

## Molality

A concentration unit that is independent of temperature is **molality ( $m$ )**, the amount of solute (in moles) divided by the mass of solvent (in kilograms).

Molality is abbreviated with a lowercase italic  $m$  while molarity is abbreviated with a capital M.

$$\text{Molality } (m) = \frac{\text{amount solute (in mol)}}{\text{mass solvent (in kg)}}$$

Notice that molality is defined with respect to kilograms *solvent*, not kilograms solution. Molality is particularly useful when we need to compare concentrations over a range of different temperatures.

## Parts by Mass and Parts by Volume

It is often convenient to report a concentration as a ratio of masses. A **parts by mass** concentration is the ratio of the mass of the solute to the mass of the solution, all multiplied by a multiplication factor:

$$\frac{\text{Mass solute}}{\text{Mass solution}} \times \text{multiplication factor}$$

The particular parts by mass unit we use, which determines the size of the multiplication factor, depends on the concentration of the solution. For example, for **percent by mass** the multiplication factor is 100:

$$\text{Percent by mass} = \frac{\text{mass solute}}{\text{mass solution}} \times 100\%$$

*Percent* means *per hundred*; a solution with a concentration of 14% by mass contains 14 g of solute per 100 g of solution.

For more dilute solutions, we might use **parts per million (ppm)**, which has a multiplication factor of  $10^6$ , or **parts per billion (ppb)**, which has a multiplication factor of  $10^9$ .

$$\text{ppm} = \frac{\text{mass solute}}{\text{mass solution}} \times 10^6$$

$$\text{ppb} = \frac{\text{mass solute}}{\text{mass solution}} \times 10^9$$

A solution with a concentration of 15 ppm by mass, for example, contains 15 g of solute per  $10^6$  g of solution.

Sometimes, we report concentrations as a ratio of volumes, especially for solutions in which both the solute and solvent are liquids. A **parts by volume** concentration is usually the ratio of the volume of the solute to the volume of the solution, all multiplied by a multiplication factor.

$$\frac{\text{Volume solute}}{\text{Volume solution}} \times \text{multiplication factor}$$

The multiplication factors are identical to those just described for parts by mass concentrations. For example, a 22% ethanol solution by volume contains 22 mL of ethanol for every 100 mL of solution.

**Using Parts by Mass (or Parts by Volume) in Calculations** We can use the parts by mass (or parts by volume) concentration of a solution as a conversion factor between mass (or volume) of the solute and mass (or volume) of the solution. For example, for a solution containing 3.5% sodium chloride by mass, we write the following conversion factor:



For dilute aqueous solutions near room temperature, the units of ppm are equivalent to milligrams solute/per liter of solution. This is because the density of a dilute aqueous solution near room temperature is 1.0 g/mL, so that 1 L has a mass of 1000 g.

This conversion factor converts from grams solution to grams NaCl. To convert the other way, we simply invert the conversion factor:



### EXAMPLE 12.3 Using Parts by Mass in Calculations

What volume (in mL) of a soft drink that is 10.5% sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) by mass contains 78.5 g of sucrose? (The density of the solution is 1.04 g/mL.)

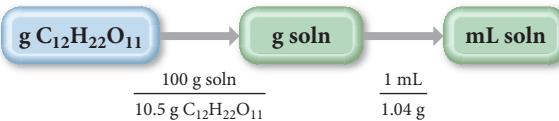
**SORT** You are given a mass of sucrose and the concentration and density of a sucrose solution, and you are asked to find the volume of solution containing the given mass.

**STRATEGIZE** Begin with the mass of sucrose in grams. Use the mass percent concentration of the solution (written as a ratio, as shown under relationships used) to find the number of grams of solution containing this quantity of sucrose. Then use the density of the solution to convert grams to milliliters of solution.

**GIVEN:** 78.5 g  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$   
10.5%  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  by mass  
density = 1.04 g/mL

**FIND:** mL

#### CONCEPTUAL PLAN



#### RELATIONSHIPS USED

$$\frac{10.5 \text{ g C}_{12}\text{H}_{22}\text{O}_{11}}{100 \text{ g soln}} \text{ (percent by mass written as ratio)}$$

$$\frac{1 \text{ mL}}{1.04 \text{ g}} \text{ (given density of the solution)}$$

**SOLVE** Begin with 78.5 g  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  and multiply by the conversion factors to arrive at the volume of solution.

#### SOLUTION

$$78.5 \text{ g C}_{12}\text{H}_{22}\text{O}_{11} \times \frac{100 \text{ g soln}}{10.5 \text{ g C}_{12}\text{H}_{22}\text{O}_{11}} \times \frac{1 \text{ mL}}{1.04 \text{ g}} = 719 \text{ mL soln}$$

**CHECK** The units of the answer are correct. The magnitude seems correct because the solution is approximately 10% sucrose by mass. Since the density of the solution is approximately 1 g/mL, the volume containing 78.5 g sucrose should be roughly 10 times larger, as calculated ( $719 \approx 10 \times 78.5$ ).

#### FOR PRACTICE 12.3

What mass of sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ), in g, is contained in 355 mL (12 ounces) of a soft drink that is 11.5% sucrose by mass? (Assume a density of 1.04 g/mL.)

#### FOR MORE PRACTICE 12.3

A water sample is found to contain the pollutant chlorobenzene with a concentration of 15 ppb (by mass). What volume of this water contains  $5.00 \times 10^2$  mg of chlorobenzene? (Assume a density of 1.00 g/mL.)

## Mole Fraction and Mole Percent

For some applications, especially those in which the ratio of solute to solvent can vary widely, the most useful way to express concentration is the amount of solute (in moles) divided by the total amount of solute and solvent (in moles). This ratio is the **mole fraction** ( $\chi_{\text{solute}}$ ):

$$\chi_{\text{solute}} = \frac{\text{amount solute (in mol)}}{\text{total amount of solute and solvent (in mol)}} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}}$$

Also in common use is the **mole percent (mol %)**, which is simply the mole fraction  $\times$  100 percent.

$$\text{mol \%} = \chi_{\text{solute}} \times 100\%$$

The mole fraction can also be defined for the solvent:

$$\chi_{\text{solvent}} = \frac{n_{\text{solvent}}}{n_{\text{solute}} + n_{\text{solvent}}}$$



## Chemistry in the Environment

### The Dirty Dozen

A number of potentially harmful chemicals—such as DDT, dioxin, and polychlorinated biphenyls (PCBs)—can make their way into water sources from industrial dumping, atmospheric emissions, agricultural use, and household dumping. Since crops, livestock, and fish consume water, they too can accumulate these chemicals. Human consumption of food or water contaminated with harmful chemicals can lead to a number of diseases and adverse health effects such as increased cancer risk, liver damage, and central nervous system damage. Governments around the world have joined forces to ban the production of a number of these kinds of chemicals—called persistent organic pollutants or POPs. The original treaty targeted 12 such substances referred to as the “dirty dozen” (Table 12.6).

**TABLE 12.6 The Dirty Dozen**

|                                 |  |
|---------------------------------|--|
| 1. Aldrin—insecticide           | 7. Furan—industrial by-product                             |
| 2. Chlordane—insecticide        | 8. Heptachlor—insecticide                                  |
| 3. DDT—insecticide              | 9. Hexachlorobenzene—fungicide, industrial by-product      |
| 4. Dieldrin—insecticide         | 10. Mirex—insecticide, fire retardant                      |
| 5. Dioxin—industrial by-product | 11. Polychlorinated biphenyls (PCBs)—electrical insulators |
| 6. Eldrin—insecticide           | 12. Toxaphene—insecticide                                  |

One problem common to all of these chemicals is their persistence in the environment. These compounds are fairly stable and do not break down under normal environmental conditions. Once they get into the environment, they stay there for a long time. A second problem with these chemicals is their contribution to a process called *bioamplification*. Because they are non-polar, these chemicals are stored and concentrated in the fatty tissues of the organisms that consume them. As larger organisms eat smaller ones they consume more of the stored chemicals. The result is an increase in the concentrations of these chemicals as they move up the food chain.

Nearly all intentional production of these chemicals has been banned. In the United States, the presence of these contaminants in water supplies is monitored by the Environmental Protection Agency (EPA). The EPA has set limits, called maximum contaminant levels (MCLs), for each of these contaminants in food and drinking water. Table 12.7 lists some MCLs for selected compounds in water supplies. Notice the units that the EPA uses to express the concentration of the contaminants, mg/L. This unit is a conversion factor between liters of water consumed and the mass (in mg) of the pollutant. According to the EPA, as long as the contaminant concentrations are below these levels, the water is safe to drink.



▲ Potentially harmful chemicals make their way into water sources in many ways.

**TABLE 12.7 EPA Maximum Contaminant Level (MCL) for Several “Dirty Dozen” Chemicals**

|                   |                 |
|-------------------|-----------------|
| Chlordane         | 0.002 mg/L      |
| Dioxin            | 0.00000003 mg/L |
| Heptachlor        | 0.0004 mg/L     |
| Hexachlorobenzene | 0.001 mg/L      |

### Question

Calculate how much of each of the chemicals in Table 12.7 at the MCL is present in 715 L of water, the approximate amount of water consumed by an adult in 1 year.

### EXAMPLE 12.4 Calculating Concentrations

A solution is prepared by dissolving 17.2 g of ethylene glycol ( $C_2H_6O_2$ ) in 0.500 kg of water. The final volume of the solution is 515 mL. For this solution, calculate the concentration in each unit.

- (a) molarity
- (b) molality
- (c) percent by mass
- (d) mole fraction
- (e) mole percent

#### SOLUTION

(a) To calculate molarity, first find the amount of ethylene glycol in moles from the mass and molar mass.

Then divide the amount in moles by the volume of the solution in liters.

$$\text{mol } C_2H_6O_2 = 17.2 \text{ g } C_2H_6O_2 \times \frac{1 \text{ mol } g \ C_2H_6O_2}{62.07 \text{ g } C_2H_6O_2} = 0.2771 \text{ mol } C_2H_6O_2$$

$$\begin{aligned}\text{Molarity (M)} &= \frac{\text{amount solute (in mol)}}{\text{volume solution (in L)}} \\ &= \frac{0.2771 \text{ mol } C_2H_6O}{0.515 \text{ L solution}} \\ &= 0.538 \text{ M}\end{aligned}$$

(b) To calculate molality, use the amount of ethylene glycol in moles from part (a), and divide by the mass of the water in kilograms.

$$\begin{aligned}\text{Molality (m)} &= \frac{\text{amount solute (in mol)}}{\text{mass solvent (in kg)}} \\ &= \frac{0.2771 \text{ mol } C_2H_6O}{0.500 \text{ kg } H_2O} \\ &= 0.554 \text{ m}\end{aligned}$$

(c) To calculate percent by mass, divide the mass of the solute by the sum of the masses of the solute and solvent and multiply the ratio by 100%.

$$\begin{aligned}\text{Percent by mass} &= \frac{\text{mass solute}}{\text{mass solution}} \times 100\% \\ &= \frac{17.2 \text{ g}}{17.2 \text{ g} + 5.00 \times 10^2 \text{ g}} \times 100\% \\ &= 3.33\%\end{aligned}$$

(d) To calculate mole fraction, first determine the amount of water in moles from the mass of water and its molar mass.

Then divide the amount of ethylene glycol in moles (from part (a)) by the total number of moles.

$$\text{mol } H_2O = 5.00 \times 10^2 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 27.75 \text{ mol } H_2O$$

$$\begin{aligned}\chi_{\text{solute}} &= \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}} \\ &= \frac{0.2771 \text{ mol}}{0.2771 \text{ mol} + 27.75 \text{ mol}} \\ &= 9.89 \times 10^{-3}\end{aligned}$$

(e) To calculate mole percent, multiply the mole fraction by 100%.

$$\begin{aligned}\text{mol \%} &= \chi_{\text{solute}} \times 100\% \\ &= 0.989\%\end{aligned}$$

#### FOR PRACTICE 12.4

A solution is prepared by dissolving 50.4 g sucrose ( $C_{12}H_{22}O_{11}$ ) in 0.332 kg of water. The final volume of the solution is 355 mL. Calculate the concentration of the solution in each unit.

- (a) molarity
- (b) molality
- (c) percent by mass
- (d) mole fraction
- (e) mole percent

**EXAMPLE 12.5** Converting between Concentration Units

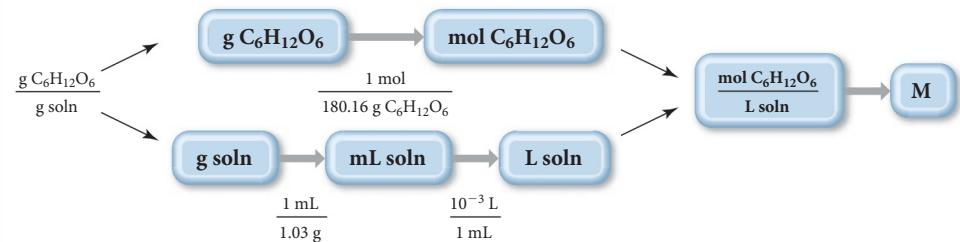

What is the molarity of a 6.56% by mass glucose ( $C_6H_{12}O_6$ ) solution? (The density of the solution is 1.03 g/mL.)

**SORT** You are given the concentration of a glucose solution in percent by mass and the density of the solution. Find the concentration of the solution in molarity.

**STRATEGIZE** Begin with the mass percent concentration of the solution written as a ratio, and separate the numerator from the denominator. Convert the numerator from g  $C_6H_{12}O_6$  to mol  $C_6H_{12}O_6$ . Convert the denominator from g soln to mL of solution and then to L solution. Then divide the numerator (now in mol) by the denominator (now in L) to obtain molarity.

**GIVEN:** 6.56%  $C_6H_{12}O_6$   
density = 1.03 g/mL

**FIND:** M

**CONCEPTUAL PLAN**

**RELATIONSHIPS USED**

$$\frac{6.56 \text{ g } C_6H_{12}O_6}{100 \text{ g soln}} \text{ (percent by mass written as ratio)}$$

$$\frac{1 \text{ mol}}{180.16 \text{ g } C_6H_{12}O_6} \text{ (from molar mass of glucose)}$$

$$\frac{1 \text{ mL}}{1.03 \text{ g}} \text{ (from given density of the solution)}$$

**SOLVE** Begin with the numerator (6.56 g  $C_6H_{12}O_6$ ) and use the molar mass to convert to mol  $C_6H_{12}O_6$ .

Convert the denominator (100 g solution) into mL of solution (using the density) and then to L of solution.

Finally, divide mol  $C_6H_{12}O_6$  by L solution to arrive at molarity.

**SOLUTION**

$$6.56 \text{ g } C_6H_{12}O_6 \times \frac{1 \text{ mol } C_6H_{12}O_6}{180.16 \text{ g } C_6H_{12}O_6} = 0.036412 \text{ mol } C_6H_{12}O_6$$

$$100 \text{ g soln} \times \frac{1 \text{ mL}}{1.03 \text{ g}} \times \frac{10^{-3} \text{ L}}{1 \text{ mL}} = 0.097087 \text{ L soln}$$

$$\frac{0.036412 \text{ mol } C_6H_{12}O_6}{0.097087 \text{ L soln}} = 0.375 \text{ M } C_6H_{12}O_6$$

**CHECK** The units of the answer are correct. The magnitude seems correct. Very high molarities (especially above 25 M) should immediately appear suspect. One liter of water contains about 55 moles of water molecules, so molarities higher than 55 M are physically impossible.

**FOR PRACTICE 12.5**

What is the molarity of a 10.5% by mass glucose ( $C_6H_{12}O_6$ ) solution? (The density of the solution is 1.03 g/mL.)

**FOR MORE PRACTICE 12.5**

What is the molality of a 10.5% by mass glucose ( $C_6H_{12}O_6$ ) solution? (The density of the solution is 1.03 g/mL.)

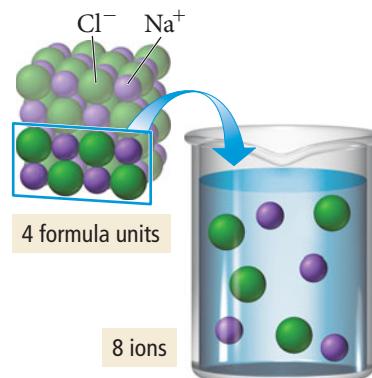
## 12.6 Colligative Properties: Vapor Pressure Lowering, Freezing Point Depression, Boiling Point Elevation, and Osmotic Pressure

Have you ever wondered why you add salt to the ice in an ice-cream maker? Or why salt is scattered on icy roads in cold climates? Salt lowers the temperature at which a salt water solution freezes. A salt and water solution will remain liquid even below 0 °C. When salt is added to ice in the ice-cream maker, an ice/water/salt mixture forms that can reach a temperature of about –10 °C, at which point the cream freezes. On the winter road, the salt allows the ice to melt when the ambient temperature is below freezing.

The depression of the freezing point of water by salt is an example of a **colligative property**, a property that depends on the number of particles dissolved in solution, not on the type of particle. In this section, we examine four colligative properties: vapor pressure lowering, freezing point depression, boiling point elevation, and osmotic pressure. Since these properties depend on the *number* of dissolved particles, nonelectrolytes are treated slightly differently than electrolytes when determining colligative properties. When 1 mol of a nonelectrolyte dissolves in water, it forms 1 mol of dissolved particles. When 1 mol of an electrolyte dissolves in water, however, it normally forms more than 1 mol of dissolved particles (as shown in Figure 12.14 ▶). For example, when 1 mol of NaCl dissolves in water, it forms 1 mol of dissolved  $\text{Na}^+$  ions and 1 mol of dissolved  $\text{Cl}^-$  ions. Therefore, the resulting solution has 2 mol of dissolved particles. The colligative properties of electrolyte solutions reflect this higher concentration of dissolved particles. In this section we examine colligative properties of non-electrolyte solutions; we then expand the concept to include electrolyte solutions in Section 12.7.



▲ In winter, salt is often applied to roads so that the ice will melt at lower temperatures.

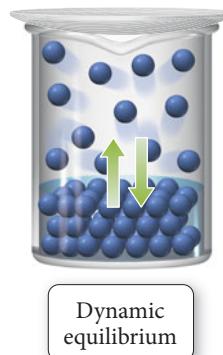


◀ FIGURE 12.14 When sodium chloride is dissolved in water, each mole of NaCl produces 2 mol of particles: 1 mol of  $\text{Na}^+$  cations and 1 mol of  $\text{Cl}^-$  anions.

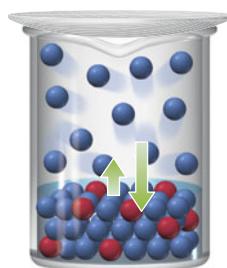
### Vapor Pressure Lowering

Recall from Section 11.5 that the vapor pressure of a liquid is the pressure of the gas above the liquid when the two are in dynamic equilibrium (that is, when the rate of vaporization equals the rate of condensation). What is the effect of a nonvolatile non-electrolyte solute on the vapor pressure of the liquid into which it dissolves? The basic answer to this question is that *the vapor pressure of the solution is lower than the vapor pressure of the pure solvent*. We can understand why this happens in two different ways.

The simplest explanation for why the vapor pressure of a solution is lower than that of the pure solvent is related to the concept of dynamic equilibrium itself. Consider the following representation of a liquid in dynamic equilibrium with its vapor. Here the rate of vaporization is equal to the rate of condensation.

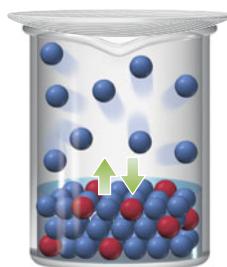


When a nonvolatile solute is added, however, the solute particles (shown in red) interfere with the ability of the solvent particles (blue) to vaporize. The rate of vaporization is thus diminished compared to that of the pure solvent.



Rate of vaporization reduced by solute

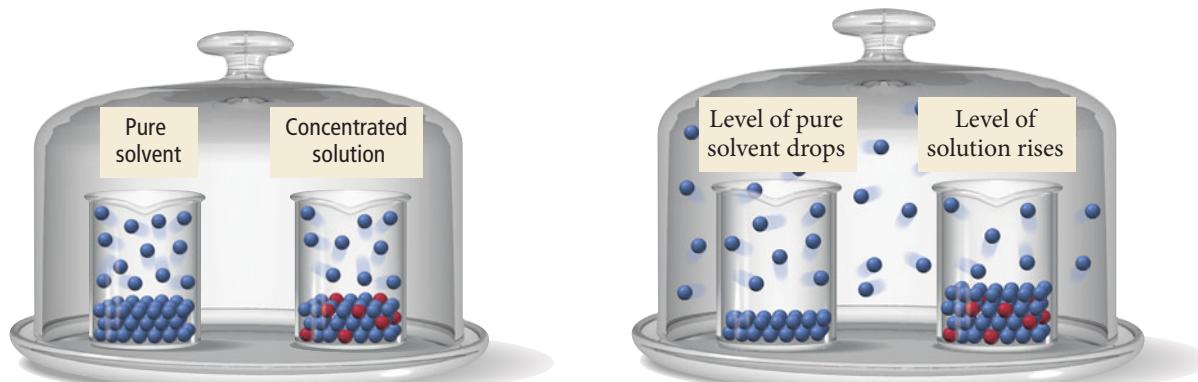
The change in the rate of vaporization creates an imbalance in the rates; the rate of condensation is now *greater* than the rate of vaporization. The net effect is that some of the molecules that were in the gas state condense into the liquid state. As they condense, the reduced number of molecules in the gas state causes the rate of condensation to decrease. Eventually the two rates become equal again, but only after the concentration of solvent molecules in the gas state has decreased.



Equilibrium reestablished but with fewer molecules in gas phase

The result is a lower vapor pressure for the solution compared to the pure solvent.

A more fundamental explanation of why the vapor pressure of a solution is lower than that of the pure solvent is related to the tendency toward mixing (toward greater entropy) that we discussed in Sections 12.1 and 12.2. Recall that a concentrated solution is a *thirsty* solution—it has the ability to draw solvent to itself. We can see a dramatic demonstration of this tendency by placing a concentrated solution of a nonvolatile solute and a beaker of the pure solvent in a sealed container. Over time, the level of the pure solvent will drop and the level of the solution will rise as molecules vaporize out of the pure solvent and condense into the solution. Notice the similarity between this process



and the dehydration caused by drinking seawater. In both cases, a concentrated solution has the ability to draw solvent to itself. The reason is nature's tendency to mix. If a pure solvent and concentrated solution are combined in a beaker, they naturally form a mixture in which the concentrated solution becomes less concentrated than it was initially. Similarly, if a pure solvent and concentrated solution are combined in a sealed container—even though they are in separate beakers—the two mix so that the concentrated solution becomes less concentrated.

The net transfer of solvent from the beaker containing pure solvent to the one containing the solution shows that the vapor pressure of the solution is lower than that of the pure solvent. As solvent molecules vaporize, the vapor pressure in the sealed container rises. Before dynamic equilibrium can be attained, however, the pressure exceeds the vapor pressure of the solution, causing molecules to condense into the solution (the beaker on the right). Therefore, molecules constantly vaporize from the pure solvent, but the solvent's vapor pressure is never reached because molecules are constantly condensing into the solution. The result is a continuous transfer of solvent molecules from the pure solvent to the solution.

We can quantify the vapor pressure of a solution with **Raoult's law**:

$$P_{\text{solution}} = \chi_{\text{solvent}} P_{\text{solvent}}^{\circ}$$

In this equation,  $P_{\text{solution}}$  is the vapor pressure of the solution,  $\chi_{\text{solvent}}$  is the mole fraction of the solvent, and  $P_{\text{solvent}}^{\circ}$  is the vapor pressure of the pure solvent at the same temperature. For example, suppose a water sample at 25 °C contains 0.90 mol of water and 0.10 mol of a nonvolatile solute such as sucrose. The pure water has a vapor pressure of 23.8 torr. We calculate the vapor pressure of the solution by substituting into Raoult's law:

$$\begin{aligned} P_{\text{solution}} &= \chi_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}^{\circ} \\ &= 0.90(23.8 \text{ torr}) \\ &= 21.4 \text{ torr} \end{aligned}$$

Notice that the vapor pressure of the solution is directly proportional to the amount of the solvent in the solution. Since the solvent particles compose 90% of all of the particles in the solution, the vapor pressure of the solution is 90% of the vapor pressure of the pure solvent.

To arrive at an equation that shows how much the vapor pressure is lowered by a solute, we define the **vapor pressure lowering ( $\Delta P$ )** as the difference in vapor pressure between the pure solvent and the solution.

$$\Delta P = P_{\text{solvent}}^{\circ} - P_{\text{solution}}$$

Then, for a two-component solution, we can substitute  $\chi_{\text{solvent}} = 1 - \chi_{\text{solute}}$  into Raoult's law.

$$\begin{aligned} P_{\text{solution}} &= \chi_{\text{solvent}} P_{\text{solvent}}^{\circ} \\ P_{\text{solution}} &= (1 - \chi_{\text{solute}}) P_{\text{solvent}}^{\circ} \\ P_{\text{solvent}}^{\circ} - P_{\text{solution}} &= \chi_{\text{solute}} P_{\text{solvent}}^{\circ} \\ \Delta P &= \chi_{\text{solute}} P_{\text{solvent}}^{\circ} \end{aligned}$$

This last equation indicates that the lowering of the vapor pressure is directly proportional to the mole fraction of the solute.

