

## 13

KINETICS: THE STUDY  
OF RATES OF REACTION

This photo shows how speed adds excitement to the movie *Mission Impossible III*. Wreckage of a high-speed chase and the explosion that the hero, Tom Cruise, barely escapes as he dashes to safety are evidence of fast chemical reactions. Kinetics is the name that describes studies of fast (and slow) chemical reactions that we will learn about in this chapter. (Stephen Vaughan/Paramount Pictures/The Kobal Collection, Ltd.)

## CHAPTER OUTLINE

- |  |   |   |
|--|---|---|
| <b>13.1</b> Five factors affect reaction rates   | <b>13.5</b> Reaction rate theories explain experimental rate laws in terms of molecular collisions  | <b>13.7</b> Experimental rate laws can be used to support or reject proposed mechanisms for a reaction    |
| <b>13.2</b> Rates of reaction are measured by monitoring change in concentration over time | <b>13.6</b> Activation energies are measured by fitting experimental data to the Arrhenius equation | <b>13.8</b> Catalysts change reaction rates by providing alternative paths between reactants and products |
| <b>13.3</b> Rate laws give reaction rate as a function of reactant concentrations          |   |   |
| <b>13.4</b> Integrated rate laws give concentration as a function of time                  |   |   |

**THIS CHAPTER IN CONTEXT** Chemical reactions run at many different speeds. Some, such as the rusting of iron or the breakdown of plastics in the environment, take place very slowly. Others, like the combustion of gasoline or the explosion of gunpowder, occur very quickly. **Chemical kinetics** is the study of the speeds (or *rates*) of chemical reactions. On a practical level, it is concerned with factors that affect the speeds of reactions and how reaction speeds can be controlled. This is essential in industry, where synthetic reactions must take place at controlled speeds. If a reaction takes weeks or months to occur, it may not be economically feasible; if it occurs too quickly or

uncontrollably, it may not be safe to carry out. For the consumer, studies on rates of decomposition allow a manufacturer to reliably determine the shelf life, or expiration date, of a product or drug. At a more fundamental level, a study of the speed of a reaction often gives clues that lead to an understanding about *how*, at a molecular level, reactants change into products. Understanding the reaction at this level of detail often allows even finer control of the reaction's speed, and suggests ways to modify the reaction to produce new types of products, or to improve the reaction's yield by preventing undesirable side reactions from occurring.

### 13.1 FIVE FACTORS AFFECT REACTION RATES

The **rate of reaction** for a given chemical change is the speed with which the reactants disappear and the products form. It is measured by the amount of products produced or reactants consumed per unit time. Usually this is done by monitoring the concentrations of the reactants or products over time, as the reaction runs (see Figure 13.1).

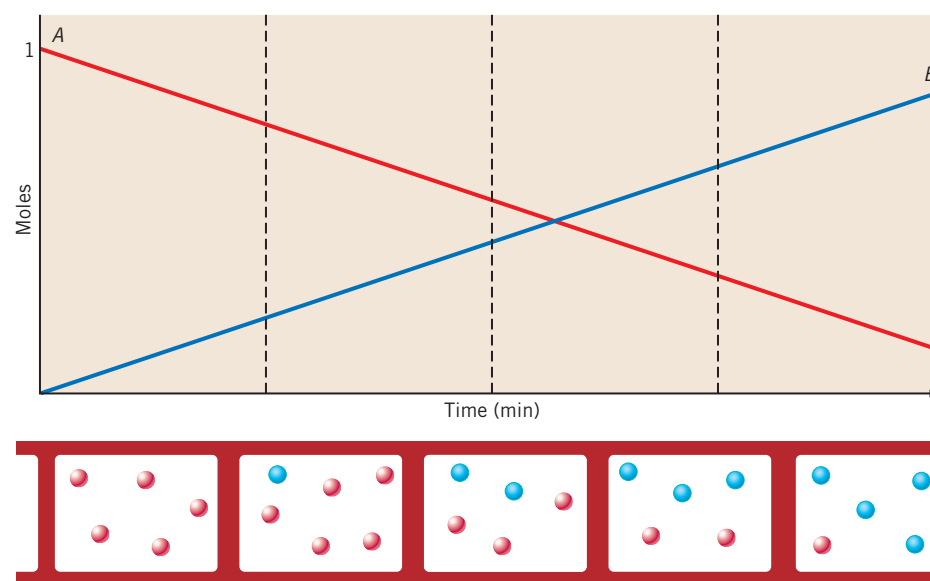
Before we take up the quantitative aspects of reaction rates, let's look qualitatively at factors that can make a reaction run faster or slower. There are five principal factors that influence reaction rates.

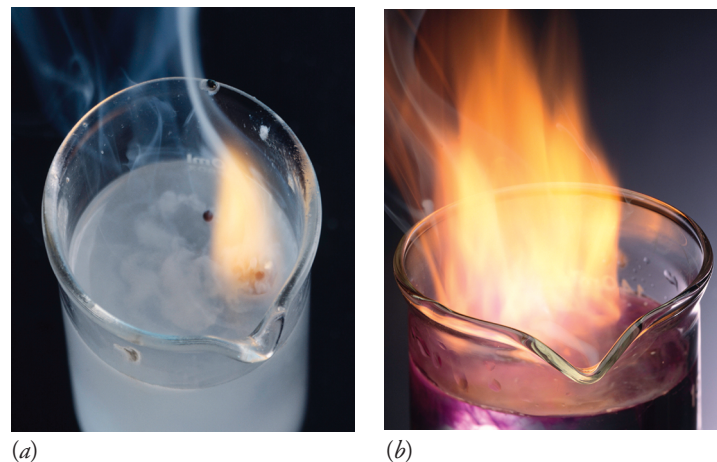
1. Chemical nature of the reactants
2. Ability of the reactants to come in contact with each other
3. Concentrations of the reactants
4. Temperature
5. Availability of rate-accelerating agents called *catalysts*

#### Chemical nature of the reactants

Bonds break and new bonds form during reactions. The most fundamental differences among reaction rates, therefore, lie in the reactants themselves, in the inherent tendencies of their atoms, molecules, or ions to undergo changes in chemical bonds. Some reactions are fast by nature and others are slow (Figure 13.2). Because sodium atoms lose electrons so easily, for example, a freshly exposed surface of metallic sodium tarnishes almost instantly when exposed to air and moisture. Under identical conditions, potassium also reacts with air and moisture, but the reaction is much faster because potassium atoms lose electrons more easily than sodium atoms.

**FIG. 13.1** Reaction rates are measured by monitoring concentration changes over time. The progress of the reaction  $A \rightarrow B$ . Note that the number of  $A$  molecules (in red) decreases with time, as the number of  $B$  molecules (in blue) increases. The steeper the concentration versus time curves are, the faster the rate of reaction is. The filmstrip represents the relative numbers of molecules of  $A$  and  $B$  at each time.





**FIG. 13.2** The chemical nature of reactants affects reaction rates. (a) Sodium loses electrons easily, so it reacts quickly with water. (b) Potassium loses electrons even more easily than sodium, so its reaction with water is explosively fast. (*Fundamental Photographs*)

### Ability of the reactants to meet

Most reactions involve two or more reactants whose particles (atoms, ions, or molecules) must collide with each other for the reaction to occur. This is why reactions are so often carried out in liquid solutions or in the gas phase, states in which the particles are able to intermingle at a molecular level and collide with each other easily.

Reactions in which all the reactants are in the same phase are called **homogeneous reactions**. Examples include the neutralization of sodium hydroxide by hydrochloric acid when both are dissolved in water, and the explosive gas-phase reaction of gasoline vapor with oxygen that can occur when the two are mixed in the right proportions. (An *explosion* is an extremely rapid reaction that quickly generates hot expanding gases.)

When the reactants are present in different phases—for example, when one is a gas and the other a liquid or a solid—the reaction is called a **heterogeneous reaction**. An example is the combustion of coal, in which solid carbon combines with gaseous oxygen. In a heterogeneous reaction, the reactants are able to meet only at the interface between the phases, so *the area of contact between the phases is a major factor in determining the rate of the reaction*. This area is controlled by the sizes of the particles of the reactants. By pulverizing a solid, the total surface area can be hugely increased (Figure 13.3). This maximizes contact between the atoms, ions, or molecules in the solid state with those in a different phase.

Although heterogeneous reactions are important, they are very complex and difficult to analyze. In this chapter, therefore, we'll focus mostly on homogeneous systems.

### Concentrations of the reactants

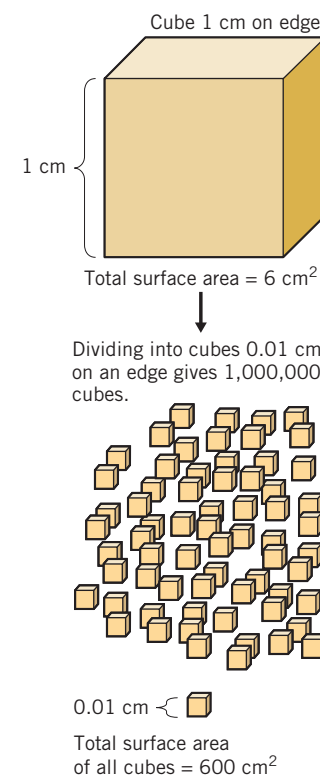
The rates of both homogeneous and heterogeneous reactions are affected by the concentrations of the reactants. For example, wood burns relatively quickly in air but extremely rapidly in pure oxygen. It has been estimated that if air were 30% oxygen instead of 20%, it would not be possible to put out forest fires. Even red hot steel wool, which only sputters and glows in air, bursts into flame when thrust into pure oxygen (see Figure 13.4).

### Temperature of the system

Almost all chemical reactions occur faster at higher temperatures than they do at lower temperatures. You may have noticed, for example, that insects move more slowly when the air is cool. An insect is a cold-blooded creature, which means that its body temperature is determined by the temperature of its surroundings. As the air cools, insects cool, and so the rates of their chemical metabolism slow down, making insects sluggish.

### Presence of catalysts

*Catalysts* are substances that increase the rates of chemical reactions without being used up. They affect every moment of our lives. Catalysts are used in the chemical industry to make



**FIG. 13.3** Effect of crushing a solid. When a single solid is subdivided into much smaller pieces, the total surface area on all of the pieces becomes very large.

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**FIG. 13.4** Effect of concentration on rate. Steel wool, after being heated to redness in a flame, burns spectacularly when dropped into pure oxygen. (OPC, Inc.)

gasoline, plastics, fertilizers, and other products that have become virtual necessities in our lives. In our bodies, substances called enzymes serve as catalysts for biochemical reactions. By making enzymes available or not, a cell is able to direct our body chemistry by controlling which chemical reactions can occur rapidly.

### 13.2 RATES OF REACTION ARE MEASURED BY MONITORING CHANGE IN CONCENTRATION OVER TIME

The qualitative factors we covered in the previous section can also be described quantitatively. To do this we need to express reaction rates in mathematical terms. Let's start with the concept of **rate**, which always implies a ratio in which a unit of time is in the denominator. Suppose, for example, that you have a job with a pay rate of ten dollars per hour. Because *per* can be translated as *divided by*, your rate of pay can be written as a fraction (abbreviating hour as hr).

$$\text{Rate of pay} = 10 \text{ dollars per hour} = \frac{10 \text{ dollars}}{1 \text{ hr}} = 10 \text{ dollars hr}^{-1}$$

where we've expressed 1/hr as  $\text{hr}^{-1}$ .

When chemical reactions occur, the concentrations of reactants decrease as they are used up, while the concentrations of the products increase as they form. So one way to describe a reaction's rate is to pick one substance in the reaction's equation and describe its change in concentration per unit of time. The result is the rate of the reaction *with respect to that substance*. Remembering that we always take "final minus initial," the rate of reaction with respect, say, to substance *X* is

$$\begin{aligned} \text{Rate with respect to } X &= \frac{(\text{conc. of } X \text{ at time } t_{\text{final}} - \text{conc. of } X \text{ at time } t_{\text{initial}})}{(t_{\text{final}} - t_{\text{initial}})} \\ &= \frac{\Delta(\text{conc. of } X)}{\Delta t} \end{aligned}$$

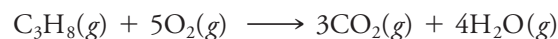
Molarity (mol/L) is normally the concentration unit, and the second (s) is the most often used unit of time. Therefore, the units for reaction rates are most frequently the following.

$$\frac{\text{mol/L}}{\text{s}}$$

Because 1/L and 1/s can also be written as  $\text{L}^{-1}$  and  $\text{s}^{-1}$ , the units for a reaction rate can be expressed as  $\text{mol L}^{-1} \text{s}^{-1}$ . For instance, if the concentration of one product of a reaction increases by 0.50 mol/L each second, the rate of its formation is  $0.50 \text{ mol L}^{-1} \text{s}^{-1}$ . Similarly, if the concentration of a reactant decreases by 0.20 mol/L per second, its rate of reaction is  $0.20 \text{ mol L}^{-1} \text{s}^{-1}$ . By convention, reaction rate is reported as a positive value whether something increases or decreases in concentration.

#### Relative rates of reaction depend on the coefficients in the equation

When we know the value of a reaction rate with respect to one substance, the coefficients of the reaction's balanced equation can be used to find the rates with respect to the other substances. For example, in the combustion of propane,



five moles of  $\text{O}_2$  *must* be consumed per unit of time for each mole of  $\text{C}_3\text{H}_8$  used in the same time. Therefore, in this reaction oxygen *must* react five times faster than propane in units of  $\text{mol L}^{-1} \text{s}^{-1}$ . Similarly,  $\text{CO}_2$  forms three times faster than  $\text{C}_3\text{H}_8$  reacts and  $\text{H}_2\text{O}$  four times faster. The magnitudes of the rates relative to each other are thus in the same relationship as the coefficients in the balanced equation.

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## EXAMPLE 13.1

## Relationships of Rates within a Reaction

Butane, the fuel in cigarette lighters, burns in oxygen to give carbon dioxide and water. If, in a certain experiment, the butane concentration is decreasing at a rate of  $0.20 \text{ mol L}^{-1} \text{ s}^{-1}$ , what is the rate at which the oxygen concentration is decreasing, and what are the rates at which the product concentrations are increasing?

**ANALYSIS:** As always we need a balanced chemical equation. Butane,  $\text{C}_4\text{H}_{10}$ , burns in oxygen to give  $\text{CO}_2$  and  $\text{H}_2\text{O}$  according to the equation



We now need to relate the rate in terms of oxygen and the products to the given rate in terms of butane. The chemical equation is the tool that links amounts of these substances to the amount of butane. The magnitudes of the rates relative to each other are in the same relationship as the coefficients in the balanced equation.

**SOLUTION:** For oxygen

$$\frac{0.20 \text{ mol } \cancel{\text{C}_4\text{H}_{10}}}{\text{L s}} \times \frac{13 \text{ mol O}_2}{2 \cancel{\text{ mol } \text{C}_4\text{H}_{10}}} = \frac{1.3 \text{ mol O}_2}{\text{L s}}$$

Oxygen is reacting at a rate of  $1.3 \text{ mol L}^{-1} \text{ s}^{-1}$ . For  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , we have similar calculations.

$$\frac{0.20 \text{ mol } \cancel{\text{C}_4\text{H}_{10}}}{\text{L s}} \times \frac{8 \text{ mol CO}_2}{2 \cancel{\text{ mol } \text{C}_4\text{H}_{10}}} = \frac{0.80 \text{ mol CO}_2}{\text{L s}}$$

$$\frac{0.20 \text{ mol } \cancel{\text{C}_4\text{H}_{10}}}{\text{L s}} \times \frac{10 \text{ mol H}_2\text{O}}{2 \cancel{\text{ mol } \text{C}_4\text{H}_{10}}} = \frac{1.0 \text{ mol H}_2\text{O}}{\text{L s}}$$

Therefore,

$$\text{Rate of formation of CO}_2 = 0.80 \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\text{Rate of formation of H}_2\text{O} = 1.0 \text{ mol L}^{-1} \text{ s}^{-1}$$

**ARE THE ANSWERS REASONABLE?** If what we've calculated is correct, then the ratio of the numerical values of the last two rates, namely 0.80 to 1.0, should check out to be the same as the ratio of the corresponding coefficients in the chemical equation, namely, 8 to 10 (the same as 0.8 to 1.0).

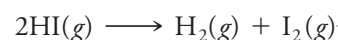
**Practice Exercise 1:** The iodate ion reacts with sulfite ions in the reaction



At what rate are the iodide and sulfate ions being produced if the sulfite ion is disappearing at a rate of  $2.4 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ ? (Hint: Recall the names of polyatomic ions.)

**Practice Exercise 2:** Hydrogen sulfide burns in oxygen to form sulfur dioxide and water. If sulfur dioxide is being formed at a rate of  $0.30 \text{ mol L}^{-1} \text{ s}^{-1}$ , what are the rates of disappearance of hydrogen sulfide and oxygen?

Because the rates of reaction of reactants and products are all related, it doesn't matter which species we pick to follow concentration changes over time. For example, to study the decomposition of hydrogen iodide, HI, into  $\text{H}_2$  and  $\text{I}_2$ ,



it is easiest to monitor the  $\text{I}_2$  concentration because it is the only colored substance in the reaction. As the reaction proceeds, purple iodine vapor forms, and there are instruments that

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**TABLE 13.1** Data, at 508 °C, for the Reaction  $2\text{HI}(g) \rightarrow \text{H}_2(g) + \text{I}_2(g)$ 

Concentration of HI (mol L <sup>-1</sup> )	Time (s)
0.100	0
0.0716	50
0.0558	100
0.0457	150
0.0387	200
0.0336	250
0.0296	300
0.0265	350

allow us to relate the intensity of the color to the iodine concentration. Then, once we know the rate of formation of iodine, we also know the rate of formation of hydrogen. It's the same because the coefficients of  $\text{H}_2$  and  $\text{I}_2$  are the same. And the rate of disappearance of HI, which has a coefficient of 2 in the equation, is twice as fast as the rate of formation of  $\text{I}_2$ .

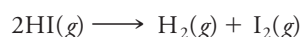
**Most reactions slow down as reactants are used up**

A reaction rate is generally not constant throughout the reaction but commonly changes as the reactants are used up. This is because the rate usually depends on the concentrations of the reactants, and these change as the reaction proceeds. For example, Table 13.1 contains data for the decomposition of hydrogen iodide at a temperature of 508 °C. The data, which show the changes in molar HI concentration over time, are plotted in Figure 13.5. Notice that the molar HI concentration drops fairly rapidly during the first 50 seconds of the reaction, which means that the initial rate is relatively fast. However, later, in the interval between 300 s and 350 s, the concentration changes by only a small amount, so the rate has slowed considerably. Thus, the steepness of the curve at any moment reflects the rate of the reaction; the steeper the curve, the higher is the rate.

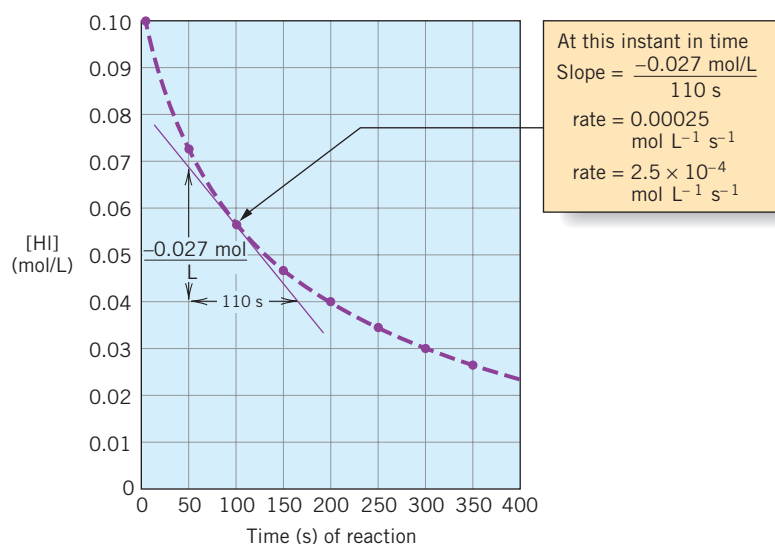
■ When we use the term “reaction rate” we mean the instantaneous rate, unless we state otherwise.

The rate at which the HI is being consumed at any particular moment is called the **instantaneous rate**. The instantaneous rate can be determined from the slope (or tangent) of the curve measured at the time we have chosen. The slope, which can be read off the graph, is the ratio (expressed positively) of the change in concentration to the change in time. In Figure 13.5, for example, the rate of the decomposition of hydrogen iodide is determined for a time 100 seconds from the start of the reaction. After the tangent to the

**FIG. 13.5** Effect of time on concentration. The data for this plot of the change in the concentration of HI with time for the reaction



at 508 °C are taken from Table 13.1. The slope is negative because we're measuring the *disappearance* of HI. But when its value is used as a rate of reaction, we express the rate as positive, as we do all rates of reaction.



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curve is drawn, we measure the concentration change (a decrease of 0.027 mol/L) and the time change (110 s) from the graph. Because the rate is based on a *decreasing* concentration, we use a minus sign for the *equation* that describes this rate so that the rate itself will be a positive quantity. We use square brackets to signify concentrations specifically in moles per liter; [HI] thus means the molar concentration of HI.

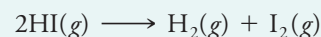
$$\text{Rate}_{(\text{with respect to HI})} = -\left(\frac{[\text{HI}]_{\text{final}} - [\text{HI}]_{\text{initial}}}{t_{\text{final}} - t_{\text{initial}}}\right) = -\left(\frac{-0.027 \text{ mol/L}}{110 \text{ s}}\right)$$

$$\text{Rate}_{(\text{with respect to HI})} = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

Thus, at this moment in the reaction, the rate with respect to HI is  $2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ . In the following example, we'll use this technique to obtain the *initial instantaneous rate* of the reaction, that is, the instantaneous rate of reaction at time zero.

