience London forces, because they are present between *all* molecules. London forces become stronger as molecules become larger, so the London forces should be stronger in propylene glycol.

Looking at the structures, we see that both contain —OH groups (one in ethanol and two in propylene glycol). This means we can expect that there will be hydrogen bonding in both liquids. Because there are more —OH groups per molecule in propylene glycol than in ethanol, we might reasonably expect that there are more opportunities for the ethylene glycol molecules to participate in hydrogen bonding. This would make the hydrogen bonding forces greater in propylene glycol.

Our analysis tells us that both kinds of attractions are stronger in propylene glycol than in ethanol, so propylene glycol should have the higher boiling point.

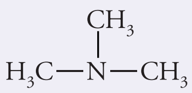
IS THE ANSWER REASONABLE? There's not much we can do to check our answer other than to review the reasoning, which is sound. (We could also check a reference book, where we would find that the boiling point of ethanol is 78.5 °C and the boiling point of propylene glycol is 188.2 °C!)

Practice Exercise 1: List the following in order of their boiling points from lowest to highest. (a) $Ca(OH)_2$, $CH_3CH_2CH_2CH_2CH_3$, CH_3CH_2OH; (b) $CH_3CH_2NH_2$, $CH_3{-}O{-}CH_3$, $HOCH_2CH_2CH_2CH_2OH$. (Hint: Determine what types of intermolecular attractive forces are important for each molecule.)

Practice Exercise 2: Propylamine and trimethylamine have the same molecular formula, C_3H_9N, but quite different structures, as shown below. Which of these substances is expected to have the higher boiling point? Why?

$CH_3{-}CH_2{-}CH_2{-}NH_2$

propylamine



$$H_3C{-}\overset{\displaystyle CH_3 \atop |}{N}{-}CH_3$$

trimethylamine

11.3 INTERMOLECULAR FORCES AND TIGHTNESS OF PACKING AFFECT THE PHYSICAL PROPERTIES OF LIQUIDS AND SOLIDS

Earlier we briefly described some properties of liquids and solids. We continue here with a more in-depth discussion, and we'll start by examining two properties that depend mostly on how tightly packed the molecules are, namely, *compressibility* and *diffusion*. Other properties depend much more on the strengths of intermolecular attractive forces, properties such as *retention of volume or shape, surface tension*, the ability of a liquid to *wet* a surface, the *viscosity* of a liquid, and a solid's or liquid's *tendency to evaporate*.

Compressibility and diffusion depend primarily on tightness of packing

Compressibility

The **compressibility** of a substance is a measure of its ability to be forced into a smaller volume. Gases are highly compressible because the molecules are far apart. However, in a liquid or solid most of the space is taken up by the molecules, and there is very little empty space into which to crowd other molecules. As a result, it is very difficult to compress liquids or solids to a smaller volume by applying pressure, so we say that these states of matter are nearly **incompressible.** This is a useful property. When you "step on the brakes" of a car, for example, you rely on the incompressibility of the brake fluid to transmit the pressure you apply with your foot to the brake shoes on the wheels. The incompressibility of liquids is also the foundation of the engineering science of *hydraulics*, which uses fluids to transmit forces that lift or move heavy objects.

Diffusion

Diffusion occurs much more rapidly in gases than in liquids, and hardly at all in solids. In gases, molecules diffuse rapidly because they travel relatively long distances between collisions, as illustrated in Figure 11.12. In liquids, however, a given molecule suffers many collisions as it moves about, so it takes longer to move from place to place and diffusion is much slower. Diffusion in solids is almost nonexistent at room temperature because the particles of a solid are held tightly in place. At high temperatures, though, the particles of a solid sometimes have enough kinetic energy to jiggle their way past each other, and diffusion can occur slowly. Such high temperature solid-state diffusion is used to make electronic devices, like transistors.

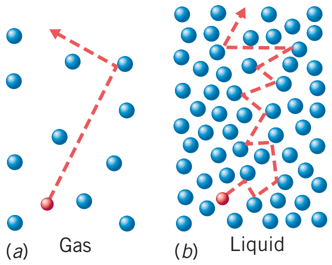


FIG. 11.12 Diffusion in a gas and a liquid viewed at the molecular level. (*a*) Diffusion in a gas is rapid because relatively few collisions occur between widely spaced molecules. (*b*) Diffusion in a liquid is slow because of many collisions between closely spaced particles.

Most physical properties depend primarily on the strengths of intermolecular attractions

Retention of volume and shape

In gases, intermolecular attractions are too weak to prevent the molecules from moving apart to fill an entire vessel, so a gas will conform to the shape and volume of its container. In liquids and solids, however, the attractions are much stronger and are able to hold the particles closely together. As a result, liquids and solids keep the same volume regardless of the size of their container. In a solid, the attractions are even stronger than in a liquid. They hold the particles more or less rigidly in place, so a solid retains its shape when moved from one container to another.

Surface tension

A property that is especially evident for liquids is *surface tension*, which is related to the tendency of a liquid to seek a shape that yields the minimum surface area. For a given volume, the shape with the minimum surface area is a sphere—it's a principle of solid geometry. This is why raindrops tend to be little spheres.

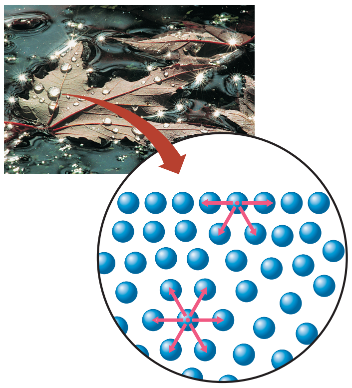
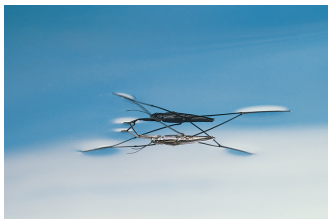


FIG. 11.13 Surface tension and intermolecular attractions. In water, as in other liquids, molecules at the surface are surrounded by fewer molecules than those below the surface. As a result, surface molecules experience fewer attractions than molecules within the liquid. *(Pat O'Hara/Stone/Getty Images.)*

To understand surface tension, we need to examine why molecules would prefer to be within a liquid rather than at its surface. In Figure 11.13 we see that a molecule *within* the liquid is surrounded by densely packed molecules on all sides, whereas one at the *surface* has neighbors beside and below it, but none above. As a result, a surface molecule is attracted to fewer neighbors than one within the liquid. With this in mind, let's imagine how we might change an interior molecule to one at the surface. To accomplish this, we would have to pull away some of the surrounding molecules. Because there are intermolecular attractions, removing neighbors requires work; so there's an increase in potential energy involved. This leads to the conclusion that *a molecule at the surface has a higher potential energy than a molecule in the bulk of the liquid.*

In general, a system becomes more stable when its potential energy decreases. For a liquid, reducing its surface area (and thereby reducing the number of molecules at the surface) lowers its potential energy. The lowest energy is achieved when the liquid has the smallest surface area possible (namely, a spherical shape). In more accurate terms, then, *the* **surface tension** *of a liquid is proportional to the energy needed to expand its surface area.*



An insect called a *water strider*, shown here, is able to walk on water because of the liquid's surface tension, which causes the water to behave as though it has a skin that resists piercing by the insect's legs. *(Hermann Eisenbeiss/Photo Researchers.)*

The tendency of a liquid to spontaneously acquire a minimum surface area explains many common observations. For example, surface tension causes the sharp edges of glass tubing to become rounded when the glass is softened in a flame, an operation called "fire polishing." Surface tension is also what allows us to fill a water glass above the rim, giving the surface a rounded appearance (Figure 11.14). The surface behaves as if it has a thin, invisible "skin" that lets the water in the glass pile up, trying to assume a spherical shape. Gravity, of course, works in opposition, tending to pull the water down. If too much water is added to the glass, the gravitational force finally wins and the skin breaks; the water overflows. If you push on the surface of a liquid, it resists expansion and pushes back, so the surface "skin" appears to resist penetration. This is what enables certain insects to "walk on water," as illustrated in the photo in the margin.

Surface tension is a property that varies with the strengths of intermolecular attractions. Liquids with strong intermolecular attractive forces have large differences in potential energy between their interior and surface molecules, and have large surface tensions.

Not surprisingly, water's surface tension is among the highest known (comparisons being at the same temperature); its intermolecular forces are hydrogen bonds, the strongest kind of dipole–dipole attraction. In fact, the surface tension of water is roughly three times that of gasoline, which consists of relatively nonpolar hydrocarbon molecules able to experience only London forces.

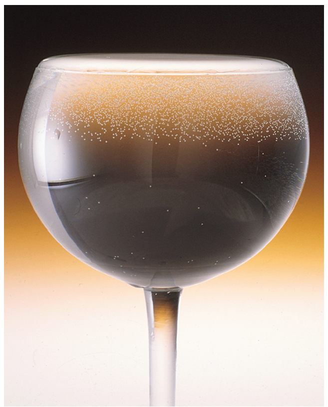


FIG. 11.14 Surface tension in a liquid. Surface tension allows a glass to be filled with water above the rim. *(Michael Watson.)*

Wetting of a surface by a liquid

A property we associate with liquids, especially water, is their ability to wet things. **Wetting** is the spreading of a liquid across a surface to form a thin film. Water wets clean glass, such as the windshield of a car, by forming a thin film over the surface of the glass (see Figure 11.15*a*). Water won't wet a greasy windshield, however. Instead, on greasy glass water forms tiny beads (see Figure 11.15*b*).

For wetting to occur, the intermolecular attractions between the liquid and the surface must be of about the same strength as the attractions within the liquid itself. Such a rough equality exists when water touches clean glass. This is because the glass surface contains lots of oxygen atoms to which water molecules can form hydrogen bonds. As a result, part of the energy needed to expand the water's surface area when wetting occurs is recovered by the formation of hydrogen bonds to the glass surface.

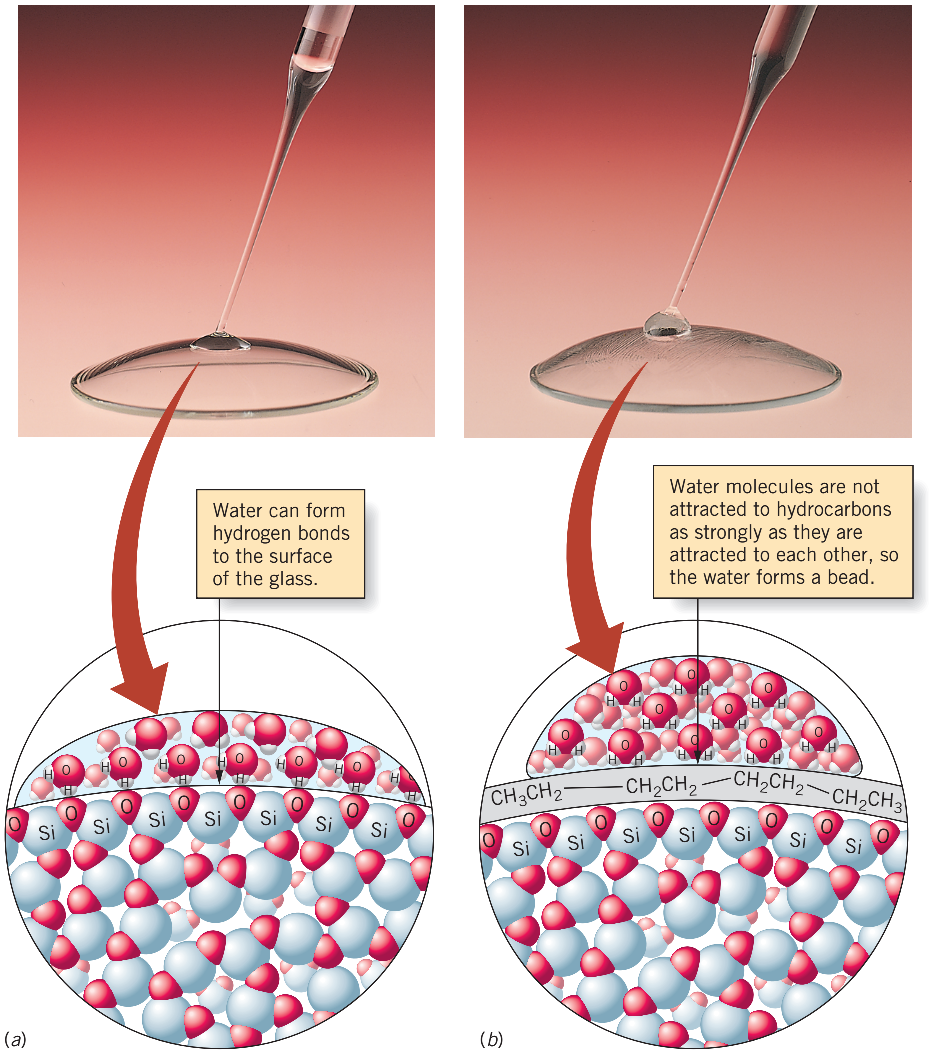


FIG. 11.15 Intermolecular attractions affect the ability of water to wet a surface. (*a*) Water wets a clean glass surface because the surface contains many oxygen atoms to which water molecules can form hydrogen bonds. (*b*) If the surface has a layer of grease, to which water molecules are only weakly attracted, the water doesn't wet it. The water resists spreading and forms a bead instead. *((a), (b) Michael Watson.)*

◻ Glass is characterized by a vast network of silicon–oxygen bonds.

When the glass is coated by a film of oil or grease, the surface exposed to the water drop becomes oil and grease and is now composed of relatively nonpolar molecules (Figure 11.15*b*). These attract other molecules (including water) largely by London forces, which are weak compared with hydrogen bonds. Therefore, the attractions *within* liquid water are much stronger than the attractions *between* water molecules and the greasy surface. The weak water-to-grease London forces can't overcome the hydrogen bonding within liquid water, so the water doesn't spread out; it forms beads instead.

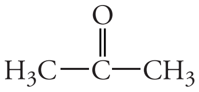
One of the reasons why detergents are used for such chores as doing laundry or washing floors is that detergents contain chemicals called **surfactants** that drastically lower the surface tension of water. This makes the water "wetter," which allows the detergent solution to spread more easily across the surface to be cleaned.

When a liquid has a low surface tension, like gasoline, we know that it has weak intermolecular attractions, and such a liquid easily wets solid surfaces. The weak attractions between molecules in gasoline, for example, are readily replaced by attractions to almost any surface, so gasoline easily spreads to a thin film. If you've ever spilled a little gasoline, you have experienced firsthand that it doesn't bead.

Viscosity

As everybody knows, syrup flows less readily or is more resistant to flow than water (both at the same temperature). Flowing is a change in the *form* of the liquid, and such resistance to a change in form is called the liquid's **viscosity.** We say that syrup is more *viscous* than water. The concept of viscosity is not confined to liquids, however, although it is with liquids that the property is most commonly associated. Solid things, even rock, also yield to forces acting to change their shapes, but normally do so only gradually and imperceptibly. Gases also have viscosity, but they respond almost instantly to form-changing forces.

Viscosity has been called the "internal friction" of a material. It is influenced both by intermolecular attractions and by molecular shape and size. For molecules of similar size, we find that as the strengths of the intermolecular attractions increase, so does the viscosity. For example, consider acetone (nail polish remover) and ethylene glycol (automotive antifreeze), each of which contains 10 atoms.



$$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

acetone

$$HO-CH_2-CH_2-OH$$

ethylene glycol

Ethylene glycol is more viscous than acetone, and looking at the molecular structures, it's easy to see why. Acetone contains a polar carbonyl group ($\gt C{=}O$), so it experiences dipole–dipole attractions as well as London forces. Ethylene glycol, on the other hand, contains two $-OH$ groups, so in addition to London forces, ethylene glycol molecules also participate in hydrogen bonding (a much stronger interaction than ordinary dipole–dipole forces). Strong hydrogen bonding in ethylene glycol makes it more viscous than acetone.

- If you've ever spilled a little acetone, you know that it flows very easily. In contrast, ethylene glycol has an "oily" thickness to it and flows more slowly.

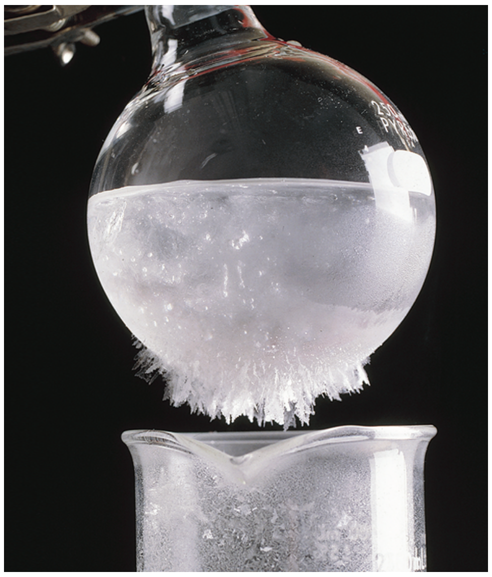
Molecular size and the ability of molecules to tangle with each other is another major factor in determining viscosity. The long, floppy, entangling molecules in heavy machine oil (almost entirely a mixture of long chain, nonpolar hydrocarbons), plus the London forces in the material, give it a viscosity roughly 600 times that of water at 15 °C. Vegetable oils, like the olive oil or corn oil used to prepare salad dressings, consist of molecules that are also large but generally nonpolar. Olive oil is roughly 100 times more viscous than water.

Viscosity also depends on temperature; as the temperature drops, the viscosity increases. When water, for example, is cooled from its boiling point to room temperature, its viscosity increases by over a factor of three. The increase in viscosity with cooling is why operators of vehicles use a "light," thin (meaning less viscous) motor oil during subzero weather.

- As the temperature drops, molecules move more slowly and intermolecular forces become more effective at restraining flow.

Evaporation and sublimation are affected by intermolecular attractions

One of the most important physical properties of liquids and solids is their tendency to undergo a change of state from liquid to gas or from solid to gas. For liquids, the change is called **evaporation.** For solids, which can also change directly to the gaseous state by evaporation without going through the liquid state, we use a special term, **sublimation.** Solid carbon dioxide is commonly called *dry ice* because it doesn't melt. Instead, at atmospheric pressure it *sublimes,* changing directly to gaseous CO_2. Naphthalene, the ingredient in some brands of moth flakes, is another substance that can sublime and seemingly disappear.



Naphthalene sublimes when heated and the vapor condenses directly to a solid when it encounters a cool surface. Here, beautiful flaky naphthalene crystals have been formed on the bottom of a flask containing ice water. *(Michael Watson.)*

To understand evaporation and sublimation, we have to examine the motions of molecules. In a solid or liquid, molecules are not stationary; they bounce around, colliding with their neighbors. At a given temperature, there is *exactly the same* distribution of kinetic energies in a liquid or a solid as there is in a gas, which means that Figure 6.4 on page 212 applies to liquids and solids, too. This figure tells us that at a given temperature a small fraction of the molecules have very large kinetic energies and therefore very high velocities. When one of these high velocity molecules is at the surface and is moving outward fast enough, it can escape the attractions of its neighbors and enter the vapor state. We say the molecule has left by evaporation (or by sublimation, if the substance is a solid).

Evaporation produces a cooling effect

One of the things we notice about the evaporation of a liquid is that it produces a cooling effect. You've experienced this if you've stepped out of a shower and been chilled by the air. The evaporation of water from your body produced this effect. In fact, our bodies use the evaporation of perspiration to maintain a constant body temperature.

We can see why liquids become cool during evaporation by examining Figure 11.16, which illustrates the kinetic energy distribution in a liquid at a particular temperature. A marker along the horizontal axis shows the minimum kinetic energy needed by a molecule to escape the attractions of its neighbors. Only molecules with kinetic energies equal to or greater than the minimum can leave the liquid. Others may begin to leave, but before they can escape they slow to a stop and then fall back. Notice in Figure 11.16 that the minimum kinetic energy needed to escape is much larger than the average, which means that when molecules evaporate they carry with them large amounts of kinetic energy. As a result, the average kinetic energy of the molecules left behind decreases. (You might think of this as being similar to removing people taller than 6 ft from a large class of students. When this is done, the average height of those who are left is less.) Because the Kelvin temperature of the remaining liquid is directly proportional to the now lower average kinetic energy, the temperature is lower; in other words, evaporation causes the liquid that remains to be cooler.