### EXAMPLE 12.6 Calculating the Vapor Pressure of a Solution Containing a Nonelectrolyte and Nonvolatile Solute

Calculate the vapor pressure at 25 °C of a solution containing 99.5 g sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) and 300.0 mL water. The vapor pressure of pure water at 25 °C is 23.8 torr. Assume the density of water to be 1.00 g/mL.

**SORT** You are given the mass of sucrose and volume of water in a solution. You are also given the vapor pressure and density of pure water and asked to find the vapor pressure of the solution.

**STRATEGIZE** Raoult's law relates the vapor pressure of a solution to the mole fraction of the solvent and the vapor pressure of the pure solvent. Begin by calculating the amount in moles of sucrose and water.

Calculate the mole fraction of the solvent from the calculated amounts of solute and solvent.

Then use Raoult's law to calculate the vapor pressure of the solution.

**SOLVE** Calculate the number of moles of each solution component.

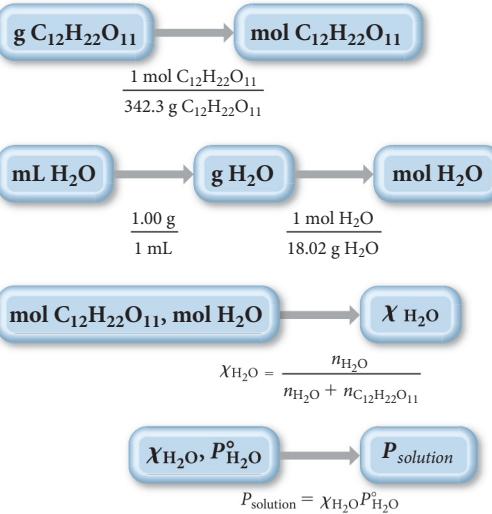
Use the number of moles of each component to calculate the mole fraction of the solvent ( $\text{H}_2\text{O}$ ).

Use the mole fraction of water and the vapor pressure of pure water to calculate the vapor pressure of the solution.

**GIVEN:** 99.5g  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$   
300.0 mL  $\text{H}_2\text{O}$   
 $P^\circ_{\text{H}_2\text{O}} = 23.8 \text{ torr at } 25^\circ\text{C}$   
 $d_{\text{H}_2\text{O}} = 1.00 \text{ g/ml}$

**FIND:**  $P_{\text{solution}}$

### CONCEPTUAL PLAN



### SOLUTION

$$99.5 \text{ g } \text{C}_{12}\text{H}_{22}\text{O}_{11} \times \frac{1 \text{ mol } \text{C}_{12}\text{H}_{22}\text{O}_{11}}{342.30 \text{ g } \text{C}_{12}\text{H}_{22}\text{O}_{11}} = 0.2907 \text{ mol } \text{C}_{12}\text{H}_{22}\text{O}_{11}$$

$$300.0 \text{ mL } \text{H}_2\text{O} \times \frac{1.00 \text{ g}}{1 \text{ mL}} \times \frac{1 \text{ mol } \text{H}_2\text{O}}{18.02 \text{ g } \text{H}_2\text{O}} = 16.65 \text{ mol } \text{H}_2\text{O}$$

$$\begin{aligned} \chi_{\text{H}_2\text{O}} &= \frac{n_{\text{H}_2\text{O}}}{n_{\text{C}_{12}\text{H}_{22}\text{O}_{11}} + n_{\text{H}_2\text{O}}} \\ &= \frac{16.65 \text{ mol}}{0.2907 \text{ mol} + 16.65 \text{ mol}} \\ &= 0.9828 \end{aligned}$$

$$\begin{aligned} P_{\text{solution}} &= \chi_{\text{H}_2\text{O}} P^\circ_{\text{H}_2\text{O}} \\ &= 0.9828 (23.8 \text{ torr}) \\ &= 23.4 \text{ torr} \end{aligned}$$

**CHECK** The units of the answer are correct. The magnitude of the answer seems right because the calculated vapor pressure of the solution is just below that of the pure liquid, as you would expect for a solution with a large mole fraction of solvent.

### FOR PRACTICE 12.6

Calculate the vapor pressure at  $25^\circ\text{C}$  of a solution containing 55.3 g ethylene glycol ( $\text{HOCH}_2\text{CH}_2\text{OH}$ ) and 285.2 g water. The vapor pressure of pure water at  $25^\circ\text{C}$  is 23.8 torr.

### FOR MORE PRACTICE 12.6

A solution containing ethylene glycol and water has a vapor pressure of 7.88 torr at  $10^\circ\text{C}$ . Pure water has a vapor pressure of 9.21 torr at  $10^\circ\text{C}$ . What is the mole fraction of ethylene glycol in the solution?

## Vapor Pressures of Solutions Containing a Volatile (Nonelectrolyte) Solute

Some solutions contain not only a volatile solvent, but also a volatile *solute*. In this case, *both* the solvent and the solute contribute to the overall vapor pressure of the solution. A solution like this may be an **ideal solution** (in which case its behavior follows Raoult's law at all concentrations for both the solvent and the solute) or it may be nonideal (in which case it does not follow Raoult's law). An ideal solution is similar in concept to an ideal gas. Just as an ideal gas follows the ideal gas law exactly, so an ideal solution follows Raoult's law exactly. In an ideal solution, the solute–solvent interactions are similar in magnitude to the solute–solute and solvent–solvent interactions. In this type of solution, the solute simply dilutes the solvent and ideal behavior is observed. The vapor pressure of each of the solution components is described by Raoult's law throughout the entire composition range of the solution. For a two-component solution containing liquids A and B, we can write:

$$P_A = \chi_A P_A^\circ$$

$$P_B = \chi_B P_B^\circ$$

The total pressure above such a solution is the sum of the partial pressures of the components:

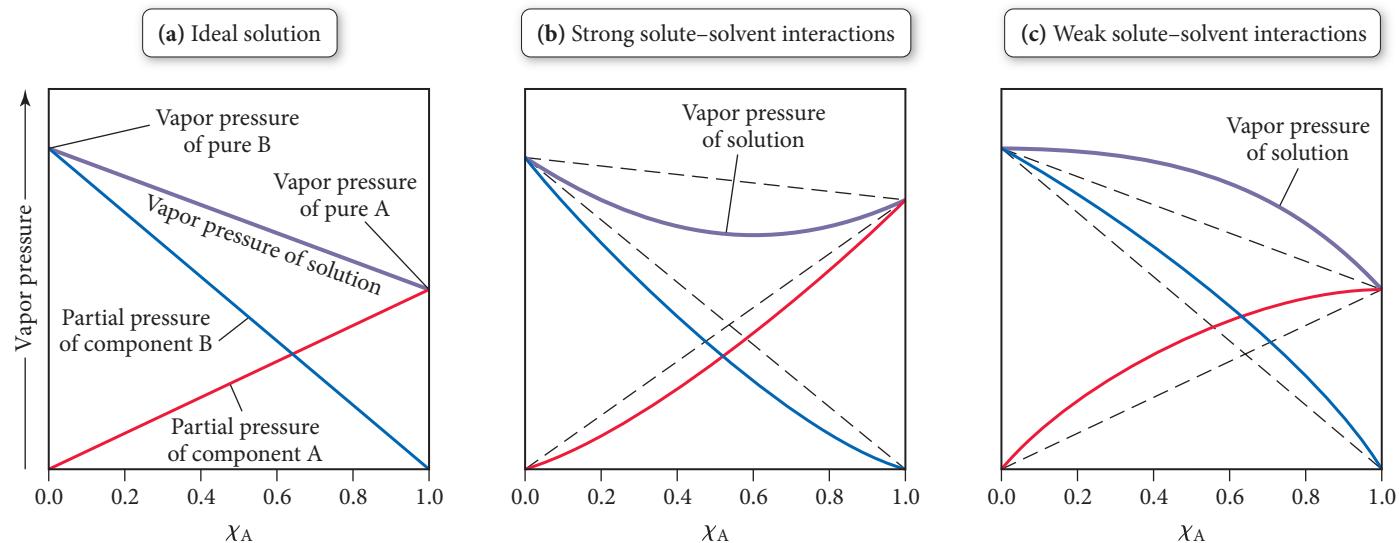
$$P_{\text{tot}} = P_A + P_B$$

Over a complete range of composition of a solution, it no longer makes sense to designate a solvent and solute, so we simply label the two components A and B.

Figure 12.15(a) ▶ is a plot of vapor pressure versus solution composition for an ideal two-component solution.

In a nonideal solution, the solute–solvent interactions are either stronger or weaker than the solvent–solvent interactions. If the solute–solvent interactions are stronger, then the solute tends to prevent the solvent from vaporizing as readily as it would otherwise. If the solution is sufficiently dilute, then the effect will be small and Raoult's law works as an approximation. However, if the solution is not dilute, the effect will be significant and the vapor pressure of the solution will be *less than* that predicted by Raoult's law, as shown in Figure 12.15(b).

### Deviations from Raoult's Law



**▲ FIGURE 12.15** Behavior of Ideal and Nonideal Solutions (a) An ideal solution follows Raoult's law for both components. (b) A solution with particularly strong solute–solvent interactions displays negative deviations from Raoult's law. (c) A solution with particularly weak solute–solvent interactions displays positive deviations from Raoult's law. (The dashed lines in parts b and c represent ideal behavior.)

If, on the other hand, the solute–solvent interactions are weaker than solvent–solvent interactions, then the solute tends to allow more vaporization than would occur with just the solvent. If the solution is not dilute, the effect will be significant and the vapor pressure of the solution will be *greater than* predicted by Raoult’s law, as shown in Figure 12.15(c).

### EXAMPLE 12.7 Calculating the Vapor Pressure of a Two-Component Solution

A solution contains 3.95 g of carbon disulfide ( $\text{CS}_2$ ) and 2.43 g of acetone ( $\text{CH}_3\text{COCH}_3$ ). The vapor pressures at 35 °C of pure carbon disulfide and pure acetone are 515 torr and 332 torr, respectively. Assuming ideal behavior, calculate the vapor pressures of each of the components and the total vapor pressure above the solution. The experimentally measured total vapor pressure of the solution at 35 °C is 645 torr. Is the solution ideal? If not, what can you say about the relative strength of carbon disulfide–acetone interactions compared to the acetone–acetone and carbon disulfide–carbon disulfide interactions?

**SORT** You are given the masses and vapor pressures of carbon disulfide and acetone and are asked to find the vapor pressures of each component in the mixture and the total pressure assuming ideal behavior.

**GIVEN:** 3.95 g  $\text{CS}_2$   
2.43 g  $\text{CH}_3\text{COCH}_3$   
 $P^\circ_{\text{CS}_2} = 515 \text{ torr (at } 35^\circ\text{C)}$   
 $P^\circ_{\text{CH}_3\text{COCH}_3} = 332 \text{ torr (at } 35^\circ\text{C)}$   
 $P_{\text{tot(exp)}} = 645 \text{ torr (at } 35^\circ\text{C)}$

**FIND:**  $P_{\text{CS}_2}$ ,  $P_{\text{CH}_3\text{COCH}_3}$ ,  $P_{\text{tot(ideal)}}$

**STRATEGIZE** This problem requires the use of Raoult’s law to calculate the partial pressures of each component. In order to use Raoult’s law, you must first calculate the mole fractions of the two components. Convert the masses of each component to moles and then use the definition of mole fraction to calculate the mole fraction of carbon disulfide. You can then find the mole fraction of acetone because the mole fractions of the two components add up to 1.

#### CONCEPTUAL PLAN

$$\begin{array}{c} 3.95 \text{ g } \text{CS}_2 \\ \longrightarrow \\ \text{mol } \text{CS}_2 \end{array} \quad \frac{1 \text{ mol } \text{CS}_2}{76.15 \text{ g } \text{CS}_2}$$

$$\begin{array}{c} 2.43 \text{ g } \text{CH}_3\text{COCH}_3 \\ \longrightarrow \\ \text{mol } \text{CH}_3\text{COCH}_3 \end{array} \quad \frac{1 \text{ mol } \text{CH}_3\text{COCH}_3}{58.08 \text{ g } \text{CH}_3\text{COCH}_3}$$

$$\begin{array}{c} \text{mol } \text{CS}_2, \text{ mol } \text{CH}_3\text{OCH}_3 \\ \longrightarrow \\ \chi_{\text{CS}_2}, \chi_{\text{CH}_3\text{COCH}_3} \end{array} \quad \chi_{\text{CS}_2} = \frac{n_{\text{CS}_2}}{n_{\text{CS}_2} + n_{\text{CH}_3\text{COCH}_3}}$$

Use the mole fraction of each component along with Raoult’s law to calculate the partial pressure of each component. The total pressure is the sum of the partial pressures.

$$\begin{aligned} P_{\text{CS}_2} &= \chi_{\text{CS}_2} P^\circ_{\text{CS}_2} \\ P_{\text{CH}_3\text{COCH}_3} &= \chi_{\text{CH}_3\text{COCH}_3} P^\circ_{\text{CH}_3\text{COCH}_3} \\ P_{\text{tot}} &= P_{\text{CS}_2} + P_{\text{CH}_3\text{COCH}_3} \end{aligned}$$

#### RELATIONSHIPS USED

$$\chi_A = \frac{n_A}{n_A + n_B} \text{ (mole fraction definition)}$$

$$P_A = \chi_A P_A^\circ \text{ (Raoult's law)}$$

|   |  |
|---|--|
| <p><b>SOLVE</b> Begin by converting the mass of each component to the amounts in moles.</p>   | <p><b>SOLUTION</b></p> $3.95 \text{ g } \text{CS}_2 \times \frac{1 \text{ mol } \text{CS}_2}{76.15 \text{ g } \text{CS}_2} = 0.05187 \text{ mol } \text{CS}_2$ $2.43 \text{ g } \text{CH}_3\text{COCH}_3 \times \frac{1 \text{ mol } \text{CH}_3\text{COCH}_3}{58.08 \text{ g } \text{CH}_3\text{COCH}_3} = 0.04184 \text{ mol } \text{CH}_3\text{COCH}_3$ |
| <p>Then calculate the mole fraction of carbon disulfide.</p>  | $\chi_{\text{CS}_2} = \frac{n_{\text{CS}_2}}{n_{\text{CS}_2} + n_{\text{CH}_3\text{COCH}_3}}$ $= \frac{0.05187 \text{ mol}}{0.05187 \text{ mol} + 0.04184 \text{ mol}}$ $= 0.5535$   |
| <p>Calculate the mole fraction of acetone by subtracting the mole fraction of carbon disulfide from 1.</p>  | $\chi_{\text{CH}_3\text{COCH}_3} = 1 - 0.5535$ $= 0.4465$  |
| <p>Calculate the partial pressures of carbon disulfide and acetone by using Raoult's law and the given values of the vapor pressures of the pure substances.</p>  | $P_{\text{CS}_2} = \chi_{\text{CS}_2} P_{\text{CS}_2}^\circ$ $= 0.5535 (515 \text{ torr})$ $= 285 \text{ torr}$ $P_{\text{CH}_3\text{COCH}_3} = \chi_{\text{CH}_3\text{COCH}_3} P_{\text{CH}_3\text{COCH}_3}^\circ$ $= 0.4465 (332 \text{ torr})$ $= 148 \text{ torr}$   |
| <p>Calculate the total pressure by summing the partial pressures.</p>   | $P_{\text{tot}}(\text{ideal}) = 285 \text{ torr} + 148 \text{ torr}$ $= 433 \text{ torr}$  |
| <p>Lastly, compare the calculated total pressure for the ideal case to the experimentally measured total pressure. Since the experimentally measured pressure is greater than the calculated pressure, we can conclude that the interactions between the two components are weaker than the interactions between the components themselves.</p> | $P_{\text{tot}}(\text{exp}) = 645 \text{ torr}$ $P_{\text{tot}}(\text{exp}) > P_{\text{tot}}(\text{ideal})$ <p>The solution is not ideal and shows positive deviations from Raoult's law. Therefore, carbon disulfide–acetone interactions must be weaker than acetone–acetone and carbon disulfide–carbon disulfide interactions.</p>                     |

**CHECK** The units of the answer (torr) are correct. The magnitude seems reasonable given the partial pressures of the pure substances.

#### FOR PRACTICE 12.7

A solution of benzene ( $\text{C}_6\text{H}_6$ ) and toluene ( $\text{C}_7\text{H}_8$ ) is 25.0% benzene by mass. The vapor pressures of pure benzene and pure toluene at 25 °C are 94.2 torr and 28.4 torr, respectively. Assuming ideal behavior, calculate the following:

- (a) The vapor pressure of each of the solution components in the mixture.
- (b) The total pressure above the solution.
- (c) The composition of the vapor in mass percent.

Why is the composition of the vapor different from the composition of the solution?

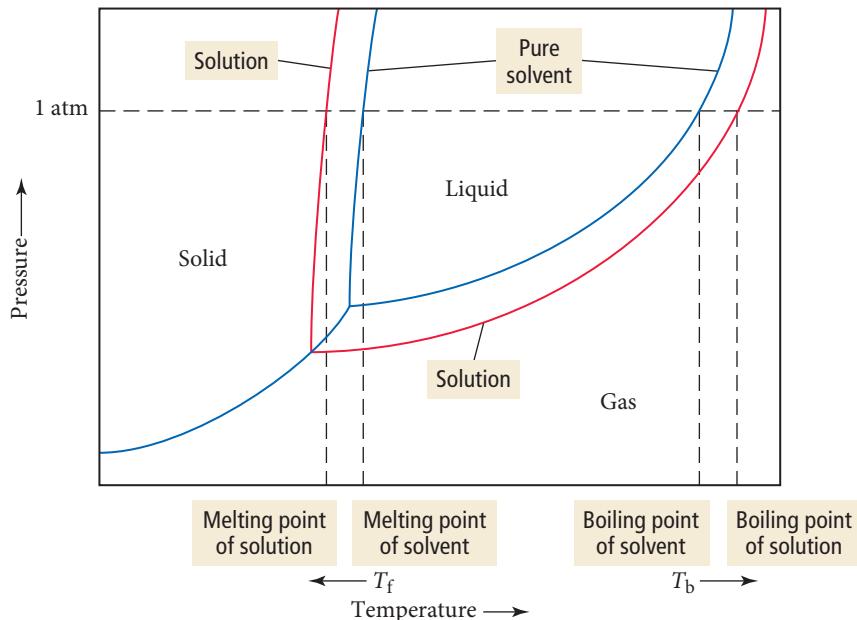
## Conceptual Connection 12.5 Raoult's Law

A solution contains equal amounts (in moles) of liquid components A and B. The vapor pressure of pure A is 100 mmHg and that of pure B is 200 mmHg. The experimentally measured vapor pressure of the solution is 120 mmHg. What are the relative strengths of the solute–solute, solute–solvent, and solvent–solvent interactions in this solution?

### Freezing Point Depression and Boiling Point Elevation

Vapor pressure lowering occurs at all temperatures. We can see the effect of vapor pressure lowering over a range of temperatures by comparing the phase diagrams for a pure solvent and for a solution containing a nonvolatile solute:

- A nonvolatile solute lowers the vapor pressure of a solution, resulting in a lower freezing point and an elevated boiling point.



Notice that the vapor pressure for the solution is shifted downward compared to that of the pure solvent. Consequently, the vapor pressure curve intersects the solid–gas curve at a lower temperature. The net effect is that the solution has a *lower melting point* and a *higher boiling point* than the pure solvent. These effects are called **freezing point depression** and **boiling point elevation**, both of which are colligative properties (like vapor pressure lowering).

The freezing point of a solution containing a nonvolatile solute is lower than the freezing point of the pure solvent. For example, antifreeze, used to prevent the freezing of engine blocks in cold climates, is an aqueous solution of ethylene glycol ( $C_2H_6O_2$ ). The more concentrated the solution, the lower the freezing point becomes.

The amount that the freezing point decreases is given by the following equation:

$$\Delta T_f = m \times K_f$$

where

- $\Delta T_f$  is the change in temperature of the freezing point in Celsius degrees (relative to the freezing point of the pure solvent), usually reported as a positive number;
- $m$  is the molality of the solution in moles solute per kilogram solvent;
- $K_f$  is the freezing point depression constant for the solvent.

For water,

$$K_f = 1.86 \text{ } ^\circ\text{C}/\text{m}$$

When an aqueous solution containing a dissolved solid solute freezes slowly, the ice that forms does not normally contain much of the solute. For example, when ice forms in ocean



- ▲ Antifreeze is an aqueous solution of ethylene glycol. The solution has a lower freezing point and higher boiling point than pure water.

**TABLE 12.8** Freezing Point Depression and Boiling Point Elevation Constants for Several Liquid Solvents

| Solvent                          | Normal Freezing Point (°C) | $K_f$ (°C/m) | Normal Boiling Point (°C) | $K_b$ (°C/m) |
|----------------------------------|----------------------------|--------------|---------------------------|--------------|
| Benzene ( $C_6H_6$ )             | 5.5                        | 5.12         | 80.1                      | 2.53         |
| Carbon tetrachloride ( $CCl_4$ ) | –22.9                      | 29.9         | 76.7                      | 5.03         |
| Chloroform ( $CHCl_3$ )          | –63.5                      | 4.70         | 61.2                      | 3.63         |
| Ethanol ( $C_2H_5OH$ )           | –114.1                     | 1.99         | 78.3                      | 1.22         |
| Diethyl ether ( $C_4H_{10}O$ )   | –116.3                     | 1.79         | 34.6                      | 2.02         |
| Water ( $H_2O$ )                 | 0.00                       | 1.86         | 100.0                     | 0.512        |

water, the ice is not salt water, but freshwater. As the ice forms, the crystal structure of the ice tends to exclude the solute particles. You can verify this yourself by partially freezing a salt water solution in the freezer. Take out the newly formed ice, rinse it several times, and taste it. Compare its taste to the taste of the original solution. The ice is much less salty.

Table 12.8 provides freezing point depression and boiling point elevation constants for several liquids. Calculating the freezing point of a solution involves substituting into the freezing point depression equation as Example 12.8 demonstrates.

### EXAMPLE 12.8 Freezing Point Depression

Calculate the freezing point of a 1.7 *m* aqueous ethylene glycol solution

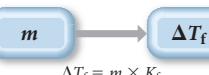
**SORT** You are given the molality of a solution and asked to find its freezing point.

**GIVEN:** 1.7 *m* solution

**FIND:** freezing point (from  $\Delta T_f$ )

**STRATEGIZE** To solve this problem, use the freezing point depression equation.

**CONCEPTUAL PLAN**



**SOLVE** Substitute into the equation to calculate  $\Delta T_f$ .

The actual freezing point is the freezing point of pure water (0.00 °C) –  $\Delta T_f$ .

**SOLUTION**

$$\begin{aligned}\Delta T_f &= m \times K_f \\ &= 1.7 \text{ } m \times 1.86 \text{ } ^\circ\text{C}/\text{m} \\ &= 3.2 \text{ } ^\circ\text{C}\end{aligned}$$

$$\begin{aligned}\text{Freezing point} &= 0.00 \text{ } ^\circ\text{C} - 3.2 \text{ } ^\circ\text{C} \\ &= -3.2 \text{ } ^\circ\text{C}\end{aligned}$$

**CHECK** The units of the answer are correct. The magnitude seems about right. The expected range for freezing points of an aqueous solution is anywhere from –10 °C to just below 0 °C. Any answers out of this range would be suspect.

#### FOR PRACTICE 12.8

Calculate the freezing point of a 2.6 *m* aqueous sucrose solution.

The boiling point of a solution containing a nonvolatile solute is higher than the boiling point of the pure solvent. In automobiles, antifreeze not only prevents the freezing of water within engine blocks in cold climates, it also prevents the boiling of water within engine blocks in hot climates. The amount that the boiling point rises in solutions is given by the equation:

$$\Delta T_b = m \times K_b$$

where

- $\Delta T_b$  is the change in temperature of the boiling point in Celsius degrees (relative to the boiling point of the pure solvent);

- $m$  is the molality of the solution in moles solute per kilogram solvent;
- $K_b$  is the boiling point elevation constant for the solvent.

For water,

$$K_b = 0.512 \text{ } ^\circ\text{C}/\text{m}$$

Calculating the boiling point of a solution involves substituting into the boiling-point elevation equation, as Example 12.9 demonstrates.

### Conceptual Connection 12.6 Boiling Point Elevation

Solution A is a 1.0 M solution with a nonionic solute and water as the solvent. Solution B is a 1.0 M solution with the same nonionic solute and ethanol as the solvent. Which solution has the greatest increase in its boiling point (relative to the pure solvent)?

#### EXAMPLE 12.9 Boiling Point Elevation

What mass of ethylene glycol ( $\text{C}_2\text{H}_6\text{O}_2$ ), in grams, must be added to 1.0 kg of water to produce a solution that boils at  $105.0 \text{ } ^\circ\text{C}$ ?



**SORT** You are given the desired boiling point of an ethylene glycol solution containing 1.0 kg of water and asked to find the mass of ethylene glycol you need to add to achieve the boiling point.

