# CHAPTER

# 16 REACTION RATES

forest fire is an enormous combustion reaction that can go on as long as it 🗖 has fuel, oxygen, and heat. The air tanker in the photograph is dropping a fire-retardant mixture to slow the spread of one of these fires. Fire retardants, which usually contain chemicals such as water, ammonium sulfate, and ammonium phosphate, work by forming a barrier between the fuel (brush and trees) and the oxygen. These chemicals help firefighters slow and eventually stop the combustion reaction. In this chapter, you will learn about the many factors that affect how fast a chemical reaction takes place.

# TART-UPACTIVITY

# **Temperature and Reaction Rates**

# **PROCEDURE**



- **2.** Submerge a second light stick in a bath of hot water (about 50°C).
- **3.** Allow each light stick to reach the same temperature as its bath.
- **4.** Remove the light sticks, and activate them.
- 5. In a dark corner of the room, observe and compare the light intensities of the two sticks.

# **ANALYSIS**

- **1.** Which stick was brighter?
- **2.** Light is emitted from the stick because of a chemical reaction. What can you conclude about how temperature affects this reaction?

# **Pre-Reading Questions**

- (1) Give two examples of units that could be used to measure a car's rate of motion.
- What can you do to slow the rate at which milk spoils?
- What is a catalytic converter in an automobile?

# CONTENTS

# **SECTION 1**

**SAFETY PRECAUTIONS** 

What Affects the Rate of a Reaction?

# **SECTION 2**

How Can Reaction Rates **Be Explained?** 



# S E C T I O N

# What Affects the Rate of a Reaction?

**Key Terms** 

- chemical kinetics
- reaction rate

# **OBJECTIVES**

- **Define** the rate of a chemical reaction in terms of concentration and time.
- **Calculate** the rate of a reaction from concentration-versus-time data.
- **Explain** how concentration, pressure, and temperature may affect the rate of a reaction.
- **Explain** why, for surface reactions, the surface area is an important factor.

# **Rates of Chemical Change**

A *rate* indicates how fast something changes with time. In a savings account, the rate of interest tells how your money is growing over time. Speed is also a rate. From the speed of one of the race cars shown in **Figure 1**, you can tell the distance that the car travels in a certain time. If a car's speed is 67 m/s (150 mi/h), you know that it travels a distance of 67 meters every second. Rates are always measured in a unit of something per time interval. The rate at which the car's wheels turn would be measured in revolutions per second. The rate at which the car burns gasoline could be measured in liters per minute.

The rate of a chemical reaction measures how quickly reactants are changed into products. Some reactions are over in as little as  $10^{-15}$  s; others may take hundreds of years. The study of reaction rates is called **chemical kinetics.** 



# chemical kinetics

the area of chemistry that is the study of reaction rates and reaction mechanisms

## **Figure 1**

The winner of the race is the car that has the highest rate of travel.

# **Rate Describes Change over Time**

At 500°C, the compound dimethyl ether slowly decomposes according to the equation below to give three products—methane, carbon monoxide, and hydrogen gas.

$$CH_3OCH_3(g) \longrightarrow CH_4(g) + CO(g) + H_2(g)$$

The concentration of dimethyl ether will keep decreasing during the reaction. Recall that the symbol  $\Delta$  represents a change in some quantity. If the concentration of dimethyl ether changes by  $\Delta$ [CH<sub>3</sub>OCH<sub>3</sub>] during a small time interval  $\Delta t$ , then the rate of the reaction is defined as

rate = 
$$\frac{-\Delta [CH_3OCH_3]}{\Delta t}$$

The sign is negative because, while  $\Delta$  [CH<sub>3</sub>OCH<sub>3</sub>] is negative, the rate during the reaction must be a positive number.

The chemical equation shows that for every mole of dimethyl ether that decomposes, 1 mol each of methane, carbon monoxide, and hydrogen is produced. Thus, the concentrations of  $CH_4$ , CO, and  $H_2$  will *increase* at the same rate that  $[CH_3OCH_3]$  *decreases*. This means that the rate for this reaction can be defined in terms of the changes in concentration of any one of the products, as shown below.

rate = 
$$\frac{-\Delta[CH_3OCH_3]}{\Delta t} = \frac{\Delta[CH_4]}{\Delta t} = \frac{\Delta[CO]}{\Delta t} = \frac{\Delta[H_2]}{\Delta t}$$

The concentrations of the products are all increasing, so the signs of their rate expressions are positive.

# Quick LAB

# **Concentration Affects Reaction Rate**

### PROCEDURE

- 1. Prepare two labeled beakers, one containing 0.001 M hydrochloric acid and the second containing 0.1 M hydrochloric acid.
- **2.** Start a **stopwatch** at the moment you drop an **effer-vescent tablet** into the first beaker.
- **3.** Stop the stopwatch when the tablet has finished dissolving.
- **4.** Repeat steps 2–3 with a second **effervescent tablet**, using the second beaker.

# **ANALYSIS**

1. What evidence is there that a chemical reaction occurred?

### SAFETY PRECAUTIONS



- **2.** Were the dissolution times different? Did the tablet dissolve faster or slower in the more concentrated solution?
- **3.** What conclusion can you draw about how the rate of a chemical reaction depends on the concentration of the reactants?

# **Balanced Coefficients Appear in the Rate Definition**

Now consider the following reaction, which is the one illustrated in **Figure 2** below.

$$2N_2O_5(s) \rightarrow 4NO_2(g) + O_2(g)$$

The stoichiometry is more complicated here because 2 mol of dinitrogen pentoxide produce 4 mol of nitrogen dioxide and 1 mol of oxygen. So, it is no longer true that the rate of decrease of the reactant concentration equals the rates of increase of the product concentrations. However, this difficulty can be overcome if, in order to define the reaction rate, we divide by the coefficients from the balanced equation. For this reaction, we get the following.

rate = 
$$\frac{-\Delta[N_2O_5]}{2\Delta t} = \frac{\Delta[NO_2]}{4\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

The definition of **reaction rate** developed in these two examples may be generalized to cover any reaction.

It is important to realize that a reaction does not have a single, specific rate. Reaction rates depend on conditions such as temperature and pressure. Also, the rate of a reaction changes *during* the reaction. Usually, the rate decreases gradually as the reaction proceeds. The rate becomes zero when the reaction is complete.



### reaction rate

the rate at which a chemical reaction takes place; measured by the rate of formation of the product or the rate of disappearance of the reactants

## Figure 2

Dinitrogen pentoxide decomposes to form oxygen and the orange-brown gas nitrogen dioxide.

Table 1	Concentratio	on Data and Ca	lculations	for the Decompo	osition of N <sub>2</sub> O <sub>5</sub>
t (s)	[NO <sub>2</sub> ] (M)	$\Delta$ [NO <sub>2</sub> ] (M)	∆ <i>t</i> (s)	$\Delta$ [NO <sub>2</sub> ]/ $\Delta$ t (M/s)	Rate (M/s)
0	0	$4.68 \times 10^{-3}$	20.0	$2.34 \times 10^{-4}$	$5.85 \times 10^{-5}$
20.0	0.00468	$4.22 \times 10^{-3}$	20.0	$2.11 \times 10^{-4}$	$5.28 \times 10^{-5}$
40.0	0.00890	$3.82 \times 10^{-3}$	20.0	$1.91 \times 10^{-4}$	$4.78 \times 10^{-5}$
60.0	0.01272	$3.44 \times 10^{-3}$	20.0	$1.72 \times 10^{-4}$	$4.30 \times 10^{-5}$
80.0	0.01616				

# **Reaction Rates Can Be Measured**

To measure a reaction rate, you need to be able to keep track of how the concentration of one or more reactants or products changes over time. There are many ways of tracking these changes depending on the reaction you are studying.

For the reaction in **Figure 2**, you could measure how quickly the concentration of one product changes by measuring a change in color. Because nitrogen dioxide is the only gas in the reaction that has a color, you could use the red-brown color of the gas mixture to calculate  $[NO_2]$ . On the other hand, because the pressure of the system changes during the reaction, you could measure this change and, with help from the gas laws, calculate the concentrations.

# **Concentrations Must Be Measured Often**

Remember that the  $\Delta t$  that occurs in the equations defining reaction rate is a *small* time interval. This means that studies of chemical kinetics require that concentrations be measured frequently. **Table 1** shows the results from a study of the following reaction.

 $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$ 

The NO<sub>2</sub> concentrations were used to calculate the reaction rate in this example, but  $[N_2O_5]$  or  $[O_2]$  data could also have been used. As expected, the reaction rate decreases with time. It takes about 900 s before the reaction is 99% complete, and at that point, the rate is only  $6.2 \times 10^{-7}$  M/s. Reaction rates are generally expressed, as they are here, in moles per liter-second or M/s.

Notice in the table how the rate is calculated from pairs of data points—two different time readings and two different concentrations of  $NO_2$ . For example, the last rate in the table comes from the calculation shown below.

rate = 
$$\frac{\Delta[\text{NO}_2]}{4\Delta t} = \frac{0.01616 \text{ M} - 0.01272 \text{ M}}{4(80.0 \text{ s} - 60.0 \text{ s})} = 4.30 \times 10^{-5} \text{ M/s}$$

This result shows the rate of the reaction after it has been going on for about 70 s.



### Figure 3

The graph shows the changes in concentration with time during the decomposition of dinitrogen pentoxide. The points represent the data used in **Table 1**.

## N<sub>2</sub>O<sub>5</sub> Decomposition Data



# **Reaction Rates Can Be Represented Graphically**

Chemists often use graphs to help them think about chemical changes. Graphs are especially helpful in the field of chemical kinetics. For one example of how a graph can be useful, we can take another look at the decomposition reaction  $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ . Figure 3 is a graph that keeps track of this reaction with three curves, which show how the concentrations of the reactant and the products change with time. Notice that the concentration of dinitrogen pentoxide steadily falls. Also note that the concentration of oxygen and the concentration of nitrogen dioxide steadily increase.

Finally, notice that the graph also shows that the concentration of nitrogen dioxide increases four times faster than the concentration of oxygen increases. This result agrees with the 4:1 ratio of nitrogen dioxide to oxygen in the balanced equation.

Now, when some quantity is plotted versus time, the slope of the line tells you how fast that quantity is changing with time. So the slopes of the three curves in **Figure 3** measure the rates of change of each concentration. The slope of a curve at a particular point is just the slope of a straight line drawn as a tangent to the curve at that point. Because oxygen is a product and its coefficient in the equation is 1, the slope of the  $O_2$  curve is simply the reaction rate.

slope of O<sub>2</sub> curve = 
$$\frac{\Delta[O_2]}{\Delta t}$$
 = rate of the reaction

A line has been drawn as a tangent to the O<sub>2</sub> curve at t = 70 s. Its slope was measured in the usual way as rise/run and is  $4.30 \times 10^{-5}$  M/s. This value agrees with the rate calculated in **Table 1** at the same instant.

# SAMPLE PROBLEM A

# **Calculating a Reaction Rate**

The data below were collected during a study of the following reaction.

$$2\mathrm{Br}^{-}(aq) + \mathrm{H}_{2}\mathrm{O}_{2}(aq) + 2\mathrm{H}_{3}\mathrm{O}^{+}(aq) \longrightarrow \mathrm{Br}_{2}(aq) + 4\mathrm{H}_{2}\mathrm{O}(l)$$

Time t (s)	[H <sub>3</sub> O <sup>+</sup> ] (M)	[Br <sub>2</sub> ] (M)
0	0.0500	0
85	0.0298	0.0101
95	0.0280	0.0110
105	0.0263	0.0118

Use two methods to calculate what the reaction rate was after 100 s.