**EXAMPLE 13.2**  
 Estimating the Initial Rate  
 of a Reaction

For the experimental data shown in Figure 13.5, what is the initial rate of the reaction



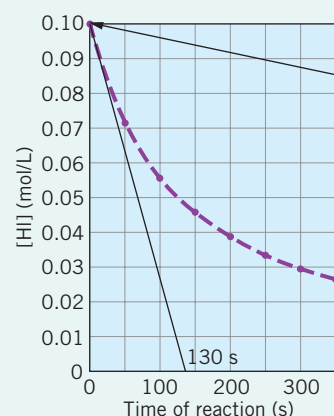
at 508 °C, with respect to HI?

**ANALYSIS:** The question asks about the initial rate, which is the instantaneous rate of the reaction at time zero. Using Figure 13.5, we can draw a tangent line to the curve showing HI concentration as a function of time at time zero. The instantaneous rate will be the slope of the tangent line. Remember that the slope of a straight line can be calculated from the coordinates of any two points ( $x_1, y_1$ ) and ( $x_2, y_2$ ) using the equation

$$\text{Slope} = \frac{y_2 - y_1}{x_2 - x_1}$$

**SOLUTION:** Remembering that a tangent line to a curve touches the curve at only one point, we can draw the line as shown in the graph below. To more precisely determine the slope of the tangent line, we should choose two points that are as far apart as possible. The point on the curve (0 s, 0.10 mol/L) and the intersection of the tangent line with the time axis (130 s, 0 mol/L) are widely separated:

$$\text{Slope} = \frac{0.10 \text{ mol/L} - 0.00 \text{ mol/L}}{0 \text{ s} - 130 \text{ s}} = -7.7 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$



At time zero, slope of the tangent line =  $-(0.10 \text{ mol/L}) / 130 \text{ s}$   
 rate =  $7.7 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

The slope is negative because the concentration of HI is decreasing as time increases. Rates are positive quantities, so we can report the initial rate of reaction as  $7.7 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ . Since the tangent line might be drawn a number of different ways, the time difference is uncertain by more than ten seconds and the rate can be reported simply as  $8 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ .

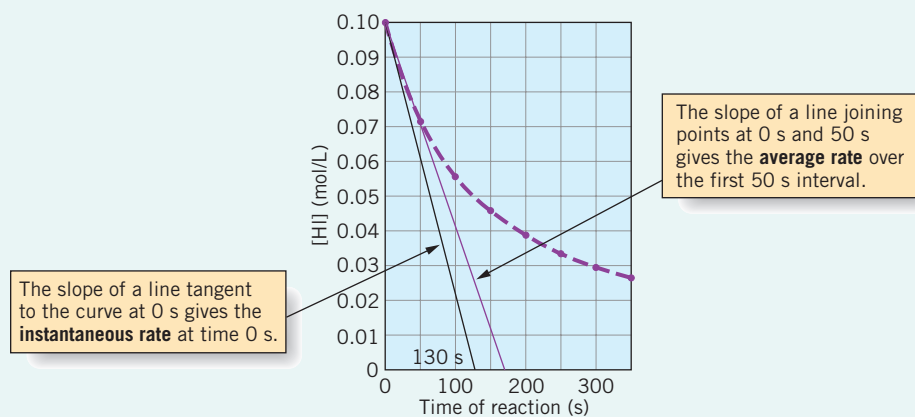
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■ The average rate is the slope of a line connecting two points on a concentration versus time graph. The instantaneous rate is the slope of a tangent line at a single point. The average and instantaneous rates are quite different from each other.

**IS THE ANSWER REASONABLE?** The instantaneous rate at time zero ought to be slightly larger than the *average rate* between zero and 50 seconds. We can compute the average rate directly from data in Table 13.1 by selecting a pair of concentrations at two different times.

$$\text{Slope} = \frac{0.0716 \text{ mol/L} - 0.100 \text{ mol/L}}{50 \text{ s} - 0 \text{ s}} = -5.7 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

Thus, the average rate from 0 to 50 s is  $5.7 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ . As expected, this is slightly less than the instantaneous rate at time zero,  $8 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ .



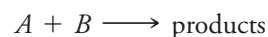
**Practice Exercise 3:** Use the graph in Figure 13.5 to estimate the rate of reaction with respect to HI 2.00 minutes after the start of the reaction. (Hint: You need to have time in seconds units to find the point where the tangent should be drawn.)

**Practice Exercise 4:** Use the graph in Figure 13.5 to estimate the rate of reaction with respect to HI 250 seconds after the start of the reaction.

### 13.3 RATE LAWS GIVE REACTION RATE AS A FUNCTION OF REACTANT CONCENTRATIONS

Thus far we have focused on a rate with respect to *one* component of a reaction. We'll now broaden our focus to consider a rate expression that includes all reactants.

The rate of a homogeneous reaction at any instant is proportional to the product of the molar concentrations of the reactants, each molarity raised to some power or exponent that has to be found by experiment. Let's consider a chemical reaction with an equation of the following form.



Its rate of reaction can be expressed as follows.

$$\text{Rate} \propto [A]^m[B]^n \quad (13.1)$$

As we said, the values of the exponents  $n$  and  $m$  are found by experiment, which we'll go into shortly.

#### Rate laws relate reaction rates and concentrations

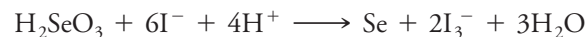
The proportionality symbol,  $\propto$ , in Equation 13.1 can be replaced by an equals sign if we introduce a proportionality constant,  $k$ , which is called the **rate constant** for the reaction. This gives Equation 13.2.

$$\text{Rate} = k[A]^m[B]^n \quad (13.2)$$

**TOOLS**  
Rate law of a reaction

## 13.3 Rate Laws Give Reaction Rate as a Function of Reactant Concentrations 527

Equation 13.2 is called the **rate law** for the reaction of  $A$  with  $B$ . Once we have found values for  $k$ ,  $n$ , and  $m$ , the rate law allows us to calculate the rate of the reaction at any set of known values of concentrations. Consider, for example, the following reaction.



Its rate law is of the form

$$\text{Rate} = k[\text{H}_2\text{SeO}_3]^x[\text{I}^-]^y[\text{H}^+]^z$$

The exponents have been found experimentally to be the following for the initial rate of this reaction (i.e., the rate when the reactants are first combined).

$$x = 1, y = 3, \text{ and } z = 2$$

At 0 °C,  $k$  equals  $5.0 \times 10^5 \text{ L}^5 \text{ mol}^{-5} \text{ s}^{-1}$ . (We have to specify the temperature because  $k$  varies with it.) Substituting the exponents and the value of  $k$  into the rate law equation gives the rate law for the reaction.

$$\text{Rate} = (5.0 \times 10^5 \text{ L}^5 \text{ mol}^{-5} \text{ s}^{-1})[\text{H}_2\text{SeO}_3][\text{I}^-]^3[\text{H}^+]^2 \quad (\text{at } 0 \text{ }^\circ\text{C})$$

We can calculate the rate of the reaction at 0 °C for any set of concentrations of  $\text{H}_2\text{SeO}_3$ ,  $\text{I}^-$ , and  $\text{H}^+$  using this rate law.

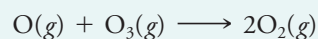
■ The value of  $k$  depends on the particular reaction being studied as well as the temperature at which the reaction occurs.

■ The units of the rate constant are such that the calculated rate will have the units  $\text{mol L}^{-1} \text{ s}^{-1}$ .

### EXAMPLE 13.3

Calculating Reaction Rate from the Rate Law

In the stratosphere, molecular oxygen ( $\text{O}_2$ ) can be broken into two oxygen atoms by ultraviolet radiation from the sun. When one of these oxygen atoms strikes an ozone ( $\text{O}_3$ ) molecule in the stratosphere, the ozone molecule is destroyed, and two oxygen molecules are created:



This reaction is part of the natural cycle of ozone destruction and creation in the stratosphere. What is the rate of ozone destruction *for this reaction alone* at an altitude of 25 km, if the rate law for the reaction is

$$\text{Rate} = 4.15 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}[\text{O}_3][\text{O}]$$

and the reactant concentrations at 25 km are the following:  $[\text{O}_3] = 1.2 \times 10^{-8} \text{ M}$  and  $[\text{O}] = 1.7 \times 10^{-14} \text{ M}$ ?

**ANALYSIS:** The tool we use for calculating the rate is the rate law. Because we already know the rate law, the answer to this question is merely a matter of substituting the given molar concentrations into this law.

**SOLUTION:** To see how the units work out, let's write all of the concentration values as well as the rate constant's units in fraction form.

$$\text{Rate} = \frac{4.15 \times 10^5 \cancel{\text{L}}}{\cancel{\text{mol}} \text{ s}} \times \left( \frac{1.2 \times 10^{-8} \cancel{\text{mol}}}{\cancel{\text{L}}} \right) \times \left( \frac{1.7 \times 10^{-14} \text{ mol}}{\text{L}} \right)$$

Performing the arithmetic and canceling the units, we see that

$$\text{Rate} = \frac{8.5 \times 10^{-17} \text{ mol}}{\text{L s}} = 8.5 \times 10^{-17} \text{ mol L}^{-1} \text{ s}^{-1}$$

**IS THE ANSWER REASONABLE?** There's obviously no simple check. Multiplying the powers of ten for the rate constant and the concentrations together reassures us that the rate is of the correct order of magnitude, and we can see that at least the answer has the correct units for a reaction rate.

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**Practice Exercise 5:** The rate law for the reaction  $2\text{NO}(g) + 2\text{H}_2(g) \longrightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(g)$  is

$$\text{Rate} = k[\text{NO}]^2[\text{H}_2]$$

If the rate of reaction is  $7.86 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$  when the concentrations of NO and  $\text{H}_2$  are both  $2 \times 10^{-6} \text{ mol L}^{-1}$  (a) what is the value of the rate constant and (b) what are the units for the rate constant? (Hint: Note the units of the reaction rate.)

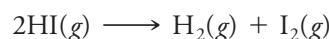
**Practice Exercise 6:** The rate law for the decomposition of HI to  $\text{I}_2$  and  $\text{H}_2$  is

$$\text{Rate} = k[\text{HI}]^2$$

Figure 13.5 shows that at  $508^\circ\text{C}$ , the rate of the reaction of HI was found to be  $2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$  when the HI concentration was  $0.0558 \text{ M}$  (see Figure 13.5). (a) What is the value of  $k$ ? (b) What are the units of  $k$ ?

### You cannot predict the rate law for a reaction from the overall balanced equation for the reaction

Although a rate law's exponents are generally unrelated to the chemical equation's coefficients, they sometimes are the same by coincidence, as is the case in the decomposition of hydrogen iodide.

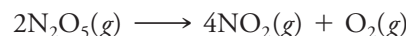


The rate law, as we've said, is

$$\text{Rate} = k[\text{HI}]^2$$

The exponent of [HI] in the rate law, namely 2, happens to match the coefficient of HI in the overall chemical equation, but *there is no way we could have predicted this match without experimental data*. Therefore, *never* simply assume the exponents and the coefficients are the same; it's a trap that many students fall into.

An exponent in a rate law is called the **order of the reaction**<sup>1</sup> with respect to the corresponding reactant. For instance, the decomposition of gaseous  $\text{N}_2\text{O}_5$  into  $\text{NO}_2$  and  $\text{O}_2$ ,



has the rate law

$$\text{Rate} = k[\text{N}_2\text{O}_5]$$

The exponent of  $[\text{N}_2\text{O}_5]$  is 1, so the reaction rate is said to be *first order* in  $\text{N}_2\text{O}_5$ . The rate law for the decomposition of HI has an exponent of 2 for the HI concentration, so its reaction rate is *second order* in HI. The rate law

$$\text{Rate} = k[\text{H}_2\text{SeO}_3][\text{I}^-]^3[\text{H}^+]^2$$

describes a reaction rate that is first order with respect to  $\text{H}_2\text{SeO}_3$ , third order with respect to  $\text{I}^-$ , and second order with respect to  $\text{H}^+$ .

The **overall order of reaction** is the sum of the orders with respect to each reactant in the rate law. The decomposition of  $\text{N}_2\text{O}_5$  is a **first-order reaction**, and the decomposition of HI is a **second-order reaction**. The overall order for the reaction with  $\text{H}_2\text{SeO}_3$  above is  $1 + 3 + 2 = 6$ .

The exponents in a rate law are usually small whole numbers, but fractional and negative exponents are occasionally found. A negative exponent means that the concentration term really belongs in the denominator, which means that as the concentration of the species increases, the rate of reaction decreases.

<sup>1</sup>The reason for describing the *order* of a reaction is to take advantage of a great convenience; namely, the mathematics involved in the treatment of the data is the same for all reactions having the same order. We will not go into this very deeply, but you should be familiar with this terminology; it's often used to describe the effects of concentration on reaction rates.

■ When the exponent on a concentration term is equal to 1, it is usually omitted.

### 13.3 Rate Laws Give Reaction Rate as a Function of Reactant Concentrations 529

There are even **zero-order reactions**. They have reaction rates that are independent of the concentration of any reactant. Zero-order reactions usually involve a small amount of a catalyst that is saturated with reactants. This is rather like the situation in a crowded supermarket with only a single checkout lane open. It doesn't matter how many people join the line; the line will move at the same rate no matter how many people are standing in it. An example of a zero-order reaction is the elimination of ethyl alcohol in the liver. Regardless of the blood alcohol level, the rate of alcohol removal by the body is constant, because the number of available catalyst molecules present in the liver is constant. Another zero-order reaction is the decomposition of gaseous ammonia into  $\text{H}_2$  and  $\text{N}_2$  on a hot platinum surface. The rate at which ammonia decomposes is the same, regardless of its concentration in the gas. The rate law for a zero-order reaction is simply

$$\text{Rate} = k$$

where the rate constant  $k$  has units of  $\text{mol L}^{-1} \text{s}^{-1}$ . The rate constant depends on the amount, quality, and available surface area of the catalyst. For example, forcing ammonia through hot platinum powder (with a high surface area) would cause it to decompose faster than simply passing it over a hot platinum surface.

**Practice Exercise 7:** The following reaction



has the rate law

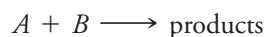
$$\text{Rate} = k[\text{BrO}_3^-][\text{SO}_3^{2-}]$$

What is the order of the reaction with respect to each reactant? What is the overall order of the reaction? (Hint: Recall that a concentration with no exponent has, in effect, an exponent of 1.)

**Practice Exercise 8:** A certain reaction has an experimental rate law that is found to be second order in  $\text{Cl}_2$  and first order in  $\text{NO}$ . Write the rate law for this reaction.

#### The order of a reaction must be determined experimentally

We've mentioned several times that the exponents in the rate law of an overall reaction must be determined experimentally. *This is the only way to know for sure what the exponents are.* To determine the exponents, we study how changes in concentration affect the rate of the reaction. For example, consider again the following hypothetical reaction.



Suppose, further, that the data in Table 13.2 have been obtained in a series of five experiments. We know the form of the rate law for the reaction will be

$$\text{Rate} = k[A]^m[B]^n$$

**TABLE 13.2** Concentration–Rate Data for the Hypothetical Reaction  $A + B \rightarrow \text{products}$

Experiment	Initial Concentrations		Initial Rate of Formation of Products ( $\text{mol L}^{-1} \text{s}^{-1}$ )
	[A] ( $\text{mol L}^{-1}$ )	[B] ( $\text{mol L}^{-1}$ )	
1	0.10	0.10	0.20
2	0.20	0.10	0.40
3	0.30	0.10	0.60
4	0.30	0.20	2.40
5	0.30	0.30	5.40

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The values of  $m$  and  $n$  can be discovered by looking for patterns in the rate data given in the table. *One of the easiest ways to reveal patterns in data is to form ratios of results using different sets of conditions.* Because this technique is quite generally useful, let's look in some detail at how it is applied to the problem of finding the rate law exponents.

For experiments 1, 2, and 3 in Table 13.2, the concentration of  $B$  has been held constant at  $0.10\text{ M}$ . Any change in the rate for these first three experiments must be due to the change in  $[A]$ . The rate law tells us that when the concentration of  $B$  is held constant, the rate must be proportional to  $[A]^m$ , so if we take the ratio of rate laws for experiments 2 and 1, we obtain

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k[A]_2^m [B]_2^n}{k[A]_1^m [B]_1^n} = \frac{k}{k} \left( \frac{[A]_2}{[A]_1} \right)^m \left( \frac{[B]_2}{[B]_1} \right)^n$$

For experiments 1 and 2, the left side of this equation is

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{0.40 \text{ mol L}^{-1} \text{ s}^{-1}}{0.20 \text{ mol L}^{-1} \text{ s}^{-1}} = 2.0$$

and on the right side of the equation the identical concentrations of  $B$  and the rate constant  $k$  cancel to give

$$\left( \frac{[A]_2}{[A]_1} \right)^m = \left( \frac{0.20 \text{ mol L}^{-1}}{0.10 \text{ mol L}^{-1}} \right)^m = 2.0^m$$

so doubling  $[A]$  in going from experiment 1 to experiment 2 doubles the rate, and the relationship reduces to  $2.0 = 2.0^m$ . For each unique combination of experiments 1, 2, and 3, we have

$$2.0 = 2.0^m \quad (\text{for experiments 2 and 1})$$

$$3.0 = 3.0^m \quad (\text{for experiments 3 and 1})$$

$$1.5 = 1.5^m \quad (\text{for experiments 3 and 2})$$

The only value of  $m$  that makes all of these equations true is  $m = 1$ . Therefore, this reaction must be first order with respect to  $A$ .

A similar method will give us the exponent on  $[B]$ . In the final three experiments, the concentration of  $B$  changes while the concentration of  $A$  is held constant. This time it is the concentration of  $B$  that affects the rate. Taking the ratio of rate laws for experiments 4 and 3, we have

$$\frac{\text{Rate}_4}{\text{Rate}_3} = \frac{k[A]_4^m [B]_4^n}{k[A]_3^m [B]_3^n}$$

that, after cancelling the identical concentrations of  $A$  and the rate constant,  $k$ , becomes

$$\frac{\text{Rate}_4}{\text{Rate}_3} = \left( \frac{[B]_4}{[B]_3} \right)^n$$

For each unique combination of experiments 3, 4, and 5, we have

$$4.0 = 2.0^n \quad (\text{for experiments 4 and 3})$$

$$9.0 = 3.0^n \quad (\text{for experiments 5 and 3})$$

$$2.25 = 1.5^n \quad (\text{for experiments 5 and 4})$$

The only value of  $n$  that makes all of these equations true is  $n = 2$ , so the reaction must be second order with respect to  $B$ .

Having determined the exponents for the concentration terms, we now know that the rate law for the reaction must be

$$\text{Rate} = k[A]^1[B]^2$$

To calculate the value of  $k$ , we substitute rate and concentration data into the rate law for any one of the sets of data.

## 13.3 Rate Laws Give Reaction Rate as a Function of Reactant Concentrations 531

**TABLE 13.3** Relationship between the Order of a Reaction and Changes in Concentration and Rate

Factor by Which the Concentration Is Changed	Factor by Which the Rate Changes	Exponent on the Concentration Term in the Rate Law
2	Rate	0
3	is	0
4	unchanged	0
2	$2 = 2^1$	1
3	$3 = 3^1$	1
4	$4 = 4^1$	1
2	$4 = 2^2$	2
3	$9 = 3^2$	2
4	$16 = 4^2$	2
2	$8 = 2^3$	3
3	$27 = 3^3$	3
4	$64 = 4^3$	3

$$k = \frac{\text{rate}}{[A]^1[B]^2}$$

Using the data from the first set in Table 13.2,

$$\begin{aligned} k &= \frac{0.20 \text{ mol L}^{-1} \text{ s}^{-1}}{(0.10 \text{ mol L}^{-1})(0.10 \text{ mol L}^{-1})^2} \\ &= \frac{0.20 \text{ mol L}^{-1} \text{ s}^{-1}}{0.0010 \text{ mol}^3 \text{ L}^{-3}} \end{aligned}$$

After canceling such units as we can, the value of  $k$  with the net units is

$$k = 2.0 \times 10^2 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$$

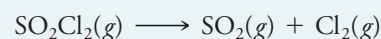
**Practice Exercise 9:** Use the data from the other four experiments (Table 13.2) to calculate  $k$  for this reaction. What do you notice about the values of  $k$ ? (Hint: Don't forget the exponents in the rate law.)

**Practice Exercise 10:** Use the rate law determined above to describe what will happen to the reaction rate under the following conditions: (a) the concentration of  $B$  is tripled, (b) the concentration of  $A$  is tripled, (c) the concentration of  $A$  is tripled and the concentration of  $B$  is halved.

Table 13.3 summarizes the reasoning used to determine the order with respect to each reactant from experimental data.

**EXAMPLE 13.4**  
Determining the Exponents of a Rate Law

Sulfuryl chloride,  $\text{SO}_2\text{Cl}_2$ , is used to manufacture the antiseptic chlorophenol. The following data were collected on the decomposition of  $\text{SO}_2\text{Cl}_2$  at a certain temperature.



Initial Concentration of $\text{SO}_2\text{Cl}_2$ ( $\text{mol L}^{-1}$ )	Initial Rate of Formation of $\text{SO}_2$ ( $\text{mol L}^{-1} \text{ s}^{-1}$ )
0.100	$2.2 \times 10^{-6}$
0.200	$4.4 \times 10^{-6}$
0.300	$6.6 \times 10^{-6}$

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What are the rate law and the value of the rate constant for this reaction?

**ANALYSIS:** The first step is to write the general form of the expected rate law so we can see which exponents have to be determined. Then we study the data to see how the rate changes when the concentration is changed by a certain factor.