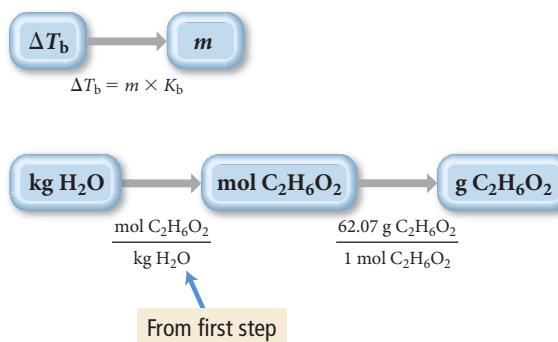
**STRATEGIZE** To solve this problem, use the boiling-point elevation equation to calculate the desired molality of the solution from  $\Delta T_b$ .

Then use that molality to determine how many moles of ethylene glycol are needed per kilogram of water. Finally, calculate the molar mass of ethylene glycol and use it to convert from moles of ethylene glycol to mass of ethylene glycol.

**GIVEN:**  $\Delta T_b = 5.0 \text{ } ^\circ\text{C}$ , 1.0 kg  $\text{H}_2\text{O}$

**FIND:** g  $\text{C}_2\text{H}_6\text{O}_2$

#### CONCEPTUAL PLAN



**RELATIONSHIPS USED**  $\text{C}_2\text{H}_6\text{O}_2$  molar mass = 62.07 g/mol  
 $\Delta T_b = m \times K_b$  (boiling point elevation)

**SOLVE** Begin by solving the boiling point elevation equation for molality and substituting the required quantities to calculate  $m$ .

#### SOLUTION

$$\Delta T_b = m \times K_b$$

$$m = \frac{\Delta T_b}{K_b} = \frac{5.0 \text{ } ^\circ\text{C}}{0.512 \frac{\text{ } ^\circ\text{C}}{\text{m}}} = 9.77 \text{ m}$$

$$1.0 \text{ kg } \text{H}_2\text{O} \times \frac{9.77 \text{ mol } \text{C}_2\text{H}_6\text{O}_2}{\text{kg } \text{H}_2\text{O}} \times \frac{62.07 \text{ g } \text{C}_2\text{H}_6\text{O}_2}{1 \text{ mol } \text{C}_2\text{H}_6\text{O}_2} = 6.1 \times 10^2 \text{ g } \text{C}_2\text{H}_6\text{O}_2$$

**CHECK** The units of the answer are correct. The magnitude might seem a little high initially, but the boiling point elevation constant is so small that a lot of solute is required to raise the boiling point by a small amount.

#### FOR PRACTICE 12.9

Calculate the boiling point of a 3.60  $m$  aqueous sucrose solution.



## Chemistry in Your Day

### Antifreeze in Frogs

Wood frogs (*Rana sylvatica*) look like most other frogs. They are a few inches long and have characteristic greenish-brown skin. However, wood frogs survive cold winters in a remarkable way—they partially freeze. In its partially frozen state, a wood frog has no heartbeat, no blood circulation, no breathing, and no brain activity. Within 1–2 hours of thawing, however, these vital functions return and the frog hops off to find food. How does the wood frog do this?

Most cold-blooded animals cannot survive freezing temperatures because the water within their cells freezes. As we learned in Section 11.9, when water freezes, it expands, irreversibly damaging cells. When the wood frog hibernates for the winter, however, it produces large amounts of glucose that is secreted into its bloodstream and fills the interior of its cells. When the temperature drops below freezing, extracellular body fluids, such as those in the frog's abdominal cavity, freeze solid. Fluids within cells, however, remain liquid because the high glucose concentration lowers their freezing point. In other words, the concentrated glucose solution within the frog's cells acts as antifreeze, preventing the water within the cells from freezing and allowing the frog to survive.



### Question

The wood frog can survive at body temperatures as low as  $-8.0\text{ }^{\circ}\text{C}$ . Calculate the molality of a glucose solution ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) required to lower the freezing point of water to  $-8.0\text{ }^{\circ}\text{C}$ .

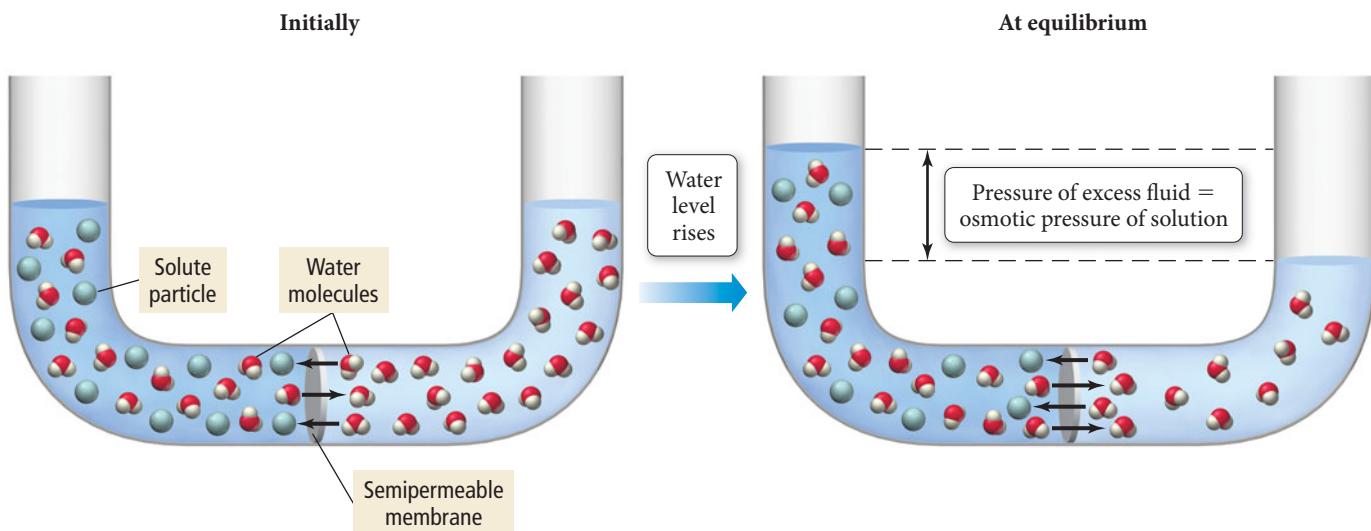
▲ The wood frog survives winter by partially freezing. It protects its cells by flooding them with glucose, which acts as an antifreeze.

## Osmotic Pressure

The process by which seawater causes dehydration (discussed in the opening section of this chapter) is **osmosis**. **Osmosis** is the flow of solvent from a solution of lower solute concentration to one of higher solute concentration. Concentrated solutions draw solvent from more dilute solutions because of nature's tendency to mix.

Figure 12.16 ▼ illustrates an osmosis cell. The left side of the cell contains a concentrated saltwater solution and the right side of the cell contains pure water. A **semipermeable membrane**—a membrane that selectively allows some substances to pass through but not

### Osmosis and Osmotic Pressure



▲ FIGURE 12.16 An Osmosis Cell In an osmosis cell, water flows from the pure-water side of the cell through the semipermeable membrane to the salt water side.

others—separates the two halves of the cell. Water flows by osmosis from the pure-water side of the cell through the semipermeable membrane and into the saltwater side. Over time, the water level on the left side of the cell rises, while the water level on the right side of the cell falls. If external pressure is applied to the water in the left cell, this process can be opposed and even stopped. The pressure required to stop the osmotic flow, called the **osmotic pressure**, is given by the following equation:

$$\Pi = MRT$$

where  $M$  is the molarity of the solution,  $T$  is the temperature (in Kelvin), and  $R$  is the ideal gas constant ( $0.08206 \text{ L} \cdot \text{atm/mol} \cdot \text{K}$ ).

### EXAMPLE 12.10 Osmotic Pressure

The osmotic pressure of a solution containing 5.87 mg of an unknown protein per 10.0 mL of solution is 2.45 torr at 25 °C. Find the molar mass of the unknown protein.

**SORT** You are given that a solution of an unknown protein contains 5.87 mg of the protein per 10.0 mL of solution. You are also given the osmotic pressure of the solution at a particular temperature and asked to find the molar mass of the unknown protein.

**STRATEGIZE** Step 1: Use the given osmotic pressure and temperature to find the molarity of the protein solution.

Step 2: Use the molarity calculated in step 1 to find the number of moles of protein in 10 mL of solution.

Step 3: Finally, use the number of moles of the protein calculated in step 2 and the given mass of the protein in 10.0 mL of solution to find the molar mass.

**SOLVE** Step 1: Begin by solving the osmotic pressure equation for molarity and substituting in the required quantities in the correct units to calculate  $M$ .

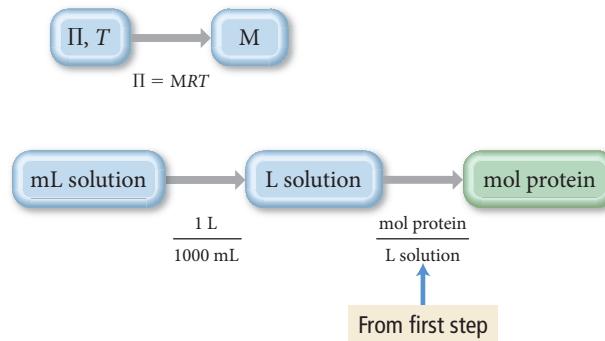
Step 2: Begin with the given volume, convert to liters, then use the molarity to find the number of moles of protein.

Step 3: Use the given mass and the number of moles from step 2 to calculate the molar mass of the protein.

**GIVEN:** 5.87 mg protein  
10.0 mL solution  
 $\Pi = 2.45 \text{ torr}$   
 $T = 25^\circ\text{C}$

**FIND:** molar mass of protein (g/mol)

#### CONCEPTUAL PLAN



$$\text{Molar mass} = \frac{\text{mass protein}}{\text{moles protein}}$$

**RELATIONSHIPS USED**  $\Pi = MRT$  (osmotic pressure equation)

#### SOLUTION

$$\Pi = MRT$$

$$M = \frac{\Pi}{RT} = \frac{2.45 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}}}{0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} (298 \text{ K})}$$

$$= 1.318 \times 10^{-4} \text{ M}$$

$$10.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{1.318 \times 10^{-4} \text{ mol}}{\text{L}}$$

$$= 1.318 \times 10^{-6} \text{ mol}$$

$$\text{Molar mass} = \frac{\text{mass protein}}{\text{moles protein}}$$

$$= \frac{5.87 \times 10^{-3} \text{ g}}{1.318 \times 10^{-6} \text{ mol}} = 4.45 \times 10^3 \text{ g/mol}$$

**CHECK** The units of the answer are correct. The magnitude might seem a little high initially, but proteins are large molecules and therefore have high molar masses.

### FOR PRACTICE 12.10

Calculate the osmotic pressure (in atm) of a solution containing 1.50 g ethylene glycol ( $\text{C}_2\text{H}_6\text{O}_2$ ) in 50.0 mL of solution at 25 °C.

## 12.7 Colligative Properties of Strong Electrolyte Solutions

At the beginning of Section 12.6, we saw that colligative properties depend on the number of dissolved particles and that electrolytes must therefore be treated slightly differently than nonelectrolytes when determining colligative properties. For example, the freezing point depression of a 0.10 *m* sucrose solution is  $\Delta T_f = 0.186$  °C. However, the freezing point depression of a 0.10 *m* sodium chloride solution is nearly twice this large. Why? Because 1 mol of sodium chloride dissociates into nearly 2 mol of ions in solution. The ratio of moles of particles in solution to moles of formula units dissolved is called the **van't Hoff factor** (*i*):

$$i = \frac{\text{moles of particles in solution}}{\text{moles of formula units dissolved}}$$

Since 1 mol of NaCl produces 2 mol of particles in solution, we expect the van't Hoff factor for NaCl to be exactly 2. In reality, this expected factor only occurs in very dilute solutions. For example, the van't Hoff factor for a 0.10 *m* NaCl solution is 1.87 and that for a 0.010 *m* NaCl solution is 1.94. The van't Hoff factor approaches the expected value at infinite dilution (as the concentration approaches zero). Table 12.9 lists the actual and expected van't Hoff factors for a number of solutes.

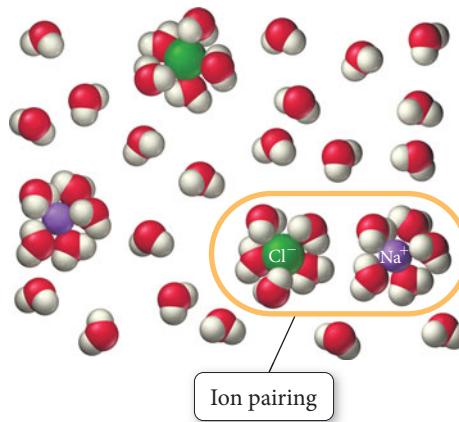
The reason that van't Hoff factors do not exactly equal expected values is that some ions effectively pair in solution. We expect the dissociation of an ionic compound to be complete in solution. In reality, however, the dissociation is not complete—at any moment, some cations pair with anions (Figure 12.17 ►), slightly reducing the number of particles in solution.

To calculate freezing point depression, boiling point elevation, and osmotic pressure of ionic solutions we use the van't Hoff factor in each equation as follows:

$$\Delta T_f = im \times K_f \text{ (freezing point depression)}$$

$$\Delta T_b = im \times K_b \text{ (boiling point elevation)}$$

$$\Pi = iMRT \text{ (osmotic pressure)}$$



◀ FIGURE 12.17 Ion Pairing

Hydrated anions and cations may get close enough together to effectively pair, lowering the concentration of particles below what would be expected.

### Conceptual Connection 12.7 Colligative Properties

Which solution has the highest boiling point?

- (a) 0.50 M  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$
- (b) 0.50 M NaCl
- (c) 0.50 M  $\text{MgCl}_2$

### EXAMPLE 12.11 Van't Hoff Factor and Freezing Point Depression

The freezing point of an aqueous  $0.050\text{ m}$   $\text{CaCl}_2$  solution is  $-0.27\text{ }^\circ\text{C}$ . What is the van't Hoff factor ( $i$ ) for  $\text{CaCl}_2$  at this concentration? How does it compare to the expected value of  $i$ ?

**SORT** You are given the molality of a solution and its freezing point. You are asked to find the value of  $i$ , the van't Hoff factor, and compare it to the expected value.

**STRATEGIZE** To solve this problem, use the freezing point depression equation including the van't Hoff factor.

**SOLVE** Solve the freezing point depression equation for  $i$ , substituting in the given quantities to calculate its value.

The expected value of  $i$  for  $\text{CaCl}_2$  is 3 because calcium chloride forms 3 mol of ions for each mole of calcium chloride that dissolves. The experimental value is slightly less than 3, probably because of ion pairing.

**GIVEN:**  $0.050\text{ m}$   $\text{CaCl}_2$  solution,  
 $\Delta T_f = 0.27\text{ }^\circ\text{C}$

**FIND:**  $i$

**CONCEPTUAL PLAN**  
 $\Delta T_f = im \times K_f$

**SOLUTION**

$$\Delta T_f = im \times K_f$$

$$i = \frac{\Delta T_f}{m \times K_f}$$

$$= \frac{0.27\text{ }^\circ\text{C}}{0.050\text{ m} \times \frac{1.86\text{ }^\circ\text{C}}{\text{m}}}$$

$$= 2.9$$

**CHECK** The answer has no units, as expected since  $i$  is a ratio. The magnitude is about right since it is close to the value you would expect upon complete dissociation of  $\text{CaCl}_2$ .

#### FOR PRACTICE 12.11

Calculate the freezing point of an aqueous  $0.10\text{ m}$   $\text{FeCl}_3$  solution using a van't Hoff factor of 3.2.

### Strong Electrolytes and Vapor Pressure

Just as the freezing point depression of a solution containing an electrolyte solute is greater than that of a solution containing the same concentration of a nonelectrolyte solute, so the vapor pressure lowering is greater (for the same reasons). The vapor pressure for a sodium chloride solution, for example, is lowered about twice as much as it is for a nonelectrolyte solution of the same concentration. To calculate the vapor pressure of a solution containing an ionic solute, we need to account for the dissociation of the solute when we calculate the mole fraction of the solvent, as shown in Example 12.12.

### EXAMPLE 12.12 Calculating the Vapor Pressure of a Solution Containing an Ionic Solute

A solution contains  $0.102\text{ mol}$   $\text{Ca}(\text{NO}_3)_2$  and  $0.927\text{ mol}$   $\text{H}_2\text{O}$ . Calculate the vapor pressure of the solution at  $55\text{ }^\circ\text{C}$ . The vapor pressure of pure water at  $55\text{ }^\circ\text{C}$  is 118.1 torr. (Assume that the solute completely dissociates.)

**SORT** You are given the number of moles of each component of a solution and asked to find the vapor pressure of the solution. You are also given the vapor pressure of pure water at the appropriate temperature.

**GIVEN:**  $0.102\text{ mol}$   $\text{Ca}(\text{NO}_3)_2$

$0.927\text{ mol}$   $\text{H}_2\text{O}$

$P_{\text{H}_2\text{O}}^\circ = 118.1\text{ torr}$  (at  $55\text{ }^\circ\text{C}$ )

**FIND:**  $P_{\text{solution}}$

**STRATEGIZE** To solve this problem, use Raoult's law as you did in Example 12.6. Calculate  $\chi_{\text{solvent}}$  from the given amounts of solute and solvent.

**CONCEPTUAL PLAN**



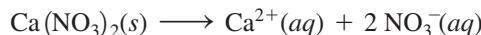
$$P_{\text{solution}} = \chi_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}^\circ$$

**SOLVE** The key to this problem is to understand the dissociation of calcium nitrate. Write an equation showing the dissociation.

Since 1 mol of calcium nitrate dissociates into 3 mol of dissolved particles, the number of moles of calcium nitrate must be multiplied by 3 when computing the mole fraction.

Use the mole fraction of water and the vapor pressure of pure water to calculate the vapor pressure of the solution.

### SOLUTION



$$\begin{aligned}\chi_{\text{H}_2\text{O}} &= \frac{n_{\text{H}_2\text{O}}}{3 \times n_{\text{Ca}(\text{NO}_3)_2} + n_{\text{H}_2\text{O}}} \\ &= \frac{0.927 \text{ mol}}{3(0.102) \text{ mol} + 0.927 \text{ mol}} \\ &= 0.7518\end{aligned}$$

$$\begin{aligned}P_{\text{solution}} &= \chi_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}^\circ \\ &= 0.7518(118.1 \text{ torr}) \\ &= 88.8 \text{ torr}\end{aligned}$$

**CHECK** The units of the answer are correct. The magnitude also seems right because the calculated vapor pressure of the solution is significantly less than that of the pure solvent, as you would expect for a solution with a significant amount of solute.

### FOR PRACTICE 12.12

A solution contains 0.115 mol H<sub>2</sub>O and an unknown number of moles of sodium chloride. The vapor pressure of the solution at 30 °C is 25.7 torr. The vapor pressure of pure water at 30 °C is 31.8 torr. Calculate the number of moles of sodium chloride in the solution.

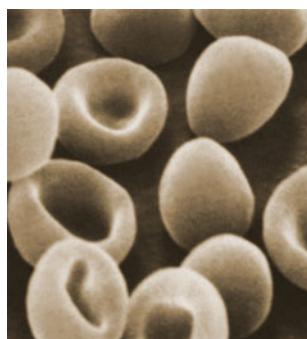
## Colligative Properties and Medical Solutions

Doctors and others healthcare workers often administer solutions to patients. The osmotic pressure of these solutions is controlled for the desired effect on the patient. Solutions having osmotic pressures greater than those of body fluids are called *hyperosmotic*. These solutions take water out of cells and tissues. When a human cell is placed in a hyperosmotic solution, it tends to shrivel as it loses water to the surrounding solution (Figure 12.18b ▼). Solutions having osmotic pressures less than those of body fluids are called *hyposmotic*. These solutions pump water into cells. When a human cell is placed in a hyposmotic solution—such as pure water, for example—water enters the cell, sometimes causing it to burst (Figure 12.18c).

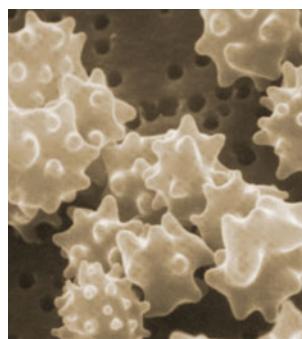
Isosmotic solution

Hyperosmotic solution

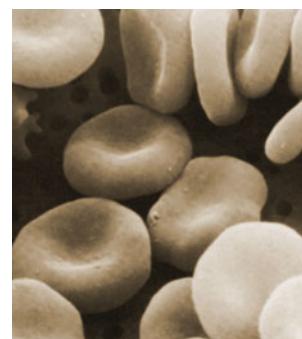
Hyposmotic solution



(a) Normal red blood cells



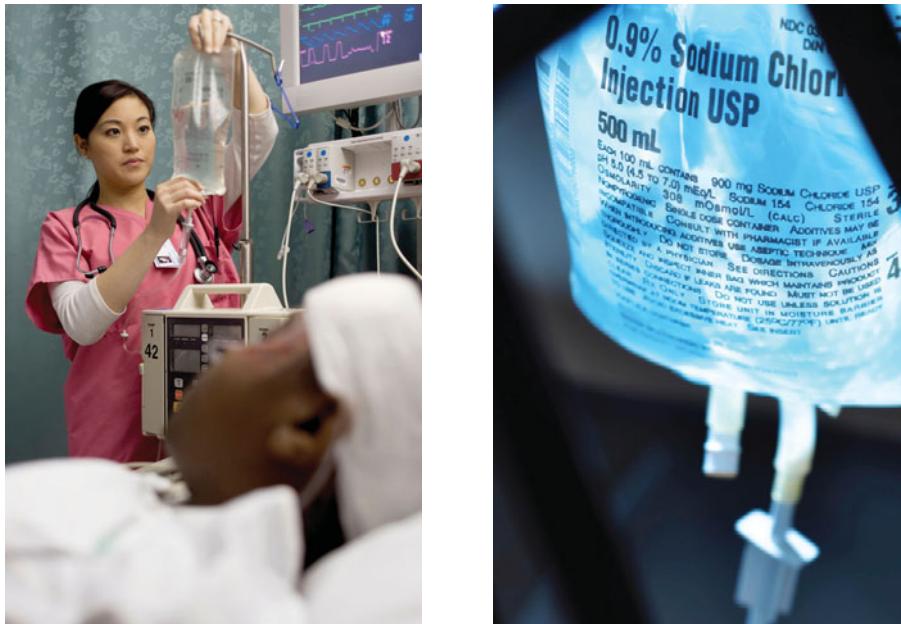
(b) Shriveled red blood cells



(c) Swollen red blood cells

**▲ FIGURE 12.18 Red Blood Cells and Osmosis** (a) In an isosmotic solution, red blood cells have the normal shape shown here. In a hyperosmotic solution (b), they lose water and shrink. In a hyposmotic solution (c), they swell up and may burst as water flows into the cell.

Intravenous solutions—those that are administered directly into a patient’s veins—must have osmotic pressures equal to those of body fluids. These solutions are called *isosmotic* (or *isotonic*). When a patient is given an IV in a hospital, the majority of the fluid is usually an isosmotic saline solution—a solution containing 0.9 g NaCl per 100 mL of solution. In medicine and in other health-related fields, solution concentrations are often reported in units that indicate the mass of the solute per given volume of solution. Also common is *percent mass to volume*—which is the mass of the solute in grams divided by the volume of the solution in milliliters times 100%. In these units, the concentration of an isotonic saline solution is 0.9% mass/volume.



► Fluids used for intravenous transfusion must be isosmotic with bodily fluids—that is, they must have the same osmotic pressure.

## 12.8 Colloids



**▲ FIGURE 12.19 A Colloid** Soapy water is an example of a colloidal dispersion. The haze is due to the scattering of light by the colloidal particles.

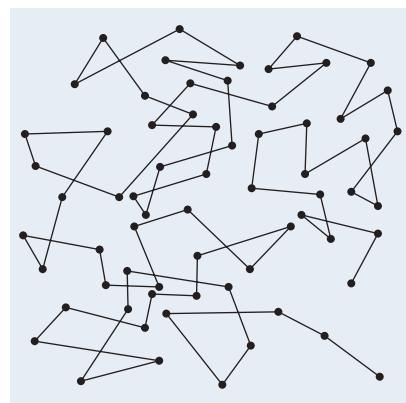
When you mix water and soap together, the resulting mixture has a distinctive haze (Figure 12.19 ▲). Soapy water is hazy because soap and water form a *colloidal dispersion*, rather than a true solution. A **colloidal dispersion**, or more simply a **colloid**, is a mixture in which a dispersed substance (which is solute-like) is finely divided in a dispersing medium (which is solvent-like). Examples of colloids including fog, smoke, whipped cream, and milk are listed in Table 12.10

Whether or not a mixture is a colloid is determined by the size of the particles it contains. If the particles are small (for example, individual small molecules), then the mixture is a solution. If the particles have a diameter greater than 1  $\mu\text{m}$  (for example, grains of sand), then the mixture is a heterogeneous mixture. Sand stirred into water will slowly settle out of the water. *If the particles are between 1 nm and 1000 nm in size, the mixture is a colloid.* Colloidal particles are small enough that they stay dispersed throughout the dispersing medium by collisions with other molecules or atoms. When you view a colloidal particle dispersed in a liquid under a microscope, you can witness its jittery motion, which proceeds along a random path, as shown in Figure 12.20 ►. This motion, called Brownian motion, is caused by collisions with molecules in the liquid. In the beginning of the twentieth century, Brownian motion was a decisive factor in confirming the molecular and atomic nature of matter.