# **1** Gather information.

During the interval  $\Delta t = 10$  s between t = 95 s and t = 105 s, the changes in the concentrations of hydronium ion and bromine were

$$\Delta[H_3O^+] = (0.0263 \text{ M}) - (0.0280 \text{ M}) = -0.0017 \text{ M}$$
$$\Delta[Br_2] = (0.0118 \text{ M}) - (0.0110) = 0.0008 \text{ M}$$

# 2 Plan your work.

For this reaction, two definitions of the reaction rate are as follows.

rate = 
$$\frac{-\Delta[H_3O^+]}{2\Delta t} = \frac{\Delta[Br_2]}{\Delta t}$$

# **3** Calculate.

From the change in hydronium ion concentration,

rate = 
$$\frac{-\Delta[H_3O^+]}{2\Delta t} = \frac{-(-0.0017 \text{ M})}{2(10 \text{ s})} = 8.5 \times 10^{-5} \text{ M/s}$$

From the change in bromine concentration,

rate = 
$$\frac{\Delta[Br_2]}{\Delta t} = \frac{0.0008 \text{ M}}{10 \text{ s}} = 8 \times 10^{-5} \text{ M/s}$$

# **4** Verify your results.

The two ways of solving the problem provide approximately the same answer.

# PRACTICE

- For the reaction in **Sample Problem A**, write the expressions that define the rate in terms of the hydrogen peroxide and bromide ion concentrations.
- 2 The initial rate of the N<sub>2</sub>O<sub>4</sub>(g)  $\rightarrow$  2NO<sub>2</sub>(g) reaction is 7.3 × 10<sup>-6</sup> M/s. What are the rates of concentration change for the two gases?
- **3** Use the data from **Sample Problem A** to calculate the reaction rate after 90 s.

# **PRACTICE HINT**

The coefficient from the chemical equation, unless it is 1, must be included when calculating a reaction rate.

# **Factors Affecting Rate**

Concentration, pressure, temperature, and surface area are the most important factors on which the rate of a chemical reaction depends. Consider each of these effects for a type of reaction that is already familiar to you—combustion.

You know that the more fuel and oxygen there is, the faster a fire burns. This is an example of the general principle that the rate of a chemical reaction increases as the concentration of a reactant increases.

Many combustion processes, such as those of sulfur or wood, take place at a surface. The larger the surface area, the greater the chances that each particle will be involved in a reaction.

# **Concentration Affects Reaction Rate**

Though there are exceptions, almost all reactions, including the one shown in **Figure 4**, increase in rate when the concentrations of the reactants are increased.

It is easy to understand why reaction rates increase as the concentrations of the reactants increase. Think about the following reaction taking place within a container.

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$$

Clearly, the reaction can take place only when a nitrogen dioxide molecule collides with a carbon monoxide molecule. If the concentration of  $NO_2$  is doubled, there are twice as many nitrogen dioxide molecules, and so the number of collisions with CO molecules will double. Only a very small fraction of those collisions will actually result in a reaction. Even so, the possibility that each reaction will take place is twice as much when the  $NO_2$  concentration is doubled.

Reaction rates decrease with time because the reaction rate depends on the concentration of the reactants. As the reaction proceeds, the reactant is consumed and its concentration declines. This change in concentration, in turn, decreases the reaction rate.





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Topic Link

Refer to the "Chemical Reactions and Equations" chapter for a discussion of collisions between molecules.

# Figure 4

Carbon burns faster in pure oxygen **a** than in air **b** because the concentration of the reacting species,  $O_2$ , is greater.

# **Concentration Affects Noncollision Reaction Rates**

Not all reactions require a collision. The gas cyclopropane has a molecule in which three bonded carbon atoms form a triangle, with two hydrogen atoms attached to each carbon atom. Above room temperature, cyclopropane slowly changes into propene.

$$(CH_2)_3(g) \longrightarrow CH_2 = CH - CH_3(g)$$

A collision is not necessary for this reaction, but the rate of the reaction still increases as the concentration of cyclopropane increases. In fact, the rate doubles if the  $(CH_2)_3$  concentration doubles. This is not surprising. Because there are twice as many molecules, their reaction is twice as likely, and so the reaction rate doubles.

# **Pressure Affects the Rates of Gas Reactions**

Pressure has almost no effect on reactions taking place in the liquid or solid states. However, it does change the rate of reactions taking place in the gas phase, such as the reaction shown in **Figure 5**.

As the gas laws confirm, doubling the pressure of a gas doubles its concentration. So changing the pressure of a gas or gas mixture is just another way of changing the concentration.

# **Temperature Greatly Influences the Reaction Rate**

All chemical reactions are affected by temperature. In almost every case, the rate of a chemical reaction *increases* with increasing temperature. The increase in rate is often very large. A temperature rise of only 10%, say from 273 K to 300 K, will frequently increase the reaction rate tenfold. Our bodies work best at around  $37^{\circ}$ C or 310 K. Even a 1°C change in body temperature affects the rates of the body's chemical reactions enough that we may become ill as a result.



### **Figure 5**

This reaction between two gases, ammonia and hydrogen chloride, forms solid ammonium chloride in a white ring near the center of the glass tube.



# Figure 6

The reactions that cause food such as these grapes to spoil occur much more slowly when food is placed in a refrigerator or freezer.



# **Temperature Affects Reactions in Everyday Life**

The fact that reaction rates respond to temperature changes is part of everyday life. In the kitchen, we increase the temperature to speed up the chemical processes of cooking food, and we lower the temperature to slow down the chemical processes of food spoilage. When you put food in a refrigerator, you slow down the chemical reactions that cause food, such as the grapes shown in **Figure 6** to decompose. Most manufacturing operations use either heating or cooling to control their processes for optimal performance.

Why do chemical reactions increase in rate so greatly when the temperature rises? You have seen, in discussing reactions such as  $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$ , that a collision between molecules (or other particles, such as ions or atoms) is necessary for a reaction to occur. A common misconception is that a rise in temperature increases the number of collisions and thereby boosts the reaction rate. It is true that a temperature rise does increase the collision frequency somewhat, but that effect is small. The main reason for the increase in reaction rate is that a temperature rise increases the fraction of molecules that have an energy great enough for collision to lead to reaction. If they are to react, molecules must collide with enough energy to rearrange bonds. A rise in temperature means that many more molecules have the required energy.

# Surface Area Can Be an Important Factor

Most of the reactions that we have considered so far happen uniformly in three-dimensional space. However, many important reactions—such as precipitations, corrosions, and many combustions—take place at surfaces. The definition of *rate* given earlier does not apply to surface reactions. Even so, these reactions respond to changes in concentration, pressure, and temperature in much the same way as do other reactions.

A feature of surface reactions is that the amount of matter that reacts is proportional to the surface area. As **Figure 7** shows, you get a bigger blaze with small pieces of wood, because the surface area of many small pieces is greater than that of one larger piece of wood.

# **Figure 7**



**a** Division of a solid makes the exposed surface of the solid larger. **b** More divisions mean more exposed surface.

**c** Hence, more surface is available for other reactant molecules to come together.

# **O** Section Review

# **UNDERSTANDING KEY IDEAS**

- **1.** What does the word *rate* mean in everyday life, and what do chemists mean by *reaction rate*?
- **2.** What is the name given to the branch of chemistry dealing with reaction rates? Why are such studies important?
- **3.** Why is a collision between molecules necessary in many reactions?
- 4. How may reaction rates be measured?
- **5.** Explain why reactant concentration influences the rate of a chemical reaction.
- **6.** Give examples of the strong effect that temperature has on chemical reactions.
- 7. What is unique about surface reactions?

# **CRITICAL THINKING**

- **8.** Why must coefficients be included in the definition of reaction rate?
- **9.** Calculating the reaction rate from a product appeared to give an answer different from that calculated from a reactant. Suggest a possible explanation.
- **10.** The usual unit for reaction rate is M/s. Suggest a different unit that could be used for reaction rate, and explain why this unit would be appropriate.
- **11.** Explain why an increase in the frequency of collisions is not an adequate explanation of the effect of temperature on reaction rate.
- **12.** Would the factors that affect the rate of a chemical reaction influence a physical change in the same way? Explain, and give an example.
- **13.** Why does pressure affect the rates of gas reactions?

# S E C T I O N

# How Can Reaction Rates Be Explained?

# **Key Terms**

- rate law
- reaction mechanism
- order
- rate-determining step
- intermediate
- activation energy
- activated complex
- catalyst
- catalysis
- enzyme

## rate law

the expression that shows how the rate of formation of product depends on the concentration of all species other than the solvent that take part in a reaction

## reaction mechanism

the way in which a chemical reaction takes place; expressed in a series of chemical equations

### order

in chemistry, a classification of chemical reactions that depends on the number of molecules that appear to enter into the reaction

# **O**BJECTIVES

- **Write** a rate law using experimental rate-versus-concentration data from a chemical reaction.
- **Explain** the role of activation energy and collision orientation in a chemical reaction.
- **Describe** the effect that catalysts can have on reaction rate and how this effect occurs.
- **Describe** the role of enzymes as catalysts in living systems, and give examples.

# **Rate Laws**

You have learned that the rate of a chemical reaction is affected by the concentration of the reactant or reactants. The **rate law** describes the way in which reactant concentration affects reaction rate. A rate law may be simple or very complicated, depending on the reaction.

By studying rate laws, chemists learn *how* a reaction takes place. Researchers in chemical kinetics can often make an informed guess about the **reaction mechanism.** In other words, they can create a model to explain how atoms move in rearranging themselves from reactants into products.

# **Determining a General Rate Law Equation**

For a reaction that involves a single reactant, the rate is often proportional to the concentration of the reactant raised to some power. That is, the rate law takes the following form.

rate = k[reactant]<sup>n</sup>

This is a general expression for the rate law. The exponent, n, is called the **order** of the reaction. It is usually a whole number, often 1 or 2, but it could be a fraction. Occasionally, n equals 0, which means that the reaction rate is independent of the reactant concentration. The term k is the *rate constant*, a proportionality constant that varies with temperature.

Reaction orders cannot be determined from a chemical equation. They must be found by experiment. For example, you might guess that n = 1 for the following reaction.

 $CH_3CHO(g) \longrightarrow CH_4(g) + CO(g)$ 

However, experiments have shown that the reaction order is 1.5.

# SAMPLE PROBLEM B

# **Determining a Rate Law**

Three experiments were performed to measure the initial rate of the reaction  $2HI(g) \rightarrow H_2(g) + I_2(g)$ . Conditions were identical in the three experiments, except that the hydrogen iodide concentrations varied. The results are shown below.

Experiment	[HI] (M)	Rate (M/s)
1	0.015	$1.1 \times 10^{-3}$
2	0.030	$4.4 \times 10^{-3}$
3	0.045	$9.9 \times 10^{-3}$

# **1** Gather information.

The general rate law for this reaction is as follows:  $rate = k[HI]^n$ n = ?

# 2 Plan your work.

Find the ratio of the reactant concentrations between experiments 1 and 2,  $\frac{[HI]_2}{[HI]_1}$ 

Then see how this affects the ratio  $\frac{(rate)_2}{(rate)_1}$  of the reaction rates.