The rate of evaporation depends on surface area, temperature, and strengths of intermolecular attractions

Later in this chapter we are going to be concerned about the *rate of evaporation* of a liquid. There are several factors that control this. You are probably already aware of one of them—the surface area of the liquid. Because evaporation occurs from the liquid's surface and not from within, it makes sense that as the surface area is increased, more molecules are able to escape

◻ To understand how temperature and intermolecular forces affect the rate of evaporation, we must compare evaporation rates from the same size surface area. In this discussion, therefore, "rate of evaporation" means "rate of evaporation *per unit surface area.*"

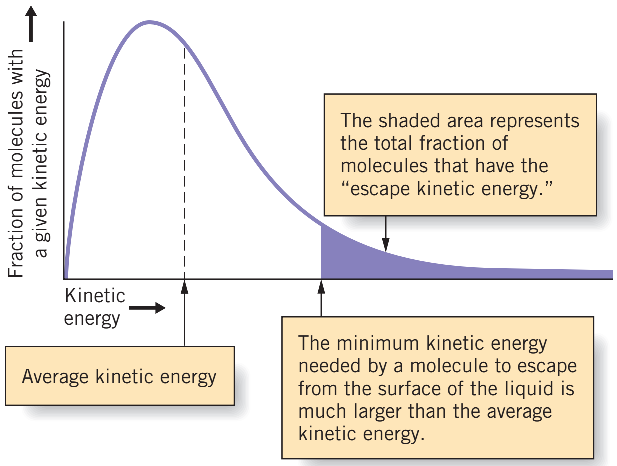
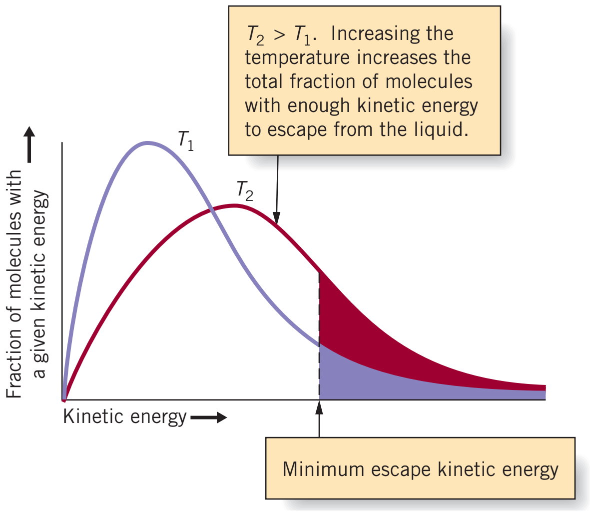


FIG. 11.16 Cooling of a liquid by evaporation. Molecules that are able to escape from the liquid have kinetic energies larger than the average. When they leave, the average kinetic energy of the molecules left behind is less, so the temperature is lower.



$T_2 > T_1$. Increasing the temperature increases the total fraction of molecules with enough kinetic energy to escape from the liquid.

Minimum escape kinetic energy

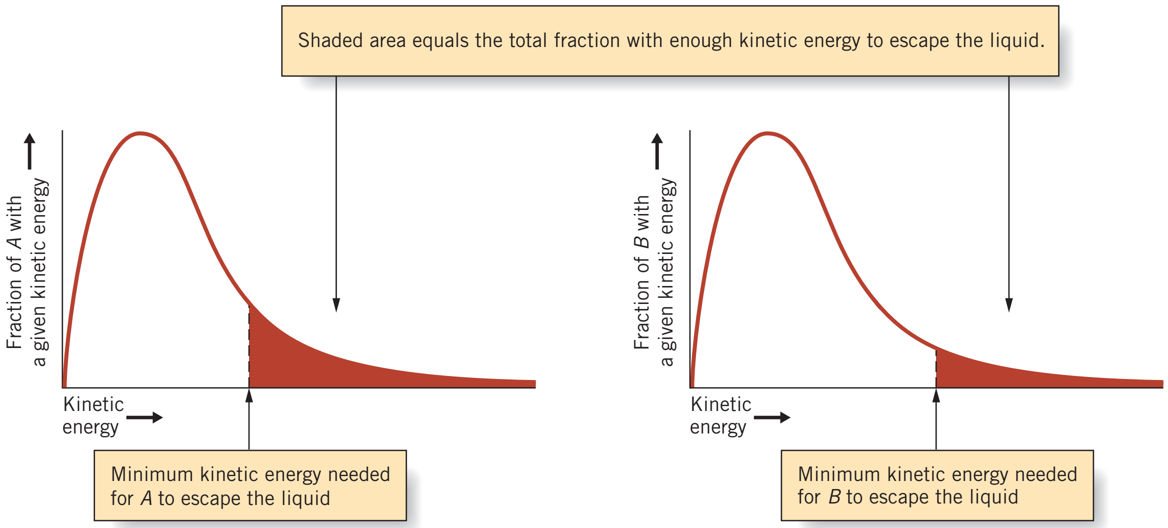
FIG. 11.17 Effect of increasing the temperature on the rate of evaporation of a liquid. At the higher temperature, the total fraction of molecules with enough kinetic energy to escape is larger, so the rate of evaporation is larger.

and the liquid evaporates more quickly. For liquids having the same surface area, the rate of evaporation depends on two factors, namely, temperature and the strengths of intermolecular attractions. Let's examine each of them separately.

TOOLS
Effect of temperature on rate of evaporation

The influence of temperature on evaporation rate is no surprise; you already know that hot water evaporates faster than cold water. The reason can be seen by studying Figure 11.17, which shows kinetic energy distributions for the *same* liquid at two temperatures. Notice two important features of the figure. First, the same minimum kinetic energy is needed for the escape of molecules at both temperatures. This minimum is determined by the kinds of attractive forces between the molecules, and is independent of temperature. Second, the shaded area of the curve represents the *total* fraction of molecules having kinetic energies equal to or greater than the minimum. At the higher temperature, the total fraction is larger, which means that at the higher temperature a greater total fraction has the ability to evaporate. As you might expect, when more molecules have the needed energy, more evaporate in a unit of time. Therefore, *the rate of evaporation per unit surface area of a given liquid is greater at a higher temperature.*

The effect of intermolecular attractions on evaporation rate can be seen by studying Figure 11.18. Here we have kinetic energy distributions for two *different* liquids—call them



Shaded area equals the total fraction with enough kinetic energy to escape the liquid.

Minimum kinetic energy needed for *A* to escape the liquid

Minimum kinetic energy needed for *B* to escape the liquid

FIG. 11.18 Kinetic energy distribution in two different liquids, *A* and *B*, at the same temperature. The minimum kinetic energy required by molecules of *A* to escape is less than that for *B* because the intermolecular attractions in *A* are weaker than in *B*. This causes *A* to evaporate faster than *B*.

A and *B*—both at the same temperature. In liquid *A*, the attractive forces are weak; they might be of the London type, for example. As we see, the minimum kinetic energy needed by *A* molecules to escape is not very large because they are not attracted very strongly to each other. In liquid *B*, the intermolecular attractive forces are much stronger; they might be hydrogen bonds, for instance. Molecules of *B*, therefore, are held more tightly to each other at the liquid's surface and must have a higher kinetic energy to evaporate. As you can see from the figure, the total fraction of molecules with enough energy to evaporate is greater for *A* than for *B*, which means that *A* evaporates faster than *B*. In general, then, *the weaker the intermolecular attractive forces, the faster is the rate of evaporation at a given temperature*. You are probably also aware of this phenomenon. At room temperature, for example, nail polish remover [acetone, $(CH_3)_2CO$], whose molecules experience weak dipole–dipole and London forces of attraction, evaporates faster than water, whose molecules feel the effects of much stronger hydrogen bonds.

TOOLS *Intermolecular forces and rate of evaporation*

11.4 CHANGES OF STATE LEAD TO DYNAMIC EQUILIBRIA

A **change of state** occurs when a substance is transformed from one physical state to another. Evaporation of a liquid and sublimation of a solid are two examples. Others are the melting of a solid such as ice and the freezing of a liquid such as water.

One of the important features about changes of state is that, at any particular temperature, they always tend toward a condition of *dynamic equilibrium*. We introduced the concept of dynamic equilibrium on page 142 with an example of a system at chemical equilibrium. The same general principles apply to a physical equilibrium, such as that between a liquid and its vapor. Let's see how such an equilibrium is established.

▫ In chemistry (unless otherwise indicated), when we use the term *equilibrium*, we always mean *dynamic equilibrium.*

When a liquid is placed in an empty container, it immediately begins to evaporate and molecules of the substance begin to collect in the space above the liquid (see Figure 11.19*a*). As they fly around in the vapor, the molecules collide with each other, with the walls of the container, and with the surface of the liquid itself. Those that strike the liquid's surface tend to stick because their kinetic energies become scattered among the surface molecules. This change, which involves vapor molecules changing to the liquid state, is called **condensation.**

Initially, when the liquid is first introduced into the container, the rate of evaporation is high, but the rate of condensation is very low because there are few molecules in the vapor state. As vapor molecules accumulate, the rate of condensation increases. This continues until the rate at which molecules are condensing becomes equal to the rate at which they are evaporating (Figure 11.19*b*). From that moment on, the number of molecules in the vapor will remain constant, because over a given period of time the

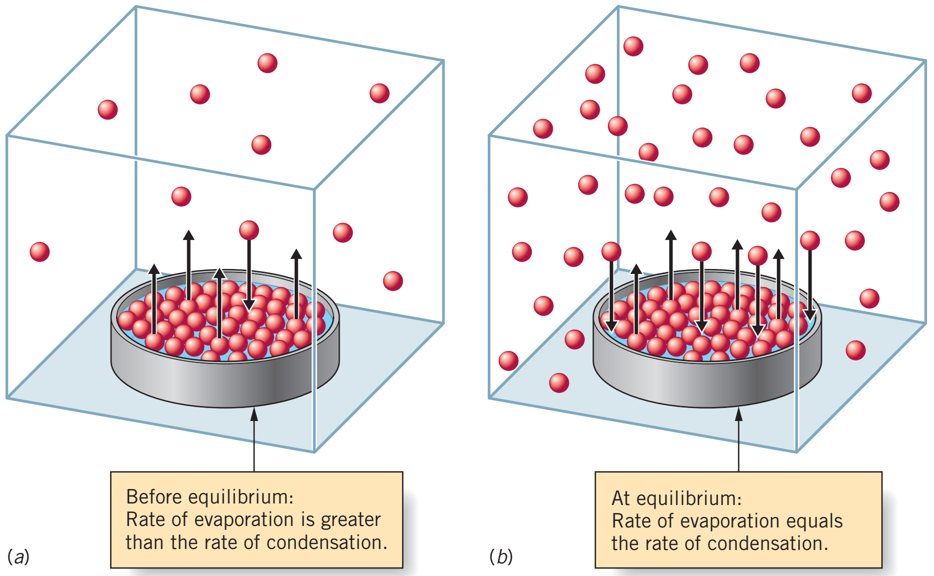


FIG. 11.19 Evaporation of a liquid into a sealed container. (*a*) The liquid has just begun to evaporate into the container. The rate of evaporation is greater than the rate of condensation. (*b*) A dynamic equilibrium is reached when the rate of evaporation equals the rate of condensation. In a given time period, the number of molecules entering the vapor equals the number that leave, so there is no net change in the number of gaseous molecules.

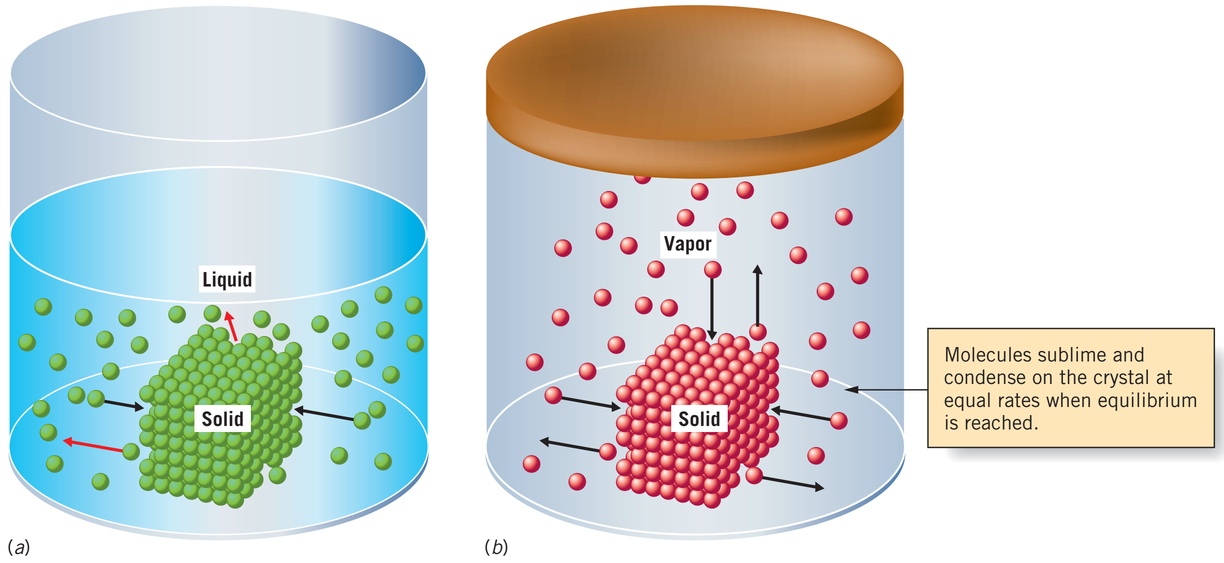


FIG. 11.20 **Solid–liquid and solid–vapor equilibria.** (*a*) As long as no heat is added or removed, melting (red arrows) and freezing (black arrows) occur at equal rates and the number of particles in the solid remains constant. (*b*) Equilibrium is established when molecules evaporate from the solid at the same rate as they condense from the vapor.

number that enters the vapor is the same as the number that leaves. At this point we have a condition of *dynamic equilibrium,* one in which two opposing effects, evaporation and condensation, are occurring at equal rates.

▫ A vapor–liquid equilibrium is possible only in a closed container. When the container is open, vapor molecules drift away and the liquid might completely evaporate.

Similar equilibria are also reached in melting and sublimation. At a temperature called the **melting point,** a solid begins to change to a liquid as heat is added. At this temperature a dynamic equilibrium can exist between molecules in the solid and those in the liquid. Molecules leave the solid and enter the liquid at the same rate as molecules leave the liquid and join the solid (Figure 11.20*a*). As long as no heat is added or removed from such a solid–liquid equilibrium mixture, melting and freezing occur at equal rates. For sublimation, the situation is exactly the same as in the evaporation of a liquid into a sealed container (see Figure 11.20*b*). After a few moments, the rates of sublimation and condensation become the same and equilibrium is established.

11.5 VAPOR PRESSURES OF LIQUIDS AND SOLIDS ARE CONTROLLED BY TEMPERATURE AND INTERMOLECULAR ATTRACTIONS

▫ A liquid with a high vapor pressure at a given temperature is said to be **volatile.**

When a liquid evaporates, the molecules that enter the vapor exert a pressure called the **vapor pressure.** From the very moment a liquid begins to evaporate into the vapor space above it, there is a vapor pressure. If the evaporation is taking place inside a sealed container, this pressure grows until finally equilibrium is reached. Once the rates of evaporation and condensation become equal, the concentration of molecules in the vapor remains constant and the vapor exerts a constant pressure. This final pressure is called the **equilibrium vapor pressure of the liquid.** In general, when we refer to the *vapor pressure,* we really mean the equilibrium vapor pressure.

Two factors determine the equilibrium vapor pressure

TOOLS
Factors that affect vapor pressure

Figure 11.21 shows plots of equilibrium vapor pressure versus temperature for a few liquids. From these graphs we see that both a liquid's temperature and its chemical composition are the major factors affecting its vapor pressure. Once we have selected a particular liquid, however, only the temperature matters. The reason is that the vapor pressure of a given liquid is a function solely of its rate of evaporation *per unit area of the liquid's surface.* When this rate is large, a large concentration of molecules in the vapor state is necessary to establish

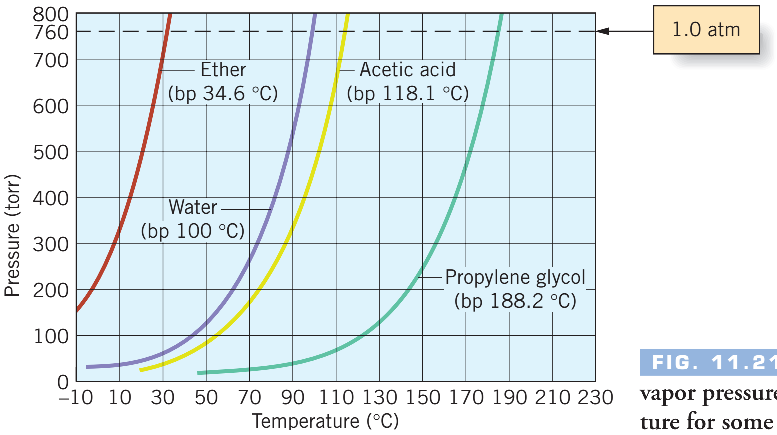


FIG. 11.21 **Variation of vapor pressure with temperature for some common liquids.**

equilibrium, which is another way of saying that the vapor pressure is relatively high when the evaporation rate is high. As the temperature of a given liquid increases, so does its rate of evaporation and so does its equilibrium vapor pressure.

As chemical composition changes in going from one liquid to another, the strengths of intermolecular attractions change. If the attractions increase, the rates of evaporation at a given temperature decrease, and the vapor pressures decrease. These data on relative vapor pressures tell us that, of the four liquids in Figure 11.21, intermolecular attractions are strongest in propylene glycol, next strongest in acetic acid, third strongest in water, and weakest in ether. Thus, *we can use vapor pressures as indications of relative strengths of the attractive forces in liquids.*

Some factors do not affect the vapor pressure

An important fact about vapor pressure is that *its magnitude doesn't depend on the* ***total*** *surface area of the liquid, nor on the volume of the liquid in the container, nor on the volume of the container itself, just as long as some liquid remains when equilibrium is reached.* The reason is because none of these factors affects the rate of evaporation *per unit surface area.*

Increasing the *total* surface area does increase the *total* rate of evaporation, but the larger area is also available for condensation; so the rate at which molecules return to the liquid also increases. The rates of both evaporation and condensation are thus affected equally, and no change occurs to the equilibrium vapor pressure.

Adding more liquid to the container can't affect the equilibrium either because evaporation occurs from the *surface*. Having more molecules in the bulk of the liquid does not change what is going on at the surface.

To understand why the vapor pressure doesn't depend on the *size* of the vapor space, consider a liquid in equilibrium with its vapor in a cylinder with a movable piston, as illustrated in Figure 11.22*a*. Withdrawing the piston (Figure 11.22*b*) increases the volume of the vapor space; as the vapor expands, the pressure it exerts becomes less, so there's a momentary drop in the pressure. The molecules of the vapor, being more spread out now, no longer strike the surface as frequently, so the rate of condensation also decreases. The rate of evaporation hasn't changed, however, so for a moment the system is not at equilibrium and the substance is evaporating faster than it is condensing (Figure 11.22*b*). This condition prevails, changing more liquid into vapor, until the concentration of molecules in the vapor has risen enough to make the condensation rate again equal to the evaporation rate (Figure 11.22*c*). At this point the vapor pressure has returned to its original value. Therefore, the net result of expanding the space above the liquid is to change more liquid into vapor, but it does not affect the equilibrium vapor pressure. Similarly, we expect that reducing the volume of the vapor space above the liquid will also not affect the equilibrium vapor pressure.

Practice Exercise 3: Considering Figure 11.22, in which direction should the piston be moved to decrease the number of molecules in the gas phase? (Hint: Consider what must happen to re-establish equilibrium after the piston is moved.)

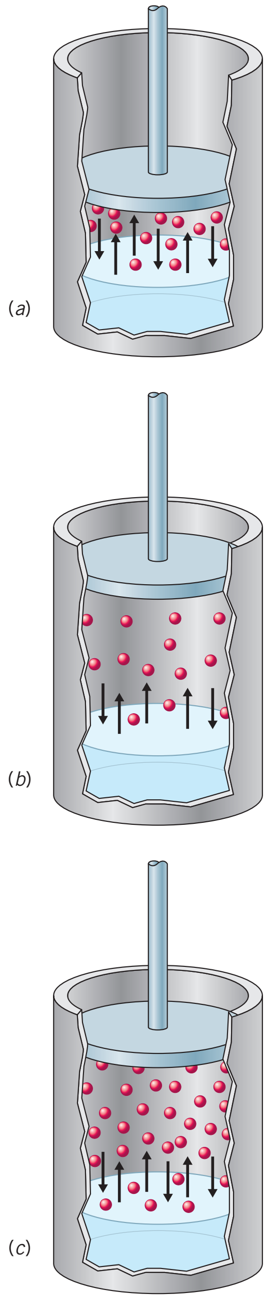


FIG. 11.22 **Effect of a volume change on the vapor pressure of a liquid.** (*a*) Equilibrium exists between liquid and vapor. (*b*) The volume is increased, which upsets the equilibrium and causes the pressure to drop. The rate of condensation is now less than the rate of evaporation, which hasn't changed. (*c*) After more liquid has evaporated, equilibrium is restored and the rates of condensation and evaporation are again equal and the vapor pressure has returned to its initial value.

Practice Exercise 4: Suppose a liquid is in equilibrium with its vapor in a piston–cylinder apparatus like that in Figure 11.22. If the piston is pushed in a short way and the system is allowed to return to equilibrium, what will have happened to the *total number* of molecules in both the liquid and the vapor?