Soap forms a colloid because of its unique structure, shown in Figure 12.21 ►. One end of the molecule is ionic and therefore interacts strongly with water molecules via ion–dipole interactions. However, the other end of the soap molecule is a long, nonpolar,

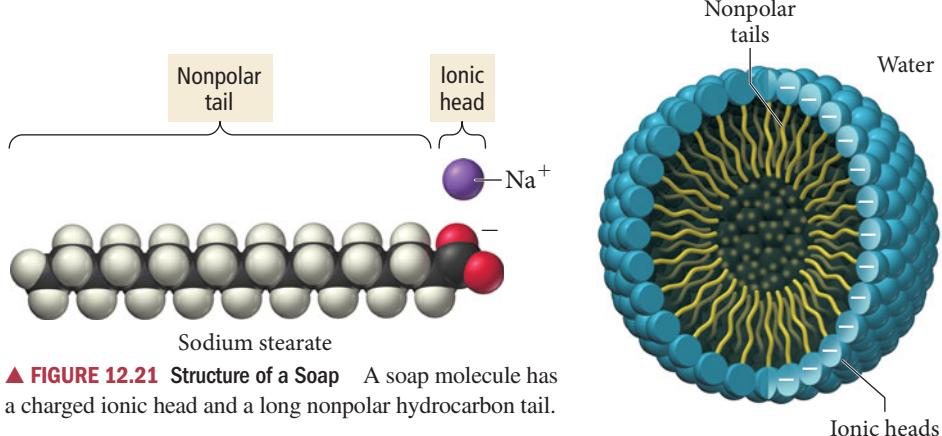
**TABLE 12.10** Types of Colloidal Dispersions

| Classification | Dispersing Substance (Solute-like) | Dispersing Medium (Solvent-like) | Example  |
|----------------|------------------------------------|----------------------------------|--|
| Aerosol        | Liquid                             | Gas                              |  Fog (water droplets in air)              |
| Solid aerosol  | Solid                              | Gas                              |  Smoke (ash in air)                       |
| Foam           | Gas                                | Liquid                           |  Whipped cream (air bubbles in butterfat) |
| Emulsion       | Liquid                             | Liquid                           |  Milk (milk fat globules in water)        |
| Solid emulsion | Liquid                             | Solid                            |  Opal (water in silica glass)            |

**▲ FIGURE 12.20** Brownian Motion

A colloidal particle exhibits Brownian motion, moving in a jerky, haphazard path as it undergoes collisions with molecules in the liquid.

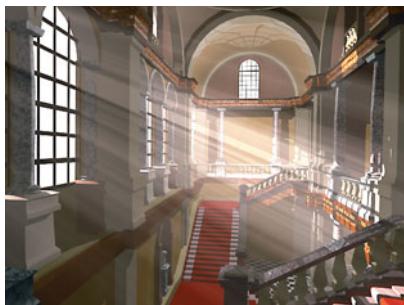
hydrocarbon tail. When enough soap is added to water, the soap molecules aggregate in structures called *micelles* (Figure 12.22 ▼). In a micelle, the nonpolar hydrocarbon tails crowd into the center of a sphere to maximize their interactions with one another. The ionic heads orient toward the surface of the sphere where they can interact with water molecules. The micelle structures are responsible for the haze seen in soapy water—they are too small to be seen by the naked eye, but they still scatter light (as particles in other

**▲ FIGURE 12.21** Structure of a Soap A soap molecule has a charged ionic head and a long nonpolar hydrocarbon tail.**▼ FIGURE 12.22** Micelle Structure

In a micelle, the nonpolar tails of soap molecules (or of other molecules that have properties that are similar to soap) are oriented inward (where they can interact with one another), and the ionic heads are oriented outward (where they can interact with the polar water molecules).



**▲ FIGURE 12.23 The Tyndall Effect** When a light beam passes through a colloidal suspension (left), it is visible because the colloid particles scatter some of the light. The beam is not visible in pure water (right), nor would it be visible in a noncolloidal solution.

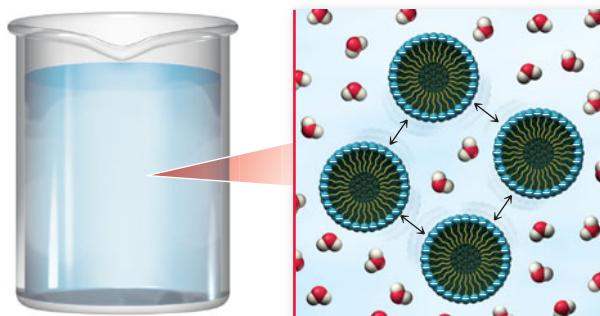


**▲** Light beams are invisible when they are not scattered by colloidally dispersed particles such as dust or mist in the air.

types of colloids do). This scattering of light by a colloidal dispersion is known as the **Tyndall effect** (Figure 12.23 ▲). You can observe the Tyndall effect in other colloids such as fog (water droplets dispersed in air) or dusty air. In fact, you can use the Tyndall effect as a test to determine whether a mixture is a solution or a colloid, since solutions contain completely dissolved solute molecules that are too small to scatter light.

Colloidal suspensions of micelles are kept stable by electrostatic repulsions that occur at their surfaces. For example, in soap, the ionic heads of the soap molecules compose the surface of the spherical particle (Figure 12.24 ▼). These ionic heads interact strongly with water molecules but repel other colloid particles. Heating a colloid composed of micelles can destroy the micelles because collisions occur with enough force to overcome the electrostatic repulsions and allow the molecules within the micelles to coalesce with those in other micelles. Similarly, adding an electrolyte to a colloidal suspension of micelles can also disrupt the electrostatic repulsions that occur between the particles and thus destroy the colloid. For this reason, soap does not work well in a salt water solution.

The particles in a colloid need not be clusters of molecules. Some colloids, such as many protein solutions, contain dispersed macromolecules. For example, blood contains dispersed hemoglobin. The hemoglobin molecules are so large that they scatter light; thus, blood is considered a colloid.



**▲ FIGURE 12.24 Micelle Repulsions** Micelles do not coalesce, because the charged surface of one micelle repels the charged surface of another.

# CHAPTER IN REVIEW

## Self Assessment Quiz

- Q1.** Which compound do you expect to be soluble in octane ( $C_8H_{18}$ )?  
 a)  $CH_3OH$    b)  $CBr_4$    c)  $H_2O$    d)  $NH_3$
- Q2.** An aqueous solution is saturated in both potassium chlorate and carbon dioxide gas at room temperature. What happens when the solution is warmed to  $85^\circ C$ ?  
 a) Potassium chlorate precipitates out of solution.  
 b) Carbon dioxide bubbles out of solution.  
 c) Potassium chlorate precipitates out of solution and carbon dioxide bubbles out of solution.  
 d) Nothing happens; all of the potassium chloride and the carbon dioxide remain dissolved in solution.
- Q3.** A 500.0 mL sample of pure water is allowed to come to equilibrium with pure oxygen gas at a pressure of 755 mmHg. What mass of oxygen gas dissolves in the water? (The Henry's law constant for oxygen gas is  $1.3 \times 10^{-3} M/atm$ ).  
 a) 15.7 g   b)  $6.5 \times 10^{-3}$  g   c) 0.041 g   d) 0.021 g
- Q4.** A potassium bromide solution is 7.55 % potassium bromide by mass and its density is 1.03 g/mL. What mass of potassium bromide is contained in 35.8 mL of the solution?  
 a) 2.78 g   b) 2.70 g   c) 4.88 g   d) 2.62 g
- Q5.** A solution contains 22.4 g glucose ( $C_6H_{12}O_6$ ) dissolved in 0.500 L of water. What is the molality of the solution? (Assume a density of 1.00 g/mL for water.)  
 a) 0.238 m   b) 44.8 m   c) 0.249 m   d) 4.03 m
- Q6.** A sodium nitrate solution is 12.5%  $NaNO_3$  by mass and has a density of 1.02 g/mL. Calculate the molarity of the solution.  
 a) 1.44 M   b) 12.8 M   c) 6.67 M   d) 1.50 M
- Q7.** Determine the vapor pressure of an aqueous ethylene glycol ( $C_2H_6O_2$ ) solution that is 14.8 %  $C_2H_6O_2$  by mass. The vapor pressure of pure water at  $25^\circ C$  is 23.8 torr.  
 a) 3.52 torr   b) 22.7 torr   c) 1.14 torr   d) 20.3 torr
- Q8.** A solution contains a mixture of substance A and substance B, both of which are volatile. The mole fraction of substance A is 0.35. At  $32^\circ C$  the vapor pressure of pure A is 87 mmHg and the vapor pressure of pure B is 122 mmHg. What is the total vapor pressure of the solution at this temperature?  
 a) 110 mmHg   b) 209 mmHg  
 c) 99.3 mmHg   d) 73.2 mmHg
- Q9.** What mass of glucose ( $C_6H_{12}O_6$ ) should be dissolved in 10.0 kg of water to obtain a solution with a freezing point of  $-4.2^\circ C$ ?  
 a) 0.023 kg   b) 4.1 kg   c) 0.41 kg   d) 14.1 kg
- Q10.** Which of these aqueous solutions has the highest boiling point?  
 a) 1.25 M  $C_6H_{12}O_6$   
 b) 1.25 M  $KNO_3$   
 c) 1.25 M  $Ca(NO_3)_2$   
 d) None of the above (they all have the same boiling point)
- Q11.** The osmotic pressure of a solution containing 22.7 mg of an unknown protein in 50.0 mL of solution is 2.88 mmHg at  $25^\circ C$ . Determine the molar mass of the protein.  
 a) 246 g/mol   b) 3.85 g/mol  
 c)  $2.93 \times 10^3$  g/mol   d) 147 g/mol
- Q12.** The enthalpy of solution for  $NaOH$  is  $-44.46\text{ kJ/mol}$ . What can you conclude about the relative magnitudes of the absolute values of  $\Delta H_{\text{solute}}$  and  $\Delta H_{\text{hydration}}$ , where  $\Delta H_{\text{solute}}$  is the heat associated with separating the solute particles and  $\Delta H_{\text{hydration}}$  is the heat associated with dissolving the solute particles in water?  
 a)  $|\Delta H_{\text{solute}}| > |\Delta H_{\text{hydration}}|$   
 b)  $|\Delta H_{\text{solute}}| < |\Delta H_{\text{hydration}}|$   
 c)  $|\Delta H_{\text{solute}}| = |\Delta H_{\text{hydration}}|$   
 d) None of the above (nothing can be concluded about the relative magnitudes)
- Q13.** A 2.4 m aqueous solution of an ionic compound with the formula  $MX_2$  has a boiling point of  $103.4^\circ C$ . Calculate the van't Hoff factor ( $i$ ) for  $MX_2$  at this concentration.  
 a) 2.8   b) 83   c) 0.73   d) 1.0
- Q14.** A solution is an equimolar mixture of two volatile components A and B. Pure A has a vapor pressure of 50 torr and pure B has a vapor pressure of 100 torr. The vapor pressure of the mixture is 85 torr. What can you conclude about the relative strengths of the intermolecular forces between particles of A and B (relative to those between particles of A and those between particles of B)?  
 a) The intermolecular forces between particles A and B are *weaker* than those between particles of A and those between particles of B.  
 b) The intermolecular forces between particles A and B are *stronger* than those between particles of A and those between particles of B.  
 c) The intermolecular forces between particles A and B are *the same as* those between particles of A and those between particles of B.  
 d) Nothing can be concluded about the relative strengths of intermolecular forces from this observation.
- Q15.** An aqueous solution is in equilibrium with a gaseous mixture containing an equal number of moles of oxygen, nitrogen, and helium. Rank the relative concentrations of each gas in the aqueous solution from highest to lowest.  
 a)  $[O_2] > [N_2] > [He]$   
 b)  $[He] > [N_2] > [O_2]$   
 c)  $[N_2] > [He] > [O_2]$   
 d)  $[N_2] > [O_2] > [He]$

## Key Terms

### Section 12.1

solution (545)  
solvent (545)  
solute (545)

### Section 12.2

aqueous solution (546)  
solubility (547)  
entropy (548)  
miscible (549)

### Section 12.3

enthalpy of solution ( $\Delta H_{\text{soln}}$ ) (552)  
heat of hydration ( $\Delta H_{\text{hydration}}$ ) (553)

### Section 12.4

dynamic equilibrium (556)  
saturated solution (556)  
unsaturated solution (556)  
supersaturated solution (556)  
recrystallization (557)  
Henry's law (558)

### Section 12.5

dilute solution (559)  
concentrated solution (559)  
molarity (M) (560)  
molality (*m*) (562)  
parts by mass (562)  
percent by mass (562)  
parts per million (ppm) (562)  
parts per billion (ppb) (562)

</div

## Key Equations and Relationships

Henry's Law: Solubility of Gases with Increasing Pressure (12.4)

$$S_{\text{gas}} = k_{\text{H}} P_{\text{gas}} \quad (k_{\text{H}} \text{ is Henry's law constant})$$

Molarity (M) of a Solution (12.5)

$$(M) = \frac{\text{amount solute (in mol)}}{\text{volume solution (in L)}}$$

Molality (m) of a Solution (12.5)

$$(m) = \frac{\text{amount solute (in mol)}}{\text{mass solvent (in kg)}}$$

Concentration of a Solution in Parts by Mass and Parts by Volume (12.5)

$$\text{Percent by mass} = \frac{\text{mass solute} \times 100\%}{\text{mass solution}}$$

$$\text{Parts per million (ppm)} = \frac{\text{mass solute} \times 10^6}{\text{mass solution}}$$

$$\text{Parts per billion (ppb)} = \frac{\text{mass solute} \times 10^9}{\text{mass solution}}$$

$$\text{Parts by volume} = \frac{\text{volume solute} \times \text{multiplication factor}}{\text{volume solution}}$$

Concentration of a Solution in Mole Fraction ( $\chi$ ) and Mole Percent (12.5)

$$\chi_{\text{solute}} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}}$$

$$\text{Mol \%} = \chi \times 100\%$$

Raoult's Law: Relationship between the Vapor Pressure of a Solution ( $P_{\text{solution}}$ ), the Mole Fraction of the Solvent ( $\chi_{\text{solvent}}$ ), and the Vapor Pressure of the Pure Solvent ( $P_{\text{solvent}}^{\circ}$ ) (12.6)

$$P_{\text{solution}} = \chi_{\text{solvent}} P_{\text{solvent}}^{\circ}$$

The Vapor Pressure of a Solution Containing Two Volatile Components (12.6)

$$P_A = \chi_A P_A^{\circ}$$

$$P_B = \chi_B P_B^{\circ}$$

$$P_{\text{tot}} = P_A + P_B$$

Relationship between Freezing Point Depression ( $\Delta T_f$ ), molality (m), and Freezing Point Depression Constant ( $K_f$ ) (12.6)

$$\Delta T_f = m \times K_f$$

Relationship between Boiling Point Elevation ( $\Delta T_b$ ), Molality (m), and Boiling Point Elevation Constant ( $K_b$ ) (12.6)

$$\Delta T_b = m \times K_b$$

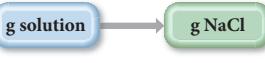
Relationship between Osmotic Pressure ( $\Pi$ ), Molarity (M), the Ideal Gas Constant ( $R$ ), and Temperature ( $T$ , in K) (12.6)

$$\Pi = MRT \quad (R = 0.08206 \text{ L} \cdot \text{atm/mol} \cdot \text{K})$$

van't Hoff Factor ( $i$ ): Ratio of Moles of Particles in Solution to Moles of Formula Units Dissolved (12.7)

$$i = \frac{\text{moles of particles in solution}}{\text{moles of formula units dissolved}}$$

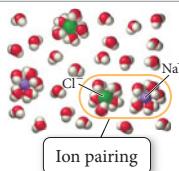
## Key Learning Outcomes

| Chapter Objectives  | Assessment   |
|---|--|
| Determining Whether a Solute Is Soluble in a Solvent (12.2)   | Example 12.1 For Practice 12.1 Exercises 31–34   |
| Using Henry's Law to Predict the Solubility of Gases with Increasing Pressure (12.4)                                      | Example 12.2 For Practice 12.2 Exercises 49, 50  |
| Calculating Concentrations of Solutions (12.5)  | Example 12.3, 12.4 For Practice 12.3, 12.4<br>For More Practice 12.3 Exercises 51–56, 63, 64 |
| Converting between Concentration Units (12.5)   | Example 12.5 For Practice 12.5 Exercises 65–68   |
| 3.5 g NaCl<br>100 g solution converts  |  |
| Determining the Vapor Pressure of a Solution Containing a Nonelectrolyte and Nonvolatile Solute (12.6)                    | Example 12.6 For Practice 12.6 For More Practice 12.6 Exercises 71, 72                       |
| Determining the Vapor Pressure of a Two-Component Solution (12.6)   | Example 12.7 For Practice 12.7 Exercises 73–76   |
| Calculating Freezing Point Depression (12.6)  | Example 12.8 For Practice 12.8 Exercises 77–82, 87, 88                                       |
| Calculating Boiling Point Elevation (12.6)  | Example 12.9 For Practice 12.9 Exercises 77, 78, 87, 88                                      |
| Determining the Osmotic Pressure (12.6)   | Example 12.10 For Practice 12.10 Exercises 83–86   |

## Key Learning Outcomes, continued

### Determining and Using the van't Hoff Factor (12.7)

### Determining the Vapor Pressure of a Solution Containing an Ionic Solute (12.7)



Example 12.11 For Practice 12.11 Exercises 91–96

Example 12.12 For Practice 12.12 Exercises 97, 98

## EXERCISES

### Review Questions

- Explain why drinking seawater results in dehydration.
- What is a solution? What are the solute and solvent?
- What does it mean to say that a substance is soluble in another substance? Which units are used in reporting solubility?
- Why do two ideal gases thoroughly mix when combined? What drives the mixing?
- What is entropy? Why is entropy important in discussing the formation of solutions?
- What kinds of intermolecular forces are involved in solution formation?
- Explain how the relative strengths of solute–solute interactions, solvent–solvent interactions, and solvent–solute interactions affect solution formation.
- What does the statement *like dissolves like* mean with respect to solution formation?
- What are three steps involved in evaluating the enthalpy changes associated with solution formation?
- What is the heat of hydration ( $\Delta H_{\text{hydration}}$ )? How does the enthalpy of solution depend on the relative magnitudes of  $\Delta H_{\text{solute}}$  and  $\Delta H_{\text{hydration}}$ ?
- Explain dynamic equilibrium with respect to solution formation. What is a saturated solution? An unsaturated solution? A supersaturated solution?
- How does the solubility of a solid in a liquid depend on temperature? How is this temperature dependence exploited to purify solids through recrystallization?
- How does the solubility of a gas in a liquid depend on temperature? How does this temperature dependence affect the amount of oxygen available for fish and other aquatic animals?

- How does the solubility of a gas in a liquid depend on pressure? How does this pressure dependence account for the bubbling that occurs upon opening a can of soda?
- What is Henry's law? For what kinds of calculations is Henry's law useful?
- What are the common units for expressing solution concentration?
- How are parts by mass and parts by volume used in calculations?
- What is the effect of a nonvolatile solute on the vapor pressure of a liquid? Why is the vapor pressure of a solution different from the vapor pressure of the pure liquid solvent?
- What is Raoult's law? For what kind of calculations is Raoult's law useful?
- Explain the difference between an ideal and a nonideal solution.
- What is the effect on vapor pressure of a solution with particularly *strong* solute–solvent interactions? With particularly *weak* solute–solvent interactions?
- Explain why the lower vapor pressure for a solution containing a nonvolatile solute results in a higher boiling point and lower melting point compared to the pure solvent.
- What are colligative properties?
- What is osmosis? What is osmotic pressure?
- Explain the meaning of the van't Hoff factor and its role in determining the colligative properties of solutions containing ionic solutes.
- Describe a colloidal dispersion. What is the difference between a colloidal dispersion and a true solution?
- What is the Tyndall effect and how can it be used to help identify colloidal dispersions?
- What keeps the particles in a colloidal dispersion from coalescing?

### Problems by Topic

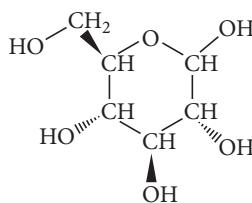
#### Solubility

- Pick an appropriate solvent from Table 12.3 to dissolve each substance. State the kind of intermolecular forces that would occur between the solute and solvent in each case.
  - motor oil (nonpolar)
  - ethanol (polar, contains an OH group)
  - lard (nonpolar)
  - potassium chloride (ionic)

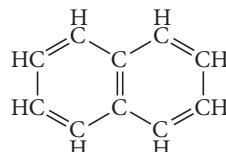
- Pick an appropriate solvent from Table 12.3 to dissolve each substance. State the kind of intermolecular forces that would occur between the solute and solvent in each case.
  - isopropyl alcohol (polar, contains an OH group)
  - sodium chloride (ionic)
  - vegetable oil (nonpolar)
  - sodium nitrate (ionic)
- Which molecule would you expect to be more soluble in water,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$  or  $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{OH}$ ?

32. Which molecule would you expect to be more soluble in water,  $\text{CCl}_4$  or  $\text{CH}_2\text{Cl}_2$ ?
33. For each compound, would you expect greater solubility in water or in hexane? Indicate the kinds of intermolecular forces that occur between the solute and the solvent in which the molecule is most soluble.

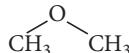
a. glucose



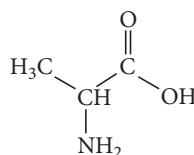
b. naphthalene



c. dimethyl ether

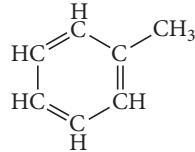


d. alanine (an amino acid)

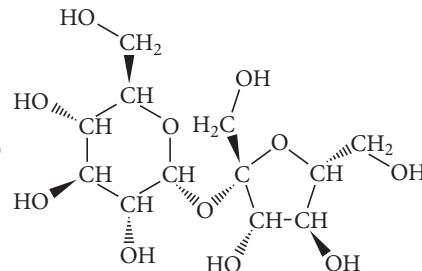


34. For each compound, would you expect greater solubility in water or in hexane? Indicate the kinds of intermolecular forces that would occur between the solute and the solvent in which the molecule is most soluble.

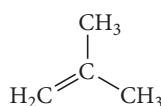
a. toluene



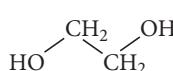
b. sucrose (table sugar)



c. isobutene



d. ethylene glycol



### Energetics of Solution Formation

35. When ammonium chloride ( $\text{NH}_4\text{Cl}$ ) is dissolved in water, the solution becomes colder.
- Is the dissolution of ammonium chloride endothermic or exothermic?
  - What can you conclude about the relative magnitudes of the lattice energy of ammonium chloride and its heat of hydration?
  - Sketch a qualitative energy diagram similar to Figure 12.7 for the dissolution of  $\text{NH}_4\text{Cl}$ .
  - Why does the solution form? What drives the process?
36. When lithium iodide ( $\text{LiI}$ ) is dissolved in water, the solution becomes hotter.
- Is the dissolution of lithium iodide endothermic or exothermic?
  - What can you conclude about the relative magnitudes of the lattice energy of lithium iodide and its heat of hydration?
  - Sketch a qualitative energy diagram similar to Figure 12.7 for the dissolution of  $\text{LiI}$ .
  - Why does the solution form? What drives the process?
37. Silver nitrate has a lattice energy of  $-820 \text{ kJ/mol}$  and a heat of solution of  $-22.6 \text{ kJ/mol}$ . Calculate the heat of hydration for silver nitrate.
38. Use the data to calculate the heats of hydration of lithium chloride and sodium chloride. Which of the two cations, lithium or sodium, has stronger ion-dipole interactions with water? Why?

| Compound      | Lattice Energy (kJ/mol) | $\Delta H_{\text{soln}}$ (kJ/mol) |
|---------------|-------------------------|-----------------------------------|
| $\text{LiCl}$ | -834                    | -37.0                             |
| $\text{NaCl}$ | -769                    | +3.88                             |

39. Lithium iodide has a lattice energy of  $-7.3 \times 10^2 \text{ kJ/mol}$  and a heat of hydration of  $-793 \text{ kJ/mol}$ . Find the heat of solution for lithium iodide and determine how much heat is evolved or absorbed when 15.0 g of lithium iodide completely dissolves in water.
40. Potassium nitrate has a lattice energy of  $-163.8 \text{ kcal/mol}$  and a heat of hydration of  $-155.5 \text{ kcal/mol}$ . How much potassium nitrate has to dissolve in water to absorb  $1.00 \times 10^2 \text{ kJ}$  of heat?