# 3 Calculate.

 $\frac{[\text{HI}]_2}{[\text{HI}]_1} = \frac{0.030 \text{ M}}{0.015 \text{ M}} = 2.0 \quad \frac{(rate)_2}{(rate)_1} = \frac{4.4 \times 10^{-3} \text{ M/s}}{1.1 \times 10^{-3} \text{ M/s}} = 4.0$ 

Thus, when the concentration changes by a factor of 2, the rate changes by 4, or  $2^2$ . Hence *n*, the reaction order, is 2.

# **4** Verify your results.

On inspecting items 1 and 3 in the table, one sees that when the concentration triples, the rate changes by a factor of 9, or  $3^2$ . This confirms that the order is 2.

# PRACTICE

- 1 In a study of the  $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$  reaction, when the ammonia concentration was changed from  $3.57 \times 10^{-3}$  M to  $5.37 \times 10^{-3}$  M, the rate increased from  $2.91 \times 10^{-5}$  M/s to  $4.38 \times 10^{-5}$  M/s. Find the reaction order.
- 2 What is the order of a reaction if its rate increases by a factor of 13 when the reactant concentration increases by a factor of 3.6?
- 3 What concentration increase would cause a tenfold increase in the rate of a reaction of order 2?
- 4 When the CH<sub>3</sub>CHO concentration was doubled in a study of the  $CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$  reaction, the rate changed from  $7.9 \times 10^{-5}$  M/s to  $2.2 \times 10^{-4}$  M/s. Confirm that the order is 3/2.

# **PRACTICE HINT**

To find a reaction order, compare a rate ratio with a concentration ratio.



# Reaction Mixtures for $NO + O_3 \longrightarrow NO_2 + O_2$



## Figure 8

Nitrogen monoxide reacts with ozone. Increasing the concentration of either NO or  $O_3$  will increase the reaction rate.

# **Rate Laws for Several Reactants**

When a reaction has more than one reactant, a term in the rate law corresponds to each. There are three concentration terms in the rate law for the following reaction.

$$2Br^{-}(aq) + H_2O_2(aq) + 2H_3O^{+}(aq) \longrightarrow Br_2(aq) + 4H_2O(l)$$

There is an order associated with each term:

rate =  $k[Br^{-}]^{n_1}[H_2O_2]^{n_2}[H_3O^{+}]^{n_3}$ 

For example,  $n_1$  is the reaction order with respect to Br<sup>-</sup>.

To be sure of the orders of reactions that have several reactants, one must perform many experiments. Often the concentration of only a single reactant is varied during a series of experiments. Then a new series is begun and a second reactant is varied, and so on.

**Figure 8** shows the results of changing conditions during a study of the reaction represented by the equation below.

$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$$

This is an important reaction because it participates in the destruction of the ozone layer high in the atmosphere. There are two terms in the rate law for this reaction, which is shown below.

rate = 
$$k[NO]^{n_1}[O_3]^{n_2}$$

In this case, it turns out that  $n_1 = n_2 = 1$ . The fact that the orders for each reactant are equal to one suggests that this reaction has a simple one-step mechanism in which an oxygen atom is transferred when the two reactant molecules collide.

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# **Rate-Determining Step Controls Reaction Rate**

Although a chemical equation can be written for the overall reaction, it does not usually show how the reaction actually takes place. For example, the reaction shown below is believed to take place in four steps, in the mechanism that follows.

$$2\mathrm{Br}^{-}(aq) + \mathrm{H}_{2}\mathrm{O}_{2}(aq) + 2\mathrm{H}_{3}\mathrm{O}^{+}(aq) \longrightarrow \mathrm{Br}_{2}(aq) + 4\mathrm{H}_{2}\mathrm{O}(l)$$

The order with respect to each of the three reactants was found to be 1.

(1) 
$$\operatorname{Br}^{-}(aq) + \operatorname{H}_{3}\operatorname{O}^{+}(aq) \rightleftharpoons \operatorname{HBr}(aq) + \operatorname{H}_{2}\operatorname{O}(l)(1)$$

(2) 
$$\operatorname{HBr}(aq) + \operatorname{H}_2\operatorname{O}_2(aq) \longrightarrow \operatorname{HOBr}(aq) + \operatorname{H}_2\operatorname{O}(l)$$

(3) 
$$\operatorname{Br}^{-}(aq) + \operatorname{HOBr}(aq) \rightleftharpoons \operatorname{Br}_{2}(aq) + \operatorname{OH}^{-}(aq)$$

(4) 
$$OH^{-}(aq) + H_3O^{+}(aq) \rightleftharpoons 2H_2O(l)$$

These four steps add up to the overall reaction that was shown above. Three of the steps are shown as equilibria; these are fast reactions. Step 2, however, is slow. If one step is slower than the others in a sequence of steps, it will control the overall reaction rate, because a reaction cannot go faster than its slowest step. Such a step is known as the **rate-determining step**. Step 2 is the rate-determining step of the mechanism shown by steps 1–4. Species such as HOBr that form during a reaction but are then consumed are called **intermediates**.

# Quick LAB



# rate-determining step

in a multistep chemical reaction, the step that has the lowest velocity, which determines the rate of the overall reaction

### intermediate

a substance that forms in a middle stage of a chemical reaction and is considered a stepping stone between the parent substance and the final product

# **Modeling a Rate-Determining Step**

# PROCEDURE

- 1. Attach a large-bore funnel above a small-bore funnel onto a ring stand. Set a large bowl on the table, directly below the funnels.
- 2. Pour one cup of sand into the top funnel, and start a stopwatch.
- **3.** When the last of the sand has fallen into the bowl, stop the stopwatch.
- **4.** Write down the elapsed time.

- **5.** Repeat steps 1 through 4 using the large-bore funnel above a **medium-bore funnel.**
- **6.** Repeat steps 1 through 4 using the medium-bore funnel above the small-bore funnel.
- **7.** Repeat steps 1 through 4 using the small-bore funnel above the large-bore funnel.

# SAFETY PRECAUTIONS



## ANALYSIS

- 1. Which combination of funnels made the process go the fastest?
- **2.** Which funnel controlled the rate of the process?
- **3.** Does reversing the order of the two funnels in a trial change the results? Explain.
- **4.** What strengths does this process have as a model for a chemical reaction? What weaknesses does it have?

# Topic Link

Refer to the "Gases" chapter for a discussion of the energy distribution of gas molecules.

### activation energy

the minimum energy required to start a chemical reaction

### activated complex

a molecule in an unstable state intermediate to the reactants and the products in the chemical reaction.

# **Reaction Pathways and Activation Energy**

If two molecules approach each other, the outer electrons of each molecule repel the outer electrons of the other. So, ordinarily, the molecules just bounce off each other. For two molecules to react, they must collide violently enough to overcome the mutual repulsion, so that the electron clouds of the two molecules merge to some extent. This merging may lead to a distortion of the shapes of the colliding molecules and, ultimately, to the creation of new bonds.

Violent collisions happen only when the colliding pair of molecules have an unusually large amount of energy. The kinetic energies of individual gas molecules vary over a wide range. Only the molecules with especially high kinetic energy are likely to react. The other molecules must wait until a succession of "lucky" collisions brings their kinetic energies up to the necessary amount.

The minimum energy that a pair of colliding molecules (or atoms or ions) need to have before a chemical change becomes a possibility is called the **activation energy** of the reaction. It is represented by the symbol  $E_a$ . No reaction is possible if the colliding pair has less energy than  $E_a$ .

# **Activation-Energy Diagrams Model Reaction Progress**

Imagine rolling a ball toward a speed bump in a parking lot. If you do not give the ball enough kinetic energy, it will roll partway up the bump, stop, reverse its direction, and come back toward you. If you give it enough energy, the ball will make it just to the top of the bump and stay there for a moment. After that, it may go either way. Given plenty of energy, the ball will pass easily over the bump. Then, gaining more kinetic energy as it descends, it will roll away down the far side of the speed bump.

The model of the ball and speed bump provides a good analogy of the reaction between two colliding molecules. Without enough kinetic energy, the two molecules will not change chemically. With a combined kinetic energy equal to the activation energy, the molecules reach a state where there is a 50:50 chance of either returning to the initial state without reacting, or of being rearranged and becoming products. This point, similar to the top of the speed bump, is called the **activated complex** or *transition state* of the reaction.

**Figure 9a** is a graph of how the energy changes as a pair of hydrogen iodide molecules collide, form an activated complex, and then go on to become hydrogen and iodine molecules. As a chemical equation, the process could be written as follows.

(reactant)		complex		(products)
initial state		activated		final state
2HI	$\rightarrow$	$H_2I_2$	$\rightarrow$	$H_2 + I_2$

In the initial state, the bonds are between the hydrogen and iodine atoms, H–I. In the activated complex, four weak bonds link the four atoms into a deformed square. In the final state the bonds link hydrogen to hydrogen, H–H, and iodine to iodine, I–I.

# Activation Energies for the Decomposition of HI and HBr





### **Figure 9**

**a** The difference in energy between the bottom of this curve and the peak is the energy of activation for the decomposition of HI.

**b** The decomposition of HBr occurs at a faster rate than the decomposition of HI because this reaction has a lower activation energy.

# **Hydrogen Bromide Requires a Different Diagram**

**Figure 8b** similarly represents how potential energy changes with reaction progress for the reaction below.

(reactant)	complex	(products)
initial state	activated	final state
2HBr —	$\rightarrow$ H <sub>2</sub> Br <sub>2</sub> –	$\rightarrow$ H <sub>2</sub> + Br <sub>2</sub>

One difference between the two graphs is that the activation energy is lower in the case of hydrogen bromide. Because the activation energy of HBr is lower than that of HI, a larger fraction of the HBr molecules have enough energy to clear the activation energy barrier than in the HI case. As a result, hydrogen bromide decomposes more quickly than hydrogen iodide does.

Notice in both **Figure 9** graphs that the initial states are not at the same energy as the final states. Note also that the products have a lower energy than the reactants in the case of the HI decomposition reaction in **Figure 9a**, while the opposite is true for hydrogen bromide decomposition in **Figure 9b**. This distinction reflects the fact that hydrogen iodide decomposition is exothermic,

$$2\text{HI}(g) \longrightarrow \text{H}_2(g) + \text{I}_2(g) \qquad \Delta H = -53 \text{ kJ}$$

while the decomposition of hydrogen bromide is endothermic.

$$2\text{HBr}(g) \longrightarrow \text{H}_2(g) + \text{Br}_2(g) \qquad \Delta H = 73 \text{ kJ}$$



Refer to the "Causes of Change" chapter for a discussion of energy changes in chemical reactions.



### Figure 10

A reaction will not occur if the collision occurs too gently, as in **a**, or with the wrong orientation as in **b**. An effective collision, as in **c**, must deliver sufficient energy and bring together the atoms that bond in the products.

# **Not All Collisions Result in Reaction**

Much of what we know about the collisions of molecules (and atoms) has come from studies of reactions between gases. However, it is believed that collisions happen similarly in solution. The principles of rate laws and activation energies apply in reactions that occur in solutions as well as in gas-phase reactions.

Collision between the reacting molecules is necessary for almost all reactions. Collision is not enough, though. The molecules must collide with enough energy to overcome the activation energy barrier. But another factor is also important. **Figure 10** illustrates the need for adequate energy and correct orientation in a collision.