Solids also have vapor pressures

Solids have vapor pressures just as liquids do. In a crystal, the particles are constantly jiggling around, bumping into their neighbors. At a given temperature there is a distribution of kinetic energies, so some particles at the surface have large enough kinetic energies to break away from their neighbors and enter the vapor state. When particles in the vapor collide with the crystal, they can be recaptured, so condensation can occur too. Eventually, the concentration of particles in the vapor reaches a point where the rate of sublimation equals the rate of condensation, and a dynamic equilibrium is established. The pressure of the vapor that is in equilibrium with the solid is called the **equilibrium vapor pressure of the solid.** As with liquids, this equilibrium vapor pressure is usually referred to simply as the vapor pressure. Like that of a liquid, the vapor pressure of a solid is determined by the strengths of the attractive forces between the particles and by the temperature.

□ In many solids, such as NaCl, the attractive forces are so strong that virtually no particles have enough kinetic energy to escape at room temperature, so essentially no evaporation occurs. Their vapor pressures at room temperature are virtually zero.

11.6 BOILING OCCURS WHEN A LIQUID'S VAPOR PRESSURE EQUALS ATMOSPHERIC PRESSURE

If you were asked to check whether a pot of water was boiling, what would you look for? The answer, of course, is *bubbles*. When a liquid boils, large bubbles usually form at many places on the inner surface of the container and rise to the top. If you were to place a thermometer into the boiling water, you would find that the temperature remains constant, regardless of how you adjust the flame under the pot. A hotter flame just makes the water bubble faster, but it doesn't raise the temperature. *Any pure liquid remains at a constant temperature while it is boiling,* a temperature that's called the liquid's *boiling point.*

If you measure the boiling point of water in Philadelphia, New York, or any place else that is nearly at sea level, your thermometer will read 100 °C or very close to it. However, if you try this experiment in Denver, Colorado, you will find that water boils at about 95 °C. Denver, at a mile above sea level, has a lower atmospheric pressure, so we find that the boiling point depends on the atmospheric pressure.

□ On the top of Mt. Everest, the world's tallest peak, water boils at only 69 °C.

These observations raise some interesting questions. Why do liquids boil? And why does the boiling point depend on the pressure of the atmosphere? The answers become apparent when we realize that inside the bubbles of a boiling liquid is the *liquid's vapor*, not air. When water boils, the bubbles contain water vapor (steam); when alcohol boils, the bubbles contain alcohol vapor. As a bubble grows, liquid evaporates into it, and the pressure of the vapor pushes the liquid aside, making the size of the bubble increase (see Figure 11.23). Opposing the bubble's internal vapor pressure, however, is the pressure of the atmosphere pushing down on the top of the liquid, attempting to collapse the bubble. The only way the bubble can exist and grow is for the vapor pressure within it to equal (maybe just slightly exceed) the pressure exerted by the atmosphere. In other words, bubbles of vapor cannot even form until the temperature of the liquid rises to a point at which the liquid's vapor pressure equals the atmospheric pressure. Thus, in scientific terms, the **boiling point** is defined as *the temperature at which the vapor pressure of the liquid is equal to the prevailing atmospheric pressure.*

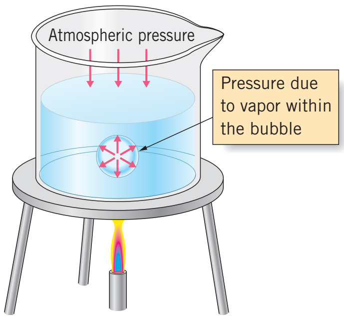


FIG. 11.23 A liquid at its boiling point. The pressure of the vapor within a bubble in a boiling liquid pushes the liquid aside against the opposing pressure of the atmosphere. Bubbles can't form unless the vapor pressure of the liquid is at least equal to the pressure of the atmosphere.

Now we can easily understand why water boils at a lower temperature in Denver than it does in New York City. Because the atmospheric pressure is lower in Denver, the water there doesn't have to be heated to as high a temperature to make its vapor pressure equal to the atmospheric pressure. The lower temperature of boiling water at places with high altitudes, like Denver, makes it necessary to cook foods longer. At the other extreme, a pressure cooker is a device that increases the pressure over the boiling water and thereby raises the boiling point. At the higher temperature, foods cook more quickly.

To make it possible to compare the boiling points of different liquids, chemists have chosen 1 atm as the reference pressure. The boiling point of a liquid at 1 atm is called its **normal boiling point.** (If a boiling point is reported without also mentioning the pressure at which it was measured, we assume it to be the normal boiling point.) Notice in Figure 11.21, page 449, that we can find the normal boiling points of ether, water, acetic acid, and propylene glycol by noting the temperatures at which their vapor pressure curves cross the 1 atm pressure line.

Boiling point is affected by intermolecular attractions

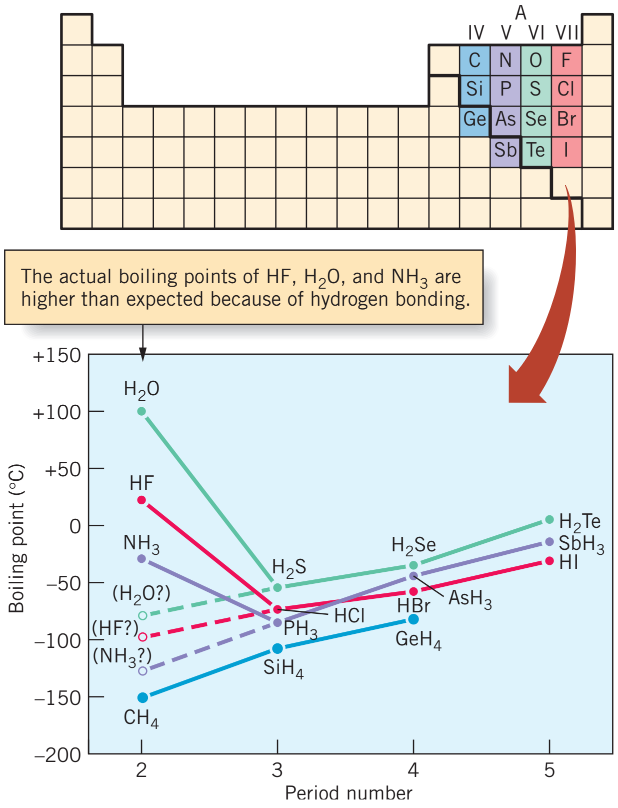
Earlier we mentioned that the boiling point is a property whose value depends on the strengths of the intermolecular attractions in a liquid. When the attractive forces are strong, the liquid has a low vapor pressure at a given temperature, so it must be heated to a high temperature to bring its vapor pressure up to atmospheric pressure. High boiling points therefore result from strong intermolecular attractions, so we often use normal boiling point data to assess relative intermolecular attractions among different liquids. (In fact, we did this in solving Example 11.1.)

The effects of intermolecular attractions on boiling point are easily seen by examining Figure 11.24, which gives the plots of the boiling points versus period numbers for some families of binary hydrogen compounds. Notice, first, the gradual increase in boiling point for the hydrogen compounds of the Group IVA elements (CH_4 through GeH_4). These compounds are composed of nonpolar tetrahedral molecules. The boiling points increase from CH_4 to GeH_4 simply because the molecules become larger and their electron clouds become more polarizable, which leads to an increase in the strengths of the London forces.

When we look at the hydrogen compounds of the other nonmetals, we find the same trend from Period 3 through Period 5. Thus, for three compounds of the Group VA series, PH_3, AsH_3, and SbH_3, there is a gradual increase in boiling point, corresponding again to the increasing strengths of London forces. Similar increases occur for the three Group VIA compounds (H_2S, H_2Se, and H_2Te) and for the three Group VIIA compounds (HCl, HBr, and HI). Significantly, however, the Period 2 members of each of these series (NH_3, H_2O, and HF) have much higher boiling points than might otherwise be expected. The reason is that each is involved in hydrogen bonding, which is a much stronger attraction than London forces.

TOOLS

Boiling ponts are related to intermolecular attractive forces



The actual boiling points of HF, H_2O, and NH_3 are higher than expected because of hydrogen bonding.

FIG. 11.24 Effects of intermolecular attractions on boiling point. Boiling points of the hydrogen compounds of elements of Groups IVA, VA, VIA, and VIIA of the periodic table. The dashed lines lead to hypothetical boiling points, if hydrogen bonding did not exist, for HF, H_2O, and NH_3.

One of the most interesting and far-reaching consequences of hydrogen bonding is that it causes water to be a liquid, rather than a gas, at temperatures near 25 °C. If it were not for hydrogen bonding, water would have a boiling point somewhere near −80 °C and could not exist as a liquid except at still lower temperatures. At such low temperatures it is unlikely that life as we know it could have developed.

Practice Exercise 5: The Dead Sea is approximately 1300 ft below sea level and its barometric pressure is approximately 830 torr. Will the boiling point of water be elevated from 100 °C by (a) less than 10 °C, (b) 10 °C to 25 °C, (c) 25 °C to 50 °C, or (d) above 50 °C? (Hint: Extrapolate from Figure 11.21.)

Practice Exercise 6: The atmospheric pressure at the top of Mt. McKinley in Alaska, 3.85 miles above sea level, is 330 torr. Use Figure 11.21 to estimate the boiling point of water at the top of the mountain.

11.7 ENERGY CHANGES OCCUR DURING CHANGES OF STATE

When a liquid or solid evaporates or a solid melts, there are increases in the distances between the particles of the substance. Particles that normally attract each other are forced apart, increasing their potential energies. Such energy changes affect our daily lives in many ways, especially the energy changes associated with the changes in state of water, changes which even control the weather on our planet. To study these energy changes, let's begin by examining how the temperature of a substance varies as it is heated.

Heating curves and cooling curves reveal changes in kinetic and potential energy

Figure 11.25*a* illustrates the way the temperature of a substance changes as we add heat to it *at a constant rate*, starting with the solid and finishing with the gaseous state of the substance. The graph is sometimes called a **heating curve** for the substance.

First, let's look at the portions of the graph that slope upward. These occur where we are increasing the temperature of the solid, liquid, and gas phases. Because temperature is related to average kinetic energy, nearly all of the heat we add in these regions of the heating curve goes to increasing the average kinetic energies of the particles. In other words, the added heat makes the particles go faster and collide with each other with more force. In addition, the slopes of the rising portions have units of degrees Celsius per joule.

▫ When a solid or liquid is heated, the volume expands only slightly, so there are only small changes in the average distance between the particles. This means that very small changes in potential energy take place, so almost all the heat added goes to increasing the kinetic energy.

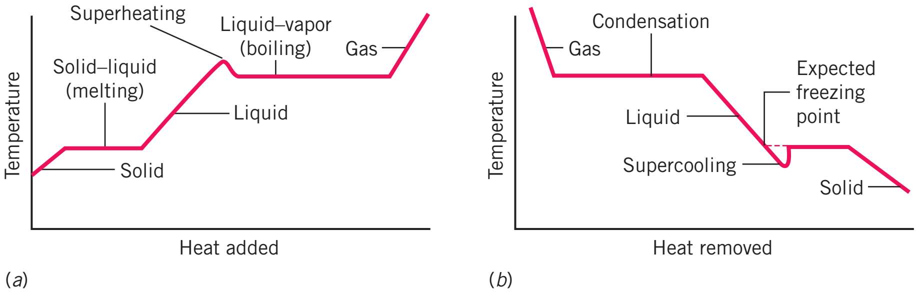


FIG. 11.25 **Heating and cooling curves.** (*a*) A heating curve observed when heat is added to a substance at a constant rate. The temperatures corresponding to the flat portions of the curve occur at the melting point and boiling point. Superheating in shown as continued heating beyond the boiling point. (*b*) A cooling curve observed when heat is removed from a substance at a constant rate. Condensation of vapor to a liquid occurs at the same temperature as the liquid boils. Supercooling is seen here as the temperature of the liquid dips below its freezing point (the same temperature as its melting point). Once a tiny crystal forms, the temperature rises to the freezing point.

This is the reciprocal of the heat capacity, meaning that the greater the slope, the lower the heat capacity. Gases have lower heat capacities than liquids and solids, therefore the heating of the gas phase has the largest slope.

In those portions of the heating curve where the temperature remains constant, the average kinetic energy of the particles is not changing. This means that all the heat being added must go to increase the *potential energies* of the particles. During melting, the particles held rigidly in the solid begin to separate slightly as they form the mobile liquid phase. The potential energy increase accompanying this process equals the amount of heat input during the melting process. During boiling, there is an even greater increase in the distance between the molecules. Here they go from the relatively tight packing in the liquid to the widely spaced distribution of molecules in the gas. This gives rise to an even larger increase in the potential energy, which we see as a longer flat region on the heating curve during the boiling of the liquid.

The opposite of a heating curve is a **cooling curve** (see Figure 11.25*b*). Here we start with a gas and gradually cool it—remove heat from it at a constant rate—until we have reached a solid.

Superheating and supercooling

Looking at Figure 11.25 again we notice two unusual features, one on each curve. There is a small "blip" on the heating curve near the transition from the liquid to a gas. A similar feature occurs when a liquid is cooled to a solid. These "blips" represent the phenomena of superheating and supercooling. Superheating occurs when the liquid is heated above the boiling point without boiling. If disturbed, a **superheated liquid** will erupt with a shower of vapor and liquid. Many people have discovered this effect when heating their favorite beverage in a microwave oven. When cooling a liquid it is possible to decrease the temperature below the freezing point without solidification occurring, creating a supercooled liquid. Once again if the supercooled liquid is disturbed, very rapid crystallization occurs. Some commercial products take advantage of supercooling to provide an instant heat source for minor injuries since the crystallization process often evolves large quantities of heat.

☐ Supercooling of a vapor is also possible. Condensation of supercooled water vapor onto solid surfaces leads to dew in warm weather and frost in freezing weather.

Molar heats of fusion, vaporization, and sublimation

TOOLS *Enthalpy changes in phase change*

Because phase changes occur at constant temperature and pressure, the potential energy changes associated with melting and vaporization can be expressed as enthalpy changes. Usually, enthalpy changes are expressed on a "per mole" basis and are given special names to identify the kind of change involved. For example, using the word **fusion** instead of "melting," *the* **molar heat of fusion, ΔH_{fusion},** *is the heat absorbed by one mole of a solid when it melts to give a liquid at the same temperature and pressure.* Similarly, *the* **molar heat of vaporization, $\Delta H_{\text{vaporization}}$,** *is the heat absorbed when one mole of a liquid is changed to one mole of vapor at a constant temperature and pressure.* Finally, *the* **molar heat of sublimation, $\Delta H_{\text{sublimation}}$,** *is the heat absorbed by one mole of a solid when it sublimes to give one mole of vapor, once again at a constant temperature and pressure*. The values of ΔH for fusion, vaporization, and sublimation are all positive because the phase change in each case is endothermic, being accompanied by a net increase in potential energy.

☐ These are also called *enthalpies* of fusion, vaporization, and sublimation.

Examples of the influence of these energy changes on our daily lives abound. For example, you've added ice to a drink to keep it cool because as the ice melts, it absorbs heat (its heat of fusion). Your body uses the heat of vaporization of water to cool itself through the evaporation of perspiration. During the summer, ice cream trucks carry dry ice because the sublimation of CO_2 absorbs its heat of sublimation and keeps the ice cream cold. And perhaps most importantly, weather on our planet is driven by the heat of vaporization of water which serves to convert solar energy into the energy of winds and storms. For example, over oceans large storms such as hurricanes rely on a continued supply of warm moist air produced by rapid evaporation of H_2O from tropical waters. Continual condensation in the high clouds forms rain and supplies the energy needed to feed the storm's winds.

Fusion means melting. The thin metal band in an electrical fuse becomes hot as electricity passes through it. It protects a circuit by melting if too much current is drawn. On the right we see a fuse that has done its job. *(Michael Watson.)*

Solidification of a liquid to a crystal, condensation of a gas to a liquid, or deposition of a gas as a solid are simply the reverse of fusion, vaporization, and sublimation processes. Therefore the heat of crystallization is equal to the heat of fusion but it has the opposite algebraic sign. Similarly the heats of condensation and deposition have the opposite signs of their counterparts.

Since heat is released when liquids condense or when gases become solids or liquids, that heat can be put to practical use. For example, a supersaturated solution of ammonium nitrate can be caused to crystallize inside a plastic bag. The heat liberated is used to treat some sports injuries with this "heat pack." Similarly, meteorologists can often use the "dew point" of the atmosphere to predict overnight low temperatures. The dew point is the temperature at which moisture in the air begins to condense. If the nighttime temperature decreases to the dew point, the heat released by the condensation of water keeps the temperature from falling much further.

FACETS OF CHEMISTRY 11.1

Determining Heats of Vaporization

The way the vapor pressure varies with temperature, which was described in Section 11.5 and Figure 11.21, depends on the heat of vaporization of a substance. The relationship, however, is not a simple proportionality. Instead, it involves *natural logarithms*, which are logarithms to the base *e* as compared to the more familiar base-10 logarithms. With modern calculators the logarithm function can be applied with the press of the *ln* key for natural logarithms and the *log* key for base-10 logarithms. The reverse process of taking an "antilogarithm" uses an *inv* or *2nd* function key with the *ln* or *log* keys on most calculators.

Rudolf Clausius (1822–1888), a German physicist, and Benoit Clapeyron (1799–1864), a French engineer, used the principles of thermodynamics (a subject that's discussed in Chapter 18) to derive the following equation that relates the vapor pressure, heat of vaporization (ΔH_{vap}), and temperature

$$\ln P = \frac{-\Delta H_{\text{vap}}}{RT} + C \qquad (1)$$

The quantity ln P is the natural logarithm of the vapor pressure, R is the gas constant expressed in energy units ($R = 8.314$ J mol^{-1} K^{-1}), T is the absolute temperature, and C is a constant. Scientists call this the **Clausius–Clapeyron equation.**

The Clausius–Clapeyron equation provides a convenient graphical method for determining heats of vaporization from experimentally measured vapor pressure–temperature data. To see this, let's rewrite the equation as follows.

$$\ln P = \left(\frac{-\Delta H_{\text{vap}}}{R}\right)\frac{1}{T} + C$$

Recall from algebra that a straight line is represented by the general equation

$$y = mx + b$$

where x and y are variables, m is the slope, and b is the intercept of the line with the y axis. In this case, we can make the substitutions

$$y = \ln P \qquad x = \frac{1}{T} \qquad m = \frac{-\Delta H_{\text{vap}}}{R} \qquad b = C$$

Therefore, we have

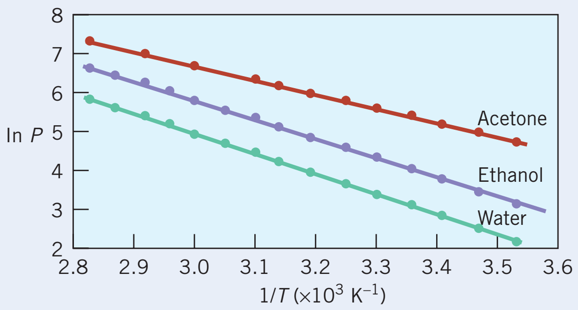
$$\begin{array}{ccccccc} \ln P & = & \left(\dfrac{-\Delta H_{\text{vap}}}{R}\right) & \dfrac{1}{T} & + & C \\ \Updownarrow & & \Updownarrow & \Updownarrow & & \Updownarrow \\ y & = & m & x & + & b \end{array}$$

Thus, a graph of ln P versus $1/T$ should give a straight line that has a slope equal to $-\Delta H_{\text{vap}}/R$. Such straight line relationships are illustrated in Figure 1 in which experimental data are plotted for water, acetone, and ethanol. From the graphs in Figure 1, the calculated values of ΔH_{vap} are as follows: for water, 43.9 kJ mol^{-1}; for acetone, 32.0 kJ mol^{-1}; and for ethanol, 40.5 kJ mol^{-1}.

Using Equation 1 above, a "two point" form of the Clausius–Clapeyron equation can be derived that can be used to calculate ΔH_{vap} if the vapor pressure is known at two different temperatures. This equation is

$$\ln \frac{P_1}{P_2} = \frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (2)$$

If we know the value of the heat of vaporization, Equation 2 can also be used to calculate the vapor pressure at some particular temperature (say, P_2 at a temperature T_2) if we already know the vapor pressure P_1 at a temperature T_1.



The numbers along the horizontal axis are equal to $1/T$ values multiplied by 1000 to make the axis easier to label.

Figure 1 A graph showing plots of ln P versus $1/T$ for acetone, ethanol, and water.

TABLE 11.4 Some Typical Heats of Vaporization

Substance	$\Delta H_{\text{vaporization}}$ (kJ mol^{-1})	Type of Attractive Force
H_2O	+43.9	Hydrogen bonding and London
NH_3	+21.7	Hydrogen bonding and London
HCl	+15.6	Dipole–dipole and London
SO_2	+24.3	Dipole–dipole and London
F_2	+5.9	London
Cl_2	+10.0	London
Br_2	+15.0	London
I_2	+22.0	London
CH_4	+8.16	London
C_2H_6	+15.1	London
C_3H_8	+16.9	London
C_6H_{14}	+30.1	London

Energy changes are related to intermolecular attractions

When a liquid evaporates or a solid sublimes, the particles go from a situation in which the attractive forces are very strong to one in which the attractive forces are so small they can almost be ignored. Therefore, the values of $\Delta H_{\text{vaporization}}$ and $\Delta H_{\text{sublimation}}$ give us directly the energy needed to separate molecules from each other. We can examine such values to obtain reliable comparisons of the strengths of intermolecular attractions.