**SOLUTION:** We expect the rate law to have the form

$$\text{Rate} = k[\text{SO}_2\text{Cl}_2]^x$$

Let's examine the data from the first two experiments. Notice that when we double the concentration from 0.100 M to 0.200 M, the initial rate doubles (from  $2.2 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}$  to  $4.4 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}$ ). If we look at the first and third, we see that when the concentration triples (from 0.100 M to 0.300 M), the rate also triples (from  $2.2 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}$  to  $6.6 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}$ ). This behavior tells us that the reaction must be first order in the  $\text{SO}_2\text{Cl}_2$  concentration. The rate law is therefore

$$\text{Rate} = k[\text{SO}_2\text{Cl}_2]^1$$

To evaluate  $k$ , we can use any of the three sets of data. Choosing the first,

$$\begin{aligned} k &= \frac{\text{rate}}{[\text{SO}_2\text{Cl}_2]^1} \\ &= \frac{2.2 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}}{0.100 \text{ mol L}^{-1}} \\ &= 2.2 \times 10^{-5} \text{ s}^{-1} \end{aligned}$$

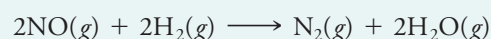
**IS THE ANSWER REASONABLE?** We should get the same value of  $k$  by picking any other pair of values. With the last pair of data, at an initial molar concentration of  $\text{SO}_2\text{Cl}_2$  of  $0.300 \text{ mol L}^{-1}$  and an initial rate of  $6.6 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}$ , we calculate  $k$  again to be  $2.2 \times 10^{-5} \text{ s}^{-1}$ .

■ We could also use experiments 2 and 3. From the second to the third, the rate increases by the same factor, 1.5, as the concentration, so by these data, too, the reaction must be first order.

### EXAMPLE 13.5

Determining the Exponents of a Rate Law

The following data were measured for the reduction of nitric oxide with hydrogen.



Initial Concentrations (mol L <sup>-1</sup> )		Initial Rate of Formation of H <sub>2</sub> O (mol L <sup>-1</sup> s <sup>-1</sup> )
[NO]	[H <sub>2</sub> ]	
0.10	0.10	$1.23 \times 10^{-3}$
0.10	0.20	$2.46 \times 10^{-3}$
0.20	0.10	$4.92 \times 10^{-3}$

What is the rate law for the reaction?

**ANALYSIS:** This time we have two reactants. To see how their concentrations affect the rate we must vary only one concentration at a time. Therefore, we choose two experiments in which the concentration of one reactant doesn't change and examine the effect of a change in the concentration of the other reactant. Then we repeat the procedure for the second reactant.

**SOLUTION:** We expect the rate law to have the form

$$\text{Rate} = k[\text{NO}]^m[\text{H}_2]^n$$

## 13.3 Rate Laws Give Reaction Rate as a Function of Reactant Concentrations 533

Let's look at the first two experiments. Here the concentration of NO remains the same, so the rate is being affected by the change in the H<sub>2</sub> concentration. When we double the H<sub>2</sub> concentration, the rate doubles, so the reaction is first order with respect to H<sub>2</sub>. This means  $n = 1$ .

Next, we need to pick two experiments in which the H<sub>2</sub> concentration doesn't change. Working with the first and third, we see that [NO] doubles and the rate increases by a factor of  $4.92/1.23 = 4.00$ . When doubling the concentration of a species quadruples the rate, the reaction is second order in that species, so  $m = 2$ .

Therefore, the rate law for the reaction is

$$\text{Rate} = k[\text{NO}]^2[\text{H}_2]$$

**IS THE ANSWER REASONABLE?** The only data that we haven't used as a pair are the data for the second and third reactions. The value of [NO] increases by 2 in going from the second to the third set of data, so this should multiply the rate by 2<sup>2</sup> or 4, if we've found the right exponents. But the value for [H<sub>2</sub>] halves at the same time, so this should take a rate that is otherwise four times as large and cut it by a factor of (1/2)<sup>1</sup> or in half. The net effect, then, is to make the rate of the third reaction two times as large as that of the second reaction, which is the observed rate change.

**Practice Exercise 11:** The following reaction is investigated to determine its rate law.

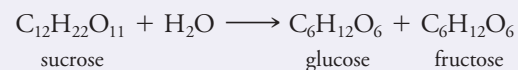


Experiments yielded the following results.

Initial Concentrations (mol L <sup>-1</sup> )		Initial Rate of Formation of N <sub>2</sub> (mol L <sup>-1</sup> s <sup>-1</sup> )
[NO]	[H <sub>2</sub> ]	
$0.40 \times 10^{-4}$	$0.30 \times 10^{-4}$	$1.0 \times 10^{-8}$
$0.80 \times 10^{-4}$	$0.30 \times 10^{-4}$	$4.0 \times 10^{-8}$
$0.80 \times 10^{-4}$	$0.60 \times 10^{-4}$	$8.0 \times 10^{-8}$

(a) Show that these data yield the same rate law as in the preceding Example. (b) What is the value of the rate constant? (c) What are the units for the rate constant? (Hint: Identify the two experiments where only the [NO] changes and the two experiments where only the [H<sub>2</sub>] varies.)

**Practice Exercise 12:** Ordinary sucrose (table sugar) reacts with water in an acidic solution to produce two simpler sugars, glucose and fructose, that have the same molecular formulas.



In a series of experiments, the following data were obtained.

Initial Sucrose Concentration (mol L <sup>-1</sup> )	Rate of Formation of Glucose (mol L <sup>-1</sup> s <sup>-1</sup> )
0.10	$6.17 \times 10^{-5}$
0.20	$1.23 \times 10^{-4}$
0.50	$3.09 \times 10^{-4}$

(a) What is the order of the reaction with respect to sucrose? (b) What is the value of the rate constant, with its units?

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**Practice Exercise 13:** A certain reaction has the following equation:  $A + B \longrightarrow C + D$ . Experiments yielded the following results.

Initial Concentrations (mol L <sup>-1</sup> )		Initial Rate of Formation of C (mol L <sup>-1</sup> s <sup>-1</sup> )
[A]	[B]	
0.40	0.30	$1.00 \times 10^{-4}$
0.60	0.30	$2.25 \times 10^{-4}$
0.80	0.60	$1.60 \times 10^{-3}$

(a) What is the rate law for the reaction? (b) What is the value of the rate constant? (c) What are the units for the rate constant? (d) What is the overall order of this reaction?

### 13.4 INTEGRATED RATE LAWS GIVE CONCENTRATION AS A FUNCTION OF TIME

The rate law tells us how the speed of a reaction varies with the concentrations of the reactants. Often, however, we are more interested in how the concentrations change over time. For instance, if we were preparing some compound, we might want to know how long it will take for the reactant concentrations to drop to some particular value, so we can decide when to isolate the products.

The relationship between the concentration of a reactant and time can be derived from a rate law using calculus. By summing or “integrating” the instantaneous rates of a reaction from the start of the reaction until some specified time  $t$ , we can obtain **integrated rate laws** that quantitatively give concentration as a function of time. The form of the integrated rate law depends on the order of the reaction. The mathematical expressions that relate concentration and time in complex reactions can be complicated, so we will concentrate on using integrated rate laws for a few simple first- and second-order reactions.

#### The natural logarithm of concentration is related linearly with time for first-order reactions

A reaction that is first order has a rate law of the type

$$\text{Rate} = k[A]$$

Using calculus<sup>2</sup> the following equation can be derived that relates the concentration of  $A$  and time.

$$\ln \frac{[A]_0}{[A]_t} = kt \quad (13.3)$$

**TOOLS**  
Integrated rate law, first-order reaction

<sup>2</sup> For a first-order reaction, the integrated rate law is obtained by calculus as follows. The instantaneous rate of change of the reactant  $A$  is given as

$$\text{Rate} = \frac{-d[A]}{dt} = k[A]$$

This can be rearranged to

$$\frac{d[A]}{[A]} = -k dt$$

Next, we integrate between  $t = 0$  and  $t = t$  as the concentration of  $A$  changes from  $[A]_0$  to  $[A]_t$ .

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = \int_0^t -k dt$$

$$\ln[A]_t - \ln[A]_0 = -kt$$

Using the properties of logarithms, this can be rearranged to give

$$\ln \frac{[A]_0}{[A]_t} = kt$$

## 13.4 Integrated Rate Laws Give Concentration as a Function of Time 535

The symbol “ln” means natural logarithm. The expression to the left of the equals sign is the natural logarithm of the ratio of  $[A]_0$  (the initial concentration of  $A$  at  $t = 0$ ) to  $[A]_t$  (the concentration of  $A$  at a time  $t$  after the start of the reaction). We take advantage of a property of logarithms that allows us to write the ratio as a difference in logarithms.

$$\ln[A]_0 - \ln[A]_t = kt$$

We can take the antilogarithm of both sides of Equation 13.3 and rearrange it to obtain the concentration at time  $t$  directly as a function of time. Taking the antilogarithm and rearranging algebraically gives<sup>3</sup>

$$[A]_t = [A]_0 e^{-kt} \quad (13.4)$$

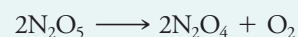
where  $e$  is the base of the system of natural logarithms ( $e = 2.718 \dots$ ). Equation 13.4 shows that the concentration of  $A$  decays (decreases) exponentially with time. Calculations can use Equation 13.3 or 13.4. When both of the concentrations are known, it is easiest to use Equation 13.3; when we wish to calculate either  $[A]_0$  or  $[A]_t$ , it may be easier to use Equation 13.4.

□  $[A]_t$  decreases exponentially because the product  $kt$  increases with time, but its negative value becomes more negative with time. As the exponent of  $e$  becomes a larger negative number the value of the expression becomes smaller.

### EXAMPLE 13.6

Concentration–Time Calculations for First-Order Reactions

Dinitrogen pentoxide is not very stable. In the gas phase or dissolved in a nonaqueous solvent, like carbon tetrachloride, it decomposes by a first-order reaction into dinitrogen tetroxide and molecular oxygen.



The rate law is

$$\text{Rate} = k[\text{N}_2\text{O}_5]$$

At 45 °C, the rate constant for the reaction in carbon tetrachloride is  $6.22 \times 10^{-4} \text{ s}^{-1}$ . If the initial concentration of  $\text{N}_2\text{O}_5$  in a carbon tetrachloride solution at 45 °C is 0.500  $M$ , what will its concentration be after exactly one hour?

**ANALYSIS:** We’re dealing with a first-order reaction and the relationship between concentration and time, so the tool we have to apply is either Equation 13.3 or 13.4. Specifically, we have to solve for an unknown concentration. The easiest form of the equation to use when one of the unknowns is a concentration term is Equation 13.4. In performing the calculation, we have to remember that the unit of  $k$  involves seconds, not hours, so we must convert the given 1 hr into seconds (1 hr = 3600 s).

**SOLUTION:** Let’s begin by listing the data.

$$\begin{aligned} [\text{N}_2\text{O}_5]_0 &= 0.500 \text{ M} & [\text{N}_2\text{O}_5]_t &= ? \text{ M} \\ k &= 6.22 \times 10^{-4} \text{ s}^{-1} & t &= 3600 \text{ s} \end{aligned}$$

Using Equation 13.4,<sup>4</sup>

$$\begin{aligned} [\text{N}_2\text{O}_5]_t &= [\text{N}_2\text{O}_5]_0 e^{-kt} \\ &= (0.500 \text{ M}) \times e^{-(6.22 \times 10^{-4} \text{ s}^{-1}) \times 3600 \text{ s}} \\ &= (0.500 \text{ M}) \times e^{-2.24} \\ &= (0.500 \text{ M}) \times 0.11 \\ &= 0.055 \text{ M} \end{aligned}$$

□ Calculating  $e^{-2.24}$  is a simple operation using a scientific calculator. In most cases it is the inverse of the ln function.

<sup>3</sup> Because of the nature of logarithms, if  $\ln x = y$ , then  $e^{\ln x} = e^y$ . But  $e^{\ln x} = x$ , so  $x = e^y$ . A similar relationship exists for common (base 10) logarithms. If  $\log x = y$ , then  $10^{\log x} = x = 10^y$ .

<sup>4</sup> There are special rules for significant figures for logarithms and antilogarithms. In writing the logarithm of a quantity, the number of digits written *after the decimal point* equals the number of significant figures in the quantity. Raising  $e$  to the  $-2.24$  power is the same as taking the antilogarithm of  $-2.24$ . Because the quantity  $-2.24$  has two digits after the decimal, the antilogarithm, 0.1064 . . . , must be rounded to 0.11 to show just two significant figures.

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After one hour, the concentration of  $\text{N}_2\text{O}_5$  will have dropped to  $0.055\text{ M}$ .

The calculation could also have been done using Equation 13.3. We would begin by solving for the concentration ratio, substituting values for  $k$  and  $t$ .

$$\ln\left(\frac{[\text{N}_2\text{O}_5]_0}{[\text{N}_2\text{O}_5]_t}\right) = (6.22 \times 10^{-4} \text{ s}^{-1}) \times 3600 \text{ s}$$

To take the antilogarithm (antiln), we raise  $e$  to the 2.24 power.

$$\begin{aligned} \text{antiln}\left[\ln\left(\frac{[\text{N}_2\text{O}_5]_0}{[\text{N}_2\text{O}_5]_t}\right)\right] &= \frac{[\text{N}_2\text{O}_5]_0}{[\text{N}_2\text{O}_5]_t} \\ \text{antiln}(2.24) &= e^{2.24} \\ &= 9.4 \text{ (rounding to 2 significant figures)} \end{aligned}$$

This means that

$$\frac{[\text{N}_2\text{O}_5]_0}{[\text{N}_2\text{O}_5]_t} = 9.4$$

Now we can substitute the known concentration,  $[\text{N}_2\text{O}_5]_0 = 0.500\text{ M}$ . This gives

$$\frac{0.500\text{ M}}{[\text{N}_2\text{O}_5]_t} = 9.4$$

Solving for  $[\text{N}_2\text{O}_5]_t$  gives

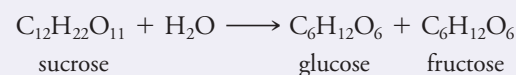
$$\begin{aligned} [\text{N}_2\text{O}_5]_t &= \frac{0.500\text{ M}}{9.4} \\ &= 0.053\text{ M} \end{aligned}$$

The answers obtained by the two methods differ slightly because of “rounding errors.” You can see that using Equation 13.4 is much easier for working this particular problem.

**IS THE ANSWER REASONABLE?** Notice that the final concentration of  $\text{N}_2\text{O}_5$  is *less* than its initial concentration. You’d know that you made a huge mistake if the calculated final concentration was larger than the initial  $0.500\text{ M}$  because reactants are used up by reactions. Also, we obtained essentially the same answer using both equations, so we can be confident it’s correct. (If you’re faced with a problem like this, you don’t have to do it both ways; we just wanted to show that either equation could be used.)

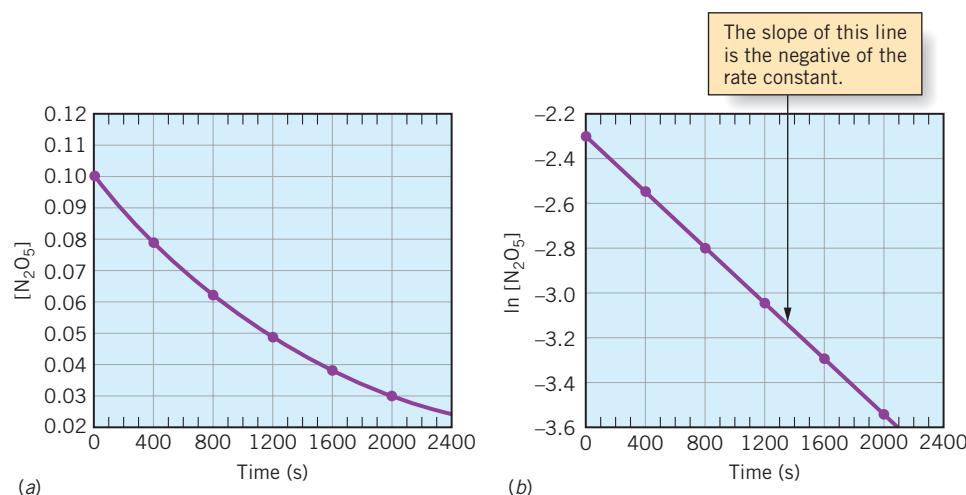
**Practice Exercise 14:** When designing a consumer product it is desirable that it have a two year shelf life. Often this means that the active ingredient in the product should not decrease by more than 5% in two years. If the reaction is first order, what rate constant must the decomposition reaction of the active ingredient have? (Hint: What are the initial and final percentages of active ingredient?)

**Practice Exercise 15:** In Practice Exercise 12, the reaction of sucrose with water in an acidic solution was described.



The reaction is first order with a rate constant of  $6.2 \times 10^{-5} \text{ s}^{-1}$  at  $35^\circ\text{C}$ , when the  $\text{H}^+$  concentration is  $0.10\text{ M}$ . Suppose, in an experiment, the initial sucrose concentration was  $0.40\text{ M}$ . (a) What will its concentration be after exactly 2 hours? (b) How many minutes will it take for the concentration of sucrose to drop to  $0.30\text{ M}$ ?

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**FIG. 13.6** The decomposition of  $\text{N}_2\text{O}_5$ . (a) A graph of concentration versus time for the decomposition at  $45^\circ\text{C}$ . (b) A straight line is obtained if the logarithm of the concentration is plotted versus time. The slope of this line equals the negative of the rate constant for the reaction.

### The rate constant can be determined graphically

Using the properties of logarithms,<sup>5</sup> Equation 13.3 can be rewritten in a form that corresponds to the equation for a straight line.

$$\begin{array}{c} \ln[A]_t = -kt + \ln[A]_0 \\ \downarrow \quad \quad \downarrow \quad \downarrow \\ y = mx + b \end{array}$$

A plot of the values of  $\ln[A]_t$  (vertical axis) versus values of  $t$  (horizontal axis) should give a straight line that has a slope equal to  $-k$ . Such a plot is illustrated in Figure 13.6 for the decomposition of  $\text{N}_2\text{O}_5$  into  $\text{N}_2\text{O}_4$  and  $\text{O}_2$  in the solvent carbon tetrachloride.

### The half-life of a reactant is a measure of its speed of reaction

The *half-life* of a reactant is a convenient way to describe how fast it reacts, particularly for a first-order process. A reactant's **half-life**,  $t_{1/2}$ , is the amount of time required for half of the reactant to disappear. A rapid reaction has a short half-life because half of the reactant disappears quickly. The equations for half-lives depend on the order of the reaction.

When a reaction, overall, is first order, the half-life of the reactant can be obtained from Equation 13.3 by setting  $[A]_t$  equal to one-half of  $[A]_0$ .

$$[A]_t = \frac{1}{2}[A]_0$$

Substituting  $\frac{1}{2}[A]_0$  for  $[A]_t$  and  $t_{1/2}$  for  $t$  in Equation 13.3, we have

$$\ln \frac{[A]_0}{\frac{1}{2}[A]_0} = kt_{1/2}$$

Noting that the left-hand side of the equation simplifies to  $\ln 2$ , and solving the equation for  $t_{1/2}$ , we have

$$t_{1/2} = \frac{\ln 2}{k} \quad (13.5)$$

Because  $k$  is a constant for a given reaction, the half-life is also a constant for any particular first-order reaction (at any given temperature). Remarkably, in other words, *the half-life of a first-order reaction is not affected by the initial concentration of the reactant*. This can be illustrated by one of the most common first-order events in nature, the change that radioactive isotopes undergo during radioactive "decay." In fact, you have probably heard the term *half-life* used in reference to the life spans of radioactive substances.

<sup>5</sup> The logarithm of a quotient,  $\ln \frac{a}{b}$ , can be written as the difference,  $\ln a - \ln b$ .

□ The equation for a straight line is usually written

$$y = mx + b$$

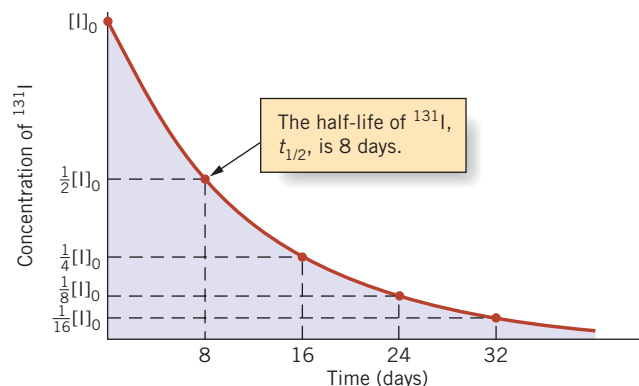
where  $x$  and  $y$  are variables,  $m$  is the slope, and  $b$  is the intercept of the line with the  $y$  axis.

□ Because  $\ln 2$  equals 0.693, Equation 13.5 is sometimes written

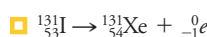
$$t_{1/2} = \frac{0.693}{k}$$



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**FIG. 13.7** First-order radioactive decay of iodine-131. The initial concentration of the isotope is represented by  $[I]_0$ .



Iodine-131, an unstable, radioactive isotope of iodine, undergoes a nuclear reaction whereby it emits a beta particle ( ${}_{-1}^0e$ ) and changes into a stable isotope of xenon.<sup>6</sup> The intensity of the radiation decreases, or *decays*, with time (see Figure 13.7). Notice that the time it takes for the first half of the  ${}^{131}\text{I}$  to disappear is 8 days. Then, during the next 8 days half of the remaining  ${}^{131}\text{I}$  disappears, and so on. Regardless of the initial amount, it takes 8 days for half of that amount of  ${}^{131}\text{I}$  to disappear, which means that the half-life of  ${}^{131}\text{I}$  is a constant.

**EXAMPLE 13.7**

## Half-life Calculations

Suppose a patient is given a certain amount of iodine-131 as part of a diagnostic procedure for a thyroid disorder. Given that the half-life of radioactive iodine-131 is 8.0 days, what fraction of the initial iodine-131 would be present in a patient after 24 days if none of it were eliminated through natural body processes?

**ANALYSIS:** We've learned that radioactive iodine-131 decays by a first-order process with a constant half-life. A period of 24 days is exactly three 8.0 day half-lives. Therefore, let's apply the half-life concept three times.

**SOLUTION:** If we take the fraction initially present to be 1, we can set up a table

Half-life	0	1	2	3
Fraction	1	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{8}$

Half of the iodine-131 is lost in the first half-life, half of that disappears in the second half-life, and so on. Therefore, the fraction remaining after three half-lives is  $\frac{1}{8}$ .