A chemical reaction produces new bonds, and those bonds are formed between specific atoms in the colliding molecules. Unless the collision brings the correct atoms close together and in the proper orientation, the molecules will not react, no matter how much kinetic energy they have. For example, if a chlorine molecule collides with the oxygen end of the nitrogen monoxide molecule, the following reaction may occur.

$$NO(g) + Cl_2(g) \longrightarrow NOCl(g) + Cl(g)$$

This reaction will not occur if the chlorine molecule strikes the nitrogen end of the molecule.

# **Catalysts Increase Reaction Rate**

Adding more reactant will usually increase the rate of a reaction. Adding extra product will sometimes cause the rate to decrease. Often, adding substances called **catalysts** to a reaction mixture will increase the reaction rate, even though the catalyst is still present and unchanged at the end of the reaction. The process, which is called **catalysis**, is shown in **Figure 11**.

Hydrogen peroxide solution, commonly used as a mild antiseptic and as a bleaching agent, decomposes only very slowly when stored in a bottle, forming oxygen as shown in the following equation.

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

Adding a drop of potassium iodide solution speeds up the reaction. On the other hand, adding a few crystals of insoluble manganese dioxide,  $MnO_2(s)$ , causes a violent decomposition to occur. The iodide ion,  $I^-(aq)$ , and manganese dioxide are two of many catalysts for the decomposition of hydrogen peroxide.

Catalysis is widely used in the chemical industry, particularly in the making of gasoline and other petrochemicals. Catalysts save enormous amounts of energy. As you probably know, carbon monoxide is a poisonous gas that is found in automobile exhaust. The following oxidation reaction could remove the health hazard, but this reaction is very slow.

$$2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$$

It is the job of the catalytic converter, built into the exhaust system of all recent models of cars, to catalyze this reaction.

Catalysis does not change the *overall* reaction at all. The stoichiometry and thermodynamics of the reaction are not changed. The changes affect only the path the reaction takes from reactant to product.



## catalyst

a substance that changes the rate of a chemical reaction without being consumed or changed significantly

### catalysis

the acceleration of a chemical reaction by a catalyst

# Figure 12

The four curves show that various catalysts reduce the activation energy for the hydrogen peroxide decomposition reaction, but by different amounts. Notice that the enzyme catalase almost cancels the activation energy.

# **Comparison of Pathways for the Decomposition of H2O2**



# **Catalysts Lower the Activation Energy Barrier**

Catalysis works by making a different pathway available between the reactants and the products. This new pathway has a different mechanism and a different rate law from that of the uncatalyzed reaction. The catalyzed pathway may involve a surface reaction, as in the decomposition of hydrogen peroxide catalyzed by manganese dioxide, and in biological reactions catalyzed by enzymes. Or, the catalytic mechanism may take place in the same phase as the uncatalyzed reaction.

The iodide-catalyzed decomposition of hydrogen peroxide is an example of catalysis that does not involve a surface. It probably works by the following mechanism.

$$I^{-}(aq) + H_2O_2(aq) \longrightarrow IO^{-}(aq) + H_2O(l)$$

(2) 
$$\operatorname{IO}^{-}(aq) + \operatorname{H}_2\operatorname{O}_2(aq) \longrightarrow \operatorname{I}^{-}(aq) + \operatorname{O}_2(g) + \operatorname{H}_2\operatorname{O}(l)$$

Notice that the iodide ion,  $I^-$ , consumed in step 1 is regenerated in step 2, and the hypoiodite ion,  $IO^-$ , generated in step 1 is consumed in step 2. In principle, a single iodide ion could break down an unlimited amount of hydrogen peroxide. This is the characteristic of all catalytic pathways—the catalyst is never used up. It is regenerated and so becomes available for use again and again.

Each pathway corresponds to a different mechanism, a different rate law, and a different activation energy. **Figure 12** shows the potential energy profiles for the uncatalyzed reaction and for catalysis by three different catalysts. Because the catalyzed pathways have lower activation energy barriers, the catalysts speed up the rate of the reaction.



(1)



# **Enzymes Are Catalysts Found in Nature**

The most efficient of the three catalysts compared in **Figure 12** is an **enzyme.** Enzymes are large protein molecules. Their biological role is to catalyze metabolic processes that otherwise would happen too slowly to help the organism. For example, the enzyme lactase catalyzes the reaction of water with the sugar lactose, present in milk. People whose bodies lack the ability to produce lactase have what is known as *lactose intolerance*.

Enzymes are very specific and catalyze only one reaction. This is because the surface of an enzyme molecule has a detailed arrangement of atoms that interacts with the target molecule (lactose, for instance). The enzyme site and the target molecule are often said to have a "lock and key" relationship to each other.

Hydrogen peroxide is a toxic metabolic product in higher animals, and the enzyme catalase is present in their blood and other tissues to destroy  $H_2O_2$ . On the other hand, the bombardier beetle stores a supply of hydrogen peroxide for use as a defense mechanism. When threatened by a predator, the beetle injects catalase into its hydrogen peroxide store. The rapidly released oxygen gas provides pressure for a spray of irritating liquid that the beetle can squirt at its enemy, as shown in **Figure 13**.



# **UNDERSTANDING KEY IDEAS**

- 1. How can reaction orders be measured?
- 2. What can be learned from reaction orders?
- **3.** Explain why not all collisions between reactant molecules lead to reaction.
- 4. What are catalysts and how do they function?
- **5.** Give an example of an enzyme-catalyzed reaction.

# **PRACTICE PROBLEMS**

- **6.** What is the order of a reaction if its rate triples when the reactant concentration triples?
- The reaction CH<sub>3</sub>NC(g) → CH<sub>3</sub>CN(g) is of order 1, with a rate of 1.3 × 10<sup>-4</sup> M/s when the reactant concentration was 0.040 M. Predict the rate when [CH<sub>3</sub>NC] = 0.025 M.
- 8. The following data relate to the reaction  $A + B \rightarrow C$ . Find the order with respect to each reactant.



## Figure 13

Bombardier beetles can repel predators such as frogs with a chemical defense mechanism powered by the catalytic decomposition of hydrogen peroxide.

## enzyme

a type of protein that speeds up metabolic reactions in plants and animals without being permanently changed or destroyed

[A](M)	[B] (M)	Rate (M/s)
0.08	0.06	0.012
0.08	0.03	0.006
0.04	0.06	0.003

# **CRITICAL THINKING**

- **9.** Which corresponds to the faster rate: a mechanism with a small activation energy or one with a large activation energy?
- **10.** If the reaction  $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$  proceeds by a one-step mechanism, what is the rate law?
- **11.** What happens if a pair of colliding molecules possesses less energy than  $E_a$ ?
- **12.** Why is the phrase "lock and key" used to describe enzyme catalysis?
- **13.** How are a catalyst and an intermediate similar? How are they different?
- 14. Draw a diagram similar to Figure 10 to show (a) an unsuccessful and (b) a successful collision between  $H_2(g)$  and  $Br_2(g)$ .

# CHAPTER HIGHLIGHTS

# **KEY IDEAS**

# **SECTION ONE** What Affects the Rate of a Reaction?

- The rate of a chemical reaction is calculated from changes in reactant or product concentration during a small time interval.
- Reaction rates generally increase with reactant concentration or, in the case of gases, pressure.
- Rate increases with temperature because at a higher temperature a greater fraction of collisions have enough energy to cause a reaction.

# **SECTION TWO** How Can Reaction Rates Be Explained?

- Rate laws, which are used to suggest mechanisms, are determined by studying how reaction rate depends on concentration.
- An activated complex occupies the energy high point on the route from reactant to product.
- Catalysts provide a pathway of lower activation energy.
- Enzymes are biological catalysts that increase the rates of reactions important to an organism.

# **KEY TERMS**

# chemical kinetics reaction rate

rate law reaction mechanism order rate-determining step intermediate activation energy activated complex catalyst catalysis enzyme

# KEY SKILLS

**Calculating a Reaction Rate** Sample Problem A p. 581 **Determining a Rate Law** Sample Problem B p. 587



# **USING KEY TERMS**

- **1.** Define *reaction rate*.
- **2.** Explain the difference between a reaction rate and a rate law.
- **3.** What is a mechanism, and what is its rate-determining step?
- **4.** Explain why the names *activated complex* and *transition state* are suitable for describing the highest energy point on a reaction's route from reactant to product.
- **5.** Explain the role of an intermediate in a reaction mechanism.
- **6.** What are enzymes, and what common features do they all share?

# **UNDERSTANDING KEY IDEAS**

# What Affects the Rate of a Reaction?

- **7.** What unit is most commonly used to express reaction rate?
- **8.** Explain how to calculate a reaction rate from concentration-versus-time data.
- **9.** Explain how a graph can be useful in defining and measuring the rate of a chemical reaction.
- **10.** Suggest ways of measuring concentration in a reaction mixture.
- **11.** Why is it necessary to divide by the coefficient in the balanced chemical equation when calculating a reaction rate? When can that step be omitted?
- **12.** What does  $\Delta$ [A] mean if A is the reactant in a chemical reaction?

# Figure 14





- **13.** In a graph like the one in **Figure 14**, what are the signs of the slopes for reactants and for products?
- **14.** Explain the effect that area has on reactions that occur on surfaces.

# **How Can Reaction Rates Be Explained?**

- **15.** Why are reaction orders not always equal to the coefficients in a chemical equation?
- **16.** Write the general expression for the rate law of a reaction with three reactants A, B, and C.
- **17.** Explain what a catalyst is and how it works.
- 18. Sketch a diagram showing how the potential energy changes with the progress of an endothermic reaction. Label the curve "Initial state," "Final state," and "Transition state." Then, draw a second curve to show the change brought about by a catalyst.
- 19. How do enzymes differ from other catalysts?

# **PRACTICE PROBLEMS**



# **Sample Problem A Calculating a Reaction Rate**

- **20.** What is the rate of the reaction  $2NO(g) + Br_2(g) \rightarrow 2NOBr$ given that the bromine concentration decreased by  $5.3 \times 10^{-5}$  M during an interval of 38 s?
- **21.** During the same 38 s interval cited in problem 20, the nitric oxide concentration decreased by  $1.04 \times 10^{-4}$  M. Recalculate the rate.
- **22.** Calculate the rate of a reaction, knowing that a graph of the concentration of a product versus time had a slope of  $3.6 \times 10^{-6}$  M/s. The product had a coefficient of 2.

# Sample Problem B Determining a Rate Law

**23.** In the reaction

 $2NO(g) + Br_2(g) \longrightarrow 2NOBr(g)$ 

doubling the  $Br_2$  concentration doubles the rate, but doubling the NO concentration quadruples the rate. Write the rate law.

- **24.** What is the reaction order if the reaction rate triples when the concentration of a reactant is increased by a factor of 3?
- **25.** The following reaction is first order.  $(CH_2)_3(g) \longrightarrow CH_2 = CH - CH_3(g)$ What change in reaction rate would you expect if the pressure of  $(CH_2)_3$  doubled?

# **MIXED REVIEW**

- **26.** Explain why, even though a collision may have energy in excess of the activation energy, reaction may not occur.
- **27.** What is meant by the *rate-determining step* in a reaction mechanism?
- **28.** When hydrogen peroxide solution, used as an antiseptic, is applied to a wound, it often bubbles. Explain why.

- **29.** Using chemical terminology, explain the purpose of food refrigeration.
- **30.** Why do reptiles move more sluggishly in cold weather?