### Solution Equilibrium and Factors Affecting Solubility

41. A solution contains 25 g of  $\text{NaCl}$  per 100.0 g of water at  $25^\circ\text{C}$ . Is the solution unsaturated, saturated, or supersaturated? (Use Figure 12.11.)
42. A solution contains 32 g of  $\text{KNO}_3$  per 100.0 g of water at  $25^\circ\text{C}$ . Is the solution unsaturated, saturated, or supersaturated? (Use Figure 12.11.)
43. A  $\text{KNO}_3$  solution containing 45 g of  $\text{KNO}_3$  per 100.0 g of water is cooled from  $40^\circ\text{C}$  to  $0^\circ\text{C}$ . What happens during cooling? (Use Figure 12.11.)
44. A  $\text{KCl}$  solution containing 42 g of  $\text{KCl}$  per 100.0 g of water is cooled from  $60^\circ\text{C}$  to  $0^\circ\text{C}$ . What happens during cooling? (Use Figure 12.11.)
45. Some laboratory procedures involving oxygen-sensitive reactants or products call for using water that has been boiled (and then cooled). Explain.
46. A person preparing a fish tank fills the tank with water that has been boiled (and then cooled). When the person puts fish into the tank, they die. Explain.

- 47.** Scuba divers breathing air at increased pressure can suffer from nitrogen narcosis—a condition resembling drunkenness—when the partial pressure of nitrogen exceeds about 4 atm. What property of gas/water solutions causes this to happen? How can a diver reverse this effect?
- 48.** Scuba divers breathing air at increased pressure can suffer from oxygen toxicity—too much oxygen in their bloodstream—when the partial pressure of oxygen exceeds about 1.4 atm. What happens to the amount of oxygen in a diver's bloodstream when he or she breathes oxygen at elevated pressures? How can this be reversed?
- 49.** Calculate the mass of nitrogen dissolved at room temperature in an 80.0 L home aquarium. Assume a total pressure of 1.0 atm and a mole fraction for nitrogen of 0.78.
- 50.** Use Henry's law to determine the molar solubility of helium at a pressure of 1.0 atm and 25 °C.

### Concentrations of Solutions

- 51.** An aqueous NaCl solution is made using 112 g of NaCl diluted to a total solution volume of 1.00 L. Calculate the molarity, molality, and mass percent of the solution. (Assume a density of 1.08 g/mL for the solution.)
- 52.** An aqueous KNO<sub>3</sub> solution is made using 72.5 g of KNO<sub>3</sub> diluted to a total solution volume of 2.00 L. Calculate the molarity, molality, and mass percent of the solution. (Assume a density of 1.05 g/mL for the solution.)
- 53.** To what volume should you dilute 50.0 mL of a 5.00 M KI solution so that 25.0 mL of the diluted solution contains 3.05 g of KI?
- 54.** To what volume should you dilute 125 mL of an 8.00 M CuCl<sub>2</sub> solution so that 50.0 mL of the diluted solution contains 4.67 g CuCl<sub>2</sub>?
- 55.** Silver nitrate solutions are often used to plate silver onto other metals. What is the maximum amount of silver (in grams) that can be plated out of 4.8 L of an AgNO<sub>3</sub> solution containing 3.4% Ag by mass? Assume that the density of the solution is 1.01 g/mL.
- 56.** A dioxin-contaminated water source contains 0.085% dioxin by mass. How much dioxin is present in 2.5 L of this water? Assume a density of 1.00 g/mL.
- 57.** A hard water sample contains 0.0085% Ca by mass (in the form of Ca<sup>2+</sup> ions). How much water (in grams) contains 1.2 g of Ca? (1.2 g of Ca is the recommended daily allowance of calcium for those between 19 and 24 years old.)
- 58.** Lead is a toxic metal that affects the central nervous system. A Pb-contaminated water sample contains 0.0011% Pb by mass. How much of the water (in mL) contains 150 mg of Pb? (Assume a density of 1.0 g/mL.)
- 59.** You can purchase nitric acid in a concentrated form that is 70.3% HNO<sub>3</sub> by mass and has a density of 1.41 g/mL. Describe exactly how you would prepare 1.15 L of 0.100 M HNO<sub>3</sub> from the concentrated solution.
- 60.** You can purchase hydrochloric acid in a concentrated form that is 37.0% HCl by mass and that has a density of 1.20 g/mL. Describe exactly how to prepare 2.85 L of 0.500 M HCl from the concentrated solution.
- 61.** Describe how to prepare each solution from the dry solute and the solvent.
- 1.00 × 10<sup>2</sup> mL of 0.500 M KCl
  - 1.00 × 10<sup>2</sup> g of 0.500 m KCl
  - 1.00 × 10<sup>2</sup> g of 5.0% KCl solution by mass

- 62.** Describe how to prepare each solution from the dry solute and the solvent.
- 125 mL of 0.100 M NaNO<sub>3</sub>
  - 125 g of 0.100 m NaNO<sub>3</sub>
  - 125 g of 1.0% NaNO<sub>3</sub> solution by mass
- 63.** A solution is prepared by dissolving 28.4 g of glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>) in 355 g of water. The final volume of the solution is 378 mL. For this solution, calculate the concentration in each unit.
- molarity
  - molality
  - percent by mass
  - mole fraction
  - mole percent
- 64.** A solution is prepared by dissolving 20.2 mL of methanol (CH<sub>3</sub>OH) in 100.0 mL of water at 25 °C. The final volume of the solution is 118 mL. The densities of methanol and water at this temperature are 0.782 g/mL and 1.00 g/mL, respectively. For this solution, calculate the concentration in each unit.
- molarity
  - molality
  - percent by mass
  - mole fraction
  - mole percent
- 65.** Household hydrogen peroxide is an aqueous solution containing 3.0% hydrogen peroxide by mass. What is the molarity of this solution? (Assume a density of 1.01 g/mL.)
- 66.** One brand of laundry bleach is an aqueous solution containing 4.55% sodium hypochlorite (NaOCl) by mass. What is the molarity of this solution? (Assume a density of 1.02 g/mL.)
- 67.** An aqueous solution contains 36% HCl by mass. Calculate the molality and mole fraction of the solution.
- 68.** An aqueous solution contains 5.0% NaCl by mass. Calculate the molality and mole fraction of the solution.
- ### Vapor Pressure of Solutions
- 69.** A beaker contains 100.0 mL of pure water. A second beaker contains 100.0 mL of seawater. The two beakers are left side by side on a lab bench for 1 week. At the end of the week, the liquid level in both beakers has decreased. However, the level has decreased more in one of the beakers than in the other. Which one and why?
- 70.** Which solution has the highest vapor pressure?
- 20.0 g of glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>) in 100.0 mL of water
  - 20.0 g of sucrose (C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>) in 100.0 mL of water
  - 10.0 g of potassium acetate KC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> in 100.0 mL of water
- 71.** Calculate the vapor pressure of a solution containing 24.5 g of glycerin (C<sub>3</sub>H<sub>8</sub>O<sub>3</sub>) in 135 mL of water at 30.0 °C. The vapor pressure of pure water at this temperature is 31.8 torr. Assume that glycerin is not volatile and dissolves molecularly (i.e., it is not ionic), and use a density of 1.00 g/mL for the water.
- 72.** A solution contains naphthalene (C<sub>10</sub>H<sub>8</sub>) dissolved in hexane (C<sub>6</sub>H<sub>14</sub>) at a concentration of 12.35% naphthalene by mass. Calculate the vapor pressure at 25 °C of hexane above the solution. The vapor pressure of pure hexane at 25 °C is 151 torr.
- 73.** A solution contains 50.0 g of heptane (C<sub>7</sub>H<sub>16</sub>) and 50.0 g of octane (C<sub>8</sub>H<sub>18</sub>) at 25 °C. The vapor pressures of pure heptane and pure octane at 25 °C are 45.8 torr and 10.9 torr, respectively. Assuming ideal behavior, answer the following:
- What is the vapor pressure of each of the solution components in the mixture?
  - What is the total pressure above the solution?
  - What is the composition of the vapor in mass percent?
  - Why is the composition of the vapor different from the composition of the solution?

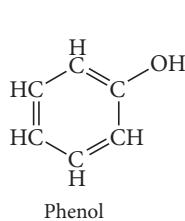
74. A solution contains a mixture of pentane and hexane at room temperature. The solution has a vapor pressure of 258 torr. Pure pentane and hexane have vapor pressures of 425 torr and 151 torr, respectively, at room temperature. What is the mole fraction composition of the mixture? (Assume ideal behavior.)
75. A solution contains 4.08 g of chloroform ( $\text{CHCl}_3$ ) and 9.29 g of acetone ( $\text{CH}_3\text{COCH}_3$ ). The vapor pressures at 35 °C of pure chloroform and pure acetone are 295 torr and 332 torr, respectively. Assuming ideal behavior, calculate the vapor pressures of each of the components and the total vapor pressure above the solution. The experimentally measured total vapor pressure of the solution at 35 °C was 312 torr. Is the solution ideal? If not, what can you say about the relative strength of chloroform–acetone interactions compared to the acetone–acetone and chloroform–chloroform interactions?
76. A solution of methanol and water has a mole fraction of water of 0.312 and a total vapor pressure of 211 torr at 39.9 °C. The vapor pressures of pure methanol and pure water at this temperature are 256 torr and 55.3 torr, respectively. Is the solution ideal? If not, what can you say about the relative strengths of the solute–solvent interactions compared to the solute–solute and solvent–solvent interactions?

### Freezing Point Depression, Boiling Point Elevation, and Osmosis

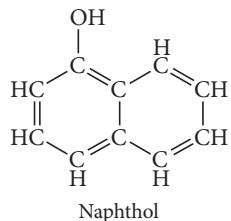
77. A glucose solution contains 55.8 g of glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) in 455 g of water. Determine the freezing point and boiling point of the solution.
78. An ethylene glycol solution contains 21.2 g of ethylene glycol ( $\text{C}_2\text{H}_6\text{O}_2$ ) in 85.4 mL of water. Determine the freezing point and boiling point of the solution. (Assume a density of 1.00 g/mL for water.)
79. Calculate the freezing point and melting point of a solution containing 10.0 g of naphthalene ( $\text{C}_{10}\text{H}_8$ ) in 100.0 mL of benzene. Benzene has a density of 0.877 g/cm<sup>3</sup>.
80. Calculate the freezing point and melting point of a solution containing 7.55 g of ethylene glycol ( $\text{C}_2\text{H}_6\text{O}_2$ ) in 85.7 mL of ethanol. Ethanol has a density of 0.789 g/cm<sup>3</sup>.
81. An aqueous solution containing 17.5 g of an unknown molecular (nonelectrolyte) compound in 100.0 g of water has a freezing point of –1.8 °C. Calculate the molar mass of the unknown compound.
82. An aqueous solution containing 35.9 g of an unknown molecular (nonelectrolyte) compound in 150.0 g of water has a freezing point of –1.3 °C. Calculate the molar mass of the unknown compound.
83. Calculate the osmotic pressure of a solution containing 24.6 g of glycerin ( $\text{C}_3\text{H}_8\text{O}_3$ ) in 250.0 mL of solution at 298 K.
84. What mass of sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) would you combine with  $5.00 \times 10^2$  g of water to make a solution with an osmotic pressure of 8.55 atm at 298 K? (Assume a density of 1.0 g/mL for the solution.)
85. A solution containing 27.55 mg of an unknown protein per 25.0 mL solution was found to have an osmotic pressure of 3.22 torr at 25 °C. What is the molar mass of the protein?
86. Calculate the osmotic pressure of a solution containing 18.75 mg of hemoglobin in 15.0 mL of solution at 25 °C. The molar mass of hemoglobin is  $6.5 \times 10^4$  g/mol.
87. Calculate the freezing point and boiling point of each aqueous solution, assuming complete dissociation of the solute.
- $0.100\text{ m K}_2\text{S}$
  - $21.5\text{ g of CuCl}_2$  in  $4.50 \times 10^2$  g water
  - $5.5\%$   $\text{NaNO}_3$  by mass (in water)
88. Calculate the freezing point and boiling point in each solution, assuming complete dissociation of the solute.
- $10.5\text{ g FeCl}_3$  in  $1.50 \times 10^2$  g water
  - $3.5\%$   $\text{KCl}$  by mass (in water)
  - $0.150\text{ m MgF}_2$
89. What mass of salt ( $\text{NaCl}$ ) should you add to 1.00 L of water in an ice cream maker to make a solution that freezes at –10.0 °C? Assume complete dissociation of the  $\text{NaCl}$  and density of 1.00 g/mL for water.
90. Determine the required concentration (in percent by mass) for an aqueous ethylene glycol ( $\text{C}_2\text{H}_6\text{O}_2$ ) solution to have a boiling point of 104.0 °C.
91. Use the van't Hoff factors in Table 12.9 to calculate each colligative property:
- the melting point of a  $0.100\text{ m}$  iron(III) chloride solution
  - the osmotic pressure of a  $0.085\text{ M}$  potassium sulfate solution at 298 K
  - the boiling point of a  $1.22\%$  by mass magnesium chloride solution
92. Assuming the van't Hoff factors in Table 12.9, calculate the mass of solute required to make each aqueous solution:
- a sodium chloride solution containing  $1.50 \times 10^2$  g of water that has a melting point of –1.0 °C
  - $2.50 \times 10^2$  mL of a magnesium sulfate solution that has an osmotic pressure of 3.82 atm at 298 K
  - an iron(III) chloride solution containing  $2.50 \times 10^2$  g of water that has a boiling point of 102 °C
93. A  $1.2\text{ m}$  aqueous solution of an ionic compound with the formula  $\text{MX}_2$  has a boiling point of 101.4 °C. Calculate the van't Hoff factor ( $i$ ) for  $\text{MX}_2$  at this concentration.
94. A  $0.95\text{ m}$  aqueous solution of an ionic compound with the formula  $\text{MX}$  has a freezing point of –3.0 °C. Calculate the van't Hoff factor ( $i$ ) for  $\text{MX}$  at this concentration.
95. A  $0.100\text{ M}$  ionic solution has an osmotic pressure of 8.3 atm at 25 °C. Calculate the van't Hoff factor ( $i$ ) for this solution.
96. A solution contains 8.92 g of  $\text{KBr}$  in 500.0 mL of solution and has an osmotic pressure of 6.97 atm at 25 °C. Calculate the van't Hoff factor ( $i$ ) for  $\text{KBr}$  at this concentration.
97. Calculate the vapor pressure at 25 °C of an aqueous solution that is 5.50%  $\text{NaCl}$  by mass. (Assume complete dissociation of the solute.)
98. An aqueous  $\text{CaCl}_2$  solution has a vapor pressure of 81.6 mmHg at 50 °C. The vapor pressure of pure water at this temperature is 92.6 mmHg. What is the concentration of  $\text{CaCl}_2$  in mass percent? (Assume complete dissociation of the solute.)

## Cumulative Problems

- 99.** The solubility of carbon tetrachloride ( $\text{CCl}_4$ ) in water at  $25^\circ\text{C}$  is 1.2 g/L. The solubility of chloroform ( $\text{CHCl}_3$ ) at the same temperature is 10.1 g/L. Why is chloroform almost ten times more soluble in water than carbon tetrachloride?
- 100.** The solubility of phenol in water at  $25^\circ\text{C}$  is 8.7 g/L. The solubility of naphthol at the same temperature is only 0.074 g/L. Examine the structures of phenol and naphthol shown here and explain why phenol is so much more soluble than naphthol.



Phenol



Naphthol

- 101.** Potassium perchlorate ( $\text{KClO}_4$ ) has a lattice energy of  $-599 \text{ kJ/mol}$  and a heat of hydration of  $-548 \text{ kJ/mol}$ . Find the heat of solution for potassium perchlorate and determine the temperature change that occurs when 10.0 g of potassium perchlorate is dissolved with enough water to make 100.0 mL of solution. (Assume a heat capacity of  $4.05 \text{ J/g} \cdot {}^\circ\text{C}$  for the solution and a density of 1.05 g/mL.)
- 102.** Sodium hydroxide ( $\text{NaOH}$ ) has a lattice energy of  $-887 \text{ kJ/mol}$  and a heat of hydration of  $-932 \text{ kJ/mol}$ . How much solution could be heated to boiling by the heat evolved by the dissolution of 25.0 g of  $\text{NaOH}$ ? (For the solution, assume a heat capacity of  $4.0 \text{ J/g} \cdot {}^\circ\text{C}$ , an initial temperature of  $25.0^\circ\text{C}$ , a boiling point of  $100.0^\circ\text{C}$ , and a density of 1.05 g/mL.)
- 103.** A saturated solution forms when 0.0537 L of argon, at a pressure of 1.0 atm and temperature of  $25^\circ\text{C}$ , is dissolved in 1.0 L of water. Calculate the Henry's law constant for argon.
- 104.** A gas has a Henry's law constant of 0.112 M/atm. What total volume of solution is needed to completely dissolve 1.65 L of the gas at a pressure of 725 torr and a temperature of  $25^\circ\text{C}$ ?
- 105.** The Safe Drinking Water Act (SDWA) sets a limit for mercury—a toxin to the central nervous system—at 0.0020 ppm by mass. Water suppliers must periodically test their water to ensure that mercury levels do not exceed this limit. Suppose water becomes contaminated with mercury at twice the legal limit (0.0040 ppm). How much of this water would a person have to consume to ingest 50.0 mg of mercury?
- 106.** Water softeners often replace calcium ions in hard water with sodium ions. Since sodium compounds are soluble, the presence of sodium ions in water does not cause the white, scaly residues caused by calcium ions. However, calcium is more beneficial to human health than sodium because calcium is a necessary part of the human diet, while high levels of sodium intake are linked to increases in blood pressure. The U.S. Food and Drug Administration (FDA) recommends that adults ingest less than 2.4 g of sodium per day. How many liters of softened water, containing a sodium concentration of 0.050% sodium by mass, would a person have to consume to exceed the FDA recommendation? (Assume a water density of 1.0 g/mL.)
- 107.** An aqueous solution contains 12.5% NaCl by mass. What mass of water (in grams) is contained in 2.5 L of the vapor above this solution at  $55^\circ\text{C}$ ? The vapor pressure of pure water at  $55^\circ\text{C}$  is 118 torr. (Assume complete dissociation of NaCl.)
- 108.** The vapor above an aqueous solution contains 19.5 mg water per liter at  $25^\circ\text{C}$ . Assuming ideal behavior, what is the concentration of the solute within the solution in mole percent?
- 109.** What is the freezing point of an aqueous solution that boils at  $106.5^\circ\text{C}$ ?
- 110.** What is the boiling point of an aqueous solution that has a vapor pressure of 20.5 torr at  $25^\circ\text{C}$ ? (Assume a nonvolatile solute.)
- 111.** An isotonic solution contains 0.90% NaCl mass to volume. Calculate the percent mass to volume for isotonic solutions containing each solute at  $25^\circ\text{C}$ . Assume a van't Hoff factor of 1.9 for all *ionic* solutes.
- KCl
  - NaBr
  - glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ )
- 112.** Magnesium citrate,  $\text{Mg}_3(\text{C}_6\text{H}_5\text{O}_7)_2$  belongs to a class of laxatives called *hyperosmotics*, which cause rapid emptying of the bowel. When a concentrated solution of magnesium citrate is consumed, it passes through the intestines, drawing water and promoting diarrhea, usually within 6 hours. Calculate the osmotic pressure of a magnesium citrate laxative solution containing 28.5 g of magnesium citrate in 235 mL of solution at  $37^\circ\text{C}$  (approximate body temperature). Assume complete dissociation of the ionic compound.
- 113.** A solution is prepared from 4.5701 g of magnesium chloride and 43.238 g of water. The vapor pressure of water above this solution is 0.3624 atm at 348.0 K. The vapor pressure of pure water at this temperature is 0.3804 atm. Find the value of the van't Hoff factor ( $i$ ) for magnesium chloride in this solution.
- 114.** When  $\text{HNO}_2$  is dissolved in water it partially dissociates according to the equation  $\text{HNO}_2 \rightleftharpoons \text{H}^+ + \text{NO}_2^-$ . A solution is prepared that contains 7.050 g of  $\text{HNO}_2$  in 1.000 kg of water. Its freezing point is  $20.2929^\circ\text{C}$ . Calculate the fraction of  $\text{HNO}_2$  that has dissociated.
- 115.** A solution of a nonvolatile solute in water has a boiling point of 375.3 K. Calculate the vapor pressure of water above this solution at 338 K. The vapor pressure of pure water at this temperature is 0.2467 atm.
- 116.** The density of a 0.438 M solution of potassium chromate ( $\text{K}_2\text{CrO}_4$ ) at 298 K is 1.063 g/mL. Calculate the vapor pressure of water above the solution. The vapor pressure of pure water at this temperature is 0.0313 atm. (Assume complete dissociation of the solute.)
- 117.** The vapor pressure of carbon tetrachloride,  $\text{CCl}_4$ , is 0.354 atm and the vapor pressure of chloroform,  $\text{CHCl}_3$ , is 0.526 atm at 316 K. A solution is prepared from equal masses of these two compounds at this temperature. Calculate the mole fraction of the chloroform in the vapor above the solution. If the vapor above the original solution is condensed and isolated into a separate flask, what would the vapor pressure of chloroform be above this new solution?

118. Distillation is a method of purification based on successive separations and recondensations of vapor above a solution. Use the result of the previous problem to calculate the mole fraction of chloroform in the vapor above a solution obtained by three successive separations and condensations of the vapors above the original solution of carbon tetrachloride and chloroform. Show how this result explains the use of distillation as a separation method.
119. A solution of 49.0%  $\text{H}_2\text{SO}_4$  by mass has a density of  $1.39 \text{ g/cm}^3$  at 293 K. A  $25.0 \text{ cm}^3$  sample of this solution is mixed with enough water to increase the volume of the solution to  $99.8 \text{ cm}^3$ . Find the molarity of sulfuric acid in this solution.
120. Find the mass of urea ( $\text{CH}_4\text{N}_2\text{O}$ ) needed to prepare 50.0 g of a solution in water in which the mole fraction of urea is 0.0770.
121. A solution contains 10.05 g of unknown compound dissolved in 50.0 mL of water. (Assume a density of 1.00 g/mL for water.) The freezing point of the solution is  $-3.16^\circ\text{C}$ . The mass percent composition of the compound is 60.97% C, 11.94% H, and the rest is O. What is the molecular formula of the compound?
122. The osmotic pressure of a solution containing 2.10 g of an unknown compound dissolved in 175.0 mL of solution at  $25^\circ\text{C}$  is 1.93 atm. The combustion of 24.02 g of the unknown compound produced 28.16 g  $\text{CO}_2$  and 8.64 g  $\text{H}_2\text{O}$ . What is the molecular formula of the compound (which contains only carbon, hydrogen, and oxygen)?
123. A 100.0 mL aqueous sodium chloride solution is 13.5% NaCl by mass and has a density of 1.12 g/mL. What would you add (solute or solvent) and what mass of it to make the boiling point of the solution  $104.4^\circ\text{C}$ ? (Use  $i = 1.8$  for NaCl.)
124. A 50.0 mL solution is initially 1.55%  $\text{MgCl}_2$  by mass and has a density of 1.05 g/mL. What is the freezing point of the solution after you add an additional 1.35 g  $\text{MgCl}_2$ ? (Use  $i = 2.5$  for  $\text{MgCl}_2$ .)