**IS THE ANSWER REASONABLE?** We could also have solved the problem using the integrated first-order rate law, Equation 13.3. We'll need the first order rate constant,  $k$ , which we can obtain from the half-life by rearranging Equation 13.5:

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{8.0 \text{ days}} = 0.0866 \text{ day}^{-1}$$

Then we can use Equation 13.3 to compute the fraction  $\frac{[A]_0}{[A]_t}$

$$\ln \frac{[A]_0}{[A]_t} = kt = (0.0866 \text{ day}^{-1})(24.0 \text{ day}) = 2.08$$

□ The fraction remaining after  $n$  half-lives is  $(\frac{1}{2})^n$ , or simply  $\frac{1}{2^n}$ .

<sup>6</sup>Iodine-131 is used in the diagnosis of thyroid disorders. The thyroid gland is a small organ located just below the Adam's apple and astride the windpipe. It uses iodide ion to make a hormone, so when a patient is given a dose of  ${}^{131}\text{I}^-$  mixed with nonradioactive  $\text{I}^-$ , both ions are taken up by the thyroid gland. The change in (temporary) radioactivity of the gland is a measure of thyroid activity.

## 13.4 Integrated Rate Laws Give Concentration as a Function of Time 539

Taking the antilogarithm of both sides, we have

$$\frac{[A]_0}{[A]_t} = e^{2.08} = 8.0$$

The initial concentration,  $[A]_0$ , is 8.0 times as large as the concentration after 24.0 days, so the fraction remaining after 24 days is  $\frac{1}{8}$ , which is exactly what we obtained much more simply above.

**Practice Exercise 16:** In Practice Exercise 12, the reaction of sucrose with water was found to be first order with respect to sucrose. The rate constant under the conditions of the experiments was  $6.17 \times 10^{-4} \text{ s}^{-1}$ . Calculate the value of  $t_{1/2}$  for this reaction in minutes. How many minutes would it take for three-quarters of the sucrose to react? (Hint: What fraction of the sucrose remains?)

**Practice Exercise 17:** From the answer to Practice Exercise 14, determine the half-life of an active ingredient that has a shelf life of 2.00 years.

### Carbon-14 dating determines the age of organic substances

Carbon-14 is a radioactive isotope that is formed in small amounts in the upper atmosphere by the action of cosmic rays on nitrogen atoms. Once formed, the carbon-14 diffuses into the lower atmosphere. It becomes oxidized to carbon dioxide and enters the earth's biosphere by means of photosynthesis. Carbon-14 thus becomes incorporated into plant substances and into the materials of animals that eat plants. As the carbon-14 decays, more is ingested by the living thing. The net effect is an overall equilibrium involving carbon-14 in the global system. As long as the plant or animal is alive, its ratio of carbon-14 atoms to carbon-12 atoms is constant. At death, an organism's remains have as much carbon-14 as they can ever have, and they now slowly lose this carbon-14 by decay. The decay is a first-order process with a rate independent of the *number* of original carbon atoms. The ratio of carbon-14 to carbon-12, therefore, can be related to the years that have elapsed between the time of death and the time of the measurement. The critical assumption in carbon-14 dating is that the steady-state availability of carbon-14 from the atmosphere has remained largely unchanged over the period for which measurements are valid.<sup>7</sup>

In contemporary biological samples the ratio  $^{14}\text{C}/^{12}\text{C}$  is about  $1.2 \times 10^{-12}$ . Thus, each fresh 1.0 g sample of biological carbon in equilibrium with the  $^{14}\text{CO}_2$  of the atmosphere has a ratio of  $5.8 \times 10^{10}$  atoms of carbon-14 to  $4.8 \times 10^{22}$  atoms of carbon-12. The ratio decreases by a factor of 2 for each half-life period of  $^{14}\text{C}$  (5730 years).

The dating of an object makes use of the fact that radioactive decay is a first-order process. If we let  $r_0$  stand for the  $^{14}\text{C}/^{12}\text{C}$  ratio at the time of death of the carbon-containing species and  $r_t$  stand for the  $^{14}\text{C}/^{12}\text{C}$  ratio now, after the elapse of  $t$  years, we can substitute into Equation 13.3 to obtain

$$\ln \frac{r_0}{r_t} = kt \quad (13.6)$$

where  $k$  is the rate constant for the decay (the *decay constant* for  $^{14}\text{C}$ ) and  $t$  is the elapsed time. We can obtain the rate constant from the half-life of  $^{14}\text{C}$  using Equation 13.5.

$$\ln 2 = kt_{1/2}$$

<sup>7</sup>The available atmospheric pool of carbon-14 atoms fluctuates somewhat with the intensities of cosmic ray showers, with slow, long-term changes in the earth's magnetic field, and with the huge injections of carbon-12 into the atmosphere from the large-scale burning of coal and petroleum in the 1900s. To reduce the uncertainties in carbon-14 dating, results of the method have been corrected against dates made by tree-ring counting. For example, an uncorrected carbon-14 dating of a Viking site at L'Anse aux Meadows, Newfoundland, gave a date of AD 895  $\pm$  30. When corrected, the date of the settlement became AD 997, almost exactly the time indicated in Icelandic sagas for Leif Eriksson's landing at "Vinland," now believed to be the L'Anse aux Meadows site.

■ In all dating experiments the amounts of sample are extremely small and extraordinary precautions must be taken to avoid contaminating specimens with "modern" materials.

■ Willard F. Libby won the Nobel Prize in Chemistry in 1960 for his discovery of the carbon-14 method for dating ancient objects.

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Substituting 5730 yr for  $t_{1/2}$  and solving for  $k$  gives  $k = 1.21 \times 10^{-4} \text{ yr}^{-1}$ . We can now substitute this value into Equation 13.6 to give

$$\ln \frac{r_0}{r_t} = (1.21 \times 10^{-4} \text{ yr}^{-1})t \quad (13.7)$$

Equation 13.7 can be used to calculate the age of a once-living object if its current  $^{14}\text{C}/^{12}\text{C}$  ratio can be measured.

**EXAMPLE 13.8**Calculating the Age of an Object by  $^{14}\text{C}$  Dating

Using a device similar to a mass spectrometer, a sample of an ancient wooden object was found to have a ratio of  $^{14}\text{C}$  to  $^{12}\text{C}$  equal to  $3.3 \times 10^{-13}$ . What is the age of the object?

**ANALYSIS:** This is a straightforward calculation that involves using Equation 13.7. We simply substitute values.

**SOLUTION:** The contemporary ratio of  $^{14}\text{C}$  to  $^{12}\text{C}$  was given earlier as  $1.2 \times 10^{-12}$ . This corresponds to  $r_0$  in Equation 13.7. Substituting into Equation 13.7 gives

$$\begin{aligned} \ln \frac{1.2 \times 10^{-12}}{3.3 \times 10^{-13}} &= (1.21 \times 10^{-4} \text{ yr}^{-1})t \\ \ln(3.6) &= (1.21 \times 10^{-4} \text{ yr}^{-1})t \end{aligned}$$

Solving for  $t$  gives an age of  $1.1 \times 10^4$  years (11,000 years).

**IS THE ANSWER REASONABLE?** We've been told that the object is ancient, so 11,000 years old seems to make sense. (Also, if you had substituted incorrectly into Equation 13.7, the answer would have been negative, and that certainly doesn't make sense!)

**Practice Exercise 18:** The  $^{14}\text{C}$  content of an ancient piece of wood was found to be one-eighth of that in living trees. How many years old is this piece of wood ( $t_{1/2} = 5730$  for  $^{14}\text{C}$ )? (Hint: Recall the relationship between the integrated rate equation and half-life.)

**Practice Exercise 19:** When using carbon-14 dating, samples that have decayed less than 5% and those that have decayed more than 95% may have unacceptably large uncertainties. With that information, what are the upper and lower limits of dates before present, BP, that can be determined?

### The reciprocal of the concentration is related linearly to time for second-order reactions

For simplicity, we will only consider a second-order reaction with a rate law of the following type.

$$\text{Rate} = k[B]^2$$

The relationship between concentration and time for a reaction with such a rate law is given by Equation 13.8, an equation that is quite different from that for a first-order reaction.

**TOOLS**

Integrated rate law, second-order reaction

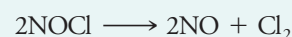
$$\frac{1}{[B]_t} - \frac{1}{[B]_0} = kt \quad (13.8)$$

$[B]_0$  is the initial concentration of  $B$  and  $[B]_t$  is the concentration at time  $t$ . The next example illustrates how Equation 13.8 is applied to calculations.

**EXAMPLE 13.9**

## Concentration–Time Calculations for Second-Order Reactions

Nitrosyl chloride,  $\text{NOCl}$ , decomposes slowly to  $\text{NO}$  and  $\text{Cl}_2$ .



The rate law shows that the rate is second order in  $\text{NOCl}$ .

$$\text{Rate} = k[\text{NOCl}]^2$$

## 13.4 Integrated Rate Laws Give Concentration as a Function of Time 541

The rate constant  $k$  equals  $0.020 \text{ L mol}^{-1} \text{ s}^{-1}$  at a certain temperature. If the initial concentration of NOCl in a closed reaction vessel is  $0.050 \text{ M}$ , what will the concentration be after 30 minutes?

**ANALYSIS:** We're given a rate law and so can see that it is for a second-order reaction and has the simple form to which our study is limited. We must calculate  $[\text{NOCl}]_t$ , the molar concentration of NOCl, after 30 minutes (1800 s). Our tool for doing this is Equation 13.8.

**SOLUTION:** Let's begin by tabulating the data.

$$\begin{aligned} [\text{NOCl}]_0 &= 0.050 \text{ M} & [\text{NOCl}]_t &= ? \text{ M} \\ k &= 0.020 \text{ L mol}^{-1} \text{ s}^{-1} & t &= 1800 \text{ s} \end{aligned}$$

The equation we wish to substitute into is

$$\frac{1}{[\text{NOCl}]_t} - \frac{1}{[\text{NOCl}]_0} = kt$$

Making the substitutions gives

$$\frac{1}{[\text{NOCl}]_t} - \frac{1}{0.050 \text{ mol L}^{-1}} = (0.020 \text{ L mol}^{-1} \text{ s}^{-1}) \times (1800 \text{ s})$$

Solving for  $1/[\text{NOCl}]_t$  gives

$$\begin{aligned} \frac{1}{[\text{NOCl}]_t} - 20 \text{ L mol}^{-1} &= 36 \text{ L mol}^{-1} \\ \frac{1}{[\text{NOCl}]_t} &= 56 \text{ L mol}^{-1} \end{aligned}$$

Taking the reciprocals of both sides gives us the value of  $[\text{NOCl}]_t$ .

$$[\text{NOCl}]_t = \frac{1}{56 \text{ L mol}^{-1}} = 0.018 \text{ mol L}^{-1} = 0.018 \text{ M}$$

The molar concentration of NOCl has decreased from  $0.050 \text{ M}$  to  $0.018 \text{ M}$  after 30 minutes.

**IS THE ANSWER REASONABLE?** The concentration of NOCl has decreased, so the answer appears to be reasonable.

**Practice Exercise 20:** For the reaction in the preceding example, determine how many minutes it would take for the NOCl concentration to drop from  $0.040 \text{ M}$  to  $0.010 \text{ M}$ . (Hint: In solving Equation 13.8 time must be a positive value.)

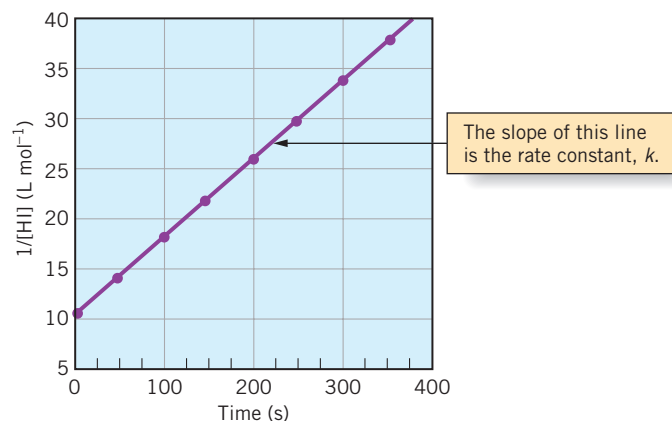
**Practice Exercise 21:** A sample of nitrosyl chloride was collected for analysis at 10:35 am. At 3:15 pm the same day the sample was analyzed and was found to contain  $0.00035 \text{ M}$  NOCl. What was the concentration of NOCl at the time the sample was collected?

### The second-order rate constant also can be determined graphically

The rate constant  $k$  for a second-order reaction, one with a rate following Equation 13.8, can be determined graphically by a method similar to that used for a first-order reaction. We can rearrange Equation 13.8 so that it corresponds to an equation for a straight line.

$$\begin{array}{c} \frac{1}{[\text{B}]_t} = kt + \frac{1}{[\text{B}]_0} \\ \updownarrow \quad \updownarrow \quad \updownarrow \\ y = mx + b \end{array}$$

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**FIG. 13.8** Second-order kinetics. A graph of  $1/[\text{HI}]$  versus time for the data in Table 13.1.

When a reaction is second order, then, a plot of  $1/[B]_t$  versus  $t$  should yield a straight line having a slope  $k$ . This is illustrated in Figure 13.8 for the decomposition of HI, using data in Table 13.1.

#### Half-lives of second-order reactions depend on concentration

The half-life of a second-order reaction *does* depend on initial reactant concentrations. We can see this by examining Figure 13.5 (page 524), which follows the decomposition of gaseous HI, a second-order reaction. The reaction begins with a hydrogen iodide concentration of  $0.10\text{ M}$ . After 125 seconds, the concentration of HI drops to  $0.050\text{ M}$ , so 125 s is the observed half-life when the initial concentration of HI is  $0.10\text{ M}$ . If we then take  $0.050\text{ M}$  as the next “initial” concentration, we find that it takes 250 seconds (at a *total* elapsed time of 375 seconds) to drop to  $0.025\text{ M}$ . If we cut the initial concentration in half, from  $0.10\text{ M}$  to  $0.05\text{ M}$ , the half-life doubles, from 125 to 250 seconds.

It can be shown that for a second-order reaction of the type we’re studying, the half-life is inversely proportional to the initial concentration of the reactant. The half-life is related to the rate constant by Equation 13.9.

$$t_{1/2} = \frac{1}{k \times (\text{initial concentration of reactant})} \quad (13.9)$$

#### EXAMPLE 13.10

Half-life Calculations

The reaction  $2\text{HI}(\text{g}) \longrightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$  has the rate law,  $\text{Rate} = k[\text{HI}]^2$ , with  $k = 0.079\text{ L mol}^{-1}\text{ s}^{-1}$  at  $508\text{ }^\circ\text{C}$ . What is the half-life for this reaction at this temperature when the initial HI concentration is  $0.10\text{ M}$ ?

**ANALYSIS:** The rate law tells us that the reaction is second order. To calculate the half-life, we need to use Equation 13.9.

**SOLUTION:** The initial concentration is  $0.10\text{ mol L}^{-1}$ ;  $k = 0.079\text{ L mol}^{-1}\text{ s}^{-1}$ . Substituting these values into Equation 13.9 gives

$$\begin{aligned} t_{1/2} &= \frac{1}{(0.079\text{ L mol}^{-1}\text{ s}^{-1})(0.10\text{ mol L}^{-1})} \\ &= 1.3 \times 10^2\text{ s} \end{aligned}$$

**IS THE ANSWER REASONABLE?** To estimate the answer we round the  $0.079$  to  $0.1$ . The estimated answer is  $\frac{1}{0.1 \times 0.1} = 100$ . This is close to our calculated value. In addition we check that the units cancel to leave only the seconds units. Both of these checks support our answer.

## 13.5 Reaction Rate Theories Explain Experimental Rate Laws in Terms of Molecular Collisions 543

**Practice Exercise 22:** The reaction  $2\text{NO}_2 \longrightarrow 2\text{NO} + \text{O}_2$  is second order with respect to  $\text{NO}_2$ . If the initial concentration of  $\text{NO}_2(g)$  is  $6.54 \times 10^{-4} \text{ mol L}^{-1}$ , what is the rate constant if the initial reaction rate is  $4.42 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1}$ ? What is the half-life of this system? (Hint: Start by setting up and solving the rate law before the integrated equation.)

**Practice Exercise 23:** Suppose that the value of  $t_{1/2}$  for a certain reaction was found to be independent of the initial concentration of the reactants. What could you say about the order of the reaction? Justify your answer.

### 13.5 REACTION RATE THEORIES EXPLAIN EXPERIMENTAL RATE LAWS IN TERMS OF MOLECULAR COLLISIONS

In Section 13.1 we mentioned that nearly all reactions proceed faster at higher temperatures. As a rule, the reaction rate increases by a factor of about 2 or 3 for each  $10^\circ\text{C}$  increase in temperature, although the actual amount of increase differs from one reaction to another. Temperature evidently has a strong effect on reaction rate. To understand why, we need to develop theoretical models that explain our observations. One of the simplest models is called *collision theory*.

#### Reaction rate is related to the number of effective collisions per second between reactant molecules

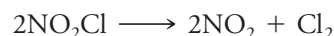
The basic postulate of **collision theory** is that the rate of a reaction is proportional to the number of *effective* collisions per second among the reactant molecules. An *effective collision* is one that actually gives product molecules. Anything that can increase the frequency of effective collisions should, therefore, increase the rate.

One of the several factors that influences the number of effective collisions per second is *concentration*. As reactant concentrations increase, the number of collisions per second of all types, including effective collisions, cannot help but increase. We'll return to the significance of concentration in Section 13.7.

Not *every* collision between reactant molecules actually results in a chemical change. We know this because the reactant atoms or molecules in a gas or a liquid undergo an enormous number of collisions per second with each other. If every collision were effective, all reactions would be over in an instant. *Only a very small fraction of all the collisions can really lead to a net change.* Why is this so?

#### Molecular orientation is important

In most reactions, when two reactant molecules collide they must be oriented correctly for a reaction to occur. For example, the reaction represented by the following equation.



appears to proceed by a two-step mechanism. One step involves the collision of an  $\text{NO}_2\text{Cl}$  molecule with a chlorine atom.



The orientation of the  $\text{NO}_2\text{Cl}$  molecule when hit by the  $\text{Cl}$  atom is important (see Figure 13.9). The poor orientation shown in Figure 13.9a cannot result in the formation of  $\text{Cl}_2$  because the two  $\text{Cl}$  atoms are not being brought close enough together for a new  $\text{Cl}-\text{Cl}$  bond to form as an  $\text{N}-\text{Cl}$  bond breaks. Figure 13.9b shows the necessary orientation if the collision of  $\text{NO}_2\text{Cl}$  and  $\text{Cl}$  is to effectively lead to products.

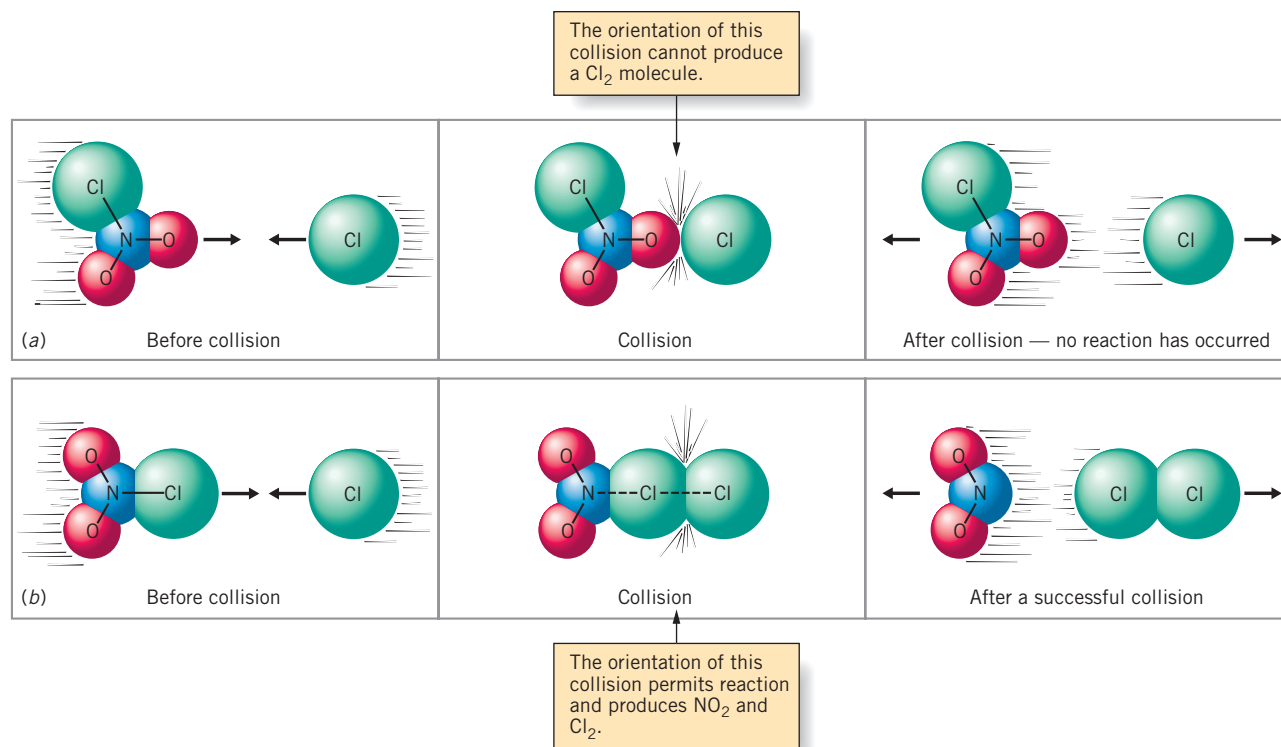
#### A minimum molecular kinetic energy is required

Not all collisions, even those correctly oriented, are energetic enough to result in products, and this is the major reason that only a small percentage of all collisions actually lead to chemical change. The colliding particles must carry into the collision a certain minimum combined molecular kinetic energy, called the **activation energy**,  $E_a$ . In a successful collision, activation energy changes over to potential energy as the particles hit each other

■ The kinetic theory provides insights for reaction rate theory.