# **CRITICAL THINKING**

- **31.** Why is it necessary, in defining the rate of a reaction, to require that  $\Delta t$  be small?
- **32.** Explain why, unlike gas-phase reactions, a reaction in solution is hardly affected at all by pressure.
- **33.** Could a catalyzed reaction pathway have an activation energy higher than the uncatalyzed reaction? Explain.
- **34.** Would you expect the concentration of a catalyst to appear in the rate law of a catalyzed reaction? Explain.

# ALTERNATIVE ASSESSMENT

35. Boilers are sometimes used to heat large buildings. Deposits of CaCO<sub>3</sub>, MgCO<sub>3</sub>, and FeCO<sub>3</sub> can hinder the boiler operation. Aqueous solutions of hydrochloric acid are commonly used to remove these deposits. The general equation for the reaction is written below.

$$MCO_{3}(s) + 2H_{3}O^{+}(aq) \rightarrow M^{2+}(aq) + 3H_{2}O(l) + CO_{2}(g)$$

In the equation, M stands for Ca, Mg, or Fe. Design an experiment to determine the effect of various HCl concentrations on the rates of this reaction. Present your design to the class.

# **CONCEPT MAPPING**



**36.** Use the following terms to create a concept map: *activation energy, alternative reaction pathway, catalysts, enzymes,* and *reaction rate.* 



Study the graph below, and answer the questions that follow. For help in interpreting graphs, see Appendix B, "Study Skills for Chemistry."

The graph relates to an experiment in which the concentrations of bromide ion, hydrogen peroxide, and bromine were monitored as the following reaction took place.

 $2\mathrm{Br}^{-}(aq) + \mathrm{H}_{2}\mathrm{O}_{2}(aq) + 2\mathrm{H}_{3}\mathrm{O}^{+}(aq) \longrightarrow$  $\mathrm{Br}_{2}(aq) + 4\mathrm{H}_{2}\mathrm{O}(l)$ 

- **37.** The three curves are lettered **a**, **b**, and **c**. Which curves have positive slopes and which have negative slopes?
- **38.** Associate each curve with one of the species being monitored.
- **39.** What were the initial concentrations of bromine and hydrogen peroxide?
- **40.** Measure the slope of each of the three curves at t = 500 s.



**41.** From each slope calculate a reaction rate. Do your three values agree?

# TECHNOLOGY AND LEARNING

# 42. Graphing Calculator

# Reaction Order

The graphing calculator can run a program that can tell you the order of a chemical reaction, provided you indicate the reactant concentrations and reaction rates for two experiments involving the same reaction.

**Go to Appendix C.** If you are using a TI-83 Plus, you can download the program **RXNORDER** and run the application as directed. If you are using another calculator, your teacher will provide you with keystrokes and data sets to use. At the prompts, enter the reactant concentrations and reaction rates. Run the program as needed to find the order of the following reactions. (All rates are given in M/s.)

- **a.**  $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$  $N_2O_5$ : conc. 1 = 0.025 M; conc. 2 = 0.040 M rate 1 = 8.1 × 10<sup>-5</sup>; rate 2 = 1.3 × 10<sup>-4</sup>
- **b.**  $2NO_2(g) \rightarrow 2NO(g) + O_2(g)$ NO<sub>2</sub>: conc. 1 = 0.040 M; conc. 2 = 0.080 M rate 1 = 0.0030; rate 2 = 0.012
- **c.**  $2H_2O_2(g) \rightarrow 2H_2O(g) + O_2(g)$  $H_2O_2$ : conc. 1 = 0.522 M; conc. 2 = 0.887 M rate  $1 = 1.90 \times 10^{-4}$ ; rate  $2 = 3.23 \times 10^{-4}$
- **d.**  $2\text{NOBr}(g) \rightarrow 2\text{NO}(g) + \text{Br}_2(g)$ NOBr: conc.  $1 = 1.27 \times 10^{-4} \text{ M}$ ; conc.  $2 = 4.04 \times 10^{-4} \text{ M}$

rate 
$$1 = 6.26 \times 10^{-5}$$
; rate  $2 = 6.33 \times 10^{-4}$ 

e.  $2HI(g) \rightarrow H_2(g) + I_2(g)$ HI: conc.  $1 = 4.18 \times 10^{-4}$  M; conc.  $2 = 8.36 \times 10^{-4}$  M rate  $1 = 3.86 \times 10^{-5}$ ; rate  $2 = 1.54 \times 10^{-4}$ 

# **STANDARDIZED TEST PREP**



# UNDERSTANDING CONCEPTS

Directions (1-3): For each question, write on a separate sheet of paper the letter of the correct answer.

- How does the potential energy of the activated complex compare with the potential energies of the reactants and products?
  - **A.** lower than the potential energies of products and of reactants
  - **B.** higher than the potential energies of products and of reactants
  - **C.** lower than the potential energy of products but higher than potential energy of reactants
  - **D.** higher than the potential energy of products but lower than potential energy of reactants

Where does the activated complex appear in a graph of how potential energy changes with reaction progress?

- **F.** at the left end of the curve
- **G.** at the right end of the curve
- **H.** at the lowest point on the curve
- **I.** at the highest point on the curve

3 Why is chemical kinetics useful?

- A. Catalysts decrease chemical costs.
- **B.** The rate law suggests possible reaction mechanisms.
- **C.** Thermodynamic data can be obtained from activation energies.
- **D.** The rate law enables the complete equation of the reaction to be derived.

# Directions (4-5): For each question, write a short response.

4 How and why is the rate of the chemical reaction  $(CH_2)_3(g) \rightarrow CH_2CHCH_3(g)$ affected by pressure?

5 Explain why the biological process of converting glucose into carbon dioxide and water occurs at a much lower temperature than combustion, even though the energy released is the same.

# **READING SKILLS**

# Directions (6–7): Read the passage below. Then answer the questions.

The energy of a corrosion reaction is used to prepare a meal that has a self-contained heat source. The heat comes from a packet containing a powder made of a magnesium-iron alloy and a separate packet of salt water. When the contents of the two packets mix, the reaction between the metal, salt water, and oxygen in the air releases enough energy to heat the food by 100°C in 15 minutes. The process is used to provide heated food or beverages to military personnel, truck drivers, and sports fans.



6 Heat can also be generated by using sodium metal in place of the magnesium iron alloy. Why would this reaction be less suitable for heating food?

- **F.** Sodium is too expensive to use for this purpose.
- **G.** The reaction with sodium generates too much energy.
- H. The reaction between sodium and salt water would proceed too slowly.
- **I.** The toxic salts of sodium might contaminate the food, making it inedible.
- How would the usefulness of the reaction 57 for heating foods change if large granules of the alloy were used instead of a powder?

# **INTERPRETING GRAPHICS**

# *Directions (8–11):* For *each* question below, record the correct answer on a separate sheet of paper.

The diagrams below show activation energies for the decomposition of HI and HBr. Use them to answer questions 8 through 11.



Activation Energies for the Decomposition of HI and HBr

8 Which of these decomposition reactions is endothermic?

- A. HBr only
- **B.** HI only
- **C.** both HBr and HI
- **D.** neither HBr nor HI

9 Which of these reactions requires an input of energy to initiate the decomposition?

- **F.** HBr only
- **G.** HI only
- **H.** both HBr and HI
- I. neither HBr nor HI

Why does hydrogen bromide decompose more quickly than hydrogen iodide?

- **A.** Bromine is a smaller atom than iodine.
- **B.** The activation energy for hydrogen bromide is smaller.
- **C.** Hydrogen bromide forms an activated complex but hydrogen iodide does not.
- **D.** The difference in energy between reactants and products is larger for hydrogen bromide.

11 How would each curve above change if a catalyst were added?

- **F.** The activation energy decreases and the energy of the reactants and products both decrease.
- **G.** The activation energy increases and the energy of the reactants and products both decrease.
- **H.** The activation energy decreases and the energy of the reactants and products remains the same.
- **I.** The activation energy increases and the energy of the reactants and products remains the same.



When using a graph to answer a question, make sure you know what variables are represented on the x- and y-axes before answering the question.



# CHAPTER

# 17 Oxidation, Reduction, and Electrochemistry

f you run out of gasoline in a car, you might have to walk to the nearest gas station for more fuel. But running out of energy when you are millions of kilometers from Earth is a different story! A robot designed to collect data on other bodies in our solar system needs a reliable, portable source of energy that can work in the absence of an atmosphere to carry out its mission. Many of the power sources for these explorer robots are batteries. In this chapter, you will learn about the processes of oxidation and reduction and how they are used in batteries to provide energy. You will also learn how these processes are used to purify metals and protect objects from corrosion.

# START-UPACTIVITY

# **Lights On**

# PROCEDURE

- **1.** Assemble **batteries**, a **light-emitting diode**, and **wires** so that the diode lights. Make a diagram of your construction.
- **2.** Remove the batteries, and reconnect them in the opposite direction. Record the results.

# **ANALYSIS**

- 1. A light-emitting diode allows electrons to move through it in only one direction—into the short leg and out of the longer leg. Based on your results, from which end of the battery must electrons leave?
- **2.** How are the atoms changing in the end of the battery from which electrons leave?
- **3.** What must happen to the electrons as they enter into the other end of the battery?
- 4. Why does a battery eventually run down?

# **Pre-Reading Questions**

- What type of charge results from losing electrons? from gaining electrons?
- 2 Name a device that converts chemical energy into electrical energy.
- Why are batteries marked with positive and negative terminals?

# SAFETY PRECAUTIONS





# **SECTION 1**

Oxidation-Reduction Reactions

# **SECTION 2**

Introduction to Electrochemistry

# **SECTION 3**

**Galvanic Cells** 

SECTION 4 Electrolytic Cells

# S E C T I O N

# **Oxidation-Reduction Reactions**

# **Key Terms**

- oxidation
- reduction
- oxidation-reduction reaction
- oxidation number
- half-reaction
- oxidizing agent
- reducing agent

# **Topic Link**

Refer to the "Ions and Ionic Compounds" and "Covalent Compounds" chapters for more information about chemical bonding.

# oxidation

a reaction that removes one or more electrons from a substance such that the substance's valence or oxidation state increases

# **O**BJECTIVES

- Identify atoms that are oxidized or reduced through electron transfer.
- **Assign** oxidation numbers to atoms in compounds and ions.
- **Identify** redox reactions by analyzing changes in oxidation numbers for different atoms in the reaction.
- 4
  - **Balance** equations for oxidation-reduction reactions through the half-reaction method.

# **Electron Transfer and Chemical Reactions**

You already know that atoms with very different electronegativities bond by an electron transfer. For example, sodium chloride is formed by the transfer of electrons from sodium atoms to chlorine atoms in the reaction shown in **Figure 1** and described by the following equation:

$$2Na(s) + Cl_2(g) \longrightarrow 2NaCl(s)$$

Though NaCl is the way the formula of sodium chloride is usually written, the compound is made up of ions. Therefore, it might be helpful to think of sodium chloride as if its formula were written  $Na^+Cl^-$  so that you remember the ions.

When the electronegativity difference between the atoms is smaller, a polar covalent bond can form when the atoms join, as shown below.

$$2\mathrm{C}(s) + \mathrm{O}_2(g) \longrightarrow 2\mathrm{CO}(g)$$

The C–O bond has some ionic character because there is an unequal sharing of electrons between the carbon atom and the oxygen atom. The oxygen atom attracts the shared electrons more strongly than the carbon atom does.