## Challenge Problems

125. The small bubbles that form on the bottom of a water pot that is being heated (before boiling) are due to dissolved air coming out of solution. Use Henry's law and the solubilities given to calculate the total volume of nitrogen and oxygen gas that should bubble out of 1.5 L of water upon warming from  $25^\circ\text{C}$  to  $50^\circ\text{C}$ . Assume that the water is initially saturated with nitrogen and oxygen gas at  $25^\circ\text{C}$  and a total pressure of 1.0 atm. Assume that the gas bubbles out at a temperature of  $50^\circ\text{C}$ . The solubility of oxygen gas at  $50^\circ\text{C}$  is 27.8 mg/L at an oxygen pressure of 1.00 atm. The solubility of nitrogen gas at  $50^\circ\text{C}$  is 14.6 mg/L at a nitrogen pressure of 1.00 atm. Assume that the air above the water contains an oxygen partial pressure of 0.21 atm and a nitrogen partial pressure of 0.78 atm.
126. The vapor above a mixture of pentane and hexane at room temperature contains 35.5% pentane by mass. What is the mass percent composition of the solution? Pure pentane and hexane have vapor pressures of 425 torr and 151 torr, respectively, at room temperature.
127. A 1.10 g sample contains only glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) and sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ). When the sample is dissolved in water to a total solution volume of 25.0 mL, the osmotic pressure of the solution is 3.78 atm at 298 K. What is the mass percent composition of glucose and sucrose in the sample?
128. A solution is prepared by mixing 631 mL of methanol with 501 mL of water. The molarity of methanol in the resulting solution is 14.29 M. The density of methanol at this temperature is 0.792 g/mL. Calculate the difference in volume between this solution and the total volume of water and methanol that were mixed to prepare the solution.
129. Two alcohols, isopropyl alcohol and propyl alcohol, have the same molecular formula,  $\text{C}_3\text{H}_8\text{O}$ . A solution of the two that is two-thirds by mass isopropyl alcohol has a vapor pressure of 0.110 atm at 313 K. A solution that is one-third by mass isopropyl alcohol has a vapor pressure of 0.089 atm at 313 K. Calculate the vapor pressure of each pure alcohol at this temperature. Explain the difference given that the formula of propyl alcohol is  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$  and that of isopropyl alcohol is  $(\text{CH}_3)_2\text{CHOH}$ .
130. A metal, M, of atomic mass 96 amu reacts with fluorine to form a salt that can be represented as  $\text{MF}_x$ . In order to determine  $x$  and therefore the formula of the salt, a boiling point elevation experiment is performed. A 9.18 g sample of the salt is dissolved in 100.0 g of water and the boiling point of the solution is found to be 374.38 K. Find the formula of the salt. (Assume complete dissociation of the salt in solution.)
131. Sulfuric acid in water dissociates completely into  $\text{H}^+$  and  $\text{HSO}_4^-$  ions. The  $\text{HSO}_4^-$  ion dissociates to a limited extent into  $\text{H}^+$  and  $\text{SO}_4^{2-}$ . The freezing point of a  $0.1000 \text{ m}$  solution of sulfuric acid in water is 272.76 K. Calculate the molality of  $\text{SO}_4^{2-}$  in the solution, assuming ideal solution behavior.
132. A solution of 75.0 g of benzene ( $\text{C}_6\text{H}_6$ ) and 75.0 g of toluene ( $\text{C}_7\text{H}_8$ ) has a total vapor pressure of 80.9 mmHg at 303 K. Another solution of 100.0 g benzene and 50.0 g toluene has a total vapor pressure of 93.9 mmHg at this temperature. Find the vapor pressure of pure benzene and pure toluene at 303 K.
133. A solution is prepared by dissolving 11.60 g of a mixture of sodium carbonate and sodium bicarbonate in 1.00 L of water. A  $300.0 \text{ cm}^3$  sample of the solution is treated with excess  $\text{HNO}_3$  and boiled to remove all the dissolved gas. A total of 0.940 L of dry  $\text{CO}_2$  is collected at 298 K and 0.972 atm. Find the molarity of the carbonate and bicarbonate in the solution.

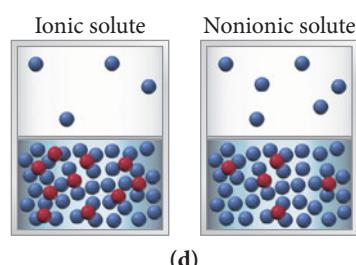
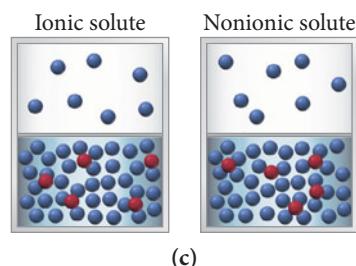
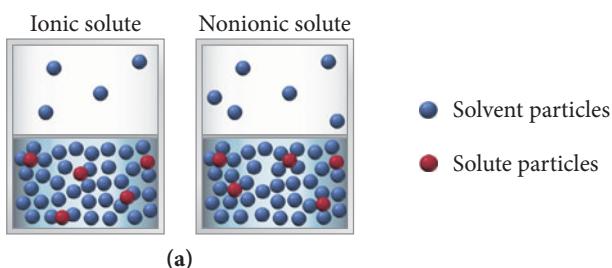
## Conceptual Problems

**134.** Substance A is a nonpolar liquid and has only dispersion forces among its constituent particles. Substance B is also a nonpolar liquid and has about the same magnitude of dispersion forces among its constituent particles as substance A. When substance A and B are combined, they spontaneously mix.

- Why do the two substances mix?
- Predict the sign and magnitude of  $\Delta H_{\text{soln}}$ .
- Determine the signs and relative magnitudes of  $\Delta H_{\text{solute}}$ ,  $\Delta H_{\text{solvent}}$ , and  $\Delta H_{\text{mix}}$ .

**135.** A power plant built on a river uses river water as a coolant. The water is warmed as it is used in heat exchangers within the plant. Should the warm water be immediately cycled back into the river? Why or why not?

**136.** The vapor pressure of a 1 M ionic solution is different from the vapor pressure of a 1 M nonelectrolyte solution. In both cases, the solute is nonvolatile. Which set of diagrams best represents the differences between the two solutions and their vapors?



**137.** If each substance listed here costs the same amount per kilogram, which would be most cost-effective as a way to lower the freezing point of water? (Assume complete dissociation for all ionic compounds.) Explain.

- $\text{HOCH}_2\text{CH}_2\text{OH}$
- $\text{NaCl}$
- $\text{KCl}$
- $\text{MgCl}_2$
- $\text{SrCl}_2$

**138.** A helium balloon inflated on one day will fall to the ground by the next day. The volume of the balloon decreases somewhat overnight but not by enough to explain why it no longer floats. (If you inflate a new balloon with helium to the same size as the balloon that fell to the ground, the newly inflated balloon floats.) Explain.

## Answers to Conceptual Problems

### Solubility

**12.1** The first alcohol on the list is methanol, which is highly polar and forms hydrogen bonds with water. It is miscible in water and has only limited solubility in hexane, which is nonpolar. However, as the carbon chain gets longer in the series of alcohols, the OH group becomes less important relative to the growing nonpolar carbon chain. Therefore, the alcohols become progressively less soluble in water and more soluble in hexane. This table demonstrates the rule of thumb *like dissolves like*. Methanol is like water and therefore dissolves in water. It is unlike hexane and therefore has limited solubility in hexane. As you move down the list, the alcohols become increasingly like hexane and increasingly unlike water and therefore become increasingly soluble in hexane and increasingly insoluble in water.

### Energetics of Aqueous Solution Formation

**12.2** You can conclude that  $|\Delta H_{\text{solute}}| < |\Delta H_{\text{hydration}}|$ . Since  $\Delta H_{\text{soln}}$  is negative, the absolute value of the negative term ( $\Delta H_{\text{hydration}}$ ) must be greater than the absolute value of the positive term ( $\Delta H_{\text{solute}}$ ).

### Solubility and Temperature

**12.3** (b) Some potassium bromide precipitates out of solution. The solubility of most solids decreases with decreasing temperature. However, the solubility of gases increases with decreasing temperature. Therefore, the nitrogen becomes more soluble and will not bubble out of solution.

**Henry's Law**

**12.4** Ammonia is the only compound on the list that is polar, so we would expect its solubility in water to be greater than those of the other gases (which are all nonpolar).

**Raoult's Law**

**12.5** The solute–solvent interactions must be stronger than the solute–solute and solvent–solvent interactions. The stronger interactions lower the vapor pressure from the expected ideal value of 150 mmHg.

**Boiling Point Elevation**

**12.6** Solution B because  $K_b$  for ethanol is greater than  $K_b$  for water.

**Colligative Properties**

**12.7** (c) The 0.50 M  $MgCl_2$  solution has the highest boiling point because it has the highest concentration of particles. We expect 1 mol of  $MgCl_2$  to form 3 mol of particles in solution (although it effectively forms slightly fewer).

# 13

## Chemical Kinetics

*Nobody, I suppose, could devote many years to the study of chemical kinetics without being deeply conscious of the fascination of time and change: this is something that goes outside science into poetry. . . .*

—Sir Cyril N. Hinshelwood (1897–1967)

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**13.3** The Rate Law: The Effect of Concentration on Reaction Rate 603

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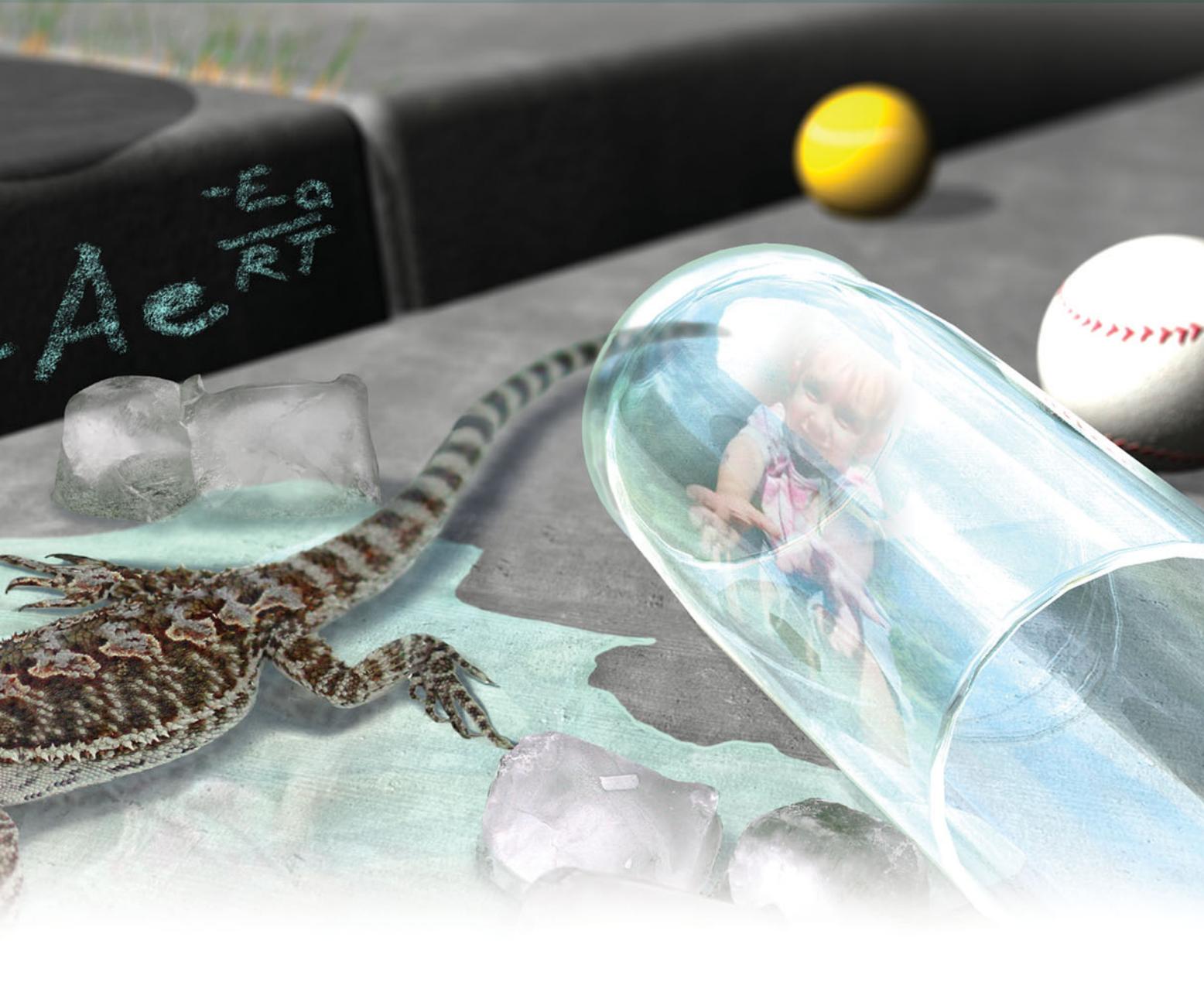
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In the passage quoted above, Oxford chemistry professor Sir Cyril Hinshelwood calls attention to an aspect of chemistry often overlooked by the casual observer—the mystery of change with time. Since the opening chapter of this book, you have learned that the goal of chemistry is to understand the macroscopic world by examining the molecular one. In this chapter, we focus on understanding how this molecular world changes with time, an area of study called chemical kinetics. The molecular world is anything but static. Thermal energy produces constant molecular motion, causing molecules to repeatedly collide with one another. In a tiny fraction of these collisions, something extraordinary happens—the electrons on one molecule or atom are attracted to the nuclei of another. Some bonds weaken and new bonds form—a chemical reaction occurs. Chemical kinetics is the study of how these kinds of changes occur in time.



## 13.1 Catching Lizards

The children who live in my neighborhood (including my own kids) have a unique way of catching lizards. Armed with cups of ice water, they chase one of these cold-blooded reptiles into a corner, and then take aim and pour the cold water directly onto the lizard's body. The lizard's body temperature drops and it becomes virtually immobilized—easy prey for little hands. The kids scoop up the lizard and place it in a tub filled with sand and leaves. They then watch as the lizard warms back up and becomes active again. They usually release the lizard back into the yard within hours. I guess you could call them catch-and-release lizard hunters.

Unlike mammals, which actively regulate their body temperature through metabolic activity, lizards are *ectotherms*—their body temperature depends on their surroundings. When splashed with cold water, a lizard's body simply gets colder. The drop in body temperature immobilizes the lizard because its movement depends on chemical reactions that occur within its muscles, and the *rates* of those reactions—how fast they occur—are highly sensitive to temperature. In other words, when the temperature drops, the reactions that produce movement in the lizard occur more slowly; therefore, the movement itself

*Pouring ice water on a lizard slows it down, making it easier to catch.*

slows down. When reptiles get cold, they become lethargic, unable to move very quickly. For this reason, reptiles try to maintain their body temperature within a narrow range by moving between sun and shade.

The rates of chemical reactions, and especially the ability to *control* those rates, are important not just in reptile movement but in many other phenomena as well. For example, a successful rocket launch depends on the rate at which fuel burns—too quickly and the rocket can explode, too slowly and it will not leave the ground. Chemists must always consider reaction rates when synthesizing compounds. No matter how stable a compound might be, its synthesis is impossible if the rate at which it forms is too slow. As we have seen with reptiles, reaction rates are important to life. In fact, the human body's ability to switch a specific reaction on or off at a specific time is achieved largely by controlling the rate of that reaction through the use of enzymes (biological molecules that we explore more fully in Section 13.7).

The first person to measure the rate of a chemical reaction carefully was Ludwig Wilhelmy. In 1850, he measured how fast sucrose, upon treatment with acid, hydrolyzed into glucose and fructose. This reaction occurred over several hours, and Wilhelmy was able to show how the rate depended on the initial amount of sugar present—the greater the initial amount, the faster the initial rate. Today we can measure the rates of reactions that occur in times as short as several femtoseconds (femto =  $10^{-15}$ ). The knowledge of reaction rates is not only practically important—giving us the ability to control how fast a reaction occurs—but also theoretically important. As you will see in Section 13.6, the rate of a reaction can tell us much about how the reaction occurs on the molecular scale.

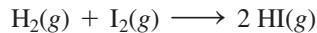
## 13.2 The Rate of a Chemical Reaction

The rate of a chemical reaction is a measure of how fast the reaction occurs, as shown in Figure 13.1 ►. If a chemical reaction has a fast rate, a large fraction of molecules react to form products in a given period of time. If a chemical reaction has a slow rate, only a relatively small fraction of molecules react to form products in a given period of time.

When we measure how fast something occurs, or more specifically the *rate* at which it occurs, we usually express the measurement as a change in some quantity per unit of time. For example, we measure the speed of a car—the rate at which it travels—in *miles per hour*, and we might measure how fast people lose weight in *pounds per week*. We report these rates in units that represent the change in what we are measuring (distance or weight) divided by the change in time.

$$\text{Speed} = \frac{\text{change in distance}}{\text{change in time}} = \frac{\Delta x}{\Delta t} \quad \text{Weight loss} = \frac{\text{change in weight}}{\text{change in time}} = \frac{\Delta \text{ weight}}{\Delta t}$$

Similarly, the rate of a chemical reaction is measured as a change in the amounts of reactants or products (usually in concentration units) divided by the change in time. For example, consider the gas-phase reaction between  $\text{H}_2(g)$  and  $\text{I}_2(g)$ :



We can define the rate of this reaction in the time interval  $t_1$  to  $t_2$  as follows:

$$\text{Rate} = -\frac{\Delta[\text{H}_2]}{\Delta t} = -\frac{[\text{H}_2]_{t_2} - [\text{H}_2]_{t_1}}{t_2 - t_1} \quad [13.1]$$

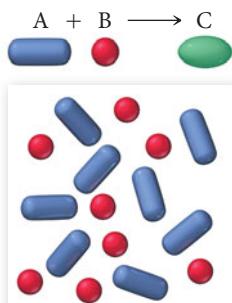
In this expression,  $[\text{H}_2]_{t_2}$  is the hydrogen concentration at time  $t_2$  and  $[\text{H}_2]_{t_1}$  is the hydrogen concentration at time  $t_1$ . The reaction rate is defined as the *negative* of the change in concentration of a reactant divided by the change in time. The negative sign is usually part of the definition when the reaction rate is defined in terms of a reactant because reactant concentrations decrease as a reaction proceeds; therefore, *the change in the concentration of a reactant is negative*. The negative sign thus makes the overall *rate* positive. (By convention, reaction rates are reported as positive quantities.)

The reaction rate can also be defined in terms of the other reactant as follows:

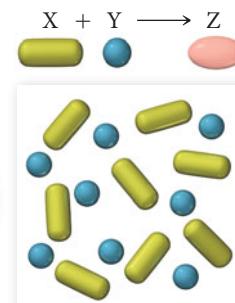
$$\text{Rate} = -\frac{\Delta[\text{I}_2]}{\Delta t} \quad [13.2]$$

Recall that  $[\text{A}]$  means the concentration of A in M ( $\text{mol/L}$ ).

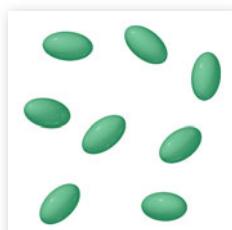
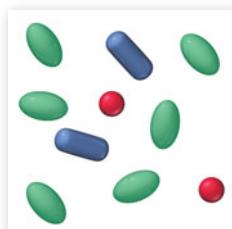
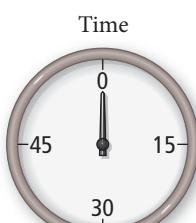
A reaction with a fast rate



A reaction with a slow rate



◀ FIGURE 13.1 The Rate of a Chemical Reaction



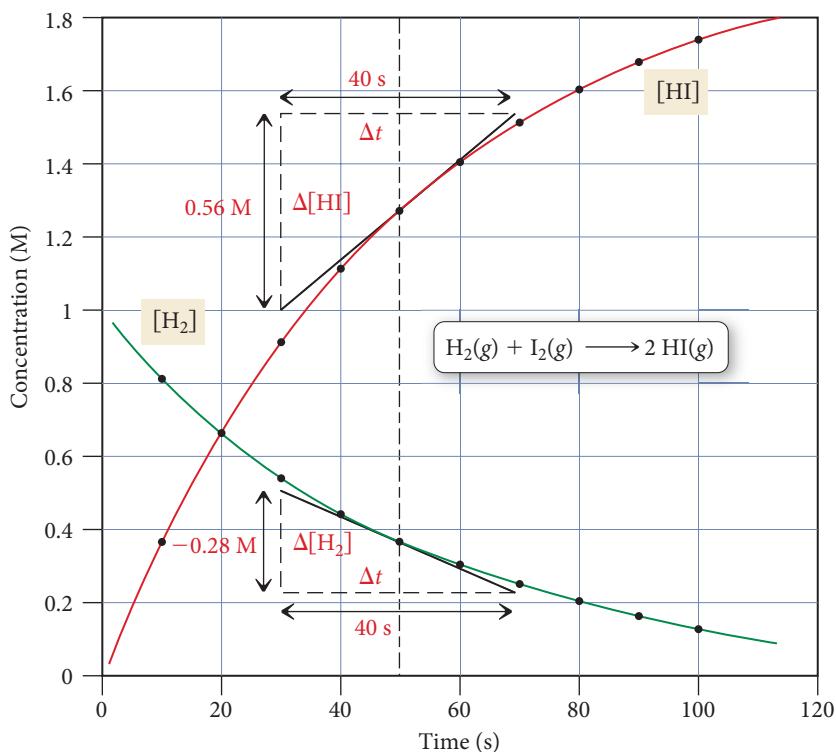
Since 1 mol of H<sub>2</sub> reacts with 1 mol of I<sub>2</sub>, the rates are defined in the same way. The rate can also be defined with respect to the *product* of the reaction as follows:

$$\text{Rate} = +\frac{1}{2} \frac{\Delta[\text{HI}]}{\Delta t} \quad [13.3]$$

Because product concentrations *increase* as the reaction proceeds, the change in concentration of a product is positive. Therefore, when the rate is defined with respect to a product, we do not include a negative sign in the definition—the rate is naturally positive. The factor of  $\frac{1}{2}$  in this definition is related to the stoichiometry of the reaction. In order to have a single rate for the entire reaction, the definition of the rate with respect to each reactant and product must reflect the stoichiometric coefficients of the reaction. For this particular reaction, 2 mol of HI is produced from 1 mol of H<sub>2</sub> and 1 mol of I<sub>2</sub>.



The concentration of HI increases at twice the rate that the concentration of H<sub>2</sub> or I<sub>2</sub> decreases. In other words, if 100 I<sub>2</sub> molecules react per second, then 200 HI molecules form per second. In order for the overall rate to have the same value when defined with respect to any of the reactants or products, the change in HI concentration must be multiplied by a factor of one-half.



**▲ FIGURE 13.2** Reactant and Product Concentrations as a Function of Time

The graph shows the concentration of one of the reactants ( $\text{H}_2$ ) and the product ( $\text{HI}$ ) as a function of time. The other reactant ( $\text{I}_2$ ) is omitted for clarity.

Consider the graph shown in Figure 13.2 ▲, which represents the changes in concentration for  $\text{H}_2$  (one of the reactants) and  $\text{HI}$  (the product) versus time. Let's examine several features of this graph individually.

### Change in Reactant and Product Concentrations

The reactant concentration, as expected, *decreases* with time because reactants are consumed in a reaction. The product concentration *increases* with time because products are formed in a reaction. The increase in  $\text{HI}$  concentration occurs at exactly twice the rate of the decrease in  $\text{H}_2$  concentration because of the stoichiometry of the reaction: 2 mol of  $\text{HI}$  form for every 1 mol of  $\text{H}_2$  consumed.

**The Average Rate of the Reaction** We can calculate the average rate of the reaction for any time interval using Equation 13.1 for  $\text{H}_2$ . The following table lists  $\text{H}_2$  concentration ( $[\text{H}_2]$ ) at various times, the change in  $\text{H}_2$  concentration for each interval ( $\Delta[\text{H}_2]$ ), the change in time for each interval ( $\Delta t$ ), and the rate for each interval ( $-\Delta[\text{H}_2]/\Delta t$ ). The rate is the average rate within the given time interval. For example, the average rate of the reaction in the time interval between 10 and 20 seconds is  $0.0149 \text{ M/s}$ , while the average rate in the time interval between 20 and 30 seconds is  $0.0121 \text{ M/s}$ . Notice that the average rate *decreases* as the reaction progresses. In other words, the reaction slows down as it proceeds. We discuss this further in the next section, where we will see that, for most reactions, the rate depends on the concentrations of the reactants. As the reactants transform to products, their concentrations decrease, and the reaction slows down.

| Time (s) | $[\text{H}_2]$ (M) | $\Delta[\text{H}_2]$ (M) | $\Delta t$ (s) | $\text{Rate} = -\Delta[\text{H}_2]/\Delta t$ (M/s) |
|----------|--------------------|--------------------------|----------------|--|
| 0.000    | 1.000              | -                        | -              | -  |
| 10.000   | 0.819              | -0.181                   | 10.000         | 0.0181   |
| 20.000   | 0.670              | -0.149                   | 10.000         | 0.0149   |
| 30.000   | 0.549              | -0.121                   | 10.000         | 0.0121   |
| 40.000   | 0.449              | -0.100                   | 10.000         | 0.0100   |
| 50.000   | 0.368              | -0.081                   | 10.000         | 0.0081   |
| 60.000   | 0.301              | -0.067                   | 10.000         | 0.0067   |
| 70.000   | 0.247              | -0.054                   | 10.000         | 0.0054   |
| 80.000   | 0.202              | -0.045                   | 10.000         | 0.0045   |
| 90.000   | 0.165              | -0.037                   | 10.000         | 0.0037   |
| 100.000  | 0.135              | -0.030                   | 10.000         | 0.0030   |

**The Instantaneous Rate of the Reaction** The instantaneous rate of the reaction is the rate at any one point in time and is represented by the instantaneous slope of the curve at that point. We can determine the instantaneous rate by calculating the slope of the tangent to the curve at the point of interest. In Figure 13.2, we have drawn the tangent lines for both  $[\text{H}_2]$  and  $[\text{HI}]$  at 50 seconds. We calculate the instantaneous rate at 50 seconds as follows:

Using  $[\text{H}_2]$

$$\text{Instantaneous rate (at 50 s)} = -\frac{\Delta[\text{H}_2]}{\Delta t} = -\frac{-0.28 \text{ M}}{40 \text{ s}} = 0.0070 \text{ M/s}$$

Using

$$\text{Instantaneous rate (at 50 s)} = +\frac{1}{2} \frac{\Delta[\text{HI}]}{\Delta t} = +\frac{1}{2} \frac{0.56 \text{ M}}{40 \text{ s}} = 0.0070 \text{ M/s}$$

As we would expect, the rate is the same whether we use one of the reactants or the product for the calculation. Notice that the instantaneous rate at 50 seconds (0.0070 M/s) is between the average rates calculated for the 10-second intervals just before and just after 50 seconds.