TOOLS

Intermolecular attractive forces are related to heats of vaporization and sublimation

In Table 11.4, notice that the heats of vaporization of water and ammonia are very large, which is just what we would expect for hydrogen-bonded substances. By comparison, CH_4, a nonpolar substance composed of atoms of similar size, has a very small heat of vaporization. Note also that polar substances such as HCl and SO_2 have fairly large heats of vaporization compared with nonpolar substances. For example, compare HCl with Cl_2. Even though Cl_2 contains two relatively large atoms, and therefore would be expected to have larger London forces than HCl, the HCl has the larger $\Delta H_{\text{vaporization}}$. This must be due to dipole–dipole attractions between polar HCl molecules—attractions that are absent in nonpolar Cl_2.

☐ The stronger the attractions, the more the potential energy will increase when the molecules become separated, and the larger will be the value of ΔH.

Heats of vaporization also reflect the factors that control the strengths of London forces. For example, the data in Table 11.4 show the effect of chain length on the intermolecular attractions between hydrocarbons; as the chain length increases from one carbon in CH_4 to six carbons in C_6H_{14}, the heat of vaporization also increases, showing that the London forces also increase. Similarly, the heats of vaporization of the halogens in Table 11.4 show that the strengths of London forces increase as the electron clouds of the particles become larger.

11.8

CHANGES IN A DYNAMIC EQUILIBRIUM CAN BE ANALYZED USING LE CHÂTELIER'S PRINCIPLE

Throughout this chapter, we have studied various dynamic equilibria. One example was the equilibrium that exists between a liquid and its vapor in a closed container. You learned that when the temperature of the liquid is increased in this system, its vapor pressure also increases. Let's briefly review why this occurs.

Initially, the liquid is in equilibrium with its vapor, which exerts a certain pressure. When the temperature is increased, equilibrium no longer exists because evaporation occurs more rapidly than condensation. Eventually, as the concentration of molecules in the vapor increases, *the system reaches a new equilibrium* in which there is more vapor and a little less liquid. The greater concentration of molecules in the vapor causes a larger pressure.

The way a liquid's equilibrium vapor pressure responds to a temperature change is an example of a general phenomenon. *Whenever a dynamic equilibrium is upset by some disturbance, the system changes in a way that will, if possible, bring the system back to equilibrium again.* It's also important to understand that in the process of regaining equilibrium, the system undergoes a net change. Thus, when the temperature of a liquid is raised, there is some net conversion of liquid into vapor as the system returns to equilibrium. When the new equilibrium is reached, the amount of liquid and the amount of vapor are not the same as they were before.

Throughout the remainder of this book, we will deal with many kinds of equilibria, both chemical and physical. It would be very time-consuming and sometimes very difficult to carry out a detailed analysis each time we wish to know the effects of some disturbance on an equilibrium system. Fortunately, there is a relatively simple and fast method for predicting the effect of a disturbance, one based on a principle proposed in 1888 by a brilliant French chemist, Henry Le Châtelier (1850–1936).

TOOLS
Le Châtelier's principle

Le Châtelier's Principle. When a dynamic equilibrium in a system is upset by a disturbance, the system responds in a *direction* that tends to counteract the disturbance and, if possible, restore equilibrium.

Let's see how we can apply Le Châtelier's principle to a liquid–vapor equilibrium that is subjected to a temperature increase. We cannot increase a temperature, of course, without adding heat. Thus, *the addition of heat is really the disturbing influence when a temperature is increased.* So let's incorporate "heat" as a member of the equation used to represent the liquid–vapor equilibrium.

$$\text{Heat} + \text{liquid} \rightleftharpoons \text{vapor} \qquad (11.1)$$

Recall that we use double arrows, $\rightleftharpoons$, to indicate a dynamic equilibrium in an equation. They imply opposing changes happening at equal rates. Evaporation is endothermic, so the heat is placed on the left side of Equation 11.1 to show that heat is absorbed by the liquid when it changes to the vapor, and that heat is released when the vapor condenses to a liquid.

Le Châtelier's principle tells us that when we add heat to raise the temperature of the equilibrium system, the system will try to adjust in a way that absorbs some of the added heat. This can happen if some liquid evaporates, because vaporization is endothermic. When liquid evaporates, the amount of vapor increases and causes the pressure to rise. Thus, we have reached the correct conclusion in a very simple way, namely, that heating a liquid must increase its vapor pressure.

We often use the term **position of equilibrium** to refer to the relative amounts of the substances on opposite sides of the double arrows in an equilibrium expression such as Equation 11.1. Thus, we can think of how a disturbance affects the position of equilibrium. For example, increasing the temperature increases the amount of vapor and decreases the amount of liquid, and we say *the position of equilibrium has shifted*; in this case, it has shifted in the direction of the vapor, or it has *shifted to the right*. In using Le Châtelier's principle, it is often convenient to think of a disturbance as "shifting the position of equilibrium" in one direction or another in the equilibrium equation.

Practice Exercise 7: Use Le Châtelier's principle to predict how a temperature increase will affect the vapor pressure of a solid. (Hint: Solid + heat $\rightleftharpoons$ vapor.)

Practice Exercise 8: Designate whether each of the following physical processes is exothermic or endothermic. Can any of them be exothermic for some substances and endothermic for others? Boiling, melting, condensing, subliming, freezing

FIG. 11.26 Crystals of table salt. The size of the tiny cubic sodium chloride crystals can be seen in comparison with a penny. *(The Photo Works.)*

11.9 CRYSTALLINE SOLIDS HAVE AN ORDERED INTERNAL STRUCTURE

When many substances freeze, or when they separate as a solid from a solution, they tend to form crystals that have highly regular features. For example, Figure 11.26 is a photograph of crystals of sodium chloride—ordinary table salt. Notice that each particle is very nearly a perfect little cube. Whenever a solution of NaCl is evaporated, the crystals that form have edges that intersect at 90° angles. Thus, cubes are the norm for NaCl.

Crystals in general tend to have flat surfaces that meet at angles that are characteristic of the substance. The regularity of these surface features reflects the high degree of order among the particles that lie within the crystal. This is true whether the particles are atoms, molecules, or ions.

Crystal structures are described by lattices and unit cells

Any repetitive pattern has a symmetrical aspect about it, whether it be a wallpaper design or the orderly packing of particles in a crystal (Figure 11.27). For example, we can easily recognize certain repeating distances between the elements of the pattern, and we can see that the lines along which the elements of the pattern repeat are at certain angles to each other.

To concentrate on the symmetrical features of a repeating structure, it is convenient to describe it in terms of a set of points that have the same repeat distances as the structure, arranged along lines oriented at the same angles. Such a pattern of points is called a **lattice,** and when we apply it to describe the packing of particles in a solid, we often call it a **crystal lattice.**

In a crystal, the number of particles is enormous. If you could imagine being at the center of even the tiniest crystal, you would find that the particles go on as far as you can see in every direction. Describing the positions of all these particles or their lattice points is impossible and, fortunately, unnecessary. All we need to do is describe the repeating unit of the lattice, which we call the *unit cell.* To see this, and to gain an insight into the usefulness of the lattice concept, let's begin in two dimensions.

In Figure 11.28 we see a two-dimensional *square lattice*, which means the lattice points lie at the corners of squares. The repeating unit of the lattice, its **unit cell,** is indicated in the drawing. If we began with this unit cell, we could produce the entire lattice by moving it repeatedly left and right and up and down by distances equal to its edge length. In this sense, all the properties of a lattice are contained in the properties of its unit cell.

An important fact about lattices is that the same lattice can be used to describe many different designs or structures. For example, in Figure 11.28*b*, we see a design formed by associating a pink heart with each lattice point. Using a square lattice, we could form any number of designs just by using different design elements (for example, a rose or a diamond) or by changing the lengths of the edges of the unit cell. *The only requirement is that the same design element must be associated with each lattice point.* In other words, if there is a rose at one lattice point, then there must be a rose at all the other lattice points.

Extending the lattice concept to three dimensions is straightforward. Illustrated in Figure 11.29 is a *simple cubic* (also called a **primitive cubic**) lattice, the simplest and most symmetrical three-dimensional lattice. Its unit cell, the **simple cubic unit cell,** is a cube with lattice points only at its eight corners. Figure 11.29*c* shows the packing of atoms in a crystal

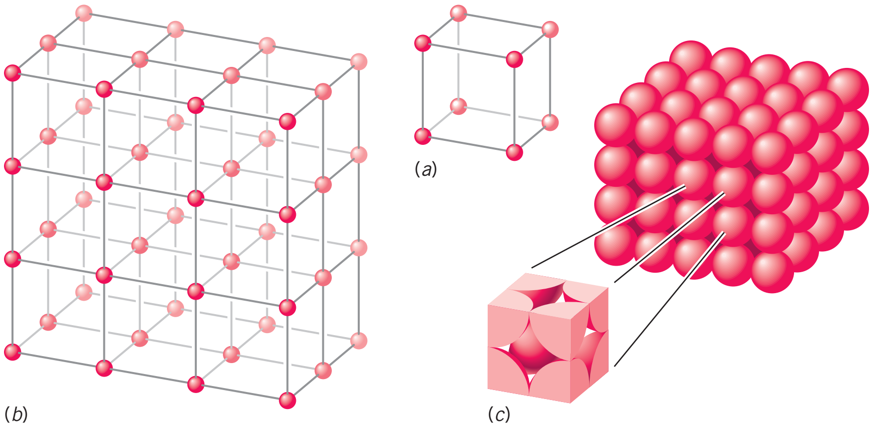


FIG. 11.29 A three-dimensional simple cubic lattice. (*a*) A simple cubic unit cell showing the locations of the lattice points. (*b*) A portion of a simple cubic lattice built by stacking simple cubic unit cells. (*c*) The crystal structure of polonium having a simple cubic lattice with identical atoms at the lattice points. Only a portion of each atom lies within this particular unit cell.

▫ A high degree of regularity is the principal feature that makes solids different from liquids. A liquid lacks this long-range repetition of structure because the particles in a liquid are jumbled and disorganized as they move about.

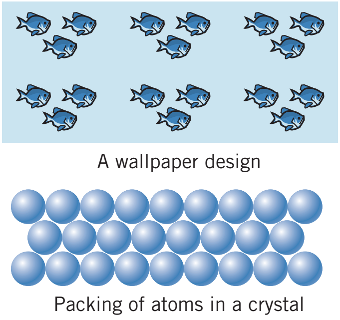


FIG. 11.27 Symmetry among repetitive patterns. A wallpaper design and particles arranged in a crystal each show a repeating pattern of structural units. The pattern can be described by the distances between the repeating units and the angles along which the repetition of structure occurs.

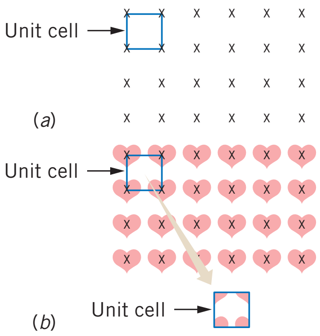


FIG. 11.28 A two-dimensional lattice. (*a*) A simple square lattice, for which the unit cell is a square with lattice points at the corners. (*b*) A wallpaper pattern formed by associating a design element (pink heart) with each lattice point. The X centered on each heart corresponds to a lattice point. The unit cell contains portions of a heart at each corner.

of polonium that crystallizes in a simple cubic lattice as well as the unit cell for that substance.[2] Notice that when the unit cell is "carved out" of the crystal, we find only part of an atom (1/8th of an atom, actually) at each corner. The rest of each atom resides in adjacent unit cells. Because the unit cell has eight corners, if we put all the corner pieces together we would obtain one complete atom. Thus, we conclude that this unit cell contains just one atom.

$$8\ \cancel{\text{corners}} \times \frac{1/8\ \text{atom}}{\cancel{\text{corner}}} = 1\ \text{atom}$$

As with the two-dimensional lattice, we could use the same simple cubic lattice to describe the structures of many different substances. The *sizes* of the unit cells would vary because the sizes of atoms vary, but the essential symmetry of the stacking would be the same in them all. This fact about lattices makes it possible to describe limitless numbers of different compounds with just a small set of three-dimensional lattices. In fact, it has been shown mathematically that there are only 14 different three-dimensional lattices possible, which means that all the chemical substances that can exist must form crystals with one or another of these 14 lattice types.

There are three cubic lattices

TOOLS
Cubic unit cells

In addition to simple cubic, two other cubic lattices are possible: face-centered cubic and body-centered cubic. The **face-centered cubic** (abbreviated **fcc) unit cell** has lattice points (and therefore, identical particles) at each of its eight corners plus another in the center of each face, as shown in Figure 11.30. Many common metals—copper, silver, gold, aluminum, and lead, for example—form crystals that have face-centered cubic lattices. Each of these metals has the same *kind* of lattice, but the *sizes* of their unit cells differ because the sizes of the atoms differ (see Figure 11.31).

The **body-centered cubic (bcc) unit cell** has lattice points at each corner plus one in the center of the cell, as illustrated in Figure 11.32. The body-centered cubic lattice is also common among a number of metals; examples are chromium, iron, and platinum. Again, these are substances with the same *kind* of lattice, but the dimensions of the lattices vary because of the *different sizes* of the particular atoms.

Not all unit cells are cubic. Some have edges of different lengths or edges that intersect at angles other than 90°. Although you should be aware of the existence of other unit cells and lattices, we will limit the remainder of our discussion to cubic lattices and their unit cells.

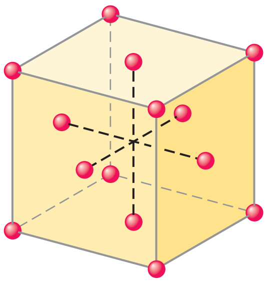


FIG. 11.30 **A face-centered cubic unit cell.** Lattice points are found at each of the eight corners and in the center of each face.

Many compounds crystallize with cubic lattices

We have seen that a number of metals have cubic lattices. The same is true for many compounds. Figure 11.33, for example, is a view of a portion of a sodium chloride crystal.

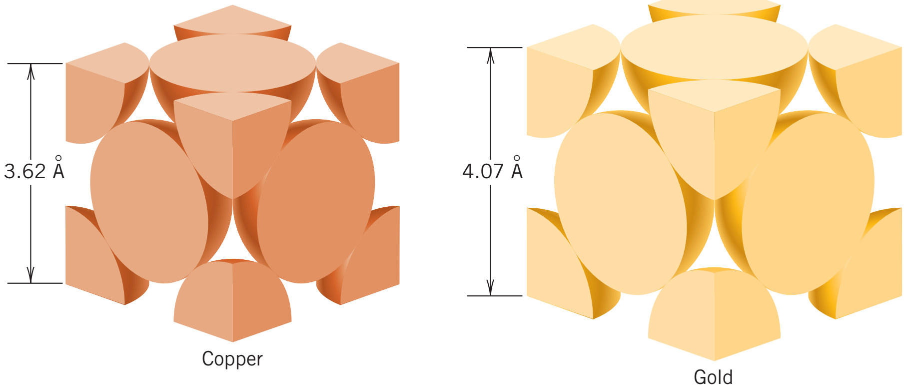


FIG. 11.31 **Unit cells for copper and gold.** These metals both crystallize in a face-centered cubic structure with similar face centered cubic unit cells. The atoms are arranged in the same way, but their unit cells have edges of different lengths because the atoms are of different sizes (1 Å = 1 × 10^{-10} m).

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[2] Polonium is the only element known to crystallize with a simple cubic lattice. Some compounds also form simple cubic lattices.

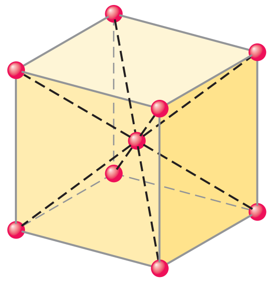


FIG. 11.32 A body-centered cubic unit cell. Lattice points are located at each of the eight corners and in the center of the unit cell.

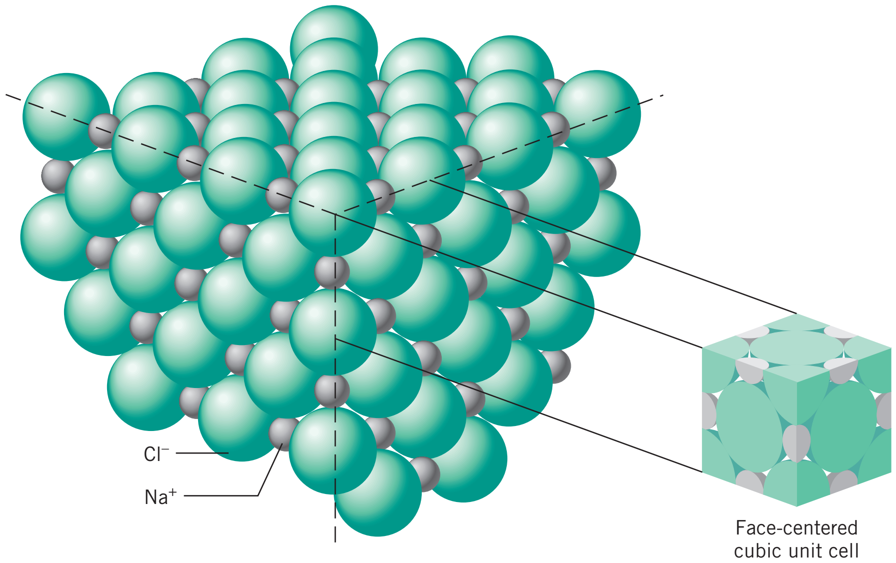


FIG. 11.33 The packing of ions in a sodium chloride crystal. Chloride ions are shown here to be associated with the lattice points of a face-centered cubic unit cell, with the sodium ions placed between the chloride ions.

The Cl^- ions (green) are shown at the lattice points that correspond to a face-centered cubic unit cell. The smaller gray spheres represent Na^+ ions. Notice that they fill the spaces between the Cl^- ions. If we look at the locations of identical particles (Cl^-, for example) we find them at lattice points that describe a face-centered cubic structure. Thus, sodium chloride is said to have a face-centered cubic lattice, and the cubic shape of this lattice is what accounts for the cubic shape of a sodium chloride crystal.

Many of the alkali halides (Group IA–VIIA compounds), such as NaBr and KCl, crystallize with fcc lattices that have the same arrangement of ions as found in NaCl. In fact, this arrangement of ions is so common that it's called the **rock salt structure** (rock salt is the mineral name of NaCl). Because sodium bromide and potassium chloride both have the same kind of lattice as sodium chloride, Figure 11.33 also could be used to describe their unit cells. The *sizes* of their unit cells are different, however, because K^+ is a larger ion than Na^+, and Br^- is larger than Cl^-.

Other examples of cubic unit cells are shown in Figures 11.34 and 11.35. The structure of cesium chloride in Figure 11.34 is simple cubic, although at first glance it may appear to be body centered. This is because in a crystal lattice, identical chemical units must be at each lattice point. In CsCl, Cs^+ ions are found at the corners, but not in the center, so the Cs^+ ions describe a simple cubic unit cell.

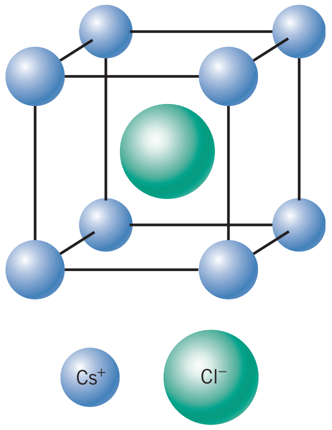


FIG. 11.34 The unit cell for cesium chloride, CsCl. The chloride ion is located in the center of the unit cell. The ions are not shown full-size to make it easier to see their locations in the unit cell.

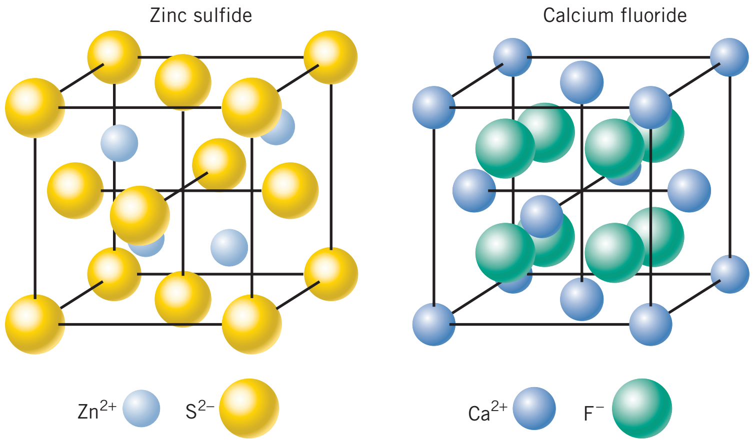


FIG. 11.35 Crystal structures based on the face-centered cubic lattice. Both zinc sulfide, ZnS, and calcium fluoride, CaF_2, have crystal structures that fit a face-centered cubic lattice. In ZnS, the sulfide ions are shown at the fcc lattice sites with the four zinc ions entirely within the unit cell. In CaF_2, the calcium ions are at the lattice points with the eight fluorides entirely within the unit cell. The ions are not shown full-size to make it easier to see their locations in the unit cells.