■ At the start of the reaction described by Figure 13.5, only about one of every billion billion ( $10^{18}$ ) collisions leads to a net chemical reaction. In each of the other collisions, the reactant molecules just bounce off each other.

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**FIG. 13.9** The importance of molecular orientation during a collision in a reaction. The key step in the decomposition of  $\text{NO}_2\text{Cl}$  to  $\text{NO}_2$  and  $\text{Cl}_2$  is the collision of a Cl atom with a  $\text{NO}_2\text{Cl}$  molecule. (a) A poorly oriented collision. (b) An effectively oriented collision.

and chemical bonds become reorganized into those of the products. For most chemical reactions, the activation energy is quite large, and only a small fraction of all well-oriented, colliding molecules have it.

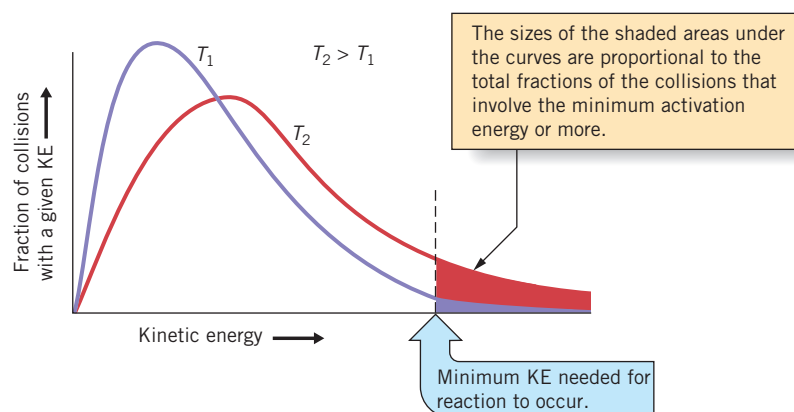
We can understand the existence of activation energy by studying in detail what actually takes place during a collision. For old bonds to break and new bonds to form, the atomic nuclei within the colliding particles must get close enough together. The molecules on a collision course must, therefore, be moving with a combined kinetic energy great enough to overcome the natural repulsions between electron clouds. Otherwise, the molecules simply veer away or bounce apart. Only fast molecules with large kinetic energies can collide with enough collision energy to enable their nuclei and electrons to overcome repulsions and thereby reach the positions required for the bond breaking and bond making that the chemical change demands.

#### Rising temperature increases reaction rates

With the concept of activation energy, we can now explain why the rate of a reaction increases so much with increasing temperature. We'll use the two curves in Figure 13.10, each corresponding to a different temperature for the same mixture of reactants. Each curve is a plot of the different *fractions* of all collisions (vertical axis) that have particular values of kinetic energy of collision (horizontal axis). (The total area under a curve then represents the total number of collisions, because all of the fractions must add up to this total.) Notice what happens to the plots when the temperature is increased; the maximum point shifts to the right and the curve flattens somewhat. However, *a modest increase in temperature generally does not affect the reaction's activation energy*. Within reason, the activation energy of a reaction is not affected by a change in temperature. In other words, as the curve flattens and shifts to the right with an increase in temperature, the value of  $E_a$  stays the same.

The shaded areas under the curves in Figure 13.10 represent the sum of all those fractions of the total collisions that equal or exceed the activation energy. This sum—we could call it the *reacting fraction*—is relatively much greater at the higher temperature than at the lower temperature because a significant fraction of the curve shifts beyond the activation

## 13.5 Reaction Rate Theories Explain Experimental Rate Laws in Terms of Molecular Collisions 545



**FIG. 13.10** Kinetic energy distributions for a reaction mixture at two different temperatures.

energy in even a modest change to a higher temperature. In other words, at the higher temperature, a much greater fraction of the collisions occurring each second results in a chemical change, so the reactants disappear faster at the higher temperature.

On the molecular scale we can write an equation that summarizes the three factors involved in the collision theory as

$$\text{Reaction rate (molecules L}^{-1} \text{ s}^{-1}) = N \times f_{\text{orientation}} \times f_{\text{KE}}$$

where  $N$  represents the collisions per second per liter of the mixture, approximately  $10^{27} \text{ s}^{-1}$ . The two other terms represent the fraction of collisions with the correct orientation,  $f_{\text{orientation}}$ , and the fraction of collisions with the required total kinetic energy,  $f_{\text{KE}}$ . To convert this to the laboratory scale rate of  $\text{mol L}^{-1} \text{ s}^{-1}$ , we divide the equation by Avogadro's number.

$$\text{Reaction rate (mol L}^{-1} \text{ s}^{-1}) = \frac{\text{reaction rate (molecules L}^{-1} \text{ s}^{-1})}{6.02 \times 10^{23} \text{ (molecules mol}^{-1}\text{)}}$$

### The transition state is the arrangement of atoms at the top of the activation energy "hill"

**Transition state theory** is used to explain in detail what happens when reactant molecules come together in a collision. Most often, those in a head-on collision slow down, stop, and then fly apart unchanged. When a collision does cause a reaction, the particles that separate are those of the products. Regardless of what happens to them, however, as the molecules on a collision course slow down, their total kinetic energy decreases as it changes into potential energy (PE). It's like the momentary disappearance of the kinetic energy of a tennis ball when it hits the racket. In the deformed racket and ball, this energy becomes potential energy, which soon changes back to kinetic energy as the ball takes off in a new direction.

### Potential energy diagrams summarize energy changes during the course of a reaction

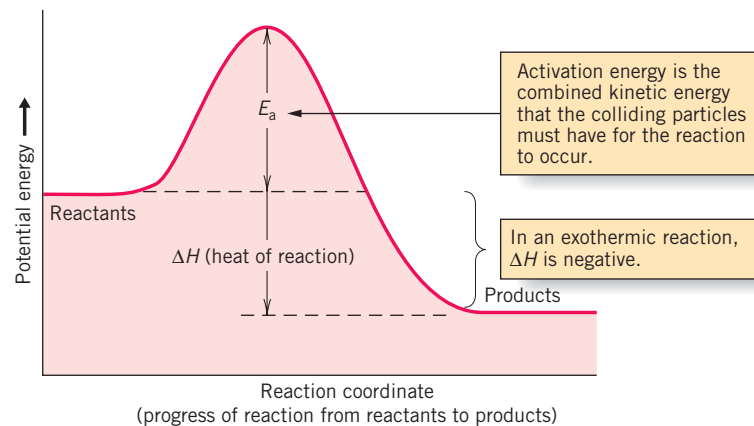
To visualize the relationship between activation energy and the development of total potential energy we sometimes use a *potential energy diagram* (see Figure 13.11). The vertical axis represents changes in *potential* energy as the kinetic energy of the colliding particles changes over to this form. The horizontal axis is called the **reaction coordinate**, and it represents the extent to which the reactants have changed to the products. It helps us follow the path taken by the reaction as reactant molecules come together and change into product molecules. Activation energy appears as a potential energy "hill" or barrier between the reactants and products. Only colliding molecules, properly oriented, that can deliver kinetic energy into potential energy at least as large as  $E_a$  are able to climb over the hill and produce products.

We can use a potential energy diagram to follow the progress of both an unsuccessful and a successful collision (see Figure 13.12). As two reactant molecules collide, we say that they begin to climb the potential energy barrier as they slow down and experience the

□ The fraction of molecules,  $f_{\text{KE}}$ , having or exceeding the activation energy,  $E_a$ , is given by the expression

$$\ln f_{\text{KE}} = \frac{-E_a}{RT}$$

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**FIG. 13.11** Potential energy diagram for an exothermic reaction.

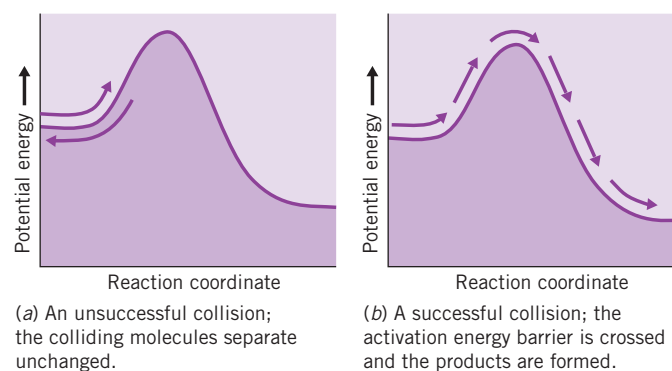
conversion of their kinetic energy into potential energy. But if their combined initial kinetic energies are equivalent to a potential energy that is less than  $E_a$ , the molecules are unable to reach the top of the hill (Figure 13.12*a*). Instead, they fall back toward the reactants. They bounce apart chemically unchanged with their original total kinetic energy; no reaction has occurred. On the other hand, if the combined kinetic energy of the colliding molecules equals or exceeds  $E_a$ , and if the molecules are oriented properly, they are able to pass over the activation energy barrier and form product molecules (Figure 13.12*b*).

#### Potential energy diagrams also show the heat of reaction

A reaction's potential energy diagram, such as that of Figure 13.11, helps us to visualize the *heat of reaction*,  $\Delta H$ , a concept introduced in Chapter 6. It's the difference between the potential energy of the products and the potential energy of the reactants. Figure 13.11 is for an *exothermic* reaction because the products have a *lower* potential energy than the reactants. In such a system, the net decrease in potential energy appears as an increase in the molecular kinetic energy of the emerging product molecules. The temperature of the system increases during an exothermic reaction because the average molecular kinetic energy of the system increases.

A potential energy diagram for an endothermic reaction is shown in Figure 13.13. Now the products have a *higher* potential energy than the reactants and, in terms of the heat of reaction, a net input of energy is needed to form the products. Endothermic reactions produce a cooling effect as they proceed because there is a net conversion of molecular kinetic energy to potential energy. As the *total* molecular kinetic energy decreases, the *average* molecular kinetic energy decreases as well, and the temperature drops.

Notice that  $E_a$  for an endothermic process is invariably greater than (or it might be equal to) the heat of reaction. If  $\Delta H$  is both positive and *high*,  $E_a$  must also be high, making such reactions very slow. However, for an exothermic reaction ( $\Delta H$  is negative) we cannot tell from  $\Delta H$  how large  $E_a$  is. It could be high, making for a slow reaction despite its being exothermic. If  $E_a$  is low, the reaction would be rapid and all its heat would appear quickly.



**FIG. 13.12** The difference between an unsuccessful and a successful collision.

## 13.5 Reaction Rate Theories Explain Experimental Rate Laws in Terms of Molecular Collisions 547

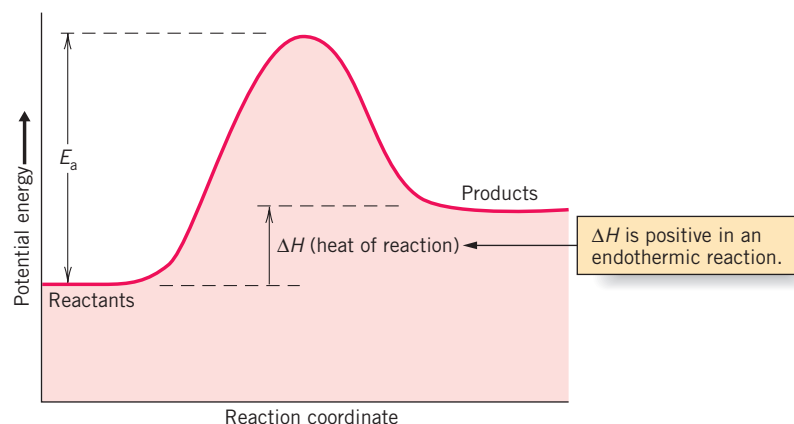


FIG. 13.13 A potential energy diagram for an endothermic reaction.

In Chapter 6 we saw that when the direction of a reaction is reversed, the sign given to the enthalpy change,  $\Delta H$ , is reversed. In other words, a reaction that is exothermic in the forward direction *must* be endothermic in the reverse direction, and vice versa. This might seem to suggest that reactions are generally reversible. Many are, but if we look again at the energy diagram for a reaction that is exothermic in the forward direction (Figure 13.11), it is obvious that in the opposite direction the reaction is endothermic *and must have a significantly higher activation energy* than the forward reaction. What differs most for the forward and reverse directions is the relative height of the activation energy barrier (see Figure 13.14).

One of the main reasons for studying activation energies is that they provide information about what actually occurs during an effective collision. For example, in Figure 13.9b on page 544, we described a way that  $\text{NO}_2\text{Cl}$  could react successfully with a Cl atom during a collision. During this collision, there is a moment when the N—Cl bond is partially broken and the new Cl—Cl bond is partially formed. This brief moment during a successful collision is called the reaction's **transition state**. The potential energy of the transition state corresponds to the high point on the potential energy diagram (see Figure 13.15). The unstable chemical species that momentarily exists at this instant,  $\text{O}_2\text{N}\cdots\text{Cl}\cdots\text{Cl}$ , with its partially formed and partially broken bonds, is called the **activated complex**.

The size of the activation energy tells us about the relative importance of bond breaking and bond making during the formation of the activated complex. A very high activation energy suggests, for instance, that bond *breaking* contributes very heavily to the formation of the activated complex because bond *breaking* is an energy-absorbing process. On the other hand, a low activation energy may mean that bonds of about equal strength are being both broken and formed simultaneously.

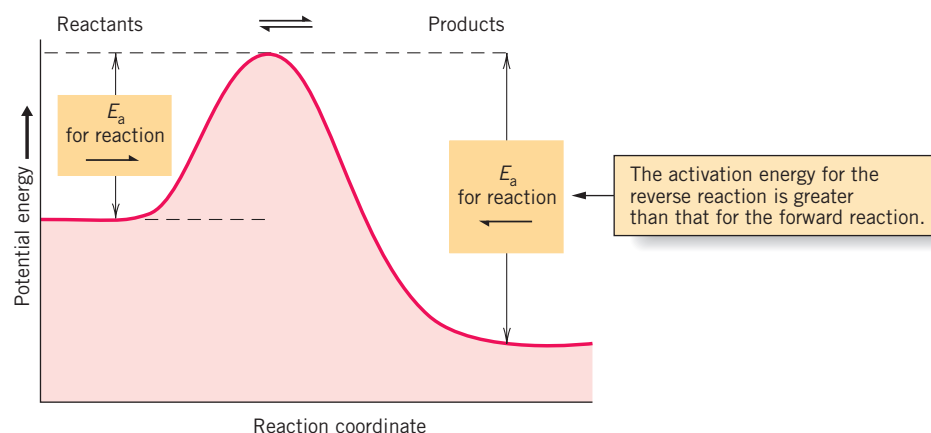
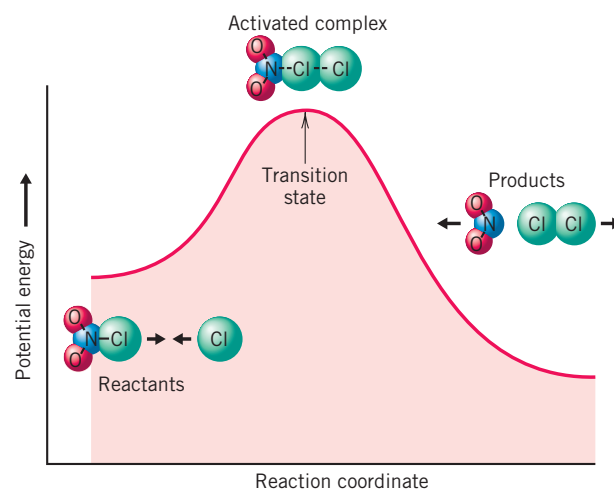


FIG. 13.14 Activation energy barrier for the forward and reverse reactions.

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**FIG. 13.15** Transition state and the activated complex. Formation of an activated complex in the reaction between  $\text{NO}_2\text{Cl}$  and  $\text{Cl}$ .  
 $\text{NO}_2\text{Cl} + \text{Cl} \longrightarrow \text{NO} + \text{Cl}_2$



## 13.6

### ACTIVATION ENERGIES ARE MEASURED BY FITTING EXPERIMENTAL DATA TO THE ARRHENIUS EQUATION

We've noted that the activation energy is a useful quantity to know because its value can provide clues to the relative importance of bond breaking and bond making during the formation of the activated complex. Determining the value of  $E_a$  is accomplished by observing how temperature affects the value of the rate constant,  $k$ .

The activation energy is linked to the rate constant by a relationship discovered in 1889 by Svante Arrhenius, whose name you may recall from our discussion of electrolytes and acids and bases in Chapter 4. The usual form of the **Arrhenius equation** is

**TOOLS**  
Arrhenius equation 

$$k = A e^{-E_a/RT} \quad (13.10)$$

where  $k$  is the rate constant,  $e$  is the base of the natural logarithm system, and  $T$  is the Kelvin temperature.  $A$  is a proportionality constant sometimes called the **frequency factor** or the **pre-exponential factor**.  $R$  is the gas constant, which we'll express in our study of kinetics in energy units, namely,  $R$  equals  $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ .<sup>8</sup>

#### The activation energy can be determined graphically

Equation 13.10 is normally used in its logarithmic form. If we take the natural logarithm of both sides, we obtain

$$\ln k = \ln A - E_a/RT$$

Let's rewrite the equation as

$$\ln k = \ln A - (E_a/R) \times (1/T) \quad (13.11)$$

<sup>8</sup> The units of  $R$  given here are actually SI units, namely, the joule (J), the mole ( $n$ ), and the kelvin (K). To calculate  $R$  in these units we need to go back to the defining equation for the universal gas law, rearranging terms.

$$R = PV/nT$$

In Chapter 10 we learned that the standard conditions of pressure and temperature are 1 atm and 273.15 K; we expressed the standard molar volume in liters, namely 22.414 L. But 1 atm equals  $1.01325 \times 10^5 \text{ N m}^{-2}$ , where N is the SI unit of force, the newton, and m is the meter, the SI unit of length. So  $\text{m}^2$  is area given in SI units. From Chapter 10, the ratio of force to area given by  $\text{N m}^{-2}$  is called the pascal, Pa, and that force times distance or N m defines one unit of energy in the SI and is called the joule, J. In the SI, volume must be expressed as  $\text{m}^3$ , to employ the SI unit of length to define volume, and 1 L equals  $10^{-3} \text{ m}^3$ . So now we can calculate  $R$  in SI units.

$$\begin{aligned} R &= \frac{(1.01325 \times 10^5 \text{ N m}^{-2}) \times (22.414 \times 10^{-3} \text{ m}^3)}{(1 \text{ mol} \times 273.15 \text{ K})} \\ &= 8.314 \text{ N m mol}^{-1} \text{ K}^{-1} = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \end{aligned}$$

### 13.6 Activation Energies Are Measured by Fitting Experimental Data to the Arrhenius Equation 549

We know that the rate constant  $k$  varies with the temperature  $T$ , which also means that the quantity  $\ln k$  varies with the quantity  $(1/T)$ . These two quantities, namely,  $\ln k$  and  $1/T$ , are variables, so Equation 13.11 is in the form of an equation for a straight line.

$$\begin{array}{ccccccc} \ln k & = & \ln A & + & (-E_a/R) & \times & (1/T) \\ \updownarrow & & \updownarrow & & \updownarrow & & \updownarrow \\ y & = & b & + & m & & x \end{array}$$

To determine the activation energy, we can make a graph of  $\ln k$  versus  $1/T$ , measure the slope of the line, and then use the relationship

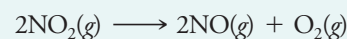
$$\text{Slope} = -E_a/R$$

to calculate  $E_a$ . Example 13.11 illustrates how this is done.

#### EXAMPLE 13.11

##### Determining Energy of Activation Graphically

Consider again the decomposition of  $\text{NO}_2$  into  $\text{NO}$  and  $\text{O}_2$ . The equation is



The following data were collected for the reaction.

Rate Constant, $k$ ( $\text{L mol}^{-1} \text{s}^{-1}$ )	Temperature ( $^{\circ}\text{C}$ )
7.8	400
10	410
14	420
18	430
24	440

Use the graphical method to determine the activation energy for the reaction in kilojoules per mole.

**ANALYSIS:** Equation 13.11 is the tool that applies. However, the use of rate data to determine the activation energy graphically requires that we plot  $\ln k$ , not  $k$ , versus the *reciprocal* of the *Kelvin* temperature, so we have to convert the given data into  $\ln k$  and  $1/T$  before we can construct the graph.

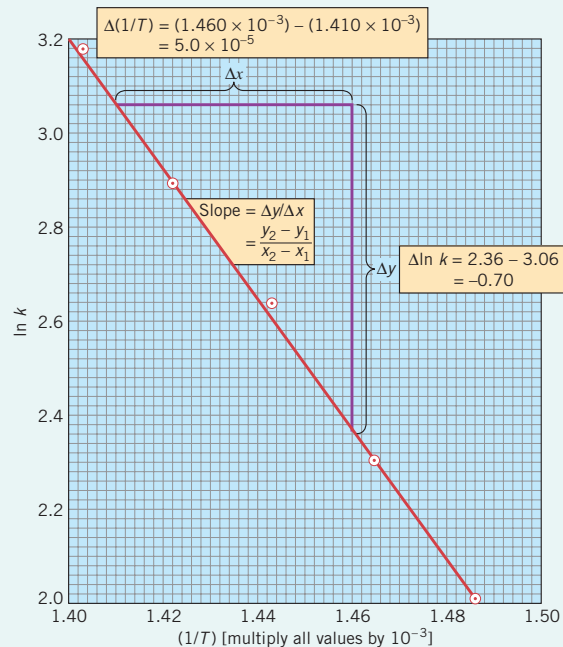
**SOLUTION:** To illustrate, using the first set of data, the conversions are

$$\begin{aligned} \ln k &= \ln(7.8) = 2.05 \\ \frac{1}{T} &= \frac{1}{(400 + 273) \text{ K}} = \frac{1}{673 \text{ K}} \\ &= 1.486 \times 10^{-3} \text{ K}^{-1} \end{aligned}$$

We are carrying extra “significant figures” for the purpose of graphing the data. The remaining conversions give the table below. Then we plot  $\ln k$  versus  $1/T$  as shown on the next page.