# **Oxidation Involves a Loss of Electrons**

In the examples above, electrons were transferred at least in part from one atom to another. The sodium atom lost an electron to the chlorine atom. The carbon atom lost some of its control over its electrons to the oxygen atom. The loss, wholly or in part, of one or more electrons is called **oxidation**.

Thus, in making NaCl, the sodium atom is oxidized from Na to Na<sup>+</sup>. Likewise, the carbon atom is oxidized when CO forms, even though the carbon atom does not become an ion.



# **Reduction Involves a Gain of Electrons**

In making NaCl, the electrons lost by the sodium atoms do not just disappear. They are gained by the chlorine atoms. The gain of electrons is described as **reduction.** The chlorine atoms are reduced as they change from  $Cl_2$  to  $2Cl^-$ .

When joining with carbon atoms to make CO, oxygen atoms do not gain electrons but gain only a partial negative charge. But because the electrons in the C—O bonds spend more time near the oxygen atoms, the change is still a reduction.

More than one electron may be gained in a reduction. In the formation of  $Li_3N$ , described by the equation below, three electrons are gained by each nitrogen atom.

 $6\text{Li}(s) + N_2(g) \longrightarrow 2\text{Li}_3N(s)$ 

# **Oxidation and Reduction Occur Together**

When oxidation happens there must also be reduction taking place. You will learn later in this chapter that oxidation and reduction can happen at different places. In most situations, however, oxidation and reduction happen in a single place. Consider HgO being broken down into its elements, as described by the following equation:

$$2 \text{HgO}(s) \longrightarrow 2 \text{Hg}(l) + \text{O}_2(g)$$

In this reaction, mercury atoms are reduced, while oxygen atoms are oxidized. A single reaction in which an oxidation and a reduction happen is called an **oxidation-reduction reaction** or *redox reaction*.

## reduction

a chemical change in which electrons are gained, either by the removal of oxygen, the addition of hydrogen, or the addition of electrons



# oxidation-reduction reaction

any chemical change in which one species is oxidized (loses electrons) and another species is reduced (gains electrons); also called *redox reaction* 

# oxidation number

the number of electrons that must be added to or removed from an atom in a combined state to convert the atom into the elemental form

# **Oxidation Numbers**

To identify whether atoms are oxidized or reduced, chemists use a model of **oxidation numbers,** which can help them identify differences in an atom of an element in different compounds. By following the set of rules described in **Skills Toolkit 1** below, you can assign an oxidation number to each atom in a molecule or in an ion. **Sample Problem A** shows how to use the rules. You can see three different oxidation numbers for atoms of manganese in **Figure 2**.

By tracking oxidation numbers, you can tell whether an atom is oxidized or reduced. If the oxidation number of an atom increases during a reaction, the atom is oxidized. If the oxidation number decreases, the atom is reduced. Like other models, oxidation numbers have limits. You should consider them a bookkeeping tool to help keep track of electrons. In some cases, additional rules are needed to find values that make sense.

# SKILLS SHOULT

# **Assigning Oxidation Numbers**

- 1. Identify the formula.
  - If no formula is provided, write the formula of the molecule or ion.

# 2. Assign known oxidation numbers.

- Place an oxidation number above each element's symbol according to the following rules.
  - **a.** The oxidation number of an atom of any free (uncombined) element in atomic or molecular form is zero.
  - **b.** The oxidation number of a monatomic ion is equal to the charge on the ion.
  - **c.** The oxidation number of an atom of fluorine in a compound is always –1 because it is the most electronegative element.
  - **d.** An atom of the more electronegative element in a binary compound is assigned the number equal to the charge it would have if it were an ion.
  - **e.** In compounds, atoms of the elements of Group 1, Group 2, and aluminum have positive

oxidation numbers of +1, +2, and +3, respectively.

- f. The oxidation number of each hydrogen atom in a compound is +1, unless it is combined with a metal atom; then it is -1.
- g. The oxidation number of each oxygen atom in compounds is usually -2. When combined with fluorine atoms, oxygen becomes +2. In peroxides, such as H<sub>2</sub>O<sub>2</sub>, an oxygen atom has an oxidation number of -1.

# **3. Calculate remaining oxidation** numbers, and verify the results.

- Use the total oxidation number of each element's atoms (the oxidation number for an atom of the element multiplied by the subscript for the element) and the following rules to calculate missing oxidation numbers.
  - **h.** The sum of the oxidation numbers for all the atoms in a molecule is zero.
  - **i.** The sum of the oxidation numbers for all atoms in a polyatomic ion is equal to the charge on that ion.



# Figure 2

An atom of manganese in its elemental form has an oxidation number of 0. In  $MnO_2$ , the oxidation number of the manganese atom is +4. In the permanganate ion,  $MnO_4^-$ , the oxidation number of the manganese atom is +7.

# SAMPLE PROBLEM A

# **Determining Oxidation Numbers**

Assign oxidation numbers to the sulfur and oxygen atoms in the pyrosulfate ion,  $S_2O_7^{2-}$ .

# **1** Identify the formula.

The pyrosulfate ion has the formula  $S_2O_7^{2-}$ .

# **2** Assign known oxidation numbers.

According to Rule **g**, the oxidation number of the O atoms is -2, so this number is written above the O symbol in the formula. Because the oxidation number of the sulfur atoms is unknown, x is written above the S symbol. Thus the formula is as follows:

 $\overset{x -2}{S_2O_7^{2-}}$ 

# **3** Calculate remaining oxidation numbers, and verify the results.

- Multiplying the oxidation numbers by the subscripts, we see that the S atoms contribute 2x and the O atoms contribute 7(-2) = -14 to the total oxidation number. To come up with the correct total charge, (Rule

  i), 2x + (-14) = -2. Solve this equation to find x = +6.
- In  $S_2O_7^{2-}$ , the oxidation number of the S atoms is +6, and the oxidation number of the O atoms is -2. The sum of the total oxidation numbers for each element is 2(+6) + 7(-2) = -2, which is the charge on the ion.

# **PRACTICE HINT**

In this book, the oxidation number for a single atom is written above its chemical symbol. However, be sure to use the total number of atoms for each element when finding the sum of the oxidation numbers for all atoms in the molecule or ion.

		PRACTICE	
Determine the			
<b>1</b> a. NH <sub>4</sub> <sup>+</sup>	<b>e.</b> H <sub>2</sub>	i. $Ca(OH)_2$	PROBLEM
<b>b.</b> Al	<b>f.</b> PbSO <sub>4</sub>	<b>j</b> . Fe <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>	SIGIL
<b>c.</b> H <sub>2</sub> O	g- KClO <sub>3</sub>	<b>k.</b> $H_2PO_4^-$	
<b>d.</b> Pb <sup>2+</sup>	<b>h.</b> BF <sub>3</sub>	I. $NH_4NO_3$	



Figure 3

Zinc metal reacts with hydrochloric acid, making bubbles of hydrogen gas.

# **Identifying Redox Reactions**

**Figure 3** shows the reaction of Zn with HCl. Is this a redox reaction? Hydrochloric acid is a solution in water of  $Cl^-$ , which plays no part in the reaction, and  $H_3O^+$ . The net change in this reaction is

$$2H_3O^+(aq) + Zn(s) \longrightarrow H_2(g) + 2H_2O(l) + Zn^{2+}(aq)$$

Using rules **a**, **b**, **f**, **g**, **h**, and **i** from **Skills Toolkit 1**, you can give oxidation numbers to all atoms as follows:

$$2\overset{+1}{\mathrm{H}_{3}}\overset{-2}{\mathrm{O}^{+}}(aq) + \overset{0}{\mathrm{Zn}}(s) \longrightarrow \overset{0}{\mathrm{H}_{2}}(g) + 2\overset{+1}{\mathrm{H}_{2}}\overset{-2}{\mathrm{O}}(l) + \overset{+2}{\mathrm{Zn}}^{2+}(aq)$$

Comparing oxidation numbers, you see that the zinc atom changes from 0 to +2 and that two hydrogen atoms change from +1 to 0. So, this is a redox reaction. In a redox reaction, the oxidation numbers of atoms that are oxidized increase, and those of atoms that are reduced decrease.

# **Half-Reactions**

In the reaction shown in **Figure 3**, each zinc atom loses two electrons and is oxidized. One way to show only this half of the overall redox reaction is by writing a **half-reaction** for the change.

$$\operatorname{Zn}(s) \longrightarrow \operatorname{Zn}^{2+}(aq) + 2e^{-}$$

Note that electrons are a product. Of course, there is also a half-reaction for reduction in which electrons are a reactant.

$$2e^- + 2H_3O^+(aq) \longrightarrow H_2(g) + 2H_2O(l)$$

By adding the two half-reactions together, you get the overall redox reaction shown earlier. Notice that enough electrons are in each half-reaction to keep the charges balanced. Keep in mind that free electrons do not actually leave the zinc atoms and float around before being picked up by the hydronium ions. Instead, they are "handed off" directly from one to the other.

## half-reaction

the part of a reaction that involves only oxidation or reduction

# **Balancing Oxidation-Reduction Equations**

Equations for redox reactions are sometimes difficult to balance. Use the steps in **Skills Toolkit 2** below to balance redox equations for reactions in acidic aqueous solution. An important step is to identify the key ions or molecules that contain atoms whose oxidation numbers change. These atoms are the starting points of the unbalanced half-reactions. For the reaction of zinc and hydrochloric acid, the unbalanced oxidation and reduction half-reactions would be as follows:

 $\operatorname{Zn}(s) \longrightarrow \operatorname{Zn}^{2+}(aq)$  and  $\operatorname{H}_3O^+(aq) \longrightarrow \operatorname{H}_2(g)$ 

These reactions are then separately balanced. Finally, the balanced equations of the two half-reactions are added together to cancel the electrons.

SKILLS

# **Balancing Redox Equations Using the Half-Reaction Method**

# 1. Identify reactants and products.

- Write the unbalanced equation in ionic form, excluding any spectator ions.
- Assign oxidation numbers, and identify the atoms that change their oxidation numbers. Ignore all species whose atoms do not change their oxidation number.

# 2. Write and balance the half-reactions.

- Separate the equation into its two half-reactions.
- For each half-reaction, do the following:
  - **a.** Balance atoms other than hydrogen and oxygen.
  - **b.** Balance oxygen atoms by adding water molecules as needed.
  - **c.** Balance hydrogen atoms by adding one hydronium ion for each hydrogen atom needed and then by adding the same number of water molecules to the other side of the equation.
  - **d.** Balance the overall charge by adding electrons as needed.

# 3. Make the electrons equal, and combine half-reactions.

- Multiply each half-reaction by an appropriate number so that both half-reactions have the same number of electrons. Now the electrons lost equal the electrons gained, so charge is conserved.
- Combine the half-reactions, and cancel anything that is common to both sides of the equation.

# 4. Verify your results.

• Double-check that all atoms and charge are balanced.

# SAMPLE PROBLEM B

# **The Half-Reaction Method**

Write and balance the equation for the reaction when an acidic solution of  $MnO_4^-$  reacts with a solution of  $Fe^{2+}$  to form a solution containing  $Mn^{2+}$  and  $Fe^{3+}$  ions.