Both zinc sulfide and calcium fluoride in Figure 11.35 have face-centered cubic unit cells that differ from that for sodium chloride, which illustrates once again how the same basic kind of lattice can be used to describe a variety of chemical structures.

Stoichiometry affects the packing of atoms in a unit cell

At this point, you may wonder why a compound crystallizes with a particular structure. Although this is a complex issue, at least one factor is the stoichiometry of the substance. Because the crystal is made up of a huge number of identical unit cells, the stoichiometry within the unit cell must match the overall stoichiometry of the compound. Let's see how this applies to sodium chloride.

EXAMPLE 11.2
Counting Atoms or Ions in a Unit Cell

How many sodium and chloride ions are there in the unit cell of sodium chloride?

ANALYSIS: To answer this question, we have to look closely at the unit cell of sodium chloride. The critical link is realizing that when the unit cell is carved out of the crystal, it encloses *parts of ions*, so we have to determine how many *whole* sodium and chloride ions can be constructed from the pieces within a given unit cell.

SOLUTION: Let's look at an "exploded" view of the NaCl unit cell, shown in Figure 11.36. We see that we have parts of chloride ions at the corners and in the center of each face. Let's add the parts.

For chloride:

$$8 \text{ corners} \times \tfrac{1}{8}\,\text{Cl}^- \text{per corner} = 1\ \text{Cl}^-$$

$$6 \text{ faces} \times \tfrac{1}{2}\,\text{Cl}^- \text{ per face} = 3\ \text{Cl}^-$$

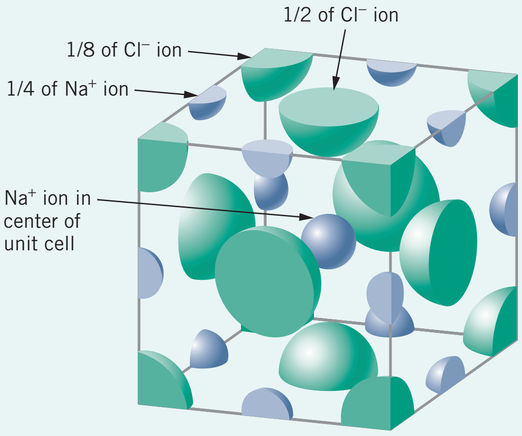


FIG. 11.36 An exploded view of the unit cell of sodium chloride.

For the sodium ions, we have parts along each of the 12 edges plus one whole Na^+ ion in the center of the unit cell. Let's add them.

For sodium:

$$12 \text{ edges} \times \tfrac{1}{4}\,\text{Na}^+ \text{ per edge} = 3\ \text{Na}^+$$

$$1\ \text{Na}^+ \text{ in the center} = 1\ \text{Na}^+$$

$$\text{Total} = 4\ \text{Na}^+$$

Thus, in one unit cell, there are four chloride ions and four sodium ions.

IS THE ANSWER REASONABLE? The ratio of the ions is 4 to 4, which is the same as 1 to 1. That's the ratio of the ions in NaCl, so the answer is correct.

Practice Exercise 9: How many calcium ions and how many fluoride ions are in the unit cell of calcium fluoride, CaF_2? (Hint: see Figure 11.35.)

Practice Exercise 10: What is the ratio of the ions in the unit cell of cesium chloride? See Figure 11.34.

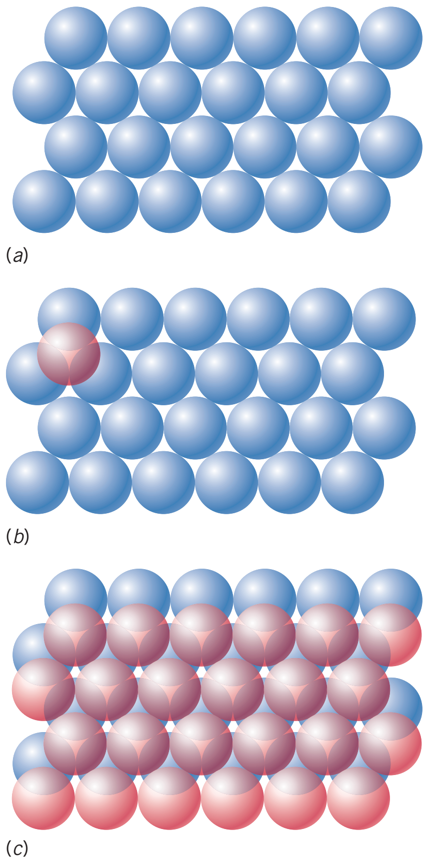
The calculation in Example 11.2 shows why NaCl can have the crystal structure it does; the unit cell has the proper ratio of cations to anions. It also shows why a compound such as CaCl_2 could *not* crystallize with the same kind of unit cell as NaCl. The sodium chloride structure demands a 1-to-1 ratio of cation to anion, so it could not be used by CaCl_2 (which has a 1-to-2 cation-to-anion ratio).

Efficiency of packing also can affect how atoms are arranged in a solid

For many solids, particularly metals, the type of crystal structure formed is controlled by maximizing the number of neighbors that surround a given atom. The more neighbors an atom has, the greater are the number of interatomic attractions and the greater is the energy lowering when the solid forms. Structures that achieve the maximum density of packing are known as **closest-packed structures,** and there are two of them that are only slightly different. To visualize how these are produced, let's look at ways to pack spheres of identical size.

Figure 11.37*a* illustrates a layer of blue spheres packed as tightly as possible. Notice that each sphere is touched by six others in this layer. When we add a second layer, each sphere (red) rests in a depression formed by three spheres in the first layer, as illustrated in Figures 11.37*b* and *c*.

The difference between the two closest-packed structures lies in the relative orientations of the spheres in the first layer and those that form the third layer. In Figure 11.38*a* the green spheres in the third layer each lie in a depression between red spheres that is directly above a depression between blue spheres in the first layer. This kind of packing is called **cubic closest packing,** abbreviated **ccp,** because when viewed from a different perspective, the atoms are located at positions corresponding to a face-centered cubic lattice. Figure 11.38*b* describes the other closest-packed structure in which a green sphere in the third layer rests in a depression between red spheres and directly above a blue sphere in the first layer. This arrangement of spheres is called **hexagonal closest packing,** abbreviated **hcp**.



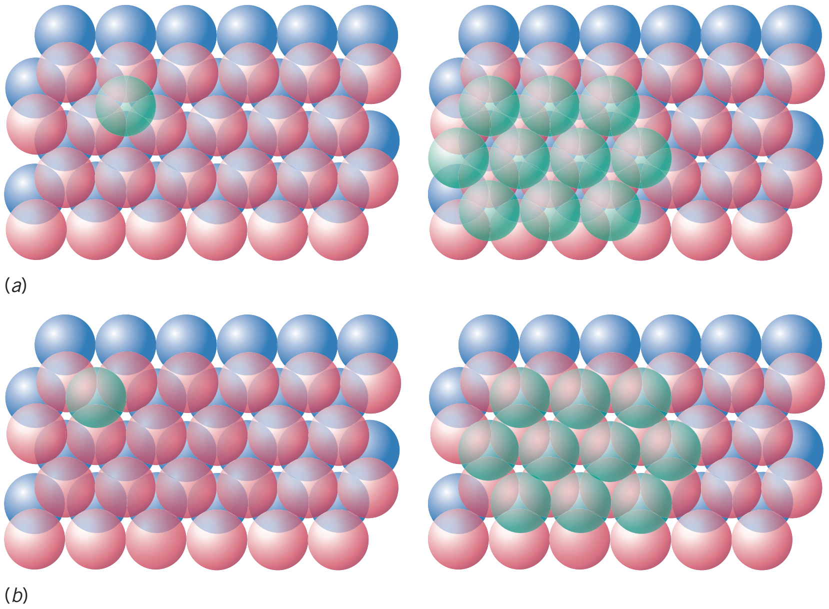


FIG. 11.37 **Packing of spheres.** (*a*) One layer of closely packed spheres. (*b*) A second layer is started by placing a sphere (colored red) in a depression formed between three spheres in the first layer. (*c*) A second layer of spheres shown slightly transparent so we can see how the atoms are stacked over the first layer.

FIG. 11.38 **Closest-packed structures.** (*a*) Cubic closest packing of spheres. (*b*) Hexagonal closest packing of spheres. In both (*a*) and (*b*) the left diagram illustrates the position of one atom on the third layer and the right diagram shows the third layer partially complete. Notice that there are subtle differences between the two modes of packing.

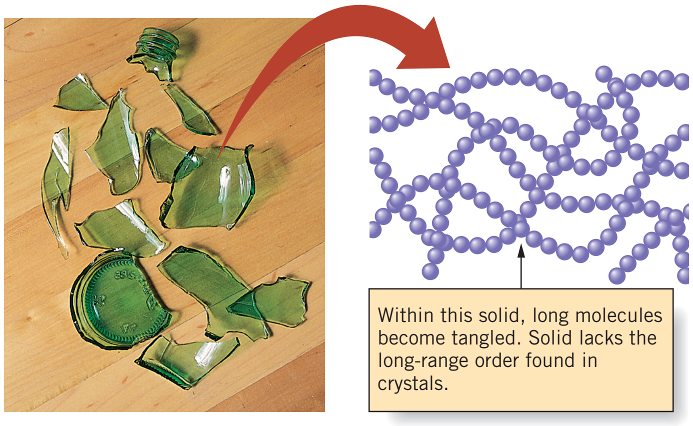


FIG. 11.39 **Glass is a noncrystalline solid.** When glass breaks, the pieces have sharp edges, but their surfaces are not flat planes. This is because in an amorphous solid like glass, long molecules (much simplified here for clarity) are tangled and disorganized, so there is no long-range order characteristic of a crystal. *(Robert Capece.)*

In the hcp structure, the layers alternate in an A-B-A-B. . . pattern, where A stands for the orientations of the first, third, fifth, etc. layers, and B stands for the orientations of the second, fourth, sixth, etc. layers. Thus, the spheres in the third, fifth, seventh, etc. layers are directly above those in the first, while spheres in the fourth, sixth, eighth, etc. layers are directly above those in the second. In the ccp structure, there is an A-B-C-A-B-C. . . pattern. The first layer is oriented like the fourth, the second like the fifth, and the third like the sixth.

Both the ccp and hcp structures yield very efficient packing of identically sized atoms. In both structures, each atom is in contact with 12 neighboring atoms: 6 atoms in its own layer, 3 atoms in the layer below, and 3 atoms in the layer above. Metals that crystallize with the ccp structure include copper, silver, gold, aluminum, and lead. Metals with the hcp structure include titanium, zinc, cadmium, and magnesium.

Not all solids are crystalline

If a cubic salt crystal is broken, the pieces still have flat faces that intersect at 90° angles. If you shatter a piece of glass, on the other hand, the pieces often have surfaces that are not flat. Instead, they tend to be smooth and curved (see Figure 11.39). This behavior illustrates a major difference between crystalline solids, such as NaCl, and noncrystalline solids, also called **amorphous solids,** such as glass.

The word *amorphous* is derived from the Greek word *amorphos,* which means "without form." Amorphous solids do not have the kinds of long-range repetitive internal structures that are found in crystals. In some ways their structures, being jumbled, are more like liquids than solids. Examples of amorphous solids are ordinary glass and many plastics. In fact, the word **glass** is often used as a general term to refer to any amorphous solid.

As suggested in Figure 11.39, substances that form amorphous solids often consist of long, chainlike molecules that are intertwined in the liquid state somewhat like long strands of cooked spaghetti. To form a crystal from the melted material, these long molecules would have to become untangled and line up in specific patterns. But as the liquid cools, the molecules slow down. Unless the liquid is cooled extremely slowly, the molecular motion decreases too rapidly for the untangling to take place, and the substance solidifies with the molecules still intertwined. As a result, amorphous solids are sometimes described as **supercooled liquids,** a term suggesting the kind of structural disorder found in liquids.

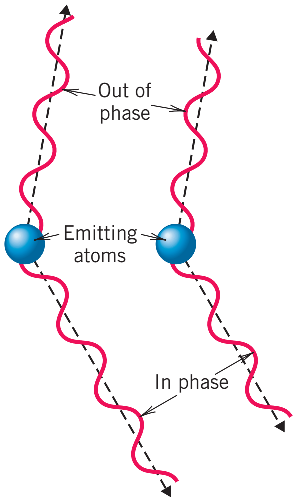


FIG. 11.40 **Diffraction of X rays from atoms in a crystal.** X rays emitted from atoms are in phase in some directions and out of phase in other directions.

11.10 X-RAY DIFFRACTION IS USED TO STUDY CRYSTAL STRUCTURES

When atoms in a crystal are bathed in X rays, they absorb some of the radiation and then emit it again in all directions. In effect, each atom becomes a tiny X-ray source. If we look at radiation from two such atoms (Figure 11.40), we find that the X rays emitted are in phase in some directions but out of phase in others. In Chapter 7 you learned that constructive (in-phase) and destructive (out-of-phase) interferences create a phenomenon called *diffraction.* X-Ray diffraction by crystals has enabled many scientists to win Nobel prizes by determining the structures of extremely complex compounds in a particularly elegant way.

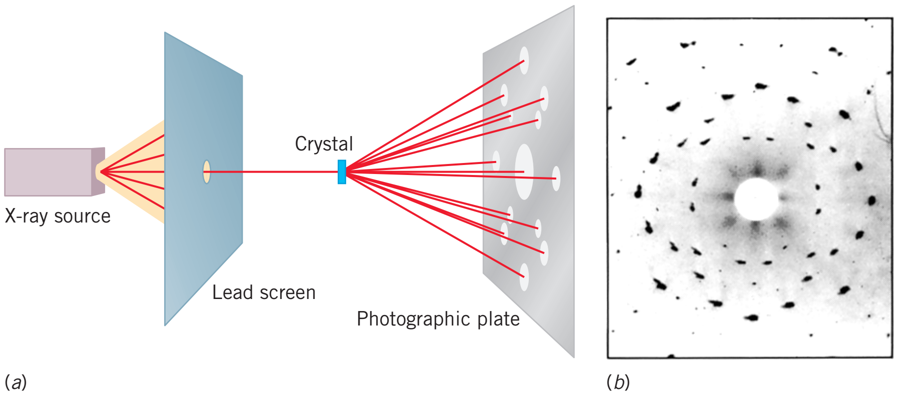


FIG. 11.41 **X-Ray diffraction.** (*a*) The production of an X-ray diffraction pattern. (*b*) An X-ray diffraction pattern produced by sodium chloride recorded on photographic film. *(Visuals Unlimited.)*

In a crystal, there are enormous numbers of atoms, evenly spaced throughout the lattice. When the crystal is bathed in X rays, intense beams are diffracted because of constructive interference, and they appear only in specific directions. In other directions, no X rays appear because of destructive interference. When the X rays coming from the crystal fall on photographic film, the diffracted beams form a **diffraction pattern** (see Figure 11.41). The film is darkened only where the X rays strike.[3]

In 1913, the British physicist William Henry Bragg and his son William Lawrence Bragg discovered that just a few variables control the appearance of an X-ray diffraction pattern. These are shown in Figure 11.42, which illustrates the conditions necessary to obtain constructive interference of the X rays from successive layers of atoms (planes of atoms) in a crystal. A beam of X rays having a wavelength λ strikes the layers at an angle θ. Constructive interference causes an intense diffracted beam to emerge at the same angle θ. The Braggs derived an equation, now called the **Bragg equation,** relating λ, θ, and the distance between the planes of atoms, d,

$$n\lambda = 2d \sin \theta \tag{11.2}$$

TOOLS
Bragg equation

where n is a whole number. The Bragg equation is the basic tool used by scientists in the study of solid structures.

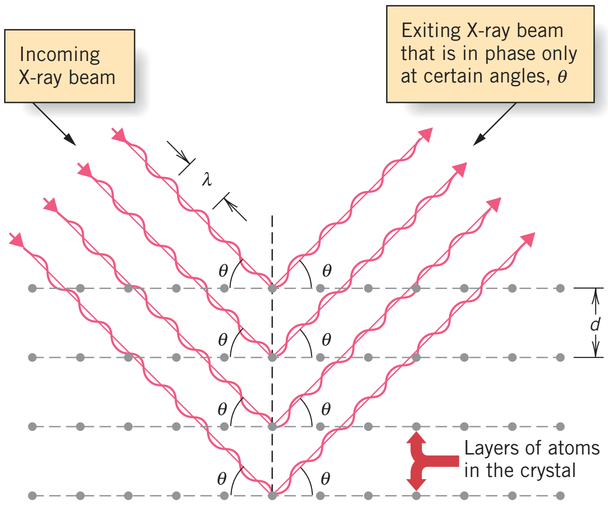


FIG. 11.42 **Diffraction of X rays from successive layers of atoms in a crystal.** The layers of atoms are separated by a distance d. The X rays of wavelength λ enter and emerge at an angle θ relative to the layers of the atoms. For the emerging beam of X rays to have any intensity, the condition $n\lambda = 2d \sin \theta$ must be fulfilled, where n is a whole number.

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[3] Modern X-ray diffraction instruments use electronic devices to detect and measure the angles and intensities of the diffracted X rays.

To determine the structure of a crystal, the angles θ at which diffracted X-ray beams emerge from a crystal are measured. These angles are used to calculate the distances between the various planes of atoms in the crystal. The calculated interplanar distances are then used to work backward to deduce where the atoms in the crystal must be located so that layers of atoms are indeed separated by these distances. This is not a simple task, and some sophisticated mathematics as well as computers are needed to accomplish it. The efforts, however, are well rewarded because the calculations give the locations of atoms within the unit cell and the distances between them. This information, plus a lot of chemical "common sense," is used by chemists to arrive at the shapes and sizes of the molecules in the crystal. Example 11.3 below provides a very simple illustration of how such data are used.

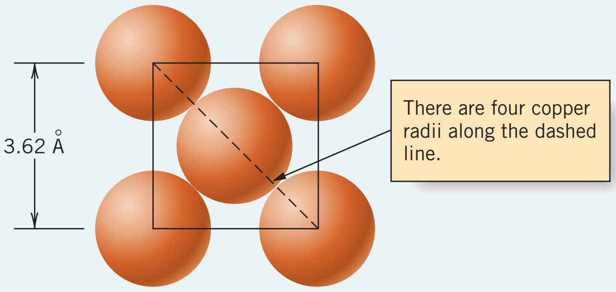
X-Ray diffraction has had a profound impact on the study of biochemical molecules. For example, the general shape of DNA molecules, the chemicals of genes, was deduced by using X-ray diffraction. Today, X-ray diffraction continues to be one of the tools used by biochemists to determine the structures of complex proteins and enzymes.

EXAMPLE 11.3

Using Crystal Structure Data to Calculate Atomic Sizes

X-Ray diffraction measurements reveal that copper crystallizes with a face-centered cubic lattice in which the unit cell length is 3.62 Å (see Figure 11.31). What is the radius of a copper atom expressed in angstroms and in picometers?

ANALYSIS: In Figure 11.31, we see that copper atoms are in contact along a diagonal (the dashed line below) that runs from one corner of a face to another corner.



There are four copper radii along the dashed line.

By geometry, we can calculate the length of this diagonal, which equals four times the radius of a copper atom. Once we calculate the radius in angstrom units we can convert to picometers using the relationships

$$1\ \text{Å} = 1 \times 10^{-10}\ \text{m}$$

$$1\ \text{pm} = 1 \times 10^{-12}\ \text{m}$$

SOLUTION: From geometry, the length of the diagonal is $\sqrt{2}$ times the length of the edge of the unit cell.

$$\text{Diagonal} = \sqrt{2} \times (3.62\ \text{Å}) = 5.12\ \text{Å}$$

If we call the radius of the copper atom r_{Cu}, then the diagonal equals $4 \times r_{\text{Cu}}$. Therefore,

$$4 \times r_{\text{Cu}} = 5.12\ \text{Å}$$

$$r_{\text{Cu}} = 1.28\ \text{Å}$$

The calculated radius of the copper atom is 1.28 Å.

Next we convert this to picometers.

$$1.28\ \cancel{\text{Å}} \times \frac{1 \times 10^{-10}\ \cancel{\text{m}}}{1\ \cancel{\text{Å}}} \times \frac{1\ \text{pm}}{1 \times 10^{-12}\ \cancel{\text{m}}} = 128\ \text{pm}$$

IS THE ANSWER REASONABLE? It's difficult to get an intuitive feel for the sizes of atoms, so we should be careful to check the calculation. The length of the diagonal seems about right; it is longer than the edge of the unit cell. If we look again at the diagram above, we can see that along the diagonal there are four copper radii. The rest of the arithmetic is okay, so our answer is correct.