$\ln k$	$1/T$ ( $\text{K}^{-1}$ )
2.05	$1.486 \times 10^{-3}$
2.30	$1.464 \times 10^{-3}$
2.64	$1.443 \times 10^{-3}$
2.89	$1.422 \times 10^{-3}$
3.18	$1.403 \times 10^{-3}$

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The slope of the curve is obtained as the ratio

$$\begin{aligned} \text{Slope} &= \frac{\Delta(\ln k)}{\Delta(1/T)} \\ &= \frac{-0.70}{5.0 \times 10^{-5} \text{ K}^{-1}} \\ &= -1.4 \times 10^4 \text{ K} = -E_a/R \end{aligned}$$

After changing signs and solving for  $E_a$  we have

$$\begin{aligned} E_a &= (8.314 \text{ J mol}^{-1} \text{ K}^{-1})(1.4 \times 10^4 \text{ K}) \\ &= 1.2 \times 10^5 \text{ J mol}^{-1} \\ &= 1.2 \times 10^2 \text{ kJ mol}^{-1} \end{aligned}$$

**IS THE ANSWER REASONABLE?** Activation energies must always have a positive sign and our result is positive. In addition, a check of the units shows that they cancel to give us the correct  $\text{kJ mol}^{-1}$ . We could try a different pair of points on the same graph to check our work.

### The activation energy can be calculated from rate constants measured at two temperatures

If the activation energy and the rate constant at a particular temperature are known, the rate constant at another temperature can be calculated using the following relationship, which can be derived from Equation 13.11,



$$\ln \left( \frac{k_2}{k_1} \right) = \frac{-E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad (13.12)$$

This equation can also be used to calculate the activation energy from rate constants measured at two different temperatures. However, the graphical method discussed earlier gives more precise values of  $E_a$ .

#### EXAMPLE 13.12

Calculating the Rate Constant at a Particular Temperature

The reaction  $2\text{NO}_2 \longrightarrow 2\text{NO} + \text{O}_2$  has an activation energy of  $111 \text{ kJ mol}^{-1}$ . At  $400^\circ\text{C}$ ,  $k = 7.8 \text{ L mol}^{-1} \text{ s}^{-1}$ . What is the value of  $k$  at  $430^\circ\text{C}$ ?

**ANALYSIS:** We know the activation energy and  $k$  at one temperature. We will need to use Equation 13.12 as our tool to obtain  $k$  at the other temperature. Since the logarithm term contains the ratio of the rate constants, we will solve for the value of this ratio, substitute the known value of  $k$ , and then solve for the unknown  $k$ .

## 13.7 Experimental Rate Laws Can Be Used to Support or Reject Proposed Mechanisms for a Reaction 551

**SOLUTION:** Let's begin by writing Equation 13.12.

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{-E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Organizing the data gives us the following table.

	$k$ (L mol <sup>-1</sup> s <sup>-1</sup> )	$T$ (K)
1	7.8	400 + 273 = 673 K
2	?	430 + 273 = 703 K

We must use  $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$  and express  $E_a$  in joules ( $E_a = 1.11 \times 10^5 \text{ J mol}^{-1}$ ). Next, we substitute values into the right side of the equation and solve for  $\ln(k_2/k_1)$ .

$$\begin{aligned}\ln\left(\frac{k_2}{k_1}\right) &= \frac{-1.11 \times 10^5 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \left(\frac{1}{703 \text{ K}} - \frac{1}{673 \text{ K}}\right) \\ &= (-1.34 \times 10^4 \text{ K})(-6.34 \times 10^{-5} \text{ K}^{-1})\end{aligned}$$

Therefore,

$$\ln\left(\frac{k_2}{k_1}\right) = 0.850$$

Taking the antilog gives the ratio of  $k_2$  to  $k_1$ .

$$\frac{k_2}{k_1} = e^{0.850} = 2.34$$

Solving for  $k_2$ ,

$$k_2 = 2.34k_1$$

Substituting the value of  $k_1$  from the data table gives

$$\begin{aligned}k_2 &= 2.34(7.8 \text{ L mol}^{-1} \text{ s}^{-1}) \\ &= 18 \text{ L mol}^{-1} \text{ s}^{-1}\end{aligned}$$

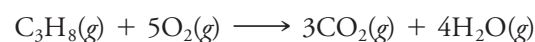
**IS THE ANSWER REASONABLE?** Although no simple check exists, we have at least found that the value of  $k$  for the higher temperature is greater than it is for the lower temperature, as it should be.

**Practice Exercise 24:** The rate constant is directly proportional to the reaction rate if the same reactant concentrations are used. When determining the stability of a consumer product, less than 5% should decompose in two years at 25 °C. What temperature should we set our oven to if we want to see that same 5% decomposition in one week? Assume the activation energy was previously determined to be 154 kJ mol<sup>-1</sup>. (Hint: All the information is here to apply the Arrhenius equation.)

**Practice Exercise 25:** The reaction  $\text{CH}_3\text{I} + \text{HI} \longrightarrow \text{CH}_4 + \text{I}_2$  was observed to have rate constants  $k = 3.2 \text{ L mol}^{-1} \text{ s}^{-1}$  at 350 °C and  $k = 23 \text{ L mol}^{-1} \text{ s}^{-1}$  at 400 °C. (a) What is the value of  $E_a$  expressed in kJ mol<sup>-1</sup>? (b) What would be the rate constant at 300 °C?

### 13.7 EXPERIMENTAL RATE LAWS CAN BE USED TO SUPPORT OR REJECT PROPOSED MECHANISMS FOR A REACTION

A balanced equation generally describes only a net overall change. Usually, however, the net change is the result of a series of simple reactions that are not at all evident from the equation. Consider, for example, the combustion of propane, C<sub>3</sub>H<sub>8</sub>.



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Anyone who has ever played billiards knows that this reaction simply cannot occur in a single, simultaneous collision between one propane molecule and five oxygen molecules. Just getting only three balls to come together with but one “click” on a flat, two-dimensional surface is extremely improbable. How unlikely it must be, then, for the *simultaneous* collision in three-dimensional space of six reactant molecules, one of which must be  $C_3H_8$  and the other five  $O_2$ . Instead, the combustion of propane proceeds very rapidly by a series of much more probable steps, involving colliding chemical species of fleeting existence. *The series of individual steps that add up to the overall observed reaction is called the **mechanism of a reaction**.* Information about reaction mechanisms is one of the dividends paid by the study of rates.

Each individual step in a reaction mechanism is a simple chemical reaction called an *elementary process*. An **elementary process** is a reaction involving collisions between molecules. As you will soon see, its rate law can be written from its own chemical equation, using coefficients as exponents for the concentration terms without requiring experiments to determine the exponents. For most reactions, the individual elementary processes cannot actually be observed; instead, we only see the net reaction. Therefore, the mechanism a chemist writes is really a *theory* about what occurs step by step as the reactants are changed to the products.

Because the individual steps in a mechanism usually cannot be observed directly, devising a mechanism for a reaction requires some ingenuity. However, we can immediately tell whether a proposed mechanism is feasible. *The overall rate law derived from the mechanism must agree with the observed rate law for the overall reaction.*

### The rate law for an elementary process can be predicted from the chemical equation for the process

Consider the following elementary process that involves collisions between two identical molecules leading directly to the products shown.



How can we predict the value of the exponent  $x$ ? Suppose the  $NO_2$  concentration were doubled. There would now be *twice* as many individual  $NO_2$  molecules and *each* would have *twice* as many neighbors with which to collide. The number of  $NO_2$ -to- $NO_2$  collisions per second would doubly double—in other words, increase by a factor of 4. This would cause the rate to increase by a factor of 4, which is  $2^2$ . Earlier we saw that when doubling a concentration leads to a fourfold increase in the rate, the concentration of that reactant is raised to the second power in the rate law. Thus, if Equation 13.13 represents an elementary process, its rate law should be

$$\text{Rate} = k[NO_2]^2$$

Notice that the exponent in the rate law for this elementary process is the same as the coefficient in the chemical equation. Similar analyses for other types of elementary processes lead to similar observations and the following statement:

The exponents in the rate law for an elementary process are equal to the coefficients of the reactants in the chemical equation for that elementary process.

Remember that this rule applies only to *elementary processes*. If all we know is the balanced equation for the overall reaction, the only way we can find the exponents of the rate law is by doing experiments.

### The rate law for the slowest step in a mechanism should agree with the experimental rate law

How does the ability to predict the rate law of an elementary process help chemists predict reaction mechanisms? To answer this question, let's look at two reactions and what are believed to be their mechanisms. (There are many other, more complicated systems, and Facets of Chemistry 13.1 describes one type, the free radical chain reaction, that is particularly important.)

■ We double the number of  $NO_2$  molecules and double the number each can collide with, so the collision frequency increases by a factor of 4.

## FACETS OF CHEMISTRY

## 13.1

**Free Radicals, Explosions, Octane Ratings, Aging and Health**

A **free radical** is a very reactive species that contains one or more unpaired electrons. Examples are chlorine atoms formed when a  $\text{Cl}_2$  molecule absorbs a photon (light) of the appropriate energy:



(A dot placed next to the symbol of an atom or molecule represents an unpaired electron and indicates that the particle is a free radical.) The reason free radicals are so reactive is because of the tendency of electrons to become paired through the formation of either ions or covalent bonds.

Free radicals are important in many gaseous reactions, including those responsible for the production of photochemical smog in urban areas. Reactions involving free radicals have useful applications, too. For example, many plastics are made by reactions that take place by mechanisms that involve free radicals. In addition, free radicals play a part in one of the most important processes in the petroleum industry, *thermal cracking*. This reaction is used to break C—C and C—H bonds in long chain hydrocarbons to produce the smaller molecules that give gasoline a higher octane rating. An example is the formation of free radicals in the thermal cracking reaction of butane. When butane is heated to 700–800 °C, one of the major reactions that occurs is



The central C—C bond of butane is shown here as a pair of dots, :, rather than the usual dash. When the bond is broken, the electron pair is divided between the two free radicals that are formed. This reaction produces two ethyl radicals,  $\text{CH}_3\text{CH}_2\cdot$ .

Free radical reactions tend to have high initial activation energies because chemical bonds must be broken to form the radicals. Once the free radicals are formed, however, reactions in which they are involved tend to be very rapid.

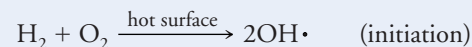
**Free Radical Chain Reactions**

In many cases, a free radical reacts with a reactant molecule to give a product molecule plus another free radical. Reactions that involve such a step are called **chain reactions**.

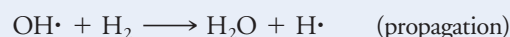
Many explosive reactions are chain reactions involving free radical mechanisms. One of the most studied reactions of this type is the formation of water from

hydrogen and oxygen. The elementary processes involved can be described according to their roles in the mechanism.

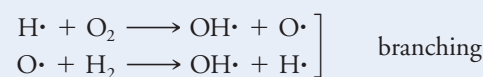
The reaction begins with an **initiation step** that gives free radicals.



The chain continues with a **propagation step**, which produces the product plus another free radical.

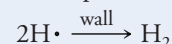


The reaction of  $\text{H}_2$  and  $\text{O}_2$  is explosive because the mechanism also contains **branching steps**.



Thus, the reaction of one  $\text{H}\cdot$  with  $\text{O}_2$  leads to the net production of two  $\text{OH}\cdot$  plus an  $\text{O}\cdot$ . Every time an  $\text{H}\cdot$  reacts with oxygen, then, there is an increase in the number of free radicals in the system. The free radical concentration grows rapidly, and the reaction rate becomes explosively fast.

Chain mechanisms also contain **termination steps**, which remove free radicals from the system. In the reaction of  $\text{H}_2$  and  $\text{O}_2$ , the wall of the reaction vessel serves to remove  $\text{H}\cdot$ , which tends to halt the chain process.

**Free Radicals and Aging**

Direct experimental evidence also exists for the presence of free radicals in functioning biological systems. These highly reactive species play many roles, but one of the most interesting is their apparent involvement in the aging process. One theory suggests that free radicals attack protein molecules in

collagen. Collagen is composed of long strands of fibers of proteins and is found throughout the body, especially in the flexible tissues of the lungs, skin, muscles, and blood vessels. Attack by free radicals seems to lead to cross-linking between these fibers, which stiffens them and makes them less flexible. The most readily observable result of this is the stiffening and hardening of the skin that accompanies aging or too much sunbathing.

People exposed to sunlight over long periods, like this woman from Nepal (a small country between India and Tibet), tend to develop wrinkles because ultraviolet radiation causes changes in their skin. (*Alison Wright/Corbis*)



## 554 Chapter 13 Kinetics: The Study of Rates of Reaction

**Free Radicals and Health**

Around 1987 evidence began to surface identifying a stable free radical, nitrogen monoxide (nitric oxide, NO), as a key inorganic molecule controlling a variety of biological functions, from the chemiluminescent flash of a firefly to beneficial effects in the human body. Amyl nitrate and nitroglycerine have been used medicinally since the early 1900s, and NO is apparently the metabolic product that makes these substances effective drugs. Currently, at an estimated rate of 3000 research

papers per year, the discoveries of the functions of NO have become major medical milestones of the 21st century. For example, this very simple, diatomic molecule can be used to treat high blood pressure, angina, pulmonary hypertension, breathing problems in newborn babies, erectile dysfunction, and even Alzheimer's and Parkinson's disease. Discovery of the effects of NO and its possible therapeutic applications led to the 1998 Nobel Prize in Medicine honoring Robert Furchgott, Louis Ignarro, and Ferid Murad.

First, consider the gaseous reaction

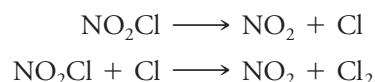


Experimentally, the rate is first order in  $\text{NO}_2\text{Cl}$ , so the rate law is

$$\text{Rate} = k[\text{NO}_2\text{Cl}] \quad (\text{experimental})$$

The first question we might ask is, Could the overall reaction (Equation 13.14) occur in a single step by the collision of two  $\text{NO}_2\text{Cl}$  molecules? The answer is no, because then it would be an elementary process and the rate law predicted for it would include a squared term,  $[\text{NO}_2\text{Cl}]^2$ . But the experimental rate law is first order in  $\text{NO}_2\text{Cl}$ . So the predicted and experimental rate laws don't agree, and we must look further to find the mechanism of the reaction.

On the basis of chemical intuition and other information that we won't discuss here, chemists believe the actual mechanism of the reaction in Equation 13.14 is the following two-step sequence of elementary processes.



■ The Cl atom formed here is called a *reactive intermediate*. We never actually observe the Cl because it reacts so quickly.

Notice that when the two reactions are added, the *intermediate*, Cl, drops out and we obtain the net overall reaction given in Equation 13.14. *Being able to add the elementary processes and thus to obtain the overall reaction is another major test of a mechanism.*

In any multistep mechanism, one step is usually much slower than the others. In this mechanism, for example, it is believed that the first step is slow and that once a Cl atom forms, it reacts very rapidly with another  $\text{NO}_2\text{Cl}$  molecule to give the final products.

The final products of a multistep reaction cannot appear faster than the products of the slow step, so the slow step in a mechanism is called the **rate-determining step** or the **rate-limiting step**. In the two-step mechanism above, then, the first reaction is the rate-determining step because the final products can't be formed faster than the rate at which Cl atoms form.

The rate-determining step is similar to a slow worker on an assembly line. The production rate depends on how quickly the slow worker works, regardless of how fast the other workers are. The factors that control the speed of the rate-determining step therefore also control the overall rate of the reaction. This means that *the rate law for the rate-determining step is directly related to the rate law for the overall reaction.*

Because the rate-determining step is an elementary process, we can predict its rate law from the coefficients of its reactants. The coefficient of  $\text{NO}_2\text{Cl}$  in its relatively slow breakdown to  $\text{NO}_2$  and Cl is 1. Therefore, the rate law predicted for the first step is

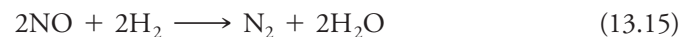
$$\text{Rate} = k[\text{NO}_2\text{Cl}] \quad (\text{predicted})$$

Notice that the predicted rate law derived for the two-step mechanism agrees with the experimentally measured rate law. Although this doesn't *prove* that the mechanism is

### 13.7 Experimental Rate Laws Can Be Used to Support or Reject Proposed Mechanisms for a Reaction 555

correct, it does provide considerable support for it. From the standpoint of kinetics, therefore, the mechanism is reasonable.

The second reaction mechanism that we will study is that of the following gas-phase reaction.

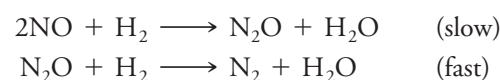


The experimentally determined rate law is

$$\text{Rate} = k[\text{NO}]^2[\text{H}_2] \quad (\text{experimental})$$

We can quickly tell from this rate law that Equation 13.15 could *not* itself be an elementary process. If it were, the exponent for  $[\text{H}_2]$  would have to be 2. Obviously, a mechanism involving two or more steps must be involved.

A chemically reasonable mechanism that yields the correct form for the rate law consists of the following two steps.

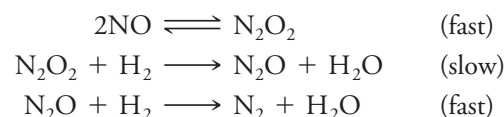


One test of the mechanism, as we said, is that the two equations must add to give the correct overall equation; and they do. Further, the chemistry of the second step has actually been observed in separate experiments.  $\text{N}_2\text{O}$  is a known compound, and it does react with  $\text{H}_2$  to give  $\text{N}_2$  and  $\text{H}_2\text{O}$ . Another test of the mechanism involves the coefficients of  $\text{NO}$  and  $\text{H}_2$  in the predicted rate law for the first step, the supposed rate-determining step.

$$\text{Rate} = k[\text{NO}]^2[\text{H}_2] \quad (\text{predicted})$$

This rate equation does match the experimental rate law, but there is still a serious flaw in the proposed mechanism. If the postulated slow step actually describes an elementary process, it would involve the simultaneous collision between three molecules, two  $\text{NO}$  and one  $\text{H}_2$ . A three-way collision is so unlikely that if it were really involved in the mechanism, the overall reaction would be extremely slow. Reaction mechanisms seldom include elementary processes that involve more than two-body or **bimolecular collisions**.

Chemists believe the reaction in Equation 13.15 proceeds by the following three-step sequence of bimolecular elementary processes.



In this mechanism the first step is proposed to be a rapidly established equilibrium in which the unstable intermediate  $\text{N}_2\text{O}_2$  forms in the forward reaction and then quickly decomposes into  $\text{NO}$  by the reverse reaction. The rate-determining step is the reaction of  $\text{N}_2\text{O}_2$  with  $\text{H}_2$  to give  $\text{N}_2\text{O}$  and a water molecule. The third step is the reaction mentioned above. Once again, notice that the three steps add to give the net overall change.

Since the second step is rate determining, the rate law for the reaction should match the rate law for this step. We predict this to be

$$\text{Rate} = k[\text{N}_2\text{O}_2][\text{H}_2] \quad (13.16)$$

However, the experimental rate law does not contain the species  $\text{N}_2\text{O}_2$ . Therefore, we must find a way to express the concentration of  $\text{N}_2\text{O}_2$  in terms of the reactants in the overall reaction. To do this, let's look closely at the first step of the mechanism, which we view as a reversible reaction.

The rate in the forward direction, in which  $\text{NO}$  is the reactant, is

$$\text{Rate (forward)} = k_f[\text{NO}]^2$$

The rate of the reverse reaction, in which  $\text{N}_2\text{O}_2$  is the reactant, is

$$\text{Rate (reverse)} = k_r[\text{N}_2\text{O}_2]$$

■ The occurrence of  $\text{N}_2\text{O}_2$  as an intermediate in the proposed mechanism can only be surmised. The compound is never present at a detectable concentration because, as supposed, it's too unstable.

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▣ Recall that in a dynamic equilibrium forward and reverse reactions occur at equal rates.

If we view this as a dynamic equilibrium, then the rate of the forward and reverse reactions are equal, which means that

$$k_f[\text{NO}]^2 = k_r[\text{N}_2\text{O}_2] \quad (13.17)$$

Since we would like to eliminate  $\text{N}_2\text{O}_2$  from the rate law in Equation 13.16, let's solve Equation 13.17 for  $[\text{N}_2\text{O}_2]$ .

$$[\text{N}_2\text{O}_2] = \frac{k_f}{k_r}[\text{NO}]^2$$

Substituting into the rate law in Equation 13.16 yields

$$\text{Rate} = k \left( \frac{k_f}{k_r} \right) [\text{NO}]^2 [\text{H}_2]$$

Combining all the constants into one ( $k'$ ) gives

$$\text{Rate} = k' [\text{NO}]^2 [\text{H}_2] \quad (\text{predicted})$$

▣ There are many reactions that do not follow simple first- or second-order rate laws and have mechanisms far more complex than those studied in this section. Even so, their more complex kinetics still serve as clues to their complex set of elementary processes.

Now the rate law derived from the mechanism matches the rate law obtained experimentally. The three-step mechanism does appear to be reasonable on the basis of kinetics.

The procedure we have worked through here applies to many reactions that proceed by mechanisms involving sequential steps. Steps that precede the rate-determining step are considered to be rapidly established equilibria involving unstable intermediates.

#### A proposed mechanism must always account for the experimental rate law

Although chemists may devise other experiments to help prove or disprove the correctness of a mechanism, one of the strongest pieces of evidence is the experimentally measured rate law for the overall reaction. No matter how reasonable a particular mechanism may appear, if its elementary processes cannot yield a predicted rate law that matches the experimental one, the mechanism is wrong and must be discarded.

**Practice Exercise 26:** Select the reactions below that may be elementary processes. For those not selected explain why they are not likely to be elementary processes.

- $2\text{N}_2\text{O}_5 \longrightarrow 2\text{N}_2\text{O}_4 + \text{O}_2$
- $\text{NO} + \text{O}_3 \longrightarrow \text{NO}_2 + \text{O}_2$
- $2\text{NO} + \text{H}_2 \longrightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$
- $\text{C}_3\text{H}_8(g) + 5\text{O}_2(g) \longrightarrow 3\text{CO}_2(g) + 4\text{H}_2\text{O}(g)$
- $\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \longrightarrow \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6$
- $3\text{H}_2 + \text{N}_2 \longrightarrow 2\text{NH}_3$

(Hint: How many molecules are likely to collide at exactly the same time?)