We can generalize our definition of reaction rate for the generic reaction:



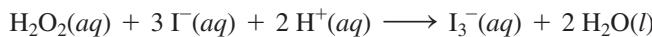
where A and B are reactants, C and D are products, and  $a$ ,  $b$ ,  $c$ , and  $d$  are the stoichiometric coefficients. We define the rate of the reaction as follows:

$$\text{Rate} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = +\frac{1}{c} \frac{\Delta[C]}{\Delta t} = +\frac{1}{d} \frac{\Delta[D]}{\Delta t} \quad [13.5]$$

From the definition, we can see that knowing the rate of change in the concentration of any one reactant or product at a point in time allows us to determine the rate of change in the concentration of any other reactant or product at that point in time (from the balanced equation). *However, predicting the rate at some future time is not possible from just the balanced equation.*

### EXAMPLE 13.1 Expressing Reaction Rates

Consider this balanced chemical equation:



In the first 10.0 seconds of the reaction, the concentration of  $\text{I}^-$  dropped from 1.000 M to 0.868 M.

- (a) Calculate the average rate of this reaction in this time interval.
- (b) Determine the rate of change in the concentration of  $\text{H}^+$  (that is,  $\Delta[\text{H}^+]/\Delta t$ ) during this time interval.

#### SOLUTION

- (a) Use Equation 13.5 to calculate the average rate of the reaction.

$$\begin{aligned} \text{Rate} &= -\frac{1}{3} \frac{\Delta[\text{I}^-]}{\Delta t} \\ &= -\frac{1}{3} \frac{(0.868 \text{ M} - 1.000 \text{ M})}{10.0 \text{ s}} \\ &= 4.40 \times 10^{-3} \text{ M/s} \end{aligned}$$

- (b) Use Equation 13.5 again for the relationship between the rate of the reaction and  $\Delta[\text{H}^+]/\Delta t$ . After solving for  $\Delta[\text{H}^+]/\Delta t$ , substitute the calculated rate from part (a) and calculate  $\Delta[\text{H}^+]/\Delta t$ .

$$\begin{aligned} \text{Rate} &= -\frac{1}{2} \frac{\Delta[\text{H}^+]}{\Delta t} \\ \frac{\Delta[\text{H}^+]}{\Delta t} &= -2(\text{rate}) \\ &= -2(4.40 \times 10^{-3} \text{ M/s}) \\ &= -8.80 \times 10^{-3} \text{ M/s} \end{aligned}$$

#### FOR PRACTICE 13.1

For the reaction shown in Example 13.1, predict the rate of change in concentration of  $\text{H}_2\text{O}_2$  ( $\Delta[\text{H}_2\text{O}_2]/\Delta t$ ) and  $\text{I}_3^-$  ( $\Delta[\text{I}_3^-]/\Delta t$ ) during this time interval.

### Conceptual Connection 13.1 Reaction Rates

For the reaction  $A + 2B \longrightarrow C$  under a given set of conditions, the initial rate is 0.100 M/s. What is  $\Delta[B]/\Delta t$  under the same conditions?

- (a)  $-0.0500 \text{ M/s}$  (b)  $-0.100 \text{ M/s}$  (c)  $-0.200 \text{ M/s}$

## Measuring Reaction Rates

In order to study the kinetics of a reaction, we must have an experimental way to measure the concentration of at least one of the reactants or products as a function of time. For example, Ludwig Wilhelmy, whose experiment on the rate of the conversion of sucrose to glucose and fructose we discussed briefly in Section 13.1, took advantage of sucrose's ability to rotate polarized light. (Polarized light is light with an electric field oriented along one plane.) When a beam of polarized light is passed through a sucrose solution, the polarization of the light is rotated clockwise. In contrast, the products of the reaction (glucose and fructose) rotate polarized light counter clockwise. By measuring the degree of polarization of light passing through a reacting solution—a technique known as polarimetry—Wilhelmy was able to determine the relative concentrations of the reactants and products as a function of time.

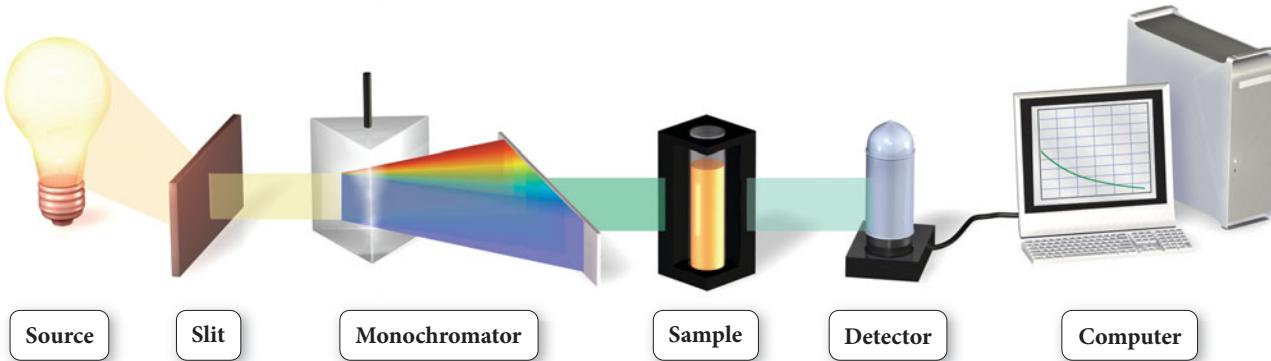
Perhaps the most common way to study the kinetics of a reaction is through spectroscopy (see Section 7.3). For example, the reaction of H<sub>2</sub> and I<sub>2</sub> to form HI can be followed spectroscopically because I<sub>2</sub> is violet and H<sub>2</sub> and HI are colorless. As I<sub>2</sub> reacts with H<sub>2</sub> to form HI, the violet color of the reaction mixture fades. The fading color can be monitored with a spectrometer, a device that passes light through a sample and measures how strongly the light is absorbed (Figure 13.3 ▶). If the sample contains the reacting mixture, the intensity of the light absorption will decrease as the reaction proceeds, providing a direct measure of the concentration of I<sub>2</sub> as a function of time. Because light travels so fast and because experimental techniques can produce very short pulses of light, spectroscopy can be used to measure reactions that happen on time scales as short as several femtoseconds.

Reactions in which the number of moles of gaseous reactants and products changes as the reaction proceeds can be readily monitored by measuring changes in pressure. Consider the reaction in which dinitrogen monoxide reacts to form nitrogen and oxygen gas:

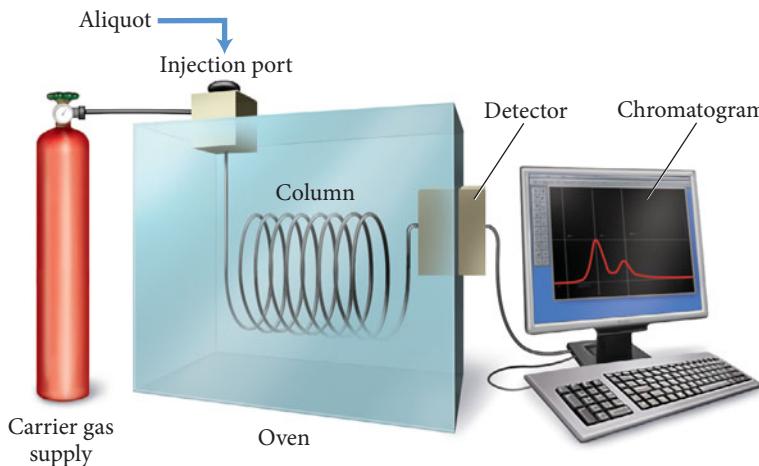


For every 2 mol of N<sub>2</sub>O that reacts, the reaction vessel will contain one additional mole of gas. As the reaction proceeds and the amount of gas increases, the pressure steadily rises. We can use the rise in pressure to determine the relative concentrations of reactants and products as a function of time.

The three techniques mentioned here—polarimetry, spectroscopy, and pressure measurement—can all be used to monitor a reaction as it occurs in a reaction vessel. Some reactions occur slowly enough that samples, or *aliquots*, can be periodically withdrawn from the reaction vessel and analyzed to determine the progress of the reaction. Instrumental techniques such as gas chromatography (Figure 13.4 ►) or mass spectrometry, as well as wet chemical techniques such as titration, can be used to measure the relative amounts of reactants or products in the aliquot. By taking aliquots at regular time intervals, we can determine the relative amounts of reactants and products as a function of time.



**▲ FIGURE 13.3 The Spectrometer** In a spectrometer, light of a specific wavelength is passed through the sample and the intensity of the transmitted light—which depends on how much light is absorbed by the sample—is measured and recorded.

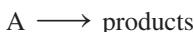


◀ FIGURE 13.4 The Gas Chromatograph

In a gas chromatograph (GC), a sample of the reaction mixture, or aliquot, is injected into a specially constructed column. Because of their characteristic physical and chemical properties, different components of the mixture pass through the column at different rates and thus exit at different times. As each component leaves the column, it is identified electronically and a chromatogram is recorded. The area under each peak in the chromatogram is proportional to the amount of one particular component in the sample mixture.

## 13.3 The Rate Law: The Effect of Concentration on Reaction Rate

The rate of a reaction often depends on the concentration of one or more of the reactants. Wilhelmy noticed this effect in 1850 for the hydrolysis of sucrose. For simplicity, let's consider a reaction in which a single reactant, A, decomposes into products:



As long as the rate of the reverse reaction (in which the products return to reactants) is negligibly slow, we can express the relationship between the rate of the reaction and the concentration of the reactant—called the **rate law**—as follows:

$$\text{Rate} = k[A]^n \quad [13.6]$$

where  $k$  is a constant of proportionality called the **rate constant** and  $n$  is the **reaction order**. The value of  $n$  (usually an integer) determines how the rate depends on the concentration of the reactant.

- If  $n = 0$ , the reaction is *zero order* and the rate is independent of the concentration of A.
- If  $n = 1$ , the reaction is *first order* and the rate is directly proportional to the concentration of A.
- If  $n = 2$ , the reaction is *second order* and the rate is proportional to the square of the concentration of A.

By definition,  $[A]^0 = 1$ , so the rate is equal to  $k$  regardless of  $[A]$ .

Although other orders are possible, including noninteger (or fractional) orders, these three are the most common.

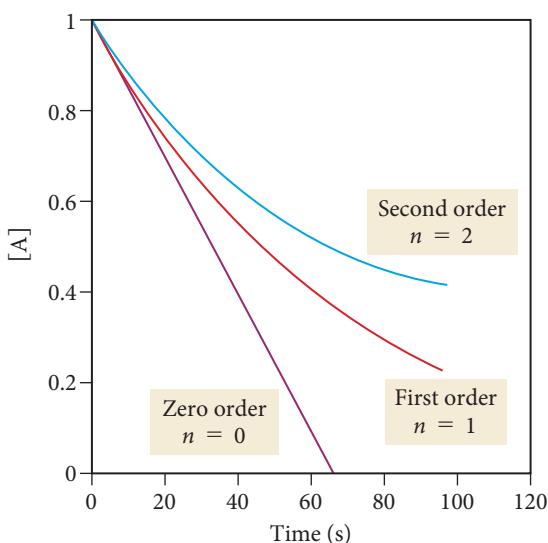
Figure 13.5 ▶ shows three plots illustrating how the *concentration of A changes with time* for the three common reaction orders with identical numerical values for the rate constant ( $k$ ) and identical initial concentrations. Figure 13.6 ▶ has three plots showing the *rate of the reaction* (the slope of the lines in Figure 13.5) as a function of the reactant concentration for each reaction order.

**Zero-Order Reaction** In a zero-order reaction, the rate of the reaction is independent of the concentration of the reactant.

$$\text{Rate} = k[A]^0 = k \quad [13.7]$$

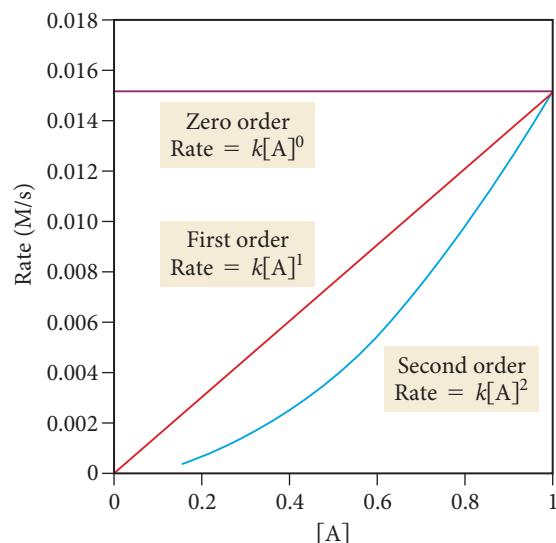
Consequently, for a zero-order reaction, the concentration of the reactant decreases linearly with time, as shown in Figure 13.5. The slope of the line is constant, indicating a constant rate. The rate is constant because the reaction does not slow down as the concentration of A decreases. The graph in Figure 13.6 shows that the rate of a zero-order reaction is the same at any concentration of A. Zero-order reactions occur under conditions where the amount of reactant actually *available for reaction* is unaffected by changes in the *overall quantity of reactant*. For example, sublimation is normally zero order because only molecules at the surface can sublime, and their concentration does not change as the amount of subliming substance decreases (Figure 13.7 ▶).

### Reactant Concentration versus Time



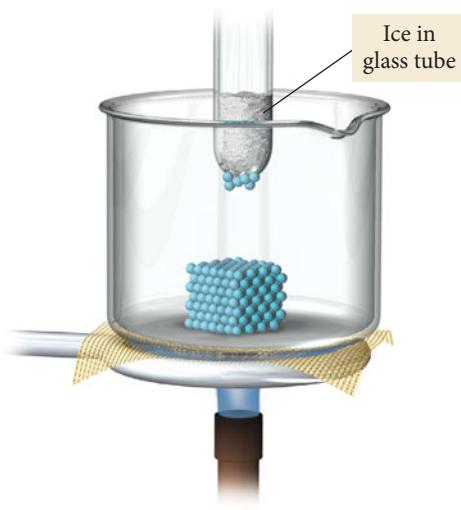
▲ FIGURE 13.5 Reactant Concentration as a Function of Time for Different Reaction Orders

### Rate versus Reactant Concentration



▲ FIGURE 13.6 Reaction Rate as a Function of Reactant Concentration for Different Reaction Orders

### Sublimation Is Zero-Order



When one layer of particles sublimes, the next layer is exposed. The number of particles available to sublime remains constant.

▲ FIGURE 13.7 Sublimation When a layer of particles sublimes, another identical layer is just below it. Consequently, the number of particles available to sublime at any one time does not change with the total number of particles in the sample, and the process is zero order.

**First-Order Reaction** In a first-order reaction, the rate of the reaction is directly proportional to the concentration of the reactant.

$$\text{Rate} = k[\text{A}]^1 \quad [13.8]$$

For a first-order reaction the rate slows down as the reaction proceeds because the concentration of the reactant decreases. You can see this in Figure 13.5—the slope of the curve (the rate) becomes less steep (slower) with time. Figure 13.6 shows the rate as a function of the concentration of A. Notice the linear relationship—the rate is directly proportional to the concentration.

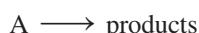
**Second-Order Reaction** In a second-order reaction, the rate of the reaction is proportional to the square of the concentration of the reactant.

$$\text{Rate} = k[\text{A}]^2 \quad [13.9]$$

Consequently, for a second-order reaction, the rate is even more sensitive to the reactant concentration. You can see this in Figure 13.5—the slope of the curve (the rate) flattens out more quickly than it does for a first-order reaction. Figure 13.6 shows the rate as a function of the concentration of A. Notice the quadratic relationship—the rate is proportional to the square of the concentration.

### Determining the Order of a Reaction

The order of a reaction can be determined only by experiment. A common way to determine reaction order is the method of initial rates. In this method, the initial rate—the rate for a short period of time at the beginning of the reaction—is measured by running the reaction several times with different initial reactant concentrations to determine the effect of the concentration on the rate. For example, let's return to our simple reaction in which a single reactant, A, decomposes into products:



In an experiment, the initial rate is measured at several different initial concentrations with the following results:

| [A] (M) | Initial Rate (M/s) |
|---------|--------------------|
| 0.10    | 0.015              |
| 0.20    | 0.030              |
| 0.40    | 0.060              |

In this data set, when the concentration of A doubles, the rate doubles—the initial rate is directly proportional to the initial concentration. The reaction is therefore first order in A, and the rate law takes the first-order form:

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

We can determine the value of the rate constant,  $k$ , by solving the rate law for  $k$  and substituting the concentration and the initial rate from any one of the three measurements (here we use the first measurement).

$$\begin{aligned}\text{Rate} &= k[\text{A}]^1 \\ k &= \frac{\text{rate}}{[\text{A}]} = \frac{0.015 \text{ M/s}}{0.10 \text{ M}} = 0.15 \text{ s}^{-1}\end{aligned}$$

Notice that the rate constant for a first-order reaction has units of  $\text{s}^{-1}$ .

The following two data sets show how measured initial rates are different for zero-order and for second-order reactions having the same initial rate at  $[\text{A}] = 0.10 \text{ M}$ :

| Zero Order ( $n = 0$ ) |                    | Second Order ( $n = 2$ ) |                    |
|------------------------|--------------------|--------------------------|--------------------|
| [A] (M)                | Initial Rate (M/s) | [A] (M)                  | Initial Rate (M/s) |
| 0.10                   | 0.015              | 0.10                     | 0.015              |
| 0.20                   | 0.015              | 0.20                     | 0.060              |
| 0.40                   | 0.015              | 0.40                     | 0.240              |

For a zero-order reaction, the initial rate is independent of the reactant concentration—the rate is the same at all measured initial concentrations. For a second-order reaction, the initial rate quadruples for a doubling of the reactant concentration—the relationship between concentration and rate is quadratic. If we are unsure about how the initial rate is changing with the initial reactant concentration, or if the numbers are not as obvious as they are in these examples, we can substitute any two initial concentrations and the corresponding initial rates into a ratio of the rate laws to determine the order ( $n$ ):

$$\frac{\text{rate 2}}{\text{rate 1}} = \frac{k[\text{A}]_2^n}{k[\text{A}]_1^n}$$

For example, we can substitute the last two measurements in the data set just given for the second-order reaction as follows:

$$\begin{aligned}\frac{0.240 \text{ M/s}}{0.060 \text{ M/s}} &= \frac{k(0.40 \text{ M})^n}{k(0.20 \text{ M})^n} \\ 4.0 &= \left(\frac{0.40}{0.20}\right)^n = 2^n\end{aligned}$$

Remember that  $\frac{x^n}{y^n} = \left(\frac{x}{y}\right)^n$

Remember that  $\log x^n = n \log x$ .

$$\begin{aligned}\log 4.0 &= \log (2^n) \\ &= n \log 2 \\ n &= \frac{\log 4}{\log 2} \\ &= 2\end{aligned}$$

The rate constants for zero- and second-order reactions have different units than for first-order reactions. The rate constant for a zero-order reaction has units of  $\text{M} \cdot \text{s}^{-1}$ , and the rate constant for a second-order reaction has units of  $\text{M}^{-1} \cdot \text{s}^{-1}$ .

### Conceptual Connection 13.2 Order of Reaction

The reaction  $\text{A} \rightarrow \text{B}$  has been experimentally determined to be second order. The initial rate is  $0.0100 \text{ M/s}$  at an initial concentration of A of  $0.100 \text{ M}$ . What is the initial rate at  $[\text{A}] = 0.500 \text{ M}$ ?

- (a)  $0.00200 \text{ M/s}$  (b)  $0.0100 \text{ M/s}$  (c)  $0.0500 \text{ M/s}$  (d)  $0.250 \text{ M/s}$

## Reaction Order for Multiple Reactants

So far, we have considered a simple reaction with only one reactant. How is the rate law defined for reactions with more than one reactant? Consider the generic reaction:



As long as the reverse reaction is negligibly slow, the rate law is proportional to the concentration of [A] raised to the  $m$  power multiplied by the concentration of [B] raised to the  $n$  power:

$$\text{Rate} = k[A]^m[B]^n \quad [13.10]$$

where  $m$  is the reaction order with respect to A and  $n$  is the reaction order with respect to B. The **overall order** is the sum of the exponents ( $m + n$ ). For example, the reaction between hydrogen and iodine has been experimentally determined to be first order with respect to hydrogen, first order with respect to iodine, and thus second order overall.



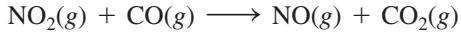
Similarly, the reaction between hydrogen and nitrogen monoxide has been experimentally determined to be first order with respect to hydrogen, second order with respect to nitrogen monoxide, and thus third order overall.



*The rate law for any reaction must always be determined by experiment*, often by the method of initial rates described previously. There is no way to simply look at a chemical equation and determine the rate law for the reaction. When the reaction has two or more reactants, the concentration of each reactant is usually varied independently of the others to determine the dependence of the rate on the concentration of that reactant. Example 13.2 shows how to use the method of initial rates to determine the order of a reaction with multiple reactants.

### EXAMPLE 13.2 Determining the Order and Rate Constant of a Reaction

Consider the reaction between nitrogen dioxide and carbon monoxide:



The initial rate of the reaction is measured at several different concentrations of the reactants with the accompanied results.

From the data, determine:

- (a) the rate law for the reaction
- (b) the rate constant ( $k$ ) for the reaction

#### SOLUTION

(a) Begin by examining how the rate changes for each change in concentration. Between the first two experiments, the concentration of  $\text{NO}_2$  doubles, the concentration of CO stays constant, and the rate quadruples, suggesting that the reaction is second order in  $\text{NO}_2$ .

Between the second and third experiments, the concentration of  $\text{NO}_2$  stays constant, the concentration of CO doubles, and the rate remains constant (the small change in the least significant figure is simply experimental error), suggesting that the reaction is zero order in CO.

Between the third and fourth experiments, the concentration of  $\text{NO}_2$  again doubles and the concentration of CO halves, yet the rate quadruples again, confirming that the reaction is second order in  $\text{NO}_2$  and zero order in CO.

| [ $\text{NO}_2$ ] (M) | [CO] (M) | Initial Rate (M/s) |
|-----------------------|----------|--------------------|
| 0.10                  | 0.10     | 0.0021             |
| 0.20                  | 0.10     | 0.0082             |
| 0.20                  | 0.20     | 0.0083             |
| 0.40                  | 0.10     | 0.033              |

| [ $\text{NO}_2$ ]     | [CO]                            | Initial Rate (M/s)    |
|-----------------------|---------------------------------|-----------------------|
| 0.10 M                | 0.10 M                          | 0.0021                |
| $\downarrow \times 2$ | $\downarrow$ constant           | $\downarrow \times 4$ |
| 0.20 M                | 0.10 M                          | 0.0082 M              |
| $\downarrow$ constant | $\downarrow \times 2$           | $\downarrow \times 1$ |
| 0.20 M                | 0.20 M                          | 0.0083 M              |
| $\downarrow \times 2$ | $\downarrow \times \frac{1}{2}$ | $\downarrow \times 4$ |
| 0.40 M                | 0.10 M                          | 0.033 M               |

Write the overall rate expression.

$$\text{Rate} = k[\text{NO}_2]^2[\text{CO}]^0 = k[\text{NO}_2]^2$$

- (b) To determine the rate constant for the reaction, solve the rate law for  $k$  and substitute the concentration and the initial rate from any one of the four measurements. In this case, we use the first measurement.

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

$$k = \frac{\text{rate}}{[\text{NO}_2]^2} = \frac{0.0021 \text{ M/s}}{(0.10 \text{ M})^2} = 0.21 \text{ M}^{-1} \cdot \text{s}^{-1}$$

### FOR PRACTICE 13.2

Consider the equation:



The initial rate of reaction is measured at several different concentrations of the reactants with the following results:

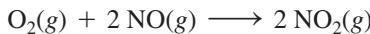
| $[\text{CHCl}_3] (\text{M})$ | $[\text{Cl}_2] (\text{M})$ | Initial Rate ( $\text{M/s}$ ) |
|------------------------------|----------------------------|-------------------------------|
| 0.010                        | 0.010                      | 0.0035                        |
| 0.020                        | 0.010                      | 0.0069                        |
| 0.020                        | 0.020                      | 0.0098                        |
| 0.040                        | 0.040                      | 0.027                         |

From the data, determine:

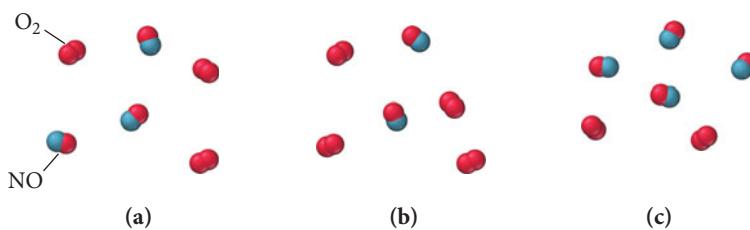
- (a) the rate law for the reaction      (b) the rate constant ( $k$ ) for the reaction

### Conceptual Connection 13.3 Rate and Concentration

This reaction was experimentally determined to be first order with respect to  $\text{O}_2$  and second order with respect to  $\text{NO}$ .



These diagrams represent reaction mixtures in which the number of each type of molecule represents its relative initial concentration. Which mixture has the fastest initial rate?