11.11 PHYSICAL PROPERTIES OF SOLIDS ARE RELATED TO THEIR CRYSTAL TYPES

Solids exhibit a wide range of properties. Some, such as diamond, are very hard whereas others, such as ice and naphthalene (moth flakes), are relatively soft. Some, such as salt crystals, have high melting points, whereas others, such as candle wax, melt at low temperatures. And some conduct electricity but others are nonconducting. Physical properties such as these depend on the kinds of particles in the solid as well as on the strengths of attractive forces holding the solid together. Even though we can't make exact predictions about such properties, some generalizations do exist. In discussing them, it is convenient to divide crystals into four types: ionic, molecular, covalent, and metallic.

Ionic crystals have cations and anions at lattice sites

Ionic crystals have ions at the lattice sites and the binding between them is mainly electrostatic, which is essentially nondirectional. As a result, the kind of lattice formed is determined mostly by the relative sizes of the ions and their charges. When the crystal forms, the ions arrange themselves to maximize attractions and minimize repulsions.

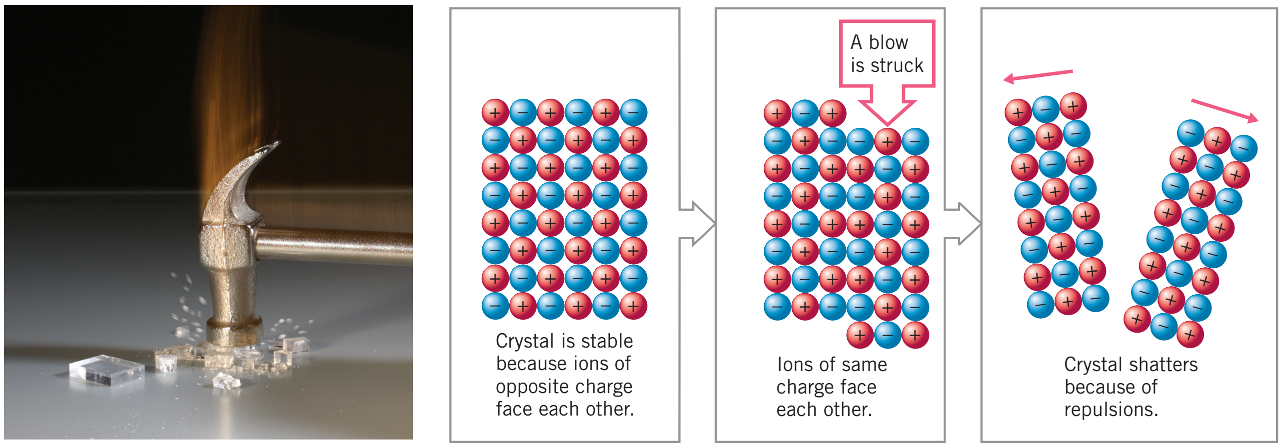
Because electrostatic forces are strong, ionic crystals tend to be hard. They also tend to have high melting points because the ions have to be given a lot of kinetic energy to enable them to break free of the lattice and enter the liquid state. The forces between ions can also be used to explain the brittle nature of many ionic compounds. For example, when struck by a hammer, a salt crystal shatters into many small pieces. A view at the atomic level reveals how this could occur (Figure 11.43). The slight movement of a layer of ions within an ionic crystal suddenly places ions of the *same* charge next to each other, and for that instant there are large repulsive forces that split the solid.

In the solid state, ionic compounds do not conduct electricity because the charges present are not able to move. When melted, however, ionic compounds are good conductors of electricity. Melting frees the electrically charged ions to move.

Molecular crystals have neutral molecules at lattice sites

Molecular crystals are solids in which the lattice sites are occupied either by atoms (as in solid argon or krypton) or by molecules (as in solid CO_2, SO_2, or H_2O). If the molecules of such solids are relatively small, the crystals tend to be soft and have low melting points because the particles in the solid experience relatively weak intermolecular attractions. In crystals of argon, for example, the attractive forces are exclusively London forces. In SO_2, which is composed of polar molecules, there are dipole–dipole attractions as well as London forces. And in water crystals (ice) the molecules are held in place primarily by strong hydrogen bonds. Molecular compounds do not conduct electricity in either the solid or liquid state because they are unable to transport electrical charges.

◻ Molecular crystals are soft because little effort is needed to separate the particles or cause them to move past each other.



Crystal is stable because ions of opposite charge face each other.

Ions of same charge face each other.

Crystal shatters because of repulsions.

FIG. 11.43 **An ionic crystal shatters when struck.** In this microview we see that striking an ionic crystal causes some of the layers to shift. This can bring ions of like charge face-to-face. The repulsions between the ions can then force parts of the crystal apart, causing the crystal to shatter. *(Andy Washnik.)*

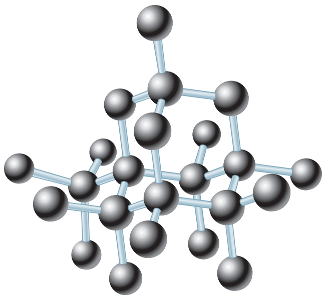


FIG. 11.44 The structure of diamond. Each carbon atom is covalently bonded to four others at the corners of a tetrahedron. This is just a tiny portion of a diamond, of course; the structure extends throughout the entire diamond crystal.

Covalent crystals have atoms at lattice sites covalently bonded to other atoms

Covalent crystals are solids in which lattice positions are occupied by atoms that are covalently bonded to other atoms at neighboring lattice sites. The result is a crystal that is essentially one gigantic molecule. These solids are sometimes called **network solids** because of the interlocking network of covalent bonds extending throughout the crystal in all directions. A typical example is diamond (see Figure 11.44). Covalent crystals tend to be very hard and to have very high melting points because of the strong attractions between covalently bonded atoms. Other examples of covalent crystals are quartz (SiO_2, found in some types of sand) and silicon carbide (SiC, a common abrasive used in sandpaper). Covalent crystals are poor conductors of electricity, although some, such as silicon, are semiconductors.

Metallic crystals have cations at lattice sites surrounded by mobile electrons

Metallic crystals have properties that are quite different from those of the other three types. Metallic crystals conduct heat and electricity well, and they have the luster characteristically associated with metals. A number of different models have been developed to explain metallic crystals. One of the simplest models views the lattice positions of a metallic crystal as being occupied by *positive ions* (nuclei plus core electrons). Surrounding them is a "cloud" of electrons formed by the valence electrons, which extends throughout the entire solid (see Figure 11.45). The electrons in this cloud belong to no single positive ion,

TOOLS
Physical properties relate to crystal type

TABLE 11.5 Types of Crystals

Crystal Type	Particles Occupying Lattice Sites	Type of Attractive Force	Typical Examples	Typical Properties
Ionic	Positive and negative ions	Attractions between ions of opposite charge	NaCl, $CaCl_2$, $NaNO_3$	Relatively hard; brittle; high melting points; nonconductors of electricity as solids, but conduct when melted
Molecular	Atoms or molecules	Dipole–dipole attractions, London forces, hydrogen bonding	HCl, SO_2, N_2, Ar, CH_4, H_2O	Soft; low melting points; nonconductors of electricity in both solid and liquid states
Covalent (network)	Atoms	Covalent bonds between atoms	Diamond, SiC, (silicon carbide), SiO_2 (sand, quartz)	Very hard; very high melting points; nonconductors of electricity
Metallic	Positive ions	Attractions between positive ions and an electron cloud that extends throughout the crystal	Cu, Ag, Fe, Na, Hg	Range from very hard to very soft; melting points range from high to low; conduct electricity in both solid and liquid states; have characteristic luster

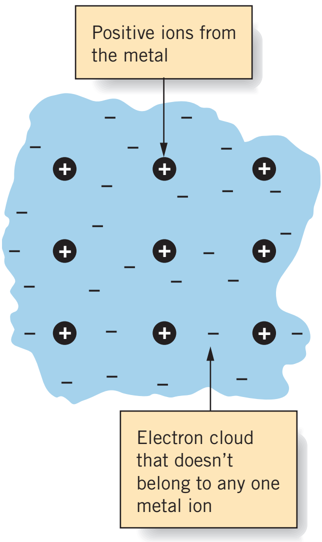


FIG. 11.45 The "electron sea" model of a metallic crystal. In this highly simplified view of a metallic solid, metal atoms lose valence electrons to the solid as a whole and exist as positive ions surrounded by a mobile "cloud" of electrons.

but rather to the crystal as a whole. Because the electrons aren't localized on any one atom, they are free to move easily, which accounts for the high electrical conductivity of metals. The electrons can also carry kinetic energy rapidly through the solid, so metals are also good conductors of heat. This model explains the luster of metals, too. When light shines on the metal, the loosely held electrons vibrate easily and readily re-emit the light with essentially the same frequency and intensity.

Some metals, like tungsten, have very high melting points (mp = 3422 °C). Others, such as sodium (mp = 97.8 °C) and mercury, which is a liquid at room temperature, have quite low melting points. To some extent, the melting point depends on the charge of the positive ions in the metallic crystal. The Group IA metals have just one valence electron, so their cores are cations with a 1+ charge, which are only weakly attracted to the "electron cloud" that surrounds them. Atoms of the Group IIA metals, however, form ions with a 2+ charge. These are attracted more strongly to the surrounding electron sea, so the Group IIA metals have higher melting points than their neighbors in Group IA. Metals with very high melting points, like tungsten, must have very strong attractions between their atoms, which suggests that there probably is some covalent bonding between them as well.

The different ways of classifying crystals and a summary of their general properties are given in Table 11.5.

EXAMPLE 11.4
Identifying Crystal Types from Physical Properties

The metal osmium, Os, forms an oxide with the formula OsO_4. The soft crystals of OsO_4 melt at 40 °C, and the resulting liquid does not conduct electricity. To which crystal type does solid OsO_4 probably belong?

ANALYSIS: You might be tempted to suggest that the compound is ionic simply because it is formed from a metal and a nonmetal. However, the properties of the compound are inconsistent with its being ionic. Therefore, we have to consider that there may be exceptions to the generalization discussed earlier about metal–nonmetal compounds. If so, what do the properties of OsO_4 suggest about its crystal type?

SOLUTION: The characteristics of the OsO_4 crystals—softness and low melting point—suggest that solid OsO_4 is a molecular solid and that it contains molecules of OsO_4. This is further supported by the fact that liquid OsO_4 does not conduct electricity, which is evidence for the lack of ions in the liquid.

IS THE ANSWER REASONABLE? There's not much we can do to check ourselves here except to review our analysis.

Practice Exercise 11: Stearic acid is an organic acid that has a chain of 18 carbon atoms. It is a soft solid with a melting point of 70 °C. What crystal type best describes this compound? (Hint: Determine the dominant attractive forces that cause stearic acid to be a solid at room temperature.)

Practice Exercise 12: Boron nitride, which has the empirical formula BN, melts at 2730 °C and is almost as hard as a diamond. What is the probable crystal type for this compound?

Practice Exercise 13: Crystals of elemental sulfur are easily crushed and melt at 113 °C to give a clear yellow liquid that does not conduct electricity. What is the probable crystal type for solid sulfur?

11.12 PHASE DIAGRAMS GRAPHICALLY REPRESENT PRESSURE–TEMPERATURE RELATIONSHIPS

TOOLS
Phase diagram

Sometimes it is useful to know under what combinations of temperature and pressure a substance will be a liquid, a solid, or a gas, or the conditions of temperature and pressure that produce an equilibrium between any two phases. A simple way to determine this is to

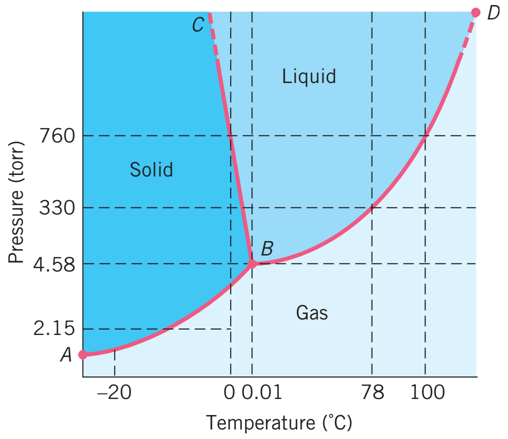


FIG. 11.46 **The phase diagram for water, distorted to emphasize certain features.** Temperatures and pressures corresponding to the dashed lines on the diagram are referred to in the text discussion.

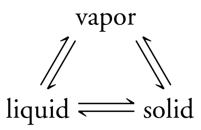
use a **phase diagram**—a graphical representation of the pressure–temperature relationships that apply to the equilibria between the phases of the substance.

Figure 11.46 is the phase diagram for water. On it, there are three lines that intersect at a common point. Points on these lines correspond to temperatures and pressures at which equilibria between phases can exist. For example, line *AB* is the vapor pressure curve for the solid (ice). Every point on this line gives a temperature and a pressure at which ice and its vapor are able to coexist in equilibrium.

□ The melting point and boiling point can be read directly from the phase diagram.

Line *BD* is the vapor pressure curve for liquid water. It gives the temperatures and pressures at which the liquid and vapor are able to coexist in equilibrium. Notice that when the temperature is 100 °C, the vapor pressure is 760 torr. Therefore, this diagram also tells us that water boils at 100 °C when the pressure is 1 atm (760 torr), because that is the temperature at which the vapor pressure equals 1 atm.

The solid–vapor equilibrium line, *AB,* and the liquid–vapor line, *BD,* intersect at a common point, *B.* Because this point is on both lines, there is equilibrium between all three phases at the same time.



□ In the SI, the triple point of water is used to define the Kelvin temperature of 273.16 K.

The temperature and pressure at which this triple equilibrium occurs define the **triple point** of the substance. For water, the triple point occurs at 0.01 °C and 4.58 torr. Every known chemical substance except helium has its own characteristic triple point, which is controlled by the balance of intermolecular forces in the solid, liquid, and vapor.

Line *BC,* which extends upward from the triple point, is the solid–liquid equilibrium line or *melting point line.* It gives temperatures and pressures at which the solid and the liquid are able to be in equilibrium. At the triple point, the melting of ice occurs at +0.01 °C (and 4.58 torr); at 760 torr, melting occurs very slightly lower, at 0 °C. Thus, we can tell that *increasing the pressure on ice lowers its melting point.*

The effect of pressure on the melting point of ice can be predicted using Le Châtelier's principle and the knowledge that a given mass of liquid water occupies *less volume* than the same mass of ice (i.e., liquid water is more dense than ice). Consider an equilibrium that is established between ice and liquid water at 0 °C and 1 atm in an apparatus like that shown in Figure 11.47,

$$H_2O(s) \rightleftharpoons H_2O(l)$$

If the piston is forced in slightly, the pressure increases. According to Le Châtelier's principle the system should respond, if possible, in a way that reduces the pressure. This can happen if some of the ice melts, so the ice–liquid mixture won't require as much space. Then the molecules won't push as hard against each other and the walls, and the pressure

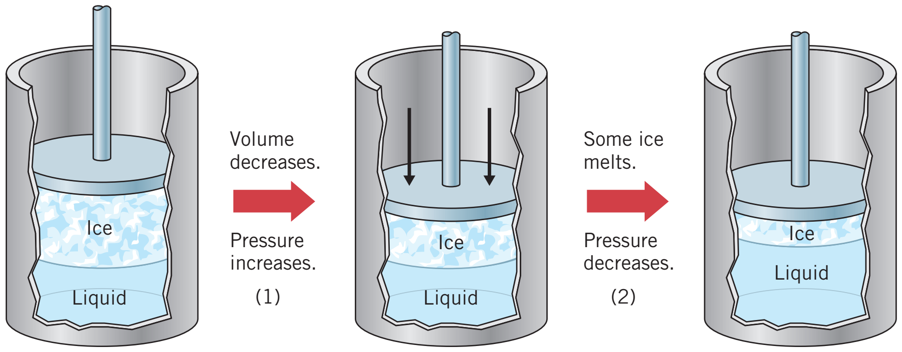


FIG. 11.47 **The effect of pressure on the equilibrium $H_2O(s) \rightleftharpoons H_2O(l)$.** (1) Pushing down on the piston decreases the volume of both the ice and liquid water by a small amount and increases the pressure. (2) Some of the ice melts, producing the more dense liquid. As the total volume of ice and liquid water decreases, the pressure drops and equilibrium is restored.

will drop. Thus, a pressure increasing disturbance to the system favors a volume decreasing change, which corresponds to the melting of some ice.

Now, suppose we have ice at a pressure just below the solid–liquid line, *BC*. If, *at constant temperature,* we raise the pressure to a point just above the line, the ice will melt and become a liquid. This could only happen if the melting point becomes lower as the pressure is raised.

Water is very unusual. Almost all other substances have melting points that increase with increasing pressure as illustrated by the phase diagram for carbon dioxide (see Figure 11.48). For CO_2 the solid–liquid line slants to the right (it slanted to the left for water). Also notice that carbon dioxide has a triple point that's above 1 atm. At atmospheric pressure, the only equilibrium that can be established is between solid carbon dioxide and its vapor. At a pressure of 1 atm, this equilibrium occurs at a temperature of −78 °C. This is the temperature of dry ice, which sublimes at atmospheric pressure at −78 °C.

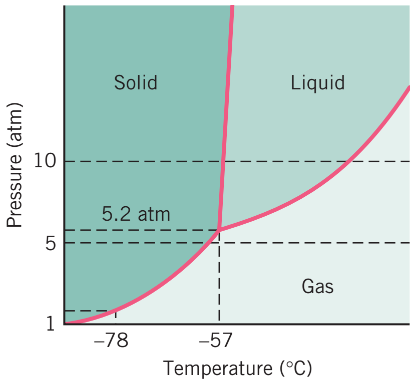


FIG. 11.48 **The phase diagram for carbon dioxide.**

Single phase regions can be identified in a phase diagram

Besides specifying phase equilibria, the three intersecting lines on a phase diagram serve to define regions of temperature and pressure at which only a single phase can exist. For example, between lines *BC* and *BD* in Figure 11.46 are temperatures and pressures at which water exists as a liquid without being in equilibrium with either vapor or ice. At 760 torr, water is a liquid anywhere between 0 °C and 100 °C. For instance, we are told by the diagram that we can't have ice with a temperature of 25 °C if the pressure is 760 torr (which, of course, you already knew; ice never has a temperature of 25 °C). The diagram also says that we can't have water vapor with a pressure of 760 torr when the temperature is 25 °C (which, again, you already knew; the temperature has to be taken to 100 °C for the vapor pressure to reach 760 torr). Instead, we are told by the phase diagram that the *only* phase for pure water at 25 °C and 1 atm is the liquid. Below 0 °C at 760 torr, water is a solid; above 100 °C at 760 torr, water is a vapor. On the phase diagram for water, the phases that can exist in the different temperature–pressure regions are marked.

EXAMPLE 11.5
Interpreting a Phase Diagram

What phase would we expect for water at 0 °C and 4.58 torr?

ANALYSIS: The words, "What phase. . .," as well as the specified temperature and pressure suggest that we refer to the phase diagram of water (Figure 11.46).

SOLUTION: First we find 0 °C on the temperature axis of the phase diagram of water. Then we move upward until we intersect a line corresponding to 4.58 torr. This intersection occurs in the "Solid" region of the diagram. At 0 °C and 4.58 torr, then, water exists as a solid.

IS THE ANSWER REASONABLE? We've seen that the freezing point of water increases slightly when we lower the pressure, so below 1 atm, water should still be a solid at 0 °C. That agrees with the answer we obtained from the phase diagram.

EXAMPLE 11.6
Interpreting a Phase Diagram

What phase changes occur if water at 0 °C is gradually compressed from a pressure of 2.15 torr to 800 torr?

ANALYSIS: Asking about "what phase changes occur" suggests once again that we use the phase diagram of water (Figure 11.46).

SOLUTION: According to the phase diagram, at 0 °C and 2.15 torr, water exists as a gas (water vapor). As the vapor is compressed, we move upward along the 0 °C line until we encounter the solid–vapor line. Here, an equilibrium will exist as compression gradually transforms the gas into solid ice. Once all the vapor has frozen, further compression raises the pressure and we continue the climb along the 0 °C line until we next encounter the solid–liquid line at 760 torr. As further compression takes place, the solid will gradually melt. After all the ice has melted, the pressure will continue to climb while the water remains a liquid. At 800 torr and 0 °C, the water will be liquid.

IS THE ANSWER REASONABLE? There's not too much we can do to check all this except to take a fresh look at the phase diagram. We do expect that above 760 torr the melting point of ice will be less than 0 °C, so at 0 °C and 800 torr we can anticipate that water will be a liquid.

Practice Exercise 14: The equilibrium line from point B to D in Figure 11.46 is present in another figure in this chapter. Identify what that line represents. (Hint: A review of the other figures will reveal the nature of the line.)

Practice Exercise 15: What phase changes will occur if water at −20 °C and 2.15 torr is heated to 50 °C under constant pressure?