**Practice Exercise 27:** Ozone,  $\text{O}_3$ , reacts with nitric oxide,  $\text{NO}$ , to form nitrogen dioxide and oxygen.



This is one of the reactions involved in the formation of photochemical smog. If this reaction occurs in a single step, what is the expected rate law for the reaction?

**Practice Exercise 28:** The mechanism for the decomposition of  $\text{NO}_2\text{Cl}$  is



What would the predicted rate law be if the second step in the mechanism were the rate-determining step?

## 13.8 Catalysts Change Reaction Rates by Providing Alternative Paths Between Reactants and Products 557

### 13.8 CATALYSTS CHANGE REACTION RATES BY PROVIDING ALTERNATIVE PATHS BETWEEN REACTANTS AND PRODUCTS

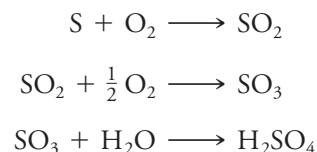
A **catalyst** is a substance that changes the rate of a chemical reaction without itself being used up. In other words, all of the catalyst added at the start of a reaction is present chemically unchanged after the reaction has gone to completion. The action caused by a catalyst is called **catalysis**. Broadly speaking, there are two kinds of catalysts. *Positive catalysts* speed up reactions, and *negative catalysts*, usually called *inhibitors*, slow reactions down. After this, when we use “catalyst” we’ll mean positive catalyst, the usual connotation.

Although the catalyst is not part of the overall reaction, it does participate by changing the mechanism of the reaction. The catalyst provides a path to the products that has a rate-determining step with a lower activation energy than that of the uncatalyzed reaction (see Figure 13.16). Because the activation energy along this new route is lower, a greater fraction of the collisions of the reactant molecules have the minimum energy needed to react, so the reaction proceeds faster.

Catalysts can be divided into two groups—**homogeneous catalysts**, which exist in the same phase as the reactants, and **heterogeneous catalysts**, which exist in a separate phase.

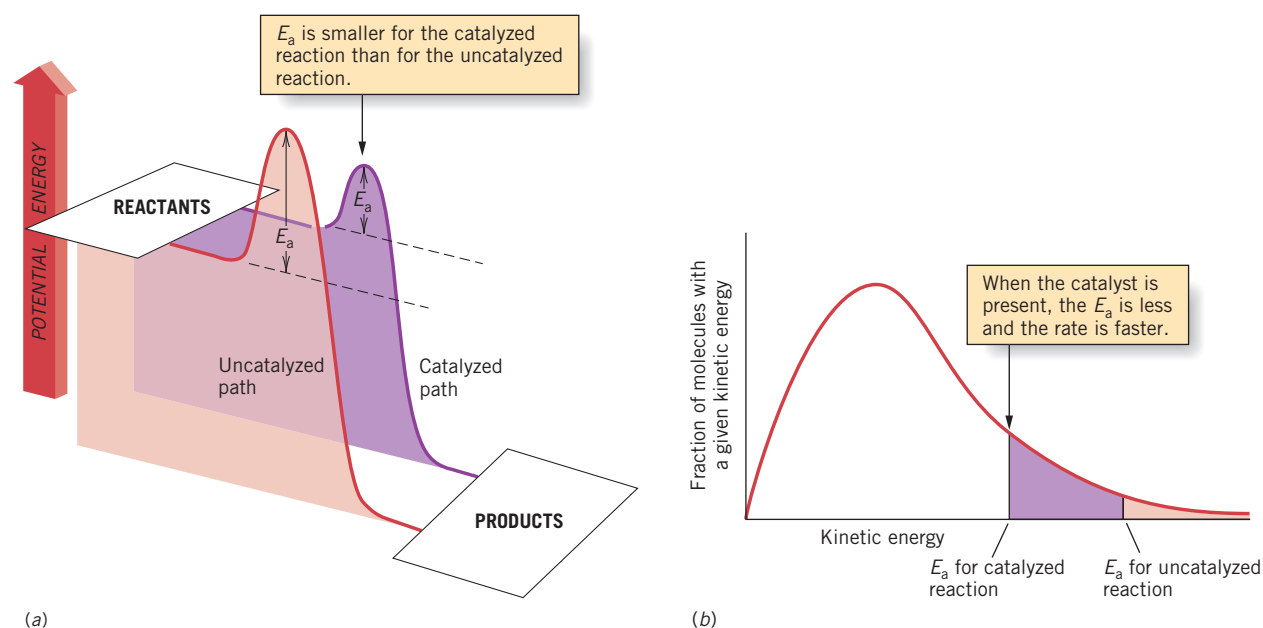
#### Homogeneous catalysts are in the same phase as the reactants

An example of homogeneous catalysis is found in the now outdated *lead chamber process* for manufacturing sulfuric acid. To make sulfuric acid by this process, sulfur is burned to give  $\text{SO}_2$ , which is then oxidized to  $\text{SO}_3$ . The  $\text{SO}_3$  is dissolved in water as it forms to give  $\text{H}_2\text{SO}_4$ .



Unassisted, the second reaction, oxidation of  $\text{SO}_2$  to  $\text{SO}_3$ , occurs slowly. In the lead chamber process, the  $\text{SO}_2$  is combined with a mixture of  $\text{NO}$ ,  $\text{NO}_2$ , air, and steam in large lead-lined reaction chambers. The  $\text{NO}_2$  readily oxidizes the  $\text{SO}_2$  to give  $\text{NO}$  and  $\text{SO}_3$ . The  $\text{NO}$  is then reoxidized to  $\text{NO}_2$  by oxygen.

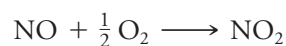
■ In the modern process for making sulfuric acid, the contact process, vanadium(V) oxide,  $\text{V}_2\text{O}_5$ , is a heterogeneous catalyst that promotes the oxidation of sulfur dioxide to sulfur trioxide.



**FIG. 13.16** Effect of a catalyst on a reaction. (a) The catalyst provides an alternative, low-energy path from the reactants to the products. (b) A larger fraction of molecules have sufficient energy to react when the catalyzed path is available.

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□ The  $\text{NO}_2$  is regenerated in the second reaction and so is recycled over and over. Thus, only small amounts of it are needed in the reaction mixture to do an effective catalytic job.

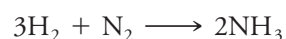


The  $\text{NO}_2$  serves as a catalyst by being an oxygen carrier and by providing a low-energy path for the oxidation of  $\text{SO}_2$  to  $\text{SO}_3$ . Notice, as must be true for any catalyst, the  $\text{NO}_2$  is regenerated; it has not been permanently changed.

### Heterogeneous catalysts are in a separate phase from the reactants

□ **Adsorption** means that molecules bind to a surface.

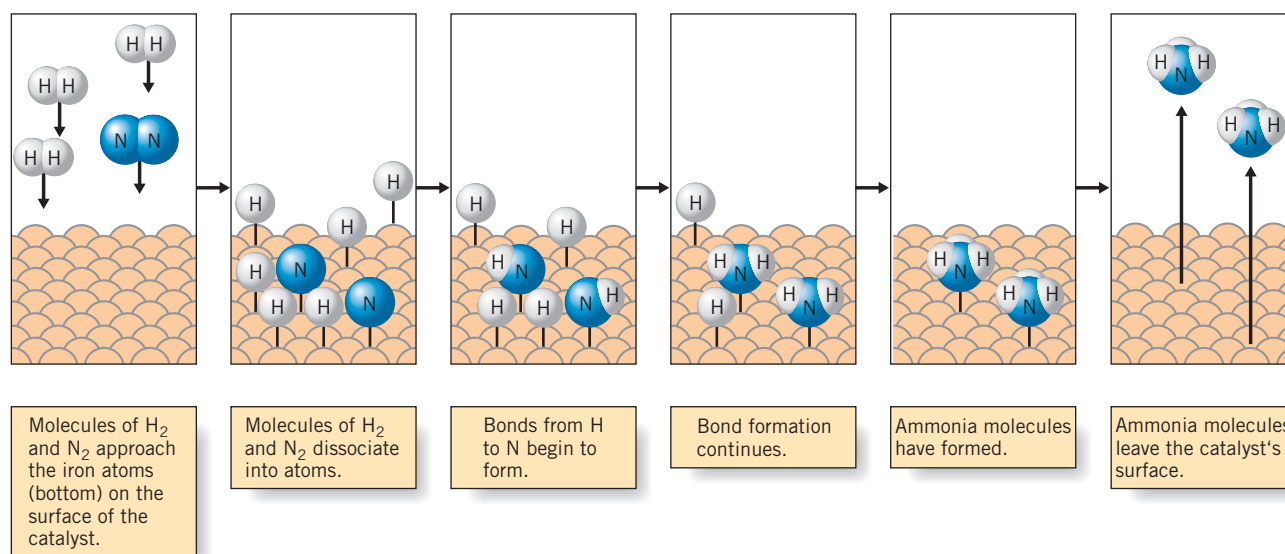
A heterogeneous catalyst is commonly a solid, and it usually functions by promoting a reaction on its surface. One or more of the reactant molecules are adsorbed onto the surface of the catalyst where an interaction with the surface increases their reactivity. An example is the synthesis of ammonia from hydrogen and nitrogen by the Haber process.



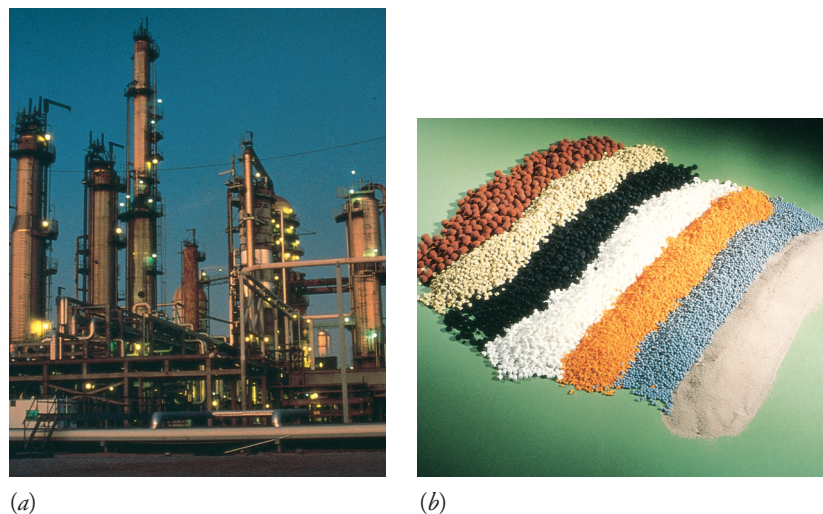
The reaction takes place on the surface of an iron catalyst that contains traces of aluminum and potassium oxides. It is thought that hydrogen molecules and nitrogen molecules dissociate while being held on the catalytic surface. The hydrogen atoms then combine with the nitrogen atoms to form ammonia. Finally, the completed ammonia molecule breaks away, freeing the surface of the catalyst for further reaction. This sequence of steps is illustrated in Figure 13.17.

Heterogeneous catalysts are used in many important commercial processes. The petroleum industry uses heterogeneous catalysts to crack hydrocarbons into smaller fragments and then re-form them into the useful components of gasoline (see Figure 13.18). The availability of such catalysts allows refineries to produce gasoline, jet fuel, or heating oil from crude oil in any ratio necessary to meet the demands of the marketplace.

A vehicle that uses unleaded gasoline is equipped with a catalytic converter (Figure 13.19) designed to lower the concentrations of exhaust gas pollutants, such as carbon monoxide, unburned hydrocarbons, and nitrogen oxides. The catalysts are nanometer size particles of platinum, ruthenium, and rhodium dispersed in a honeycomb of a high temperature ceramic. The large ratio of surface area to mass enables the catalytic converter to react large volumes of exhaust efficiently. Air is introduced into the exhaust stream that then passes over a catalyst that adsorbs  $\text{CO}$ ,  $\text{NO}$ , and  $\text{O}_2$ . The  $\text{NO}$  dissociates into  $\text{N}$  and  $\text{O}$  atoms, and the  $\text{O}_2$  also dissociates into atoms. Pairing of nitrogen



**FIG. 13.17** The Haber process. Catalytic formation of ammonia molecules from hydrogen and nitrogen occurs on the surface of a catalyst.



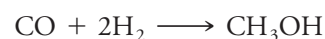
**FIG. 13.18** Catalysts are very important in the petroleum industry. (a) Catalytic cracking towers at a Standard Oil refinery. (b) A variety of catalysts are available as beads, powders, or in other forms for various refinery operations. (Courtesy American Petroleum Institute/Courtesy Englehard Corporation)

atoms then produces  $N_2$ , and oxidation of  $CO$  by oxygen atoms produces  $CO_2$ . Unburned hydrocarbons are also oxidized to  $CO_2$  and  $H_2O$ . The catalysts in catalytic converters are deactivated or “poisoned” by lead-based octane boosters like tetraethyl lead  $[Pb(C_2H_5)_4]$ . “Leaded” gasoline was finally banned in 1995. Leaded gasoline also posed an environmental hazard from the lead emitted in automobile exhaust.

The poisoning of catalysts is also a major problem in many industrial processes. Methyl alcohol (methanol,  $CH_3OH$ ), for example, is a promising fuel that can be made from coal and steam by the reaction



followed by



A catalyst for the second step is copper(I) ion held in solid solution with zinc oxide. However, traces of sulfur, a contaminant in coal, must be avoided because sulfur reacts with the catalyst and destroys its catalytic activity.

### Enzymes are biological catalysts

In living systems, complex protein-based molecules called **enzymes** catalyze almost every reaction that occurs in living cells. Enzymes contain a specially shaped area called an active site that lowers the energy of the transition state of the reaction being catalyzed. This causes the reaction rate to increase significantly. Many poisons have been shown to work by blocking important enzyme systems. Heavy metals bind to sulfur-containing groups and distort the active site. Molecular modeling is used to design drug molecules to have optimum shapes to fit enzymatic active sites.



**FIG. 13.19** A modern catalytic converter of the type used in about 80% of new cars. Part of the converter has been cut away to reveal the porous ceramic material that serves as the support for the catalyst. (Courtesy AC Spark Plug)

## SUMMARY

**Reaction Rates.** The speeds or **rates** of reactions are controlled by five factors: (1) the nature of the reactants, (2) the ability of reactants to meet, (3) the concentrations of the reactants, (4) the temperature, and (5) the presence of catalysts. The rates of **heterogeneous reactions** are determined largely by the area of contact between the phases; the rates of **homogeneous reactions** are determined by the concentrations of the reactants. The rate is

measured by monitoring the change in reactant or product concentrations with time.

$$\text{Rate} = \Delta(\text{concentration})/\Delta(\text{time})$$

In any chemical reaction, the rates of formation of products and the rates of disappearance of reactants are related by the coefficients of the balanced overall chemical equation.

## 560 Chapter 13 Kinetics: The Study of Rates of Reaction

**Rate Laws.** The **rate law** for a reaction relates the reaction rate to the molar concentrations of the reactants. The rate is proportional to the product of the molar concentrations of the reactants, each raised to an appropriate power. These exponents must be determined by experiments in which the concentrations are varied and the effects of the variations on the rate are measured. The proportionality constant,  $k$ , is called the **rate constant**. Its value depends on temperature but not on the concentrations of the reactants. The sum of the exponents in the rate law is the **order** (or overall order) of the reaction.

**Concentration and Time.** Equations exist that relate the concentration of a reactant at a given time  $t$  to the initial concentration and the rate constant. The time required for half of a reactant to disappear is the **half-life**,  $t_{1/2}$ . For a first-order reaction, the half-life is a constant that depends only on the rate constant for the reaction; it is independent of the initial concentration. The half-life for a second-order reaction is inversely proportional both to the initial concentration of the reactant and to the rate constant.

**Theories of Reaction Rate.** According to **collision theory**, the rate of a reaction depends on the number per second of **effective collisions** of the reactant particles, which is only an extremely small fraction of the total number of collisions per second. This fraction is so small partly because the reactant molecules must be suitably oriented, but mostly because the colliding molecules must jointly possess a minimum molecular kinetic energy called the **activation energy**,  $E_a$ . As the temperature increases, a larger fraction of the collisions have this necessary energy, making more collisions effective each second and the reaction faster.

**Transition state theory** visualizes how the energies of molecules and the orientations of their nuclei interact as they collide. In this theory, the energy of activation is viewed as an energy barrier on the reaction's potential energy diagram. The *heat of reaction* is the net potential energy difference between the reactants

and the products. In reversible reactions, the values of  $E_a$  for both the forward and reverse reactions can be identified on an energy diagram. The species at the high point on an energy diagram is the **activated complex** and is said to be in the **transition state**.

**Determining the Activation Energy.** The **Arrhenius equation** lets us see how changes in activation energy and temperature affect a rate constant. The Arrhenius equation also lets us determine  $E_a$  either graphically or by a calculation using the appropriate form of the Arrhenius equation. The calculation requires two rate constants determined at two temperatures. The graphical method uses more values of rate constants at more temperatures and thus usually yields more accurate results. The activation energy and the rate constant at one temperature can be used to calculate the rate constant at another temperature.

**Reaction Mechanisms.** The detailed sequence of elementary processes that lead to the net chemical change is the **mechanism** of the reaction. Since intermediates usually cannot be detected, the mechanism is a theory. Support for a mechanism comes from matching the predicted rate law for the mechanism with the rate law obtained from experimental data. For the **rate-determining step** or for any **elementary process** the corresponding rate law has exponents equal to the coefficients in the balanced equation for the elementary process.

**Catalysts.** **Catalysts** are substances that change a reaction rate but are not consumed by the reaction. Negative catalysts inhibit reactions. Positive catalysts provide alternative paths for reactions for which at least one step has a smaller activation energy than the uncatalyzed reaction. **Homogeneous catalysts** are in the same phase as the reactants. **Heterogeneous catalysts** provide a path of lower activation energy by having a surface on which the reactants are adsorbed and react. Catalysts in living systems are called **enzymes**.



## TOOLS FOR PROBLEM SOLVING

In this chapter you learned to apply the following concepts as tools in solving problems dealing with aspects of chemical kinetics. Study each tool 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. Remember that at times tools from previous chapters will be needed along with the new ones in this chapter.

**Rate law of a reaction** (page 526) A rate law allows us to calculate the rate of reaction for a given set of reactant concentrations. It also serves as a guide in devising reasonable reaction mechanisms. Exponents for the concentrations in the rate law are always determined experimentally as described on page 529. Rate constants determined at different temperatures are used in the Arrhenius equation described below.

$$\text{Rate} = k[A]^n[B]^m$$

**Integrated first-order rate law** (page 534) For a first-order reaction with known  $k$ , this equation is used when we need to calculate the concentration of a reactant at some specified time after the start of the reaction. We could also calculate the time required for the concentration to drop to some specified value. This equation is also used for carbon-14 dating of organic materials.

$$\ln \frac{[A]_0}{[A]_t} = kt$$

**Integrated second-order rate law** (page 540) For a second-order reaction of the form,  $\text{Rate} = k[B]^2$ , with known  $k$ , this equation is used to calculate the concentration of a reactant at some specified time after the start of the reaction, or the time required for the concentration to drop to some specified value.

$$\frac{1}{[B]_t} - \frac{1}{[B]_0} = kt$$

**Half-lives of a first-order reaction** (page 537) This equation relates the rate constant to the half-life,  $t_{1/2}$ , for first-order reactions. Use of half-lives can be a convenient alternative to the integrated first-order rate law to determine the concentration of a reactant after it has reacted for a whole number of number of half-lives. The amount of reactant left after  $n$  half-lives is equal to  $(1/2)^n$ .

$$\ln 2 = kt_{1/2}$$

**Arrhenius equation** (pages 548 and 550) This equation relates the rate constant,  $k$ , to the activation energy,  $E_a$ , and temperature. Activation energies are determined by measuring rate constants at a variety of temperatures and graphically analyzing the data (see page 549). This equation is also used to determine the shelf life of a wide variety of consumer products.

$$k = A e^{-E_a/RT} \quad \ln \left( \frac{k_2}{k_1} \right) = \frac{-E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

## 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](http://www.wiley.com/college/brady). OH = an Office Hours video is available for this problem.

### REVIEW QUESTIONS

#### Factors That Affect Reaction Rate

**13.1** Give an example from everyday experience of (a) a very fast reaction, (b) a moderately fast reaction, and (c) a slow reaction.

**13.2** Suppose we compared two reactions, one requiring the simultaneous collision of three molecules and the other requiring a collision between two molecules. From the standpoint of statistics, and all other factors being equal, which reaction should be faster? Explain your answer.

**13.3** How does an instantaneous rate of reaction differ from an average rate of reaction?

**13.4** Explain how the initial instantaneous rate of reaction can be determined from experimental concentration versus time data.

**13.5** What is a *homogeneous reaction*? What is a *heterogeneous reaction*? Give examples.

**13.6** Why are chemical reactions usually carried out in solution?

**13.7** What is the major factor that affects the rate of a heterogeneous reaction?

**13.8** How does particle size affect the rate of a heterogeneous reaction? Why?

**13.9** The rate of hardening of epoxy glue depends on the amount of hardener that is mixed into the glue. What factor affecting reaction rates does this illustrate?

**13.10** A Polaroid instant photograph develops faster if it's kept warm than if it is exposed to cold. Why?

**13.11** Insects have no way of controlling their body temperatures like mammals do. In cool weather, they become sluggish and move less quickly. How can this be explained using the principles developed in this chapter?

**13.12** On the basis of what you learned in Chapter 11, why do foods cook faster in a pressure cooker than in an open pot of boiling water?

**13.13** Persons who have been submerged in very cold water and who are believed to have drowned sometimes can be revived. On the other hand, persons who have been submerged in warmer water for the same length of time have died. Explain this in terms of factors that affect the rates of chemical reactions.