# **1** Identify reactants and products.

• The unbalanced equation in ionic form is as follows:

 $H_3O^+(aq) + MnO_4^-(aq) + Fe^{2+}(aq) \longrightarrow Mn^{2+}(aq) + Fe^{3+}(aq)$ 

• Oxidation numbers for the atoms are as follows:

$${}^{+1}_{H_3}{}^{-2}_{O^+} + {}^{+7}_{Mn}{}^{-2}_{O_4} + {}^{+2}_{Fe}{}^{2+} \longrightarrow {}^{+2}_{Mn}{}^{2+}_{O^+} + {}^{+3}_{Fe}{}^{3-}_{O^+}$$

• Atoms of Mn and Fe change oxidation numbers.

# **2** Write and balance the half-reactions.

Unbalanced:  $Fe^{2+} \rightarrow Fe^{3+}$  $MnO_4^- \rightarrow Mn^{2+}$ Balance O:  $Fe^{2+} \rightarrow Fe^{3+}$  $MnO_4^- \rightarrow Mn^{2+} + 4H_2O$ Balance H:  $Fe^{2+} \rightarrow Fe^{3+}$  $8H_3O^+ + MnO_4^- \rightarrow Mn^{2+} + 12H_2O$ Balance  $e^-$ :  $Fe^{2+} \rightarrow Fe^{3+} + e^ 5e^- + 8H_3O^+ + MnO_4^- \rightarrow Mn^{2+} + 12H_2O$ 

# 3 Make the electrons equal, and combine half-reactions.

Multiply the half-reaction that involves iron by 5 to make the numbers of electrons the same in each half-reaction. Add the half-reactions, and cancel the electrons to get the final balanced equation:

 $8\mathrm{H}_{3}\mathrm{O}^{+}(aq) + \mathrm{MnO}_{4}^{-}(aq) + 5\mathrm{Fe}^{2+}(aq) \longrightarrow \mathrm{Mn}^{2+}(aq) + 5\mathrm{Fe}^{3+}(aq) + 12\mathrm{H}_{2}\mathrm{O}(l)$ 

# **4** Verify your results.

Note that there are equal numbers of all atoms and a net charge of +17 on each side of the equation.

# PRACTICE

Use the half-reaction method to write a balanced equation for each of the following reactions in acidic, aqueous solution.

- The reactants are Fe(s) and  $O_2(aq)$ , and the products are  $Fe^{3+}(aq)$  and  $H_2O(l)$ .
- **2** Al(*s*) is placed in the acidic solution and forms  $H_2(g)$  and Al<sup>3+</sup>(*aq*).
- 3 The reactants are sodium bromide and hydrogen peroxide, and the products are bromine and water.
- 4 The reactants are manganese dioxide and a soluble copper(I) salt, and the products are soluble manganese(II) and copper(II) salts.

# **PRACTICE HINT**

To help avoid confusion between charges and oxidation numbers, the sign of a charge is written last and the sign of an oxidation number is written first. Thus the  $Fe^{2+}$  ion has a 2+ charge and a +2 oxidation number.



# **Identifying Agents in Redox Reactions**

In **Sample Problem B**, the permanganate ion caused the oxidation of the iron(II) ion. Substances that cause the oxidation of other substances are called **oxidizing agents.** They accept electrons easily and so are reduced. Common oxidizing agents are oxygen, hydrogen peroxide, and halogens.

**Reducing agents** cause reduction to happen and are themselves oxidized. The iron(II) ion caused the reduction of the permanganate ion and was the reducing agent. Common ones are metals, hydrogen, and carbon.

# oxidizing agent

the substance that gains electrons in an oxidation-reduction reaction and is reduced

# reducing agent

a substance that has the potential to reduce another substance

# **O** Section Review

# **UNDERSTANDING KEY IDEAS**

- **1.** Explain oxidation and reduction in terms of electron transfer.
- **2.** How can you identify a reaction as a redox reaction?
- **3.** Describe how an oxidation-reduction reaction may be broken down into two half-reactions, and explain why the latter are useful in balancing redox equations.
- **4.** Compare the number of electrons lost in an oxidation half-reaction with the number of electrons gained in the corresponding reduction half-reaction.
- **5.** Describe what an oxidizing agent and a reducing agent are.

# **PRACTICE PROBLEMS**

**6.** Assign oxidation numbers to the atoms in each of the following:

a. 
$$H_2SO_3$$
 c.  $SF_6$ 

**b.** 
$$Cl_2$$
 **d.**  $NO_3^-$ 

- **7.** Assign oxidation numbers to the atoms in each of the following:
  - **a.** CH<sub>4</sub> **c.** NaHCO<sub>3</sub>
  - **b.**  $HSO_3^-$  **d.**  $NaBiO_3$
- Identify the oxidation number of a Cr atom in each of the following: CrO<sub>3</sub>, CrO, Cr(s), CrO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, and CrO<sub>4</sub><sup>2-</sup>.

**9.** Which of the following equations represent redox reactions? For each redox reaction, determine which atom is oxidized and which is reduced, and identify the oxidizing agent and the reducing agent.

**a.** MgO(s) + H<sub>2</sub>CO<sub>3</sub>(aq) 
$$\rightarrow$$

$$MgCO_3(s) + H_2O(l)$$

**b.** 
$$2KNO_3(s) \rightarrow 2KNO_2(s) + O_2(g)$$

**c.** 
$$H_2(g) + CuO(s) \longrightarrow Cu(s) + H_2O(l)$$

**d.** NaOH(
$$aq$$
) + HCl( $aq$ )  $\rightarrow$ 

 $NaCl(aq) + H_2O(l)$ 

**e.** 
$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$$

**f.** 
$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(aq)$$

**10.** Use the half-reaction method in acidic, aqueous solution to balance each of the following redox reactions:

**a.** 
$$\operatorname{Cl}^{-}(aq) + \operatorname{Cr}_{2}\operatorname{O}_{7}^{2-}(aq) \longrightarrow$$
  
 $\operatorname{Cl}_{2}(g) + \operatorname{Cr}^{3+}(aq)$   
**b.**  $\operatorname{Cu}(s) + \operatorname{Ag}^{+}(aq) \longrightarrow \operatorname{Cu}^{2+}(aq) + \operatorname{Ag}(s)$   
**c.**  $\operatorname{Br}_{2}(l) + \operatorname{I}^{-}(aq) \longrightarrow \operatorname{I}_{2}(s) + \operatorname{Br}^{-}(aq)$ 

- **d.**  $I^{-}(aq) + NO_{2}^{-}(aq) \longrightarrow NO(g) + I_{2}(s)$
- **11.** Determine which atom is oxidized and which is reduced, and identify the oxidizing agent and the reducing agent for each reaction in item 10.

# **CRITICAL THINKING**

**12.** How is it possible for hydrogen peroxide to be both an oxidizing agent and a reducing agent?

# S E C T I O N



# Introduction to Electrochemistry

# **Key Terms**

- electrochemistry
- voltage
- electrode
- electrochemical cell
- cathode
- anode

## electrochemistry

the branch of chemistry that is the study of the relationship between electric forces and chemical reactions



# **Figure 4**

When the switch of a flashlight is closed, electrons "pushed" by the battery are forced through the thin tungsten filament of the bulb. This flow of electrons makes the filament hot enough to emit light.

# **O**BJECTIVES

**Describe** the relationship between voltage and the movement of electrons.

- **Identify** the parts of an electrochemical cell and their functions.
- Write electrode reactions for cathodes and anodes.

# **Chemistry Meets Electricity**

The science of **electrochemistry** deals with the connections between chemistry and electricity. It is an important subject because it is involved in many of the things you use every day. Electrochemical devices change electrical energy into chemical energy and vice versa. A simple flashlight is an everyday example of something that converts chemical energy into electrical energy, which is then converted into light energy.

**Figure 4** shows the components of a typical flashlight. The power source is two batteries or cells. Each cell has a metal terminal at each end. If you examine a battery, you will find a  $\oplus$  or + symbol near the top identifying the positive terminal. The bottom is the negative terminal, and is possibly unmarked or marked with a  $\ominus$  or – symbol. By closing the switch, you turn the flashlight on. Electrons move from the negative terminal of the lower battery, through a metal circuit that includes the light bulb, and continue to the positive terminal of the upper battery. The circuit is completed by electrons and ions moving charge through each of the batteries and electrons moving charge from the upper battery to the lower one. When you turn off the flashlight, you break the pathway, and the movement of electrons and ions stops.

# "Electrical Pressure" Is Expressed in Volts

Electrochemical reactions in a battery cause a greater electron density in the negative terminal than in the positive terminal. Electrons repel each other, so there is a higher "pressure" on the electrons in the negative terminal, which drives the electrons out of the battery and through the flashlight.

Electrical "pressure," often called *electric potential*, or **voltage**, is expressed in units of *volts*. The voltage of an ordinary flashlight cell is 1.5 volts or 1.5 V. When two cells are placed end-to-end, as in **Figure 4**, the voltages add together, so the overall voltage driving electrons is 3.0 V. The movement of electrons or other charged particles is described as *electric current* and is expressed in units of *amperes*.

# **Components of Electrochemical Cells**

A flashlight battery is an electrochemical cell. An **electrochemical cell** consists of two electrodes separated by an electrolyte. An **electrode** is a conductor that connects with a nonmetallic part of a circuit. You have learned about two kinds of conductors. One kind includes metals, which conduct electric current through moving electrons. The second kind includes electrolyte solutions, which conduct through moving ions.

# **The Cathode Is Where Reduction Occurs**

*Electrode reactions* happen on the surfaces of electrodes. **Figure 5** shows half of an electrochemical cell. The copper strip is an electrode because it is a conductor in contact with the electrolyte solution. The reaction on this electrode is the reduction described by the following equation:

$$\operatorname{Cu}^{2+}(aq) + 2e^{-} \longrightarrow \operatorname{Cu}(s)$$

The copper electrode is a **cathode** because reduction happens on it.

# voltage

the potential difference or electromotive force, measured in volts; it represents the amount of work that moving an electric charge between two points would take

## electrochemical cell

a system that contains two electrodes separated by an electrolyte phase

# electrode

a conductor used to establish electrical contact with a nonmetallic part of a circuit, such as an electrolyte

## cathode

the electrode on whose surface reduction takes place





# **The Anode Is Where Oxidation Occurs**

The electrons that cause reduction at the cathode are pushed there from a reaction at the second electrode of a cell. The **anode** is the electrode on which oxidation occurs. **Figure 6** shows the second half of the electrochemical cell. The zinc strip is an electrode because it is a conductor in contact with the solution. The reaction on this electrode is the oxidation described by the following equation:

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^{-}$$

The zinc electrode is an anode because oxidation happens on it.

The electrode reactions described here would have been called halfreactions in the last section. The difference is that a half-reaction is a helpful model, but the electrons shown are never really free. An electrode reaction describes reality because the electrons actually move from one electrode to another to continue the reaction.

# **Pathways for Moving Charges**

The electrode reactions cannot happen unless the electrodes are part of a complete circuit. So, a cell must have pathways to move charges. Wires are often used to connect the electrodes through a meter or a light bulb. Electrons carry charges in the wires and electrodes.

Ions in solution carry charges between the electrolytes to complete the circuit. A porous barrier, as shown in **Figure 7**, or a salt bridge keeps the solutions from mixing, but lets the ions move. In the cell shown, charge is carried through the barrier by a combination of  $Zn^{2+}(aq)$  ions moving to the right and  $SO_4^{2-}(aq)$  ions moving to the left. Understand that positive charge may be carried from left to right through this cell either by negative particles (electrons or anions) moving from right to left or by cations moving from left to right.