Practice Exercise 16: What phase will water be in if it is at a pressure of 330 torr and a temperature of 50 °C?

Above the critical temperature only one phase is possible

For water (Figure 11.46), the vapor pressure line for the liquid, which begins at point *B*, terminates at point *D*, which is known as the **critical point.** The temperature and pressure at *D* are called the **critical temperature, T_c,** and **critical pressure, P_c.** Above the critical temperature, a distinct liquid phase cannot exist, *regardless of the pressure.*

Figure 11.49 illustrates what happens to a substance as it approaches its critical point. In Figure 11.49*a*, we see a liquid in a container with some vapor above it. We can distinguish

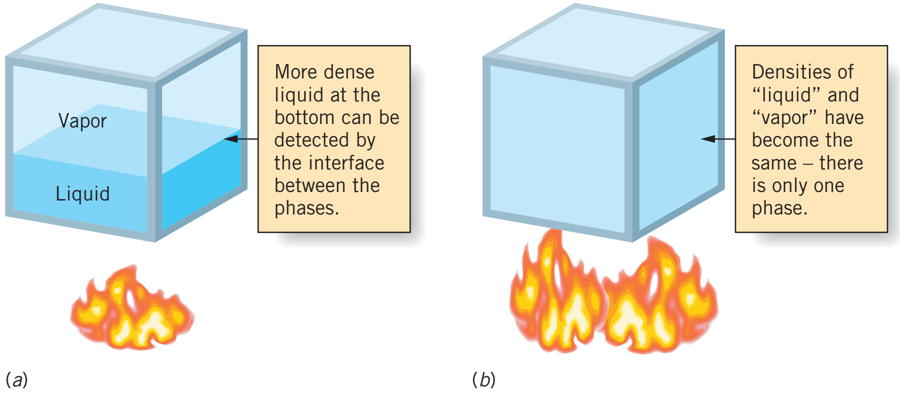


FIG. 11.49 **Changes that are observed when a liquid is heated in a sealed container.** (*a*) Below the critical temperature. (*b*) Above the critical temperature.

FACETS OF CHEMISTRY 11.2

Decaffeinated Coffee and Supercritical Carbon Dioxide

Many people prefer to avoid caffeine, yet still enjoy a cup of coffee. For them, decaffeinated coffee is just the thing. To satisfy this demand, coffee producers remove caffeine from the coffee beans before roasting them. Several methods have been used, some of which use solvents such as methylene chloride (CH_2Cl_2) or ethyl acetate ($CH_3CO_2C_2H_5$) to dissolve the caffeine. Even though only trace amounts of these solvents remain after the coffee beans are dried, there are those who would prefer not to have any such chemicals in their coffee. And that's where carbon dioxide comes into the picture.

It turns out that supercritical carbon dioxide is an excellent solvent for many organic substances, including caffeine. To make it, gaseous CO_2 is heated to a temperature above its critical temperature of 31 °C, typically to about 80 °C. It is then compressed to about 200 atm. This gives it a density near that of a liquid, but with some properties of a gas. The fluid has a very low viscosity and readily penetrates coffee beans that have been softened with steam, drawing out the water and caffeine. After several hours, the CO_2 has removed as much as 97% of the caffeine, and the fluid containing the water and caffeine is then drawn off. When the pressure of the supercritical CO_2 solution is reduced, the CO_2 turns to a gas and the water and caffeine separate. The caffeine is recovered and sold to beverage or pharmaceutical companies. Meanwhile, the pressure over the coffee beans is also reduced and the beans are warmed to about 120 °C, causing residual CO_2 to evaporate. Because CO_2 is not a toxic gas, any small traces of CO_2 that remain are totally harmless.

(Andy Washnik.)

Decaffeination of coffee is not the only use of supercritical CO_2. It is also used to extract the essential flavor ingredients in spices and herbs for use in a variety of products. As with coffee, using supercritical CO_2 as a solvent completely avoids any potential harm that might be caused by small residual amounts of other solvents.

between the two phases because they have different densities, which causes them to bend light differently. This allows us to see the interface, or surface, between the more dense liquid and the less dense vapor. If this liquid is now heated, two things happen. First, more liquid evaporates. This causes an increase in the number of molecules per cubic centimeter of vapor which, in turn, causes the density of the vapor to increase. Second, the liquid expands (just like mercury does in a thermometer). This means that a given mass of liquid occupies more volume, so its density decreases. As the temperature of the liquid and vapor continue to increase, the vapor density rises and the liquid density falls; they approach each other. Eventually the densities become equal, and a separate liquid phase no longer exists; everything is the same (see Figure 11.49*b*). The highest temperature at which a liquid phase still exists is the critical temperature, and the pressure of the vapor at this temperature is the critical pressure. A substance that has a temperature above its critical temperature and a density near its liquid density is described as a **supercritical fluid.** Supercritical fluids have some unique properties that make them excellent solvents, and one that is particularly useful is supercritical carbon dioxide, which is used as a solvent to decaffeinate coffee.

◻ This interface between liquid and gas is called the **meniscus.**

The values of the critical temperature and critical pressure are unique for every chemical substance and are controlled by the intermolecular attractions (see Table 11.6). Notice

TABLE 11.6 **Some Critical Temperatures and Pressures**

Compound	T_c (°C)	P_c (atm)
Water	374.1	217.7
Ammonia	132.5	112.5
Carbon dioxide	31	72.9
Ethane (C_2H_6)	32.2	48.2
Methane (CH_4)	−82.1	45.8
Helium	−267.8	2.3

that liquids with strong intermolecular attractions, like water, tend to have high critical temperatures. Under pressure, the strong attractions between the molecules are able to hold them together in a liquid state even when the molecules are jiggling about violently at an elevated temperature. In contrast, substances with weak intermolecular attractions, such as methane and helium, have low critical temperatures. For these substances, even the small amounts of kinetic energy possessed by the molecules at low temperatures is sufficient to overcome the intermolecular attractions and prevent the molecules from sticking together as a liquid, despite being held close together under high pressure.

At room temperature, some gases will liquefy and others will not

When a gaseous substance has a temperature below its critical temperature, it is capable of being liquefied by compressing it. For example, carbon dioxide is a gas at room temperature (approximately 25 °C). This is below its critical temperature of 31 °C. If the $CO_2(g)$ is gradually compressed, a pressure will eventually be reached that lies on the liquid–vapor curve for CO_2, and further compression will cause the CO_2 to liquefy. In fact, that's what happens when a CO_2 fire extinguisher is filled; the CO_2 that's pumped in is a liquid under a high pressure. If you shake a filled CO_2 fire extinguisher, you can feel the liquid sloshing around inside, provided the temperature of the fire extinguisher is below 31 °C (88 °F). When the fire extinguisher is used, a valve releases the pressurized CO_2, which rushes out to extinguish the fire.

□ On a very hot day, when the temperature is in the 90s, a filled CO_2 fire extinguisher won't give the sensation that it's filled with a liquid. At such temperatures, the CO_2 is in a supercritical state and no separate liquid phase exists.

Gases such as O_2 and N_2, which have critical temperatures far below 0 °C, can never be liquids at room temperature. When they are compressed, they simply become high-pressure gases. To make liquid N_2 or O_2, the gases must be made very cold as well as being compressed to high pressures.

SUMMARY

Physical Properties: Gases, Liquids, and Solids. Gases expand to fill the entire volume of a container. Liquids and solids retain a constant volume if transferred from one container to another. Solids also retain a constant shape. These characteristics are related to how tightly packed the particles are and to the relative strengths of the intermolecular attractions in the different states of matter. Most physical properties depend primarily on intermolecular attractions. In gases, these attractions are weak because the molecules are so far apart. They are much stronger in liquids and solids, where the particles are packed together tightly.

Intermolecular Attractions. Polar molecules attract each other by **dipole–dipole attractions,** which arise because the positive end of one dipole attracts the negative end of another. Nonpolar molecules are attracted to each other by **London dispersion forces,** which are **instantaneous dipole–induced dipole attractions.** London forces are present between all particles, including atoms, polar and nonpolar molecules, and ions. Among different substances, London forces increase with an increase in size of a particle's electron cloud; they also increase with increasing chain length among molecules such as the hydrocarbons. Compact molecules experience weaker London forces than similar long chain molecules. For large molecules, the cumulative effect of large numbers of weak London force interactions can be quite strong and outweigh other intermolecular attractions. **Hydrogen bonding,** a special case of dipole–dipole attractions, occurs between molecules in which hydrogen is covalently bonded to a small, very electronegative atom—principally, nitrogen, oxygen, or fluorine. Hydrogen bonding is much stronger than the other types of intermolecular attractions. **Ion–dipole attractions** occur when ions interact with polar substances. **Ion–induced dipole attractions** result when an ion creates a dipole in a neighboring molecule or ion.

General Properties of Liquids and Solids. Properties that depend mostly on closeness of packing of particles are **compressibility** (or the opposite, incompressibility) and **diffusion.** Diffusion is slow in liquids and almost nonexistent in solids at room temperature. Properties that depend mostly on the strengths of intermolecular attractions are **retention of volume and shape, surface tension,** and **ease of evaporation. Surface tension** is related to the energy needed to expand a liquid's surface area. A liquid can **wet** a surface if its molecules are attracted to the surface about as strongly as they are attracted to each other. **Evaporation** of liquids and solids is endothermic and produces a cooling effect. The overall rate of evaporation increases with increasing surface area. The rate of evaporation from a given surface area of a liquid increases with increasing temperature, and with decreasing intermolecular attractions. Evaporation of a solid is called **sublimation.**

Changes of State. Changes from one physical state to another, such as melting, vaporization, or sublimation, can occur as dynamic equilibria. In a **dynamic equilibrium,** opposing processes occur continually at equal rates, so over time there is no apparent change in the composition of the system. For liquids and solids, equilibria are established when vaporization occurs in a sealed container. A solid is in equilibrium with its liquid at the melting point.

Vapor Pressures. When the rates of evaporation and condensation of a liquid are equal, the vapor above the liquid exerts a pressure called the **equilibrium vapor pressure** (or more commonly, just the **vapor pressure**). The vapor pressure is controlled by the rate of evaporation *per unit surface area.* When the intermolecular attractive forces are large, the rate of evaporation is small and the vapor pressure is small. Vapor pressure increases with increasing temperature because the rate of evaporation increases as the temperature rises. The vapor pressure is independent of the *total* surface area of the liquid. Solids have vapor pressures just as liquids do.

Boiling Point. A substance boils when its vapor pressure equals the prevailing atmospheric pressure. The **normal boiling point** of a liquid is the temperature at which its vapor pressure equals 1 atm. Substances with high boiling points have strong intermolecular attractions.

Energy Changes Associated with Changes of State. On a **heating curve,** flat portions correspond to phase changes in which the heat added changes the potential energies of the particles without changing their average kinetic energy. **Superheating** sometimes occurs when a liquid is heated above its boiling point. On a **cooling curve, supercooling** sometimes occurs when the temperature of the liquid drops below the freezing point of the substance. The enthalpy changes for melting, vaporization of a liquid, and sublimation are the **molar heat of fusion,** ΔH_{fusion}, the **molar heat of vaporization,** $\Delta H_{\text{vaporization}}$, and the **molar heat of sublimation,** $\Delta H_{\text{sublimation}}$, respectively. They are all endothermic and are related in size as follows: $\Delta H_{\text{fusion}} < \Delta H_{\text{vaporization}} < \Delta H_{\text{sublimation}}$. The sizes of these enthalpy changes are large for substances with strong intermolecular attractive forces.

Le Châtelier's Principle. When the equilibrium in a system is upset by a disturbance, the system changes in a direction that minimizes the disturbance and, if possible, brings the system back to equilibrium. By this principle, we find that raising the temperature favors an endothermic change. Decreasing the volume favors a change toward a more dense phase.

Crystalline Solids. Crystalline solids have highly ordered arrangements of particles within them, which can be described in terms of repeating three-dimensional arrays of points called **lattices.** The simplest portion of a lattice is its **unit cell.** Many structures can be described with the same lattice by associating different units (atoms, molecules, or ions) to lattice points and by changing the dimensions of the unit cell. Three cubic unit cells are possible—**simple cubic, face-centered cubic,** and **body-centered cubic.** Sodium chloride and many other alkali metal halides crystallize in the **rock salt structure,** which contains four formula units per unit cell. Two modes of closest packing of atoms are **cubic closest packing (ccp)** and **hexagonal closest packing (hcp).** The ccp structure has an A-B-C-A-B-C. . . alternating stacking of layers of spheres; the hcp structure has an A-B-A-B-. . . stacking of layers. **Amorphous** solids lack the internal structure of crystalline solids. Glass is an amorphous solid and is sometimes called a **supercooled liquid.**

X-Ray Diffraction. Information about crystal structures is obtained experimentally from **X-ray diffraction patterns** produced by constructive and destructive interference of X rays scattered by atoms. Distances between planes of atoms in a crystal can be calculated by the Bragg equation, $n\lambda = 2d \sin \theta$, where n is a whole number, λ is the wavelength of the X rays, d is the distance between planes of atoms producing the diffracted beam, and θ is the angle at which the diffracted X-ray beam emerges relative to the planes of atoms producing the diffracted beam.

Crystal Types. Crystals can be divided into four general types: **ionic, molecular, covalent,** and **metallic.** Their properties depend on the kinds of particles within the lattice and on the attractions between the particles, as summarized in Table 11.5.

Phase Diagrams. Temperatures and pressures at which equilibria can exist between phases are given graphically in a **phase diagram.** The three equilibrium lines intersect at the **triple point.** The liquid–vapor line terminates at the **critical point.** At the **critical temperature,** a liquid has a vapor pressure equal to its **critical pressure.** Above the critical temperature a liquid phase cannot be formed; the single phase that exists is called a **supercritical fluid.** The equilibrium lines also divide a phase diagram into temperature–pressure regions in which a substance can exist in just a single phase. Water is different from most substances in that its melting point decreases with increasing pressure.

TOOLS FOR PROBLEM SOLVING

The concepts that you've learned in this chapter are collected below. They can be applied as tools in solving problems. Study each one carefully so that you know what each is used for. When faced with solving a problem, recall what each tool does and consider whether it will be helpful in finding a solution. This will aid you in selecting the tools you need. If necessary, refer to this table when working on the Review Problems that follow.

Relationship between intermolecular forces and molecular structure *(page 433)* From molecular structure, we can determine whether a molecule is polar or not and whether it has N—H or O—H bonds. This lets us predict and compare the strengths of intermolecular attractions. You should be able to identify when dipole–dipole, London, and hydrogen bonding occurs. See the summary Table 11.3 on page *440*.

Factors that affect rates of evaporation and vapor pressure *(pages 446, 447, and 448)* They allow us to compare the relative rates of evaporation based on temperature and the strengths of intermolecular forces in substances. They also allow us to compare the strengths of intermolecular forces based on the relative magnitudes of vapor pressures at a given temperature.

Boiling points of substances *(page 451)* They allow us to compare the strengths of intermolecular forces in substances based on their boiling points.

Enthalpy changes during phase changes *(pages 453 and 455)* They allow us to compare the strengths of intermolecular forces in substances based on relative values of $\Delta H_{\text{vaporization}}$ and $\Delta H_{\text{sublimation}}$.

Le Châtelier's principle *(page 456)* Le Châtelier's principle enables us to predict the direction in which the position of equilibrium is shifted when a dynamic equilibrium is upset by a disturbance. You should be able to predict how the position of equilibrium between phases is affected by temperature and pressure changes.

Bragg equation *(page 463)*

$$n\lambda = 2d \sin \theta$$

Using the wavelength of X rays and angles at which X rays are diffracted from a crystal, the distances between planes of atoms can be calculated.

Unit cell structures for simple cubic, face-centered cubic, and body-centered cubic lattices *(page 458)* By knowing the arrangements of atoms in these unit cells, we can use the dimensions of the unit cell to calculate atomic radii and other properties.

Properties of crystal types *(page 466)* By examining certain physical properties of a solid (hardness, melting point, electrical conductivity in the solid and liquid state), we can often predict the nature of the particles that occupy lattice sites in the solid and the kinds of attractive forces between them.

Phase diagram *(page 467)* We use a phase diagram to identify temperatures and pressures at which equilibrium can exist between phases of a substance, and to identify conditions under which only a single phase can exist.

QUESTIONS, PROBLEMS, AND EXERCISES

Answers to problems whose numbers are printed in color are given in Appendix B. More challenging problems are marked with asterisks. ILW = Interactive Learningware solution is available at www.wiley.com/college/brady. OH = an Office Hours video is available for this problem.

REVIEW QUESTIONS

Comparisons among the States of Matter

11.1 Why are the intermolecular attractive forces stronger in liquids and solids than they are in gases?

11.2 Compare the behavior of gases, liquids, and solids when they are transferred from one container to another.

11.3 For a given substance, how do the intermolecular attractive forces compare in its gaseous, liquid, and solid states?

Intermolecular Attractions

11.4 Which kinds of attractive forces, intermolecular or intramolecular, are responsible for chemical properties? Which kind are responsible for physical properties?

11.5 Describe *dipole–dipole attractions*.

11.6 What are *London forces*? How are they affected by the sizes of the atoms in a molecule? How are they affected by the number of atoms in a molecule? How are they affected by the shape of a molecule?

11.7 Define *polarizability*. How does this property affect the strengths of London forces?

11.8 Which nonmetals, besides hydrogen, are most often involved in hydrogen bonding? Why these and not others?

11.9 Which is expected to have the higher boiling point, C_8H_{18} or C_4H_{10}? Explain your choice.

11.10 Ethanol and dimethyl ether have the same molecular formula, C_2H_6O. Ethanol boils at 78.4 °C, whereas dimethyl ether boils at −23.7 °C. Their structural formulas are

CH_3CH_2OH	CH_3OCH_3
ethanol	dimethyl ether

Explain why the boiling point of the ether is so much lower than the boiling point of ethanol.

11.11 How do the strengths of covalent bonds and dipole–dipole attractions compare? How do the strengths of ordinary dipole–dipole attractions compare with the strengths of hydrogen bonds?

11.12 For each pair, in which compound are the ion–induced dipole attractions stronger? (a) CaO or CaS, (b) MgO or Al_2O_3

General Properties of Liquids and Solids

11.13 Name two physical properties of liquids and solids that are controlled primarily by how tightly packed the particles are. Name three that are controlled mostly by the strengths of the intermolecular attractions.

11.14 Why does diffusion occur more slowly in liquids than in gases? Why does diffusion occur extremely slowly in solids?

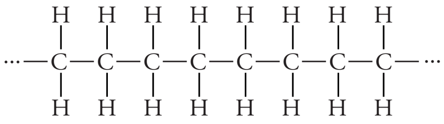
11.15 On the basis of kinetic theory, would you expect the rate of diffusion in a liquid to increase or decrease as the temperature is increased? Explain your answer.

11.16 What is *surface tension*? Why do molecules at the surface of a liquid behave differently from those within the interior?

11.17 Which liquid is expected to have the larger surface tension at a given temperature, CCl_4 or H_2O? Explain your answer.

11.18 What does *wetting* of a surface mean? What is a *surfactant?* What is its purpose and how does it function?

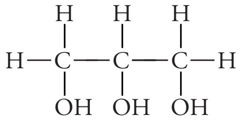
11.19 Polyethylene plastic consists of long chains of carbon atoms, each of which is also bonded to hydrogens, as shown below:



$$\cdots-\underset{\substack{|\\H}}{\overset{\substack{H\\|}}{C}}-\underset{\substack{|\\H}}{\overset{\substack{H\\|}}{C}}-\underset{\substack{|\\H}}{\overset{\substack{H\\|}}{C}}-\underset{\substack{|\\H}}{\overset{\substack{H\\|}}{C}}-\underset{\substack{|\\H}}{\overset{\substack{H\\|}}{C}}-\underset{\substack{|\\H}}{\overset{\substack{H\\|}}{C}}-\underset{\substack{|\\H}}{\overset{\substack{H\\|}}{C}}-\underset{\substack{|\\H}}{\overset{\substack{H\\|}}{C}}-\cdots$$

Water forms beads when placed on a polyethylene surface. Why?

11.20 The structural formula for glycerol is



$$H-\underset{\substack{|\\OH}}{\overset{\substack{H\\|}}{C}}-\underset{\substack{|\\OH}}{\overset{\substack{H\\|}}{C}}-\underset{\substack{|\\OH}}{\overset{\substack{H\\|}}{C}}-H$$

Would you expect this liquid to wet glass surfaces? Explain your answer.

11.21 On the basis of what happens on a molecular level, why does evaporation lower the temperature of a liquid?

11.22 On the basis of the distribution of kinetic energies of the molecules of a liquid, explain why increasing the liquid's temperature increases the rate of evaporation.

11.23 How is the rate of evaporation of a liquid affected by increasing the surface area of the liquid? How is the rate of evaporation affected by the strengths of intermolecular attractive forces?

11.24 During the cold winter months, snow often disappears gradually without melting. How is this possible? What is the name of the process responsible for this phenomenon?