#### Concentration and Rate; Rate Laws

**13.14** What are the units of reaction rate?

**13.15** What are the units of the rate constant for (a) a first-order reaction, (b) a second-order reaction, and (c) a zero-order reaction?

**13.16** How does the dependence of reaction rate on concentration differ between a zero-order and a first-order reaction?

**13.17** Is there any way of using the coefficients in the balanced overall equation for a reaction to predict with certainty what the exponents are in the rate law?

**13.18** If the concentration of a reactant is doubled and the reaction rate is unchanged, what must be the order of the reaction with respect to that reactant?

**13.19** If the concentration of a reactant is doubled and the reaction rate doubles, what must be the order of the reaction with respect to that reactant?

**13.20** If the concentration of a reactant is doubled, by what factor will the rate increase if the reaction is second order with respect to that reactant?

**13.21** In an experiment, the concentration of a reactant was tripled. The rate increased by a factor of 27. What is the order of the reaction with respect to that reactant?

**13.22** Biological reactions usually involve the interaction of an enzyme with a *substrate*, the substance that actually undergoes the chemical change. In many cases, the rate of reaction depends on the concentration of the enzyme but is independent of the substrate concentration. What is the order of the reaction with respect to the substrate in such instances?

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**13.23** A reaction has the following rate law:

$$\text{Rate} = k[A]^2[B][C]$$

What are the units of the rate constant,  $k$ ?

## Concentration and Time, Half-lives

**13.24** How is the half-life of a first-order reaction affected by the initial concentration of the reactant?

**13.25** How is the half-life of a second-order reaction affected by the initial reactant concentration?

**13.26** Derive the equations for  $t_{1/2}$  for first- and second-order reactions from Equations 13.3 and 13.8, respectively.

**13.27** The integrated rate law for a zero-order reaction is

$$[A]_t - [A]_0 = -kt$$

Derive an equation for the half-life of a zero-order reaction.

## Effect of Temperature on Rate

**13.28** What is the basic postulate of collision theory?

**13.29** What two factors influence the effectiveness of molecular collisions in producing chemical change?

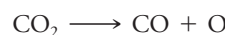
**13.30** In terms of the kinetic theory, why does an increase in temperature increase the reaction rate?

**13.31** Draw the potential energy diagram for an endothermic reaction. Indicate on the diagram the activation energy for both the forward and reverse reactions. Also indicate the heat of reaction.

**13.32** Explain, in terms of the law of conservation of energy, why an endothermic reaction leads to a cooling of the reaction mixture (provided heat cannot enter from outside the system).

**13.33** Draw a potential energy diagram for an exothermic reaction and indicate on the diagram the location of the transition state.

**13.34** The decomposition of carbon dioxide,



has a very large activation energy of approximately  $460 \text{ kJ mol}^{-1}$ . Explain why this is consistent with a mechanism that involves the breaking of a  $\text{C}=\text{O}$  bond.

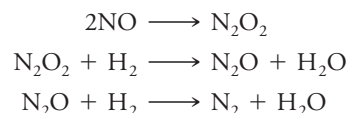
## Reaction Mechanisms

**13.35** What is the definition of an *elementary process*? How are elementary processes related to the mechanism of a reaction?

**13.36** What is a *rate-determining step*?

**13.37** In what way is the rate law for a reaction related to the rate-determining step?

**13.38** A reaction has the following mechanism.

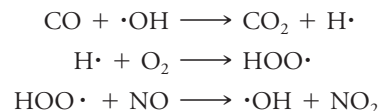


What is the net overall change that occurs in this reaction? Identify any intermediates in the reaction.

**13.39** If the reaction  $\text{NO}_2 + \text{CO} \longrightarrow \text{NO} + \text{CO}_2$  occurs by a one-step collision process, what would be the expected rate law

for the reaction? The actual rate law is  $\text{Rate} = k[\text{NO}_2]^2$ . Could the reaction actually occur by a one-step collision between  $\text{NO}_2$  and  $\text{CO}$ ? Explain.

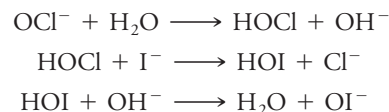
**13.40** Oxidation of  $\text{NO}$  to  $\text{NO}_2$ —one of the reactions in the production of smog—appears to involve carbon monoxide. A possible mechanism is



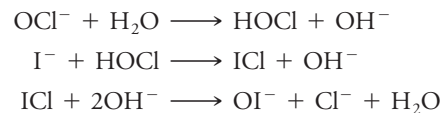
(The formulas with dots represent extremely reactive species with unpaired electrons and are called *free radicals*.) Write the net chemical equation for the reaction.

**13.41** Show that the following two mechanisms give the same net overall reaction.

## Mechanism 1



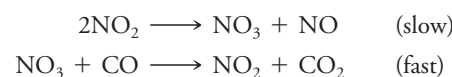
## Mechanism 2



**13.42** The experimental rate law for the reaction



is  $\text{rate} = k[\text{NO}_2]^2$ . If the mechanism is



show that the predicted rate law is the same as the experimental rate law.

## Catalysts

**13.43** How does a catalyst increase the rate of a chemical reaction?

**13.44** What is a *homogeneous catalyst*? How does it function, in general terms?

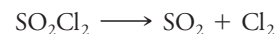
**13.45** What is the difference in meaning between the terms *adsorption* and *absorption*? (If necessary, use a dictionary.) Which one applies to heterogeneous catalysts?

**13.46** What does the catalytic converter do in the exhaust system of an automobile? Why should leaded gasoline not be used in cars equipped with catalytic converters?

## REVIEW PROBLEMS

## Measuring Rates of Reaction

**13.47** The following data were collected at a certain temperature for the decomposition of sulfuryl chloride,  $\text{SO}_2\text{Cl}_2$ , a chemical used in a variety of organic syntheses.



Time (min)	[SO <sub>2</sub> Cl <sub>2</sub> ] (mol L <sup>-1</sup> )
0	0.1000
100	0.0876
200	0.0768
300	0.0673
400	0.0590
500	0.0517
600	0.0453
700	0.0397
800	0.0348
900	0.0305
1000	0.0267
1100	0.0234

Make a graph of concentration versus time and determine the rate of formation of SO<sub>2</sub> at  $t = 200$  minutes and  $t = 600$  minutes.

**13.48** The following data were collected for the decomposition of acetaldehyde, CH<sub>3</sub>CHO (used in the manufacture of a variety of chemicals including perfumes, dyes, and plastics), into methane and carbon monoxide. The data were collected at a temperature of 530 °C.

$$\text{CH}_3\text{CHO} \longrightarrow \text{CH}_4 + \text{CO}$$

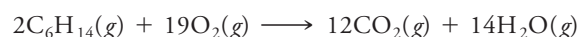
[CH <sub>3</sub> CHO] (mol L <sup>-1</sup> )	Time (s)
0.200	0
0.153	20
0.124	40
0.104	60
0.090	80
0.079	100
0.070	120
0.063	140
0.058	160
0.053	180
0.049	200

Make a graph of concentration versus time and determine the rate of reaction of CH<sub>3</sub>CHO after 60 seconds and after 120 seconds.

**13.49** In the reaction  $3\text{H}_2 + \text{N}_2 \longrightarrow 2\text{NH}_3$ , how does the rate of disappearance of hydrogen compare to the rate of disappearance of nitrogen? How does the rate of appearance of NH<sub>3</sub> compare to the rate of disappearance of nitrogen?

**OH 13.50** For the reaction  $2A + B \longrightarrow 3C$ , it was found that the rate of disappearance of  $B$  was  $0.30 \text{ mol L}^{-1} \text{ s}^{-1}$ . What were the rate of disappearance of  $A$  and the rate of appearance of  $C$ ?

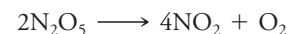
**13.51** In the combustion of hexane (a low-boiling component of gasoline),



it was found that the rate of reaction of C<sub>6</sub>H<sub>14</sub> was  $1.20 \text{ mol L}^{-1} \text{ s}^{-1}$ .

- What was the rate of reaction of O<sub>2</sub>?
- What was the rate of formation of CO<sub>2</sub>?
- What was the rate of formation of H<sub>2</sub>O?

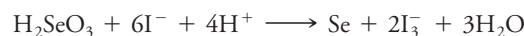
**13.52** At a certain moment in the reaction



N<sub>2</sub>O<sub>5</sub> is decomposing at a rate of  $2.5 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}$ . What are the rates of formation of NO<sub>2</sub> and O<sub>2</sub>?

### Rate Laws for Reactions

**13.53** Estimate the rate of the reaction

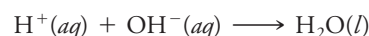


given the rate law for the reaction at 0 °C is

$$\text{Rate} = (5.0 \times 10^5 \text{ L}^5 \text{ mol}^{-5} \text{ s}^{-1})[\text{H}_2\text{SeO}_3][\text{I}^-]^3[\text{H}^+]^2$$

and the reactant concentrations are  $[\text{H}_2\text{SeO}_3] = 2.0 \times 10^{-2} \text{ M}$ ,  $[\text{I}^-] = 2.0 \times 10^{-3} \text{ M}$ , and  $[\text{H}^+] = 1.0 \times 10^{-3} \text{ M}$ .

**13.54** Estimate the rate of the reaction

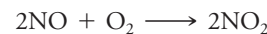


given that the rate law for the reaction is

$$\text{Rate} = (1.3 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1})[\text{OH}^-][\text{H}^+]$$

for neutral water where  $[\text{H}^+] = 1.0 \times 10^{-7} \text{ M}$  and  $[\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$ .

**OH 13.55** The oxidation of NO (released in small amounts in the exhaust of automobiles) produces the brownish-red gas NO<sub>2</sub>, which is a component of urban air pollution.



The rate law for the reaction is  $\text{Rate} = k[\text{NO}]^2[\text{O}_2]$ . At 25 °C,  $k = 7.1 \times 10^9 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$ . What would be the rate of the reaction if  $[\text{NO}] = 0.0010 \text{ mol L}^{-1}$  and  $[\text{O}_2] = 0.034 \text{ mol L}^{-1}$ ?

**13.56** The rate law for the decomposition of N<sub>2</sub>O<sub>5</sub> is

$$\text{Rate} = k[\text{N}_2\text{O}_5]$$

If  $k = 1.0 \times 10^{-5} \text{ s}^{-1}$ , what is the reaction rate when the N<sub>2</sub>O<sub>5</sub> concentration is  $0.0010 \text{ mol L}^{-1}$ ?

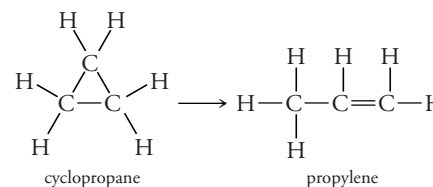
**13.57** The following data were collected for the reaction



Initial Concentrations (mol L <sup>-1</sup> )		Initial rate of reaction
[M]	[N]	(mol L <sup>-1</sup> s <sup>-1</sup> )
0.010	0.010	$2.5 \times 10^{-3}$
0.020	0.010	$5.0 \times 10^{-3}$
0.020	0.030	$4.5 \times 10^{-2}$

What is the rate law for the reaction? What is the value of the rate constant (with correct units)?

**13.58** Cyclopropane, C<sub>3</sub>H<sub>6</sub>, is a gas used as a general anesthetic. It undergoes a slow molecular rearrangement to propylene.



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At a certain temperature, the following data were obtained relating concentration and rate.

Initial Concentration of $C_3H_6$ (mol L <sup>-1</sup> )	Rate of Formation of Propylene (mol L <sup>-1</sup> s <sup>-1</sup> )
0.050	$2.95 \times 10^{-5}$
0.100	$5.90 \times 10^{-5}$
0.150	$8.85 \times 10^{-5}$

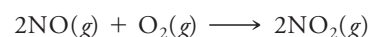
What is the rate law for the reaction? What is the value of the rate constant, with correct units?

**13.59** The reaction of iodide ion with hypochlorite ion,  $OCl^-$  (the active ingredient in a “chlorine bleach” such as Clorox), follows the equation  $OCl^- + I^- \longrightarrow OI^- + Cl^-$ . It is a rapid reaction that gives the following rate data.

Initial Concentrations (mol L <sup>-1</sup> )		Rate of Formation of $Cl^-$ (mol L <sup>-1</sup> s <sup>-1</sup> )
$[OCl^-]$	$[I^-]$	
$1.7 \times 10^{-3}$	$1.7 \times 10^{-3}$	$1.75 \times 10^4$
$3.4 \times 10^{-3}$	$1.7 \times 10^{-3}$	$3.50 \times 10^4$
$1.7 \times 10^{-3}$	$3.4 \times 10^{-3}$	$3.50 \times 10^4$

What is the rate law for the reaction? Determine the value of the rate constant with its correct units.

**13.60** The formation of small amounts of nitric oxide, NO, in automobile engines is the first step in the formation of smog. As noted in Problem 13.55, nitric oxide is readily oxidized to nitrogen dioxide by the reaction



The following data were collected in a study of the rate of this reaction.

Initial Concentrations (mol L <sup>-1</sup> )		Rate of Formation of $NO_2$ (mol L <sup>-1</sup> s <sup>-1</sup> )
$[O_2]$	$[NO]$	
0.0010	0.0010	7.10
0.0040	0.0010	28.4
0.0040	0.0030	255.6

What is the rate law for the reaction? What is the rate constant with its correct units?

**13.61** At a certain temperature the following data were collected for the reaction  $2ICl + H_2 \longrightarrow I_2 + 2HCl$

Initial Concentrations (mol L <sup>-1</sup> )		Initial Rate of Formation of $I_2$ (mol L <sup>-1</sup> s <sup>-1</sup> )
$[ICl]$	$[H_2]$	
0.10	0.10	0.0015
0.20	0.10	0.0030
0.10	0.0500	0.00075

Determine the rate law and the rate constant (with correct units) for the reaction.

**13.62** The following data were obtained for the reaction of  $(CH_3)_3CBr$  with hydroxide ion at 55 °C.



Initial Concentrations (mol L <sup>-1</sup> )		Initial Rate of Formation of $(CH_3)_3COH$ (mol L <sup>-1</sup> s <sup>-1</sup> )
$[(CH_3)_3CBr]$	$[OH^-]$	
0.10	0.10	$1.0 \times 10^{-3}$
0.20	0.10	$2.0 \times 10^{-3}$
0.30	0.10	$3.0 \times 10^{-3}$
0.10	0.20	$1.0 \times 10^{-3}$
0.10	0.30	$1.0 \times 10^{-3}$

What is the rate law for the reaction? What is the value of the rate constant (with correct units) at this temperature?

## Concentration and Time

**13.63** Data for the decomposition of  $SO_2Cl_2$  according to the equation  $SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$  were given in Problem 13.47. Show graphically that these data fit a first-order rate law. Graphically determine the rate constant for the reaction.

**13.64** For the data in Problem 13.48, decide graphically whether the reaction is first or second order. Determine the rate constant for the reaction described in that problem.

**13.65** The decomposition of  $SO_2Cl_2$  described in Problem 13.47 has a first-order rate constant  $k = 2.2 \times 10^{-5} \text{ s}^{-1}$  at 320 °C. If the initial  $SO_2Cl_2$  concentration in a container is 0.0040 M, what will its concentration be (a) after 1.00 hour and (b) after 1.00 day?

**13.66** If it takes 75.0 min for the concentration of a reactant to drop to 20% of its initial value in a first-order reaction, what is the rate constant for the reaction in the units  $\text{min}^{-1}$ ?

**13.67** The concentration of a drug in the body is often expressed in units of milligrams per kilogram of body weight. The initial dose of a drug in an animal was 25.0 mg/kg body weight. After 2.00 hours, this concentration had dropped to 15.0 mg/kg body weight. If the drug is eliminated metabolically by a first-order process, what is the rate constant for the process in units of  $\text{min}^{-1}$ ?

**13.68** In the preceding problem, what must the initial dose of the drug be in order for the drug concentration 3.00 hours afterward to be 5.0 mg/kg body weight?

**13.69** The decomposition of hydrogen iodide follows the equation  $2HI(g) \longrightarrow H_2(g) + I_2(g)$ . The reaction is second order and has a rate constant equal to  $1.6 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$  at 700 °C. If the initial concentration of HI in a container is  $3.4 \times 10^{-2} \text{ M}$ , how many minutes will it take for the concentration to be reduced to  $8.0 \times 10^{-4} \text{ M}$ ?

**13.70** The second-order rate constant for the decomposition of HI at 700 °C was given in the preceding problem. At  $2.5 \times 10^3$  minutes after a particular experiment had begun, the HI concen-



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\*13.88 What percentage of cesium chloride made from cesium-137 ( $t_{1/2}=30$  yr; beta emitter) remains after 150 yr? What chemical product forms?

\*13.89 One of the reactions that occurs in polluted air in urban areas is  $2\text{NO}_2(g) + \text{O}_3(g) \longrightarrow \text{N}_2\text{O}_5(g) + \text{O}_2(g)$ . It is believed that a species with the formula  $\text{NO}_3$  is involved in the mechanism, and the observed rate law for the overall reaction is  $\text{Rate} = k[\text{NO}_2][\text{O}_3]$ . Propose a mechanism for this reaction that includes the species  $\text{NO}_3$  and is consistent with the observed rate law.

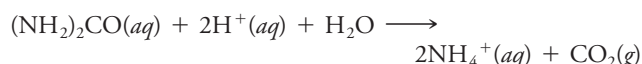
\*13.90 Suppose a reaction occurs with the mechanism



in which the first step is a very rapid reversible reaction that can be considered to be essentially an equilibrium (forward and reverse reactions occurring at the same rate) and the second is a slow step.

- Write the rate law for the forward reaction in step (1).
- Write the rate law for the reverse reaction in step (1).
- Write the rate law for the rate-determining step.
- What is the chemical equation for the net reaction that occurs in this chemical change?
- Use the results of parts (a) and (b) to rewrite the rate law of the rate-determining step in terms of the concentrations of the reactants in the overall balanced equation for the reaction.

OH 13.91 The decomposition of urea,  $(\text{NH}_2)_2\text{CO}$ , in 0.10  $M$  HCl follows the equation



At 60 °C,  $k = 5.84 \times 10^{-6} \text{ min}^{-1}$  and at 70 °C,  $k = 2.25 \times 10^{-5} \text{ min}^{-1}$ . If this reaction is run at 80 °C starting with a urea concentration of 0.0020  $M$ , how many minutes will it take for the urea concentration to drop to 0.0012  $M$ ?

13.92 Show that for a reaction that obeys the general rate law

$$\text{Rate} = k[A]^n$$

a graph of  $\log(\text{rate})$  versus  $\log[A]$  should yield a straight line with a slope equal to the order of the reaction. For the reaction in Problem 13.47, measure the rate of the reaction at  $t = 150, 300, 450,$  and  $600$  s. Then graph  $\log(\text{rate})$  versus  $\log[\text{SO}_2\text{Cl}_2]$  and determine the order of the reaction with respect to  $\text{SO}_2\text{Cl}_2$ .

OH \*13.93 It was mentioned that the rates of many reactions approximately double for each 10 °C rise in temperature. Assuming a starting temperature of 25 °C, what would the activation energy be, in  $\text{kJ mol}^{-1}$ , if the rate of a reaction were to be twice as large at 35 °C?

\*13.94 The development of a photographic image on film is a process controlled by the kinetics of the reduction of silver halide by a developer. The time required for development at a particular temperature is inversely proportional to the rate constant for the process. Below are published data on development times for Kodak's Tri-X film using Kodak D-76 developer. From these data, estimate the activation energy (in units of  $\text{kJ mol}^{-1}$ ) for the development process. Also estimate the development time at 15 °C.

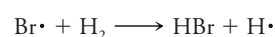
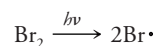
Temperature (°C)	Development Time (minutes)
18	10
20	9
21	8
22	7
24	6

13.95 The rate at which crickets chirp depends on the ambient temperature, because crickets are cold-blooded insects whose body temperature follows the temperature of their environment. It has been found that the Celsius temperature can be estimated by counting the number of chirps in 8 seconds and then adding 4. In other words,  $t_C = (\text{number of chirps in 8 seconds}) + 4$ .

- Calculate the number of chirps in 8 seconds for temperatures of 20, 25, 30, and 35 °C.
- The number of chirps per unit of time is directly proportional to the rate constant for a biochemical reaction involved in the cricket's chirp. On the basis of this assumption, make a graph of  $\ln(\text{chirps in 8 s})$  versus  $(1/T)$ . Calculate the activation energy for the biochemical reaction involved.
- How many chirps would a cricket make in 8 seconds at a temperature of 40 °C?

\*13.96 The cooking of an egg involves the denaturation of a protein called albumen. The time required to achieve a particular degree of denaturation is inversely proportional to the rate constant for the process. This reaction has a high activation energy,  $E_a = 418 \text{ kJ mol}^{-1}$ . Calculate how long it would take to cook a traditional three-minute egg on top of Mt. McKinley in Alaska on a day when the atmospheric pressure there is 355 torr.

\*13.97 The following question is based on Facets of Chemistry 13.1. The reaction of hydrogen and bromine appears to follow the mechanism



- Identify the initiation step in the mechanism.
- Identify any propagation steps.
- Identify the termination step.
- The mechanism also contains the reaction



How does this reaction affect the rate of formation of HBr?

### EXERCISES IN CRITICAL THINKING

13.98 Provide three examples of ordinary occurrences that mimic a reaction mechanism and have a rate-limiting step.

13.99 Can a reaction have a negative activation energy? Explain your response.

## Questions, Problems, and Exercises 567

**13.100** Assume you have a three-step mechanism. Would the potential energy diagram have three peaks? If so, how would you distinguish the rate-limiting step?

**13.101** What range of ages can C-14 dating reliably determine?

**13.102** Why are initial reaction rates used to determine rate laws?

**13.103** If a reaction is reversible (i.e., the products can react to re-form the reactants) what would the rate law look like?

**\*13.104** The ozone layer protects us from high energy radiation. Description of the ozone layer is a kinetics problem concerning the formation and destruction of ozone to produce a steady state. How can we write this mathematically assuming that the processes are elementary reactions?

**\*13.105** How would you measure an extremely fast reaction?