### anode

the electrode on whose surface oxidation takes place; anions migrate toward the anode, and electrons leave the system from the anode



Electrodes Porous barrier

## **Figure 7**

The light bulb is powered by the reaction in this cell.

# **The Complete Cell**

**Figure 7** shows a complete cell composed of the electrodes shown separately in earlier figures. The overall process when the anode reaction is added to the cathode reaction for this cell is the same as the following redox reaction:

$$\operatorname{Zn}(s) + \operatorname{Cu}^{2+}(aq) \longrightarrow \operatorname{Zn}^{2+}(aq) + \operatorname{Cu}(s)$$

Although the two electrode reactions occur at the same time, they occur at different places in the cell. This is an important distinction from the redox reactions discussed in the last section.



# **UNDERSTANDING KEY IDEAS**

- **1.** What is voltage?
- **2.** How does voltage relate to the movement of electrons?
- **3.** List the components of an electrochemical cell, and describe the function of each.
- **4.** What are the names of the electrodes in an electrochemical cell? What type of reaction happens on each?
- **5.** Describe the difference in how charge flows in wires and in electrolyte solutions.
- **6.** A 12 V car battery has six cells connected end-to-end. What is the voltage of a single cell?
- **7.** Will the reaction below happen at an anode or a cathode? Explain.

$$\operatorname{Fe}(\operatorname{CN})_6^{3-}(aq) + e^- \longrightarrow \operatorname{Fe}(\operatorname{CN})_6^{4-}(aq)$$

**8.** Describe the changes in oxidation number that happen in an anode reaction and in a cathode reaction.

# **CRITICAL THINKING**

- **9.** What would happen if you put one of the batteries in backward in a two-cell flashlight?
- **10.** What would happen if you put both batteries in backward in a two-cell flashlight?



- **12.** Write an electrode reaction in which you change  $Br^{-}(aq)$  to  $Br_{2}(aq)$ . Would this reaction happen at an anode or a cathode?
- **13.** Write an electrode reaction in which  $\operatorname{Sn}^{4+}(aq)$  is changed to  $\operatorname{Sn}^{2+}(aq)$ . Would this reaction happen at an anode or a cathode?
- **14.** If you wanted to use an electrochemical cell to deposit a thin layer of silver metal onto a bracelet, which electrode would you make the bracelet? Explain using the equation for the electrode reaction that would occur.
- 15. What would happen at each electrode if batteries were connected to the cell in Figure 7 so that electrons flowed in the opposite direction of the direction described in the text?
- **16.** Compare the equations for electrode reactions with the equations for half-reactions.
- 17. Write the electrode reactions for a cell that involves only Cu(s) and Cu<sup>2+</sup>(aq) in which the anode reaction is the reverse of the cathode reaction. What is the net result of operating this cell?
- **18.** Is it correct to say that the net chemical result of an electrochemical cell is a redox reaction? Explain.

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# S E C T I O N



# **Galvanic Cells**

# **Key Terms**

- corrosion
- standard electrode potential

# **OBJECTIVES**

- **Describe** the operation of galvanic cells, including dry cells, lead-acid batteries, and fuel cells.
- Identify conditions that lead to corrosion and ways to prevent it.
- **Calculate** cell voltage from a table of standard electrode potentials.

# **Types of Galvanic Cells**

A battery is one kind of *galvanic cell*, a device that can change chemical energy into electrical energy. In these cells, a spontaneous reaction happens that causes electrons to move. **Figure 8** shows a kind of galvanic cell known as a Daniell cell. Daniell cells were used as energy sources in the early days of electrical research. Of course, Daniell cells would be impractical to use in a radio or portable computer today. There are many other kinds of galvanic cells. These include dry cells, lead-acid batteries, and fuel cells.

# Figure 8

As a result of the reaction in a galvanic cell, the bulb lights up as electrons move in the wires from the anode to the cathode.





# **Dry Cells**

Although the Daniell cell was useful for supplying energy in the lab, it wasn't very portable because it held solutions. The energy source that you know as a *battery* and use in radios and remote controls is a dry cell. In a dry cell, moist electrolyte pastes are used instead of solutions. This cell was invented over a century ago by Georges Leclanché, a French chemist. His original design was close to that shown on the left in **Figure 9.** A carbon rod, the battery's positive terminal, connects with a wet paste of carbon; ammonium chloride,  $NH_4Cl$ ; manganese(IV) oxide,  $MnO_2$ ; starch; and water. When the cell is used, the carbon rod is the cathode, and the following electrode reaction happens:

Cathode:  $2MnO_2(s) + 2NH_4^+(aq) + 2e^- \rightarrow Mn_2O_3(s) + 2NH_3(aq) + H_2O(l)$ 

The zinc case serves as the negative terminal of the battery. When the cell is used, zinc dissolves in the following electrode reaction:

Anode: 
$$\operatorname{Zn}(s) + 4\operatorname{NH}_3(aq) \longrightarrow 2e^- + \operatorname{Zn}(\operatorname{NH}_3)_4^{2+}(aq)$$

The white powder that you see on old corroded batteries is the chloride salt of this  $Zn(NH_3)_4^{2+}(aq)$  complex ion.

The  $NH_4^+(aq)$  ion is a weak acid, and for this reason the Leclanché cell is called the *acidic* version of the dry cell. The *alkaline cell*, shown in **Figure 9**, is a newer, better version. The ingredients of the alkaline cell are similar to the acidic version, but the carbon cathode is replaced by a piece of brass, and ammonium chloride is replaced by potassium hydroxide. The presence of this strong base gives the alkaline cell its name. The electrode reactions that occur when the cell is used are described by the equations below.

Cathode: 
$$2MnO_2(s) + H_2O(l) + 2e^- \rightarrow Mn_2O_3(s) + 2OH^-(aq)$$
  
Anode:  $Zn(s) + 2OH^-(aq) \rightarrow 2e^- + Zn(OH)_2(s)$ 

A sturdy steel shell is needed to prevent the caustic contents from leaking out of the battery. Because of this extra packaging, alkaline cells are more expensive than cells of the older, acidic version. Figure 9 Two familiar kinds of dry cells use different electrolytes. The electrolytes make the cell on the left acidic and the cell on the right alkaline.



# Listen Up

# PROCEDURE

- 1. Press a zinc strip and a copper strip into a raw potato. The strips should be about 0.5 cm apart but should not touch one another.
- **2.** While listening to the **ear-phone**, touch one wire from the earphone to one of the

metal strips and the other wire from the earphone to the second metal strip using **alligator clips.** Record your observations.

**3.** While listening to the earphone, touch both wires to a single metal strip. Record your observations.

## SAFETY PRECAUTIONS



### ANALYSIS

- Compare your results from step 2 with your results from step 3. Suggest an explanation for any similarities or differences.
- **2.** Suggest an explanation for the sound.

# **Lead-Acid Batteries**

The batteries just discussed are called *dry cells* because the water is not free, but absorbed in pastes. In contrast, the Daniell cell and the lead-acid battery use aqueous solutions of electrolytes, so they should be used in an upright position.

Most car batteries are lead-acid storage batteries. Usually they have six cells mounted side-by-side in a single case, as shown in **Figure 10**. Though many attempts have been made to replace the heavy lead-acid battery by lighter alternatives, no other material has been found that can reliably and economically give the large surges of electrical energy needed to start a cold engine.

A fully charged lead-acid cell is made up of a stack of alternating lead and lead(IV) oxide plates isolated from each other by thin porous separators. All these components are in a concentrated solution of sulfuric acid. The positive terminal of one cell is linked to the negative terminal of the next cell in the same way that the batteries in the flashlight were connected. This arrangement of cells causes the outermost terminals of the lead-acid battery to have a voltage of 12.0 V. When the cell is used, it acts as a galvanic cell with the following reactions:

Cathode: 
$$PbO_2(s) + HSO_4(aq) + 3H_3O^+(aq) + 2e^- \longrightarrow PbSO_4(s) + 5H_2O(l)$$

Anode:  $Pb(s) + HSO_4(aq) + H_2O(l) \rightarrow 2e^- + PbSO_4(s) + H_3O^+(aq)$ 

Notice that PbSO<sub>4</sub> is produced at both electrodes.

Unlike the Daniell and Leclanché cells, the lead-acid cell is rechargeable. So, when the battery runs down, you do not need to replace it. Instead, an electric current is applied in a direction opposite to that discussed above. As a result of the input of energy, the reactions are reversed. The cell is eventually restored to its charged state. During recharge, the cell functions as an *electrolytic cell*, which you will learn about in the next section.





# Figure 10

The lead-acid battery is used to store energy in almost all vehicles. Although the cutaway view shows a single  $PbO_2$  plate and a single Pb plate in each cell, there are actually several of each.

# **Fuel Cells**

In a *fuel cell*, the oxidizing and reducing agents are brought in, often as gases, from outside of the cell, rather than being part of it. Unlike a dry cell, a fuel cell can work forever, in principle, changing chemical energy into electrical energy. **Figure 11** models a fuel cell that uses the reactions below.

Cathode:  $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$ 

Anode:  $2H_2(g) + 4OH^-(aq) \rightarrow 4e^- + 4H_2O(l)$ 

Because fuel cells directly change chemical energy into electrical energy, they are very efficient and are cleaner than the burning of fuels in power plants to generate electrical energy. Research into fuel cells continues, and fuel cells are used in a few experimental power plants.



## Figure 11

The reactions in this fuel cell take place at carbon electrodes that contain metal catalysts. The water formed is removed as a gas.

# **Corrosion Cells**

Oxygen is so reactive that many metals spontaneously oxidize in air. Fortunately, many of these reactions are slow. The disintegration of metals is called **corrosion.** Usually  $O_2(g)$  is the oxidizing agent, but the direct reaction of  $O_2$  with the metal is not usually how corrosion happens.

Water is usually involved in corrosion. Consider the corrosion of iron. Hydrated iron(III) oxide, or rust, forms by the following overall reaction:

$$4\text{Fe}(s) + 3\text{O}_2(aq) + 4\text{H}_2\text{O}(l) \longrightarrow 2\text{Fe}_2\text{O}_3 \cdot 2\text{H}_2\text{O}(s)$$

However, the reaction mechanism is more complicated than this equation suggests. An even simpler version of what happens is shown in **Figure 12.** The iron dissolves by the oxidation half-reaction

$$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^{-}$$

 $Fe^{2+}$  then gets oxidized to  $Fe^{3+}$  in a further reaction. Any oxidation must be accompanied by a reduction taking place at the same time, but not necessarily at the same location. In fact, the electrons produced by the oxidation are consumed by the reduction of oxygen at a cathodic site elsewhere on the iron's surface. The reduction half-reaction is

$$O_2(aq) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$$

Electrons move in the metal and ions move in the water layer between the two reaction sites, as in an electrochemical cell. In fact, a corrosion cell is an unwanted galvanic cell. Chemical energy is converted into electrical energy, which heats the metal.

The three ingredients—oxygen, water, and ions—needed for the corrosion of metals are present almost everywhere on Earth. Even pure rainwater contains a few  $H_3O^+$  and  $HCO_3^-$  ions from dissolved carbon dioxide. Higher ion concentrations—from airborne salt near the ocean, from acidic air pollutants, or from salts spread on icy roads—make corrosion worse in certain areas.



## corrosion

the gradual destruction of a metal or alloy as a result of chemical processes such as oxidation or the action of a chemical agent