Changes of State and Equilibrium

11.25 What terms do we use to describe the following changes of state?
(a) solid → gas, (b) liquid → gas, (c) gas → liquid,
(d) solid → liquid, (e) liquid → solid

11.26 When a molecule escapes from the surface of a liquid by evaporation, it has a kinetic energy that's much larger than the average KE. Why is it likely that after being in the vapor for a while its kinetic energy will be much less? If this molecule collides with the surface of the liquid, is it likely to bounce out again?

11.27 Why does a molecule of a vapor that collides with the surface of a liquid tend to be captured by the liquid, even if the incoming molecule has a large kinetic energy?

11.28 When an equilibrium is established in the evaporation of a liquid into a sealed container, we refer to it as a *dynamic equilibrium*. Why?

11.29 Viewed at a molecular level, what is happening when a dynamic equilibrium is established between the liquid and solid forms of a substance? What is the temperature called at which there is an equilibrium between a liquid and a solid?

11.30 Is it possible to establish an equilibrium between a solid and its vapor? Explain.

Vapor Pressure

11.31 Define *equilibrium vapor pressure.* Why do we call the equilibrium involved a *dynamic equilibrium*?

11.32 Explain why changing the volume of a container in which there is a liquid–vapor equilibrium has no effect on the equilibrium vapor pressure.

11.33 Why doesn't a change in the surface area of a liquid cause a change in the equilibrium vapor pressure?

11.34 What effect does increasing the temperature have on the equilibrium vapor pressure of a liquid? Why?

11.35 Why does moisture condense on the outside of a cool glass of water in the summertime?

11.36 Why do we feel more uncomfortable in humid air at 90 °F than in dry air at 90 °F?

Boiling Points of Liquids

11.37 Define *boiling point* and *normal boiling point.*

11.38 Why does the boiling point vary with atmospheric pressure?

11.39 Mt. Kilimanjaro in Tanzania is the tallest peak in Africa (19,340 ft). The normal barometric pressure at the top of this mountain is about 345 torr. At what Celsius temperature would water be expected to boil there? (See Figure 11.21.)

11.40 When liquid ethanol begins to boil, what is present inside the bubbles that form?

11.41 The radiator cap of an automobile engine is designed to maintain a pressure of approximately 15 lb/in.^{2} above normal atmospheric pressure. How does this help prevent the engine from "boiling over" in hot weather?

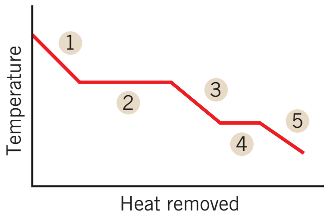
11.42 Butane, C_4H_{10}, has a boiling point of -0.5 °C (which is 31 °F). Despite this, liquid butane can be seen sloshing about inside a typical butane lighter, even at room temperature. Why isn't the butane boiling inside the lighter at room temperature?

11.43 Why does H_2S have a lower boiling point than H_2Se? Why does H_2O have a much higher boiling point than H_2S?

11.44 An $H-F$ bond is more polar than an $O-H$ bond, so HF forms stronger hydrogen bonds than H_2O. Nevertheless, HF has a lower boiling point than H_2O. Explain why this is so.

Energy Changes That Accompany Changes of State

11.45 Below is a cooling curve for one mole of a substance.



(a) On which portions of this graph do we find the average kinetic energy of the molecules of the substance changing?
(b) On which portions of this graph is the amount of heat removed related primarily to a lowering of the potential energy of the molecules?
(c) Which portion of the graph corresponds to the release of the heat of vaporization?
(d) Which portion of the graph corresponds to the release of the heat of fusion?
(e) Which is larger, the heat of fusion or the heat of vaporization?
(f) On the graph, indicate the melting point of the solid.
(g) On the graph, indicate the boiling point of the liquid.
(h) On the drawing, indicate how supercooling of the liquid would affect the graph.

11.46 Why is $\Delta H_{\text{vaporization}}$ larger than ΔH_{fusion}? How does $\Delta H_{\text{sublimation}}$ compare with $\Delta H_{\text{vaporization}}$? Explain your answer.

11.47 Would the "heat of condensation," $\Delta H_{\text{condensation}}$, be exothermic or endothermic?

11.48 Hurricanes can travel for thousands of miles over warm water, but they rapidly lose their strength when they move over a large land mass or over cold water. Why?

11.49 Ethanol (grain alcohol) has a molar heat of vaporization of 39.3 kJ mol^{-1}. Ethyl acetate, a common solvent, has a molar heat of vaporization of 32.5 kJ mol^{-1}. Which of these substances has the larger intermolecular attractions?

11.50 A burn caused by steam is much more serious than one caused by the same amount of boiling water. Why?

11.51 Arrange the following substances in order of their increasing values of $\Delta H_{\text{vaporization}}$: (a) HF, (b) CH_4, (c) CF_4, and (d) HCl.

Le Châtelier's Principle

11.52 State Le Châtelier's principle in your own words.

11.53 What do we mean by the *position of equilibrium*?

11.54 Use Le Châtelier's principle to predict the effect of adding heat in the equilibrium: $\text{solid} + \text{heat} \rightleftharpoons \text{liquid}$.

11.55 Use Le Châtelier's principle to explain why lowering the temperature lowers the vapor pressure of a solid.

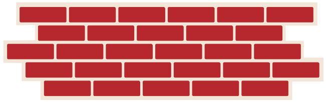
Crystalline Solids and X-Ray Diffraction

11.56 What is the difference between a crystalline solid and an amorphous solid?

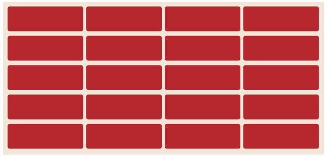
11.57 What is a *lattice*? What is a *unit cell*?

11.58 What relationship is there between a crystal lattice and its unit cell?

11.59 The diagrams below illustrate typical arrangements of paving bricks in a patio or driveway. Sketch the unit cells that correspond to these patterns of bricks.

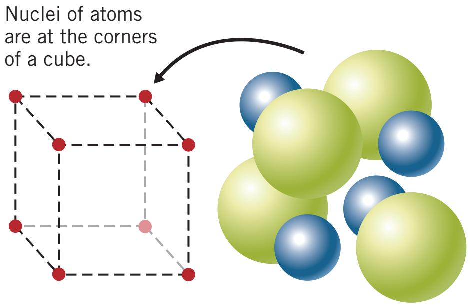


(a)



(b)

11.60 Below is illustrated the way the atoms of two different elements are packed in a certain solid. The nuclei occupy positions at the corners of a cube. Is this cube the unit cell for this substance? Explain your answer.



11.61 Make a sketch of a layer of sodium ions and chloride ions in a NaCl crystal. Indicate how the ions are arranged in a face-centered cubic pattern, regardless of whether we place lattice points at the Cl^- ions or Na^+ ions.

11.62 How do the crystal structures of copper and gold differ? In what way are they similar? On the basis of the locations of the elements in the periodic table, what kind of crystal structure would you expect for silver?

11.63 What kind of lattice does zinc sulfide have? What kind of lattice does calcium fluoride have?

11.64 Only 14 different kinds of crystal lattices are possible. How can this be true, considering the fact that there are millions of different chemical compounds that are able to form crystals?

11.65 Write the Bragg equation and define the symbols.

11.66 Why can't $CaCl_2$ or $AlCl_3$ form crystals with the same structure as NaCl?

Crystal Types

11.67 What kinds of particles are located at the lattice sites in a metallic crystal?

11.68 What kinds of attractive forces exist between particles in (a) molecular crystals, (b) ionic crystals, and (c) covalent crystals?

11.69 Why are covalent crystals sometimes called *network solids*?

Amorphous Solids

11.70 What does the word *amorphous* mean?

11.71 What is an *amorphous solid*? Compare what happens when crystalline and amorphous solids are broken into pieces.

Phase Diagrams

11.72 For most substances, the solid is more dense than the liquid. Use Le Châtelier's principle to explain why the melting point of such substances should *increase* with increasing pressure. Sketch the phase diagram for such a substance, being sure to have the solid–liquid equilibrium line slope in the correct direction.

11.73 Define *critical temperature* and *critical pressure.*

11.74 What is a *supercritical fluid*? Why is supercritical CO_2 used to decaffeinate coffee?

11.75 What phases of a substance are in equilibrium at the triple point?

11.76 Why doesn't CO_2 have a normal boiling point?

11.77 At room temperature, hydrogen can be compressed to very high pressures without liquefying. On the other hand, butane becomes a liquid at high pressure (at room temperature). What does this tell us about the critical temperatures of hydrogen and butane?

REVIEW PROBLEMS

Intermolecular Attractions and Molecular Structure

11.78 Which liquid evaporates faster at 25 °C, diethyl ether (an anesthetic) or butanol (a solvent used in the preparation of shellac and varnishes)? Both have the molecular formula $C_4H_{10}O$, but their structural formulas are different, as shown below.

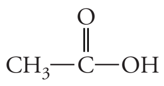
$CH_3CH_2CH_2CH_2OH$ — butanol

$CH_3CH_2—O—CH_2CH_3$ — diethyl ether

OH **11.79** Which compound should have the higher vapor pressure at 25 °C, butanol or diethyl ether? Which should have the higher boiling point?

11.80 What kinds of intermolecular attractive forces (dipole–dipole, London, hydrogen bonding) are present in the following substances?
(a) HF (b) PCl_3 (c) SF_6 (d) SO_2

11.81 What kinds of intermolecular attractive forces are present in the following substances?

(a) 
$CH_3—\overset{\overset{\displaystyle O}{\|}}{C}—OH$ (b) H_2S (c) SO_3 (d) CH_3NH_2

OH **11.82** Consider the compounds $CHCl_3$ (chloroform, an important solvent that was once used as an anesthetic) and $CHBr_3$ (bromoform, which has been used as a sedative). Compare the strengths of their dipole–dipole attractions and the strengths of their London forces. Their boiling points are 61 °C and 149 °C, respectively. For these compounds, which kinds of attractive forces (dipole–dipole or London) are more important in determining their boiling points? Justify your answer.

11.83 Carbon dioxide does not liquefy at atmospheric pressure, but instead forms a solid that sublimes at −78 °C. Nitrogen dioxide forms a liquid that boils at 21 °C at atmospheric pressure. How do these data support the statement that CO_2 is a linear molecule whereas NO_2 is nonlinear?

11.84 Which should have the higher boiling point, ethanol (CH_3CH_2OH, found in alcoholic beverages) or ethanethiol (CH_3CH_2SH, a foul-smelling liquid found in the urine of rabbits that have feasted on cabbage)?

11.85 How do the strengths of London forces compare in $CO_2(l)$ and $CS_2(l)$? Which of these is expected to have the higher boiling point? (Check your answer by referring to the *Handbook of Chemistry and Physics*, which is available in your school library.)

OH **11.86** Below are the vapor pressures of some relatively common chemicals measured at 20 °C. Arrange these substances in order of increasing intermolecular attractive forces.

Benzene, C_6H_6	80 torr
Acetic acid, $HC_2H_3O_2$	11.7 torr
Acetone, C_3H_6O	184.8 torr
Diethyl ether, $C_4H_{10}O$	442.2 torr
Water	17.5 torr

11.87 The boiling points of some common substances are given here. Arrange these substances in order of increasing strengths of intermolecular attractions.

Ethanol, C_2H_5OH	78.4 °C
Ethylene glycol, $C_2H_4(OH)_2$	197.2 °C
Water	100 °C
Diethyl ether, $C_4H_{10}O$	34.5 °C

Energy Changes That Accompany Changes of State

OH **11.88** The molar heat of vaporization of water at 25 °C is +43.9 kJ mol^{-1}. How many kilojoules of heat would be required to vaporize 125 mL (0.125 kg) of water?

11.89 The molar heat of vaporization of acetone, C_3H_6O, is 30.3 kJ mol^{-1} at its boiling point. How many kilojoules of heat would be liberated by the condensation of 5.00 g of acetone?

11.90 Suppose 45.0 g of water at 85 °C is added to 105.0 g of ice at 0 °C. The molar heat of fusion of water is 6.01 kJ mol^{-1}, and the specific heat of water is 4.18 J/g °C. On the basis of these data, (a) what will be the final temperature of the mixture and (b) how many grams of ice will melt?

11.91 A cube of solid benzene (C_6H_6) at its melting point and weighing 10.0 g is placed in 10.0 g of water at 30 °C. Given that the heat of fusion of benzene is 9.92 kJ mol^{-1}, to what temperature will the water have cooled by the time all of the benzene has melted?

Crystalline Solids and X-Ray Diffraction

11.92 How many zinc and sulfide ions are present in the unit cell of zinc sulfide? (See Figure 11.35.)

11.93 How many copper atoms are within the face-centered cubic unit cell of copper? (Hint: See Figure 11.31 and add up all the *parts* of atoms in the fcc unit cell.)

OH ILW **11.94** The atomic radius of nickel is 1.24 Å. Nickel crystallizes in a face-centered cubic lattice. What is the length of the edge of the unit cell expressed in angstroms and in picometers?

11.95 Silver forms face-centered cubic crystals. The atomic radius of a silver atom is 144 pm. Draw the face of a unit cell with the nuclei of the silver atoms at the lattice points. The atoms are in contact along the diagonal. Calculate the length of an edge of this unit cell.

11.96 Potassium ions have a radius of 133 pm, and bromide ions have a radius of 195 pm. The crystal structure of potassium bromide is the same as for sodium chloride. Estimate the length of the edge of the unit cell in potassium bromide.

11.97 The unit cell edge in sodium chloride has a length of 564.0 pm. The sodium ion has a radius of 95 pm. What is the *diameter* of a chloride ion?

OH **11.98** Calculate the angles at which X rays of wavelength 229 pm will be observed to be defracted from crystal planes spaced (a) 1000 pm apart and (b) 250 pm apart. Assume $n = 1$ for both calculations.

11.99 Calculate the interplanar spacings (in picometers) that correspond to defracted beams of X rays at $\theta = 20.0°$, 27.4°, and 35.8°, if the X rays have a wavelength of 141 pm. Assume that $n = 1$.

11.100 Cesium chloride forms a simple cubic lattice in which Cs^+ ions are at the corners and a Cl^- ion is in the center (see Figure 11.34). The cation–anion contact occurs along the *body diagonal* of the unit cell. (The body diagonal starts at one corner and then runs through the center of the cell to the opposite corner.) The length of the edge of the unit cell is 412.3 pm. The Cl^- ion has a radius of 181 pm. Calculate the radius of the Cs^+ ion.

11.101 Rubidium chloride has the rock salt structure. Cations and anions are in contact along the edge of the unit cell, which is 658 pm long. The radius of the chloride ion is 181 pm. What is the radius of the Rb^+ ion?

Crystal Types

11.102 Tin(IV) chloride, $SnCl_4$, has soft crystals with a melting point of −30.2 °C. The liquid is nonconducting. What type of crystal is formed by $SnCl_4$?

11.103 Elemental boron is a semiconductor, is very hard, and has a melting point of about 2250 °C. What type of crystal is formed by boron?

11.104 Columbium is another name for one of the elements. This element is shiny, soft, and ductile. It melts at 2468 °C, and the solid conducts electricity. What kind of solid does columbium form?

11.105 Elemental phosphorus consists of soft white "waxy" crystals that are easily crushed and melt at 44 °C. The solid does not conduct electricity. What type of crystal does phosphorus form?

11.106 Indicate which type of crystal (ionic, molecular, covalent, metallic) each of the following would form when it solidifies. (a) Br_2, (b) LiF, (c) MgO, (d) Mo, (e) Si, (f) PH_3, (g) NaOH

11.107 Indicate which type of crystal (ionic, molecular, covalent, metallic) each of the following would form when it solidifies: (a) O_2, (b) H_2S, (c) Pt, (d) KCl, (e) Ge, (f) $Al_2(SO_4)_3$, (g) Ne

Phase Diagrams

11.108 Sketch the phase diagram for a substance that has a triple point at −15.0 °C and 0.30 atm, melts at −10.0 °C at 1 atm, and has a normal boiling point of 90 °C.

11.109 Based on the phase diagram of the preceding problem, below what pressure will the substance undergo sublimation? How does the density of the liquid compare with the density of the solid?

11.110 According to Figure 11.48, what phase(s) should exist for CO_2 at (a) −60 °C and 6 atm, (b) −60 °C and 2 atm, (c) −40 °C and 10 atm, and (d) −57 °C and 5.2 atm?

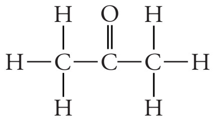
OH **11.111** Looking at the phase diagram for CO_2 (Figure 11.48), how can we tell that solid CO_2 is more dense than liquid CO_2?

ADDITIONAL EXERCISES

11.112 Make a list of *all* of the attractive forces that exist in solid Na_2SO_3.

OH **11.113** Calculate the mass of water vapor present in 10.0 L of air at 20 °C if the relative humidity is 75%.

11.114 Should acetone molecules be attracted to water molecules more strongly than to other acetone molecules? Explain your answer. The structure of acetone is shown below.



OH **11.115** Acetic acid has a heat of fusion of 10.8 kJ mol^{-1} and a heat of vaporization of 24.3 kJ mol^{-1}.

$$HC_2H_3O_2(s) \longrightarrow HC_2H_3O_2(l) \quad \Delta H_{\text{fusion}} = 10.8 \text{ kJ mol}^{-1}$$

$$HC_2H_3O_2(l) \longrightarrow HC_2H_3O_2(g) \quad \Delta H_{\text{vaporization}} = 24.3 \text{ kJ mol}^{-1}$$

Use Hess's law to estimate the value for the heat of sublimation of acetic acid, in kilojoules per mole.

***11.116** Melting point is sometimes used as an indication of the extent of covalent bonding in a compound—the higher the melting point, the more ionic the substance. On this basis, oxides of metals seem to become less ionic as the charge on the metal ion increases. Thus, Cr_2O_3 has a melting point of 2266 °C whereas CrO_3 has a melting point of only 196 °C. The explanation often given is similar in some respects to explanations of the variations in the strengths of certain intermolecular attractions given in this chapter. Provide an explanation for the greater degree of electron sharing in CrO_3 as compared with Cr_2O_3.

***11.117** When warm moist air sweeps in from the ocean and rises over a mountain range, it expands and cools. Explain how this cooling is related to the attractive forces between gas molecules. Why does this cause rain to form? When the air drops down the far side of the range, its pressure rises as it is compressed. Explain why this causes the air temperature to rise. How does the humidity of this air compare with the air that originally came in off the ocean? Now, explain why the coast of California is lush farmland, whereas valleys (such as Death Valley) that lie to the east of the tall Sierra Nevada are arid and dry.

OH ***11.118** Gold crystallizes in a face-centered cubic lattice. The edge of the unit cell has a length of 407.86 pm. The density of gold is 19.31 g cm^{-3}. Use these data and the atomic mass of gold to calculate the value of Avogadro's number.

11.119 Gold crystallizes with a face-centered cubic unit cell with an edge length of 407.86 pm. Calculate the atomic radius of gold in units of picometers.

***11.120** Calculate the amount of empty space (in pm^3) in simple cubic, body-centered cubic, and face-centered cubic unit cells if the lattice points are occupied by identical atoms with a diameter of 1.00 pm. Which of these structures gives the most efficient packing of atoms.

11.121 Silver has an atomic radius of 144 pm. What would be the density of silver (in g cm^{-3}) if it were to crystallize in (a) a simple cubic lattice, (b) a body-centered cubic lattice, and (c) a face-centered cubic lattice? The actual density of silver is 10.6 g cm^{-3}. Which cubic lattice does silver have?

***11.122** Potassium chloride crystallizes with the rock salt structure. When bathed in X rays, the layers of atoms corresponding to the surfaces of the unit cell produce a diffracted beam of X rays at an angle of 12.8°. Calculate the density of KCl.

11.123 Why do clouds form when the humid air of a weather system called a *warm front* encounters the cool, relatively dry air of a *cold front*?

EXERCISES IN CRITICAL THINKING

11.124 Supercritical CO_2 is used to decaffeinate coffee. Propose other uses for supercritical fluids.

11.125 Freshly precipitated crystals are usually very small. Over time the crystals tend to grow larger. How can we use the concept of dynamic equilibrium to explain this phenomenon?

11.126 What are some "everyday" applications of Le Châtelier's principle? For example, we turn up the heat in an oven to cook a meal faster.

11.127 Lubricants, oils, greases, etc. are very important in everyday life. Explain how a lubricant works in terms of intermolecular forces.

11.128 Galileo's thermometer is a tube of liquid that has brightly colored glass spheres that float or sink depending on the temperature. Using your knowledge from the past two chapters, explain all of the processes that are involved in this thermometer.

11.129 Use the Clausius–Clapeyron equation to plot the vapor pressure curve of a gas that has a heat of vaporization of 21.7 kJ mol^{-1} and a boiling point of 48 °C. Compare your results to the other vapor pressure curves in this chapter.

11.130 Will the near weightless environment of the international space station have any effect on intermolecular forces and chemical reactions? What types of chemical reactions may benefit from a weightless environment?