## 13.4 The Integrated Rate Law: The Dependence of Concentration on Time

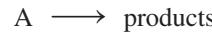
The rate laws we have examined so far show the relationship between *the rate of a reaction and the concentration of a reactant*. But we often want to know the relationship between *the concentration of a reactant and time*. For example, the presence of chlorofluorocarbons (CFCs) in the atmosphere threatens the ozone layer. One of the reasons that CFCs pose such a significant threat is that the reactions that consume them are so slow (see Table 13.1). Legislation has significantly reduced CFC emissions, but even if we were to completely stop adding CFCs to the atmosphere, their concentration would decrease only very slowly. Nonetheless, we would like to know how their concentration changes with time. How much will be left in 20 years? In 50 years?

**TABLE 13.1 Atmospheric Lifetimes of Several CFCs**

| CFC Name   | Structure  | Atmospheric Lifetime* |
|--|--|-----------------------|
| CFC-11 ( $\text{CCl}_3\text{F}$ )<br>Trichlorofluoromethane                            |  | 45 years              |
| CFC-12 ( $\text{CCl}_2\text{F}_2$ )<br>Dichlorodifluoromethane                         |  | 100 years             |
| CFC-113 ( $\text{C}_2\text{F}_3\text{Cl}_3$ )<br>1,1,2-Trichloro-1,2,2-trifluoroethane |  | 85 years              |
| CFC-114 ( $\text{C}_2\text{F}_4\text{Cl}_2$ )<br>1,2-Dichlorotetrafluoroethane         |  | 300 years             |
| CFC-115 ( $\text{C}_2\text{F}_5\text{Cl}$ )<br>Monochloropentafluoroethane             |  | 1700 years            |

\*Data taken from EPA site (under section 602 of Clean Air Act).

The **integrated rate law** for a chemical reaction is a relationship between the concentrations of the reactants and time. For simplicity, we return to a single reactant decomposing into products:



The integrated rate law for this reaction depends on the order of the reaction; let's examine each of the common reaction orders individually.

**First-Order Integrated Rate Law** If our simple reaction is first order, the rate is directly proportional to the concentration of A:

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

Since  $\text{Rate} = -\Delta[\text{A}]/\Delta t$ , we can write:

$$-\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}] \quad [13.11]$$

In this form, the rate law is also known as the *differential rate law*.

Although we do not show the steps here, we can use calculus (see End-of-Chapter Exercise 112) to integrate the differential rate law and obtain the first-order *integrated rate law*:

$$\begin{aligned}\ln[\text{A}]_t &= -kt + \ln[\text{A}]_0 \\ \ln[\text{A}]_t - \ln[\text{A}]_0 &= -kt \\ \ln \frac{[\text{A}]_t}{[\text{A}]_0} &= -kt\end{aligned}$$

$$\ln[\text{A}]_t = -kt + \ln[\text{A}]_0 \quad [13.12]$$

or

$$\ln \frac{[\text{A}]_t}{[\text{A}]_0} = -kt \quad [13.13]$$

Remember that  $\ln A - \ln B = \ln(A/B)$ .

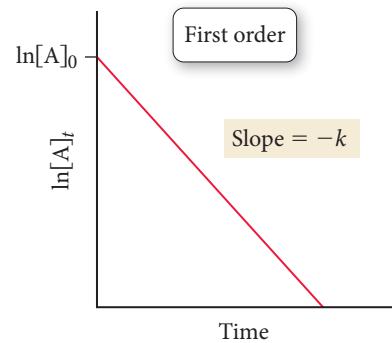
where  $[\text{A}]_t$  is the concentration of A at any time  $t$ ,  $k$  is the rate constant, and  $[\text{A}]_0$  is the initial concentration of A. These two forms of the equation are equivalent, as shown in the margin.

Notice that the integrated rate law shown in Equation 13.12 has the form of an equation for a straight line.

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

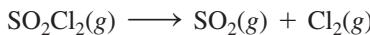
$$y = mx + b$$

For a first-order reaction, a plot of the natural log of the reactant concentration as a function of time yields a straight line with a slope of  $-k$  and a  $y$ -intercept of  $\ln[A]_0$ , as shown in Figure 13.8 ►. (Note that the slope is negative but that the rate constant is always positive.)



### EXAMPLE 13.3 The First-Order Integrated Rate Law: Using Graphical Analysis of Reaction Data

Consider the equation for the decomposition of  $\text{SO}_2\text{Cl}_2$ :



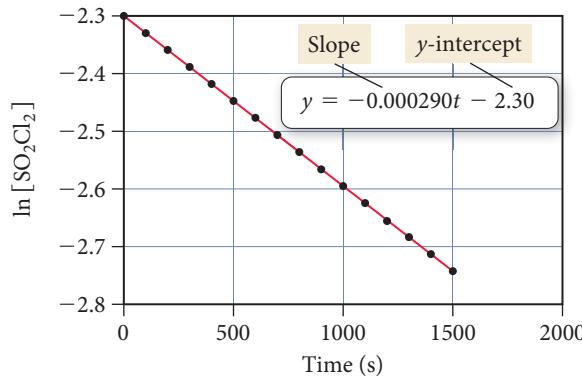
The concentration of  $\text{SO}_2\text{Cl}_2$  was monitored at a fixed temperature as a function of time during the decomposition reaction, and the following data were tabulated:

| Time (s) | $[\text{SO}_2\text{Cl}_2]$ (M) | Time (s) | $[\text{SO}_2\text{Cl}_2]$ (M) |
|----------|--------------------------------|----------|--------------------------------|
| 0        | 0.100                          | 800      | 0.0793                         |
| 100      | 0.0971                         | 900      | 0.0770                         |
| 200      | 0.0944                         | 1000     | 0.0748                         |
| 300      | 0.0917                         | 1100     | 0.0727                         |
| 400      | 0.0890                         | 1200     | 0.0706                         |
| 500      | 0.0865                         | 1300     | 0.0686                         |
| 600      | 0.0840                         | 1400     | 0.0666                         |
| 700      | 0.0816                         | 1500     | 0.0647                         |

Show that the reaction is first order, and determine the rate constant for the reaction.

#### SOLUTION

In order to show that the reaction is first order, prepare a graph of  $\ln[\text{SO}_2\text{Cl}_2]$  versus time as shown.



The plot is linear, confirming that the reaction is indeed first order. To obtain the rate constant, fit the data to a line. The slope of the line will be equal to  $-k$ . Since the slope of the best fitting line (which is most easily determined on a graphing calculator or with spreadsheet software such as Microsoft Excel) is  $-2.90 \times 10^{-4}\text{s}^{-1}$ , the rate constant is therefore  $+2.90 \times 10^{-4}\text{s}^{-1}$ .

#### FOR PRACTICE 13.3

Use the graph and the best fitting line in Example 13.3 to predict the concentration of  $\text{SO}_2\text{Cl}_2$  at 1900 s.

▲ FIGURE 13.8 First-Order Integrated Rate Law For a first-order reaction, a plot of the natural log of the reactant concentration as a function of time yields a straight line. The slope of the line is equal to  $-k$  and the  $y$ -intercept is  $\ln[A]_0$ .

**EXAMPLE 13.4** The First-Order Integrated Rate Law: Determining the Concentration of a Reactant at a Given Time

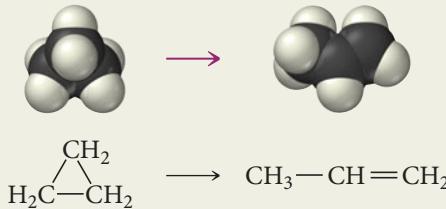

In Example 13.3, you determined that the decomposition of  $\text{SO}_2\text{Cl}_2$  (under the given reaction conditions) is first order and has a rate constant of  $+2.90 \times 10^{-4}\text{s}^{-1}$ . If the reaction is carried out at the same temperature, and the initial concentration of  $\text{SO}_2\text{Cl}_2$  is 0.0225 M, what will the  $\text{SO}_2\text{Cl}_2$  concentration be after 865 s?

|  |  |
|--|--|
| <b>SORT</b> You are given the rate constant of a first-order reaction and the initial concentration of the reactant and asked to find the concentration at 865 seconds.                              | <b>GIVEN:</b> $k = +2.90 \times 10^{-4}\text{s}^{-1}$<br>$[\text{SO}_2\text{Cl}_2]_0 = 0.0225\text{ M}$  |
| <b>STRATEGIZE</b> Refer to the first-order integrated rate law to determine the information you are asked to find.   | <b>EQUATION</b> $\ln[\text{A}]_t = -kt + \ln[\text{A}]_0$  |
| <b>SOLVE</b> Substitute the rate constant, the initial concentration, and the time into the integrated rate law.<br><br>Solve the integrated rate law for the concentration of $[\text{SOCl}_2]_t$ . | <b>SOLUTION</b><br>$\begin{aligned} \ln[\text{SO}_2\text{Cl}_2]_t &= -kt + \ln[\text{SO}_2\text{Cl}_2]_0 \\ \ln[\text{SO}_2\text{Cl}_2]_t &= -(2.90 \times 10^{-4}\text{s}^{-1})865\text{ s} + \ln(0.0225) \\ \ln[\text{SO}_2\text{Cl}_2]_t &= -0.251 - 3.79 \\ [\text{SO}_2\text{Cl}_2]_t &= e^{-4.04} \\ &= 0.0175\text{ M} \end{aligned}$ |

**CHECK** The concentration is smaller than the original concentration as expected. If the concentration were larger than the initial concentration, this would indicate a mistake in the signs of one of the quantities on the right-hand side of the equation.

**FOR PRACTICE 13.4**

Cyclopropane rearranges to form propene in the gas phase.



The reaction is first order in cyclopropane and has a measured rate constant of  $3.36 \times 10^{-5}\text{s}^{-1}$  at 720 K. If the initial cyclopropane concentration is 0.0445 M, what will the cyclopropane concentration be after 235.0 minutes?

**Second-Order Integrated Rate Law** If our simple reaction ( $\text{A} \longrightarrow \text{products}$ ) is second order, the rate is proportional to the square of the concentration of A:

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

Since  $\text{Rate} = -\Delta[\text{A}]/\Delta t$ , we can write:

$$-\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]^2 \quad [13.14]$$

Again, although we do not show the steps here, this differential rate law can be integrated to obtain the *second-order integrated rate law*:

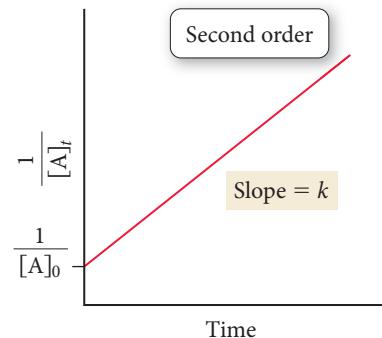
$$\frac{1}{[\text{A}]_t} = kt + \frac{1}{[\text{A}]_0} \quad [13.15]$$

The second-order integrated rate law is also in the form of an equation for a straight line:

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

$$y = mx + b$$

However, you must plot the inverse of the concentration of the reactant as a function of time. The plot yields a straight line with a slope of  $k$  and an intercept of  $1/[A]_0$  as shown in Figure 13.9 ►.



### EXAMPLE 13.5 The Second-Order Integrated Rate Law: Using Graphical Analysis of Reaction Data

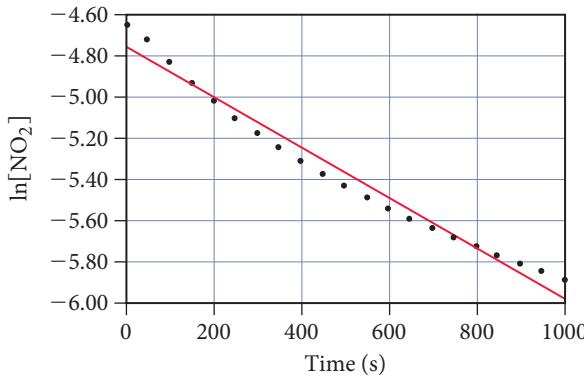
Consider the equation for the decomposition of  $\text{NO}_2$ :



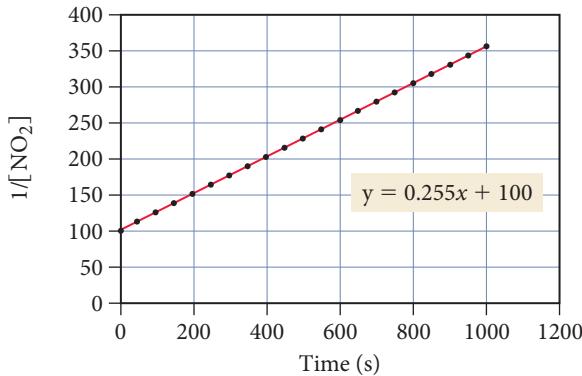
The concentration of  $\text{NO}_2$  is monitored at a fixed temperature as a function of time during the decomposition reaction and the data tabulated in the margin at right. Show by graphical analysis that the reaction is not first order and that it is second order. Determine the rate constant for the reaction.

#### SOLUTION

In order to show that the reaction is *not* first order, prepare a graph of  $\ln[\text{NO}_2]$  versus time as shown.



The plot is *not* linear (the straight line does not fit the data points), confirming that the reaction is not first order. In order to show that the reaction is second order, prepare a graph of  $1/[\text{NO}_2]$  versus time as shown.

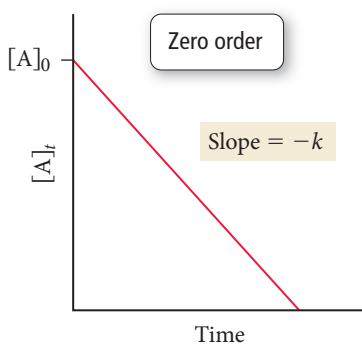


This graph is linear (the data points fit well to a straight line), confirming that the reaction is indeed second order. To obtain the rate constant, determine the slope of the best fitting line. The slope is  $0.255 \text{ M}^{-1} \cdot \text{s}^{-1}$ ; therefore, the rate constant is  $0.255 \text{ M}^{-1} \cdot \text{s}^{-1}$ .

#### FOR PRACTICE 13.5

Use the graph and the best fitting line in Example 13.5 to predict the concentration of  $\text{NO}_2$  at 2000 s.

| Time (s) | $[\text{NO}_2]$ (M) |
|----------|---------------------|
| 0        | 0.01000             |
| 50       | 0.00887             |
| 100      | 0.00797             |
| 150      | 0.00723             |
| 200      | 0.00662             |
| 250      | 0.00611             |
| 300      | 0.00567             |
| 350      | 0.00528             |
| 400      | 0.00495             |
| 450      | 0.00466             |
| 500      | 0.00440             |
| 550      | 0.00416             |
| 600      | 0.00395             |
| 650      | 0.00376             |
| 700      | 0.00359             |
| 750      | 0.00343             |
| 800      | 0.00329             |
| 850      | 0.00316             |
| 900      | 0.00303             |
| 950      | 0.00292             |
| 1000     | 0.00282             |



**▲ FIGURE 13.10 Zero-Order Integrated Rate Law** For a zero-order reaction, a plot of the reactant concentration as a function of time yields a straight line. The slope of the line is equal to  $-k$  and the  $y$ -intercept is  $[A]_0$ .

**Zero-Order Integrated Rate Law** If our simple reaction is zero order, the rate is proportional to a constant:

$$\text{Rate} = k[A]^0 = k$$

Since  $\text{Rate} = -\Delta[A]/\Delta t$ , we can write:

$$-\frac{\Delta[A]}{\Delta t} = k \quad [13.16]$$

We can integrate this differential rate law to obtain the *zero-order integrated rate law*:

$$[A]_t = -kt + [A]_0 \quad [13.17]$$

The zero-order integrated rate law in Equation 13.17 is also in the form of an equation for a straight line. A plot of the concentration of the reactant as a function of time yields a straight line with a slope of  $-k$  and an intercept of  $[A]_0$ , as shown in Figure 13.10 ▲.

## The Half-Life of a Reaction

The **half-life** ( $t_{1/2}$ ) of a reaction is the time required for the concentration of a reactant to fall to one-half of its initial value. For example, if a reaction has a half-life of 100 seconds, and if the initial concentration of the reactant is 1.0 M, the concentration will fall to 0.50 M in 100 s. The half-life expression—which defines the dependence of half-life on the rate constant and the initial concentration—is different for different reaction orders.

**First-Order Reaction Half-Life** From the definition of half-life, and from the integrated rate law, we can derive an expression for the half-life. For a first-order reaction, the integrated rate law is:

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

At a time equal to the half-life ( $t = t_{1/2}$ ), the concentration is exactly half of the initial concentration: ( $[A]_t = \frac{1}{2}[A]_0$ ). Therefore, when  $t = t_{1/2}$  we can write the following expression:

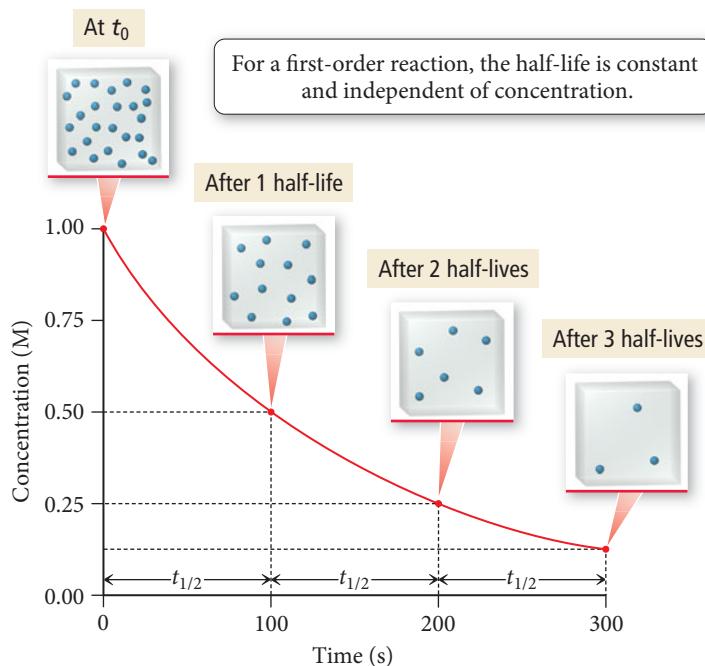
$$\ln \frac{\frac{1}{2}[A]_0}{[A]_0} = \ln \frac{1}{2} = -kt_{1/2} \quad [13.18]$$

Solving for  $t_{1/2}$ , and substituting  $-0.693$  for  $\ln \frac{1}{2}$ , we arrive at the expression for the half-life of a first-order reaction:

$$t_{1/2} = \frac{0.693}{k} \quad [13.19]$$

Notice that, for a first-order reaction,  $t_{1/2}$  is independent of the initial concentration. For example, if  $t_{1/2}$  is 100 s, and if the initial concentration is 1.0 M, the concentration falls to 0.50 M in 100 s, to 0.25 M in another 100 s, to 0.125 M in another 100 s, and so on (Figure 13.11 ▶). Even though the concentration is changing as the reaction proceeds, the half-life (how long it takes for the concentration to halve) is constant. A constant half-life is unique to first-order reactions, making the concept of half-life particularly useful for first-order reactions.

### Half-Life for a First-Order Reaction



**◀ FIGURE 13.11** Half-Life: Concentration versus Time for a First-Order Reaction For this reaction, the concentration decreases by one-half every 100 seconds ( $t_{1/2} = 100$  s). The blue spheres represent reactant molecules (the products are omitted for clarity).

#### EXAMPLE 13.6 Half-Life

Molecular iodine dissociates at 625 K with a first-order rate constant of  $0.271\text{ s}^{-1}$ .

What is the half-life of this reaction?

#### SOLUTION

Because the reaction is first order, the half-life is given by Equation 13.19. Substitute the value of  $k$  into the expression and calculate  $t_{1/2}$ .

$$\begin{aligned}t_{1/2} &= \frac{0.693}{k} \\&= \frac{0.693}{0.271/\text{s}} = 2.56\text{ s}\end{aligned}$$

#### FOR PRACTICE 13.6

A first-order reaction has a half-life of 26.4 seconds. How long does it take for the concentration of the reactant in the reaction to fall to one-eighth of its initial value?

**Second-Order Reaction Half-Life** For a second-order reaction, the integrated rate law is:

$$\frac{1}{[\text{A}]_t} = kt + \frac{1}{[\text{A}]_0}$$

At a time equal to the half-life ( $t = t_{1/2}$ ), the concentration is exactly one-half of the initial concentration ( $[\text{A}]_t = \frac{1}{2}[\text{A}]_0$ ). We can therefore write the following expression at  $t = t_{1/2}$ :

$$\frac{1}{\frac{1}{2}[\text{A}]_0} = kt_{1/2} + \frac{1}{[\text{A}]_0} \quad [13.20]$$

And then solve for  $t_{1/2}$ :

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

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

$$t_{1/2} = \frac{1}{k[A]_0}$$

[13.21]

Notice that, for a second-order reaction, the half-life depends on the initial concentration. So if the initial concentration of a reactant in a second-order reaction is 1.0 M, and the half-life is 100 s, the concentration falls to 0.50 M in 100 s. However, the time it takes for the concentration to fall to 0.25 M is now *longer than 100 s* because the initial concentration has decreased. Thus, the half-life continues to get longer as the concentration decreases.

**Zero-Order Reaction Half-Life** For a zero-order reaction, the integrated rate law is:

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

Making the substitutions ( $t = t_{1/2}$ ;  $[A]_t = \frac{1}{2}[A]_0$ ), we can write the expression at  $t = t_{1/2}$ :

$$\frac{1}{2}[A]_0 = -kt_{1/2} + [A]_0 \quad [13.22]$$

We then solve for  $t_{1/2}$ :

$$t_{1/2} = \frac{[A]_0}{2k}$$

[13.23]

Notice that, for a zero-order reaction, the half-life also depends on the initial concentration; however, unlike in the second order case, the two are directly proportional—the half-life gets *shorter* as the concentration decreases.

#### Summarizing Basic Kinetic Relationships (see Table 13.2):

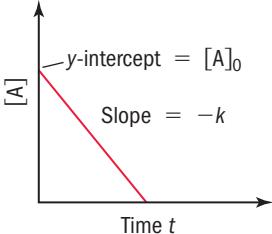
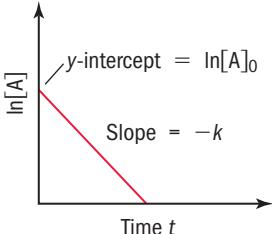
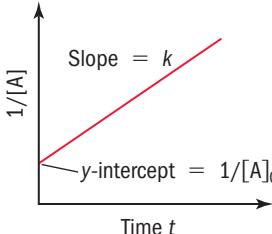
- ▶ The reaction order and rate law must be determined experimentally.
- ▶ The rate law relates the *rate* of the reaction to the *concentration* of the reactant(s).
- ▶ The integrated rate law (which is mathematically derived from the rate law) relates the *concentration* of the reactant(s) to *time*.
- ▶ The half-life is the time it takes for the concentration of a reactant to fall to one-half of its initial value.
- ▶ The half-life of a first-order reaction is independent of the initial concentration.
- ▶ The half-lives of zero-order and second-order reactions depend on the initial concentration.

### Conceptual Connection 13.4 Rate Law and Integrated Rate Law

A decomposition reaction, with a rate that is observed to slow down as the reaction proceeds, is found to have a half-life that depends on the initial concentration of the reactant. Which statement is most likely true for this reaction?

- A plot of the natural log of the concentration of the reactant as a function of time is linear.
- The half-life of the reaction increases as the initial concentration increases.
- A doubling of the initial concentration of the reactant results in a quadrupling of the rate.

**TABLE 13.2 Rate Law Summary Table**

| Order | Rate Law        | Units of k                       | Integrated Rate Law  | Straight-Line Plot  | Half-Life Expression                                       |
|-------|-----------------|----------------------------------|--|---|--|
| 0     | Rate = $k[A]^0$ | M·s <sup>-1</sup>                | $[A]_t = -kt + [A]_0$  |   | $t_{1/2} = \frac{[A]_0}{2k} = \frac{1}{k} \frac{[A]_0}{2}$ |
| 1     | Rate = $k[A]^1$ | s <sup>-1</sup>                  | $\ln[A]_t = -kt + \ln[A]_0$<br>$\ln \frac{[A]_t}{[A]_0} = -kt$ |   | $t_{1/2} = \frac{0.693}{k} = \frac{1}{k} (0.693)$          |
| 2     | Rate = $k[A]^2$ | M <sup>-1</sup> ·s <sup>-1</sup> | $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$                       |  | $t_{1/2} = \frac{1}{k[A]_0} = \frac{1}{k} \frac{1}{[A]_0}$ |

## 13.5 The Effect of Temperature on Reaction Rate

In the opening section of this chapter, you learned that lizards become lethargic when their body temperature drops because the chemical reactions that control their muscle movement slow down at lower temperatures. The rates of chemical reactions are, in general, highly sensitive to temperature. For example, at around room temperature, a 10 °C increase in temperature increases the rate of a typical biological reaction by two or three times. How do we explain this highly sensitive temperature dependence?

Recall that the rate law for a reaction is Rate =  $k[A]^n$ . The temperature dependence of the reaction rate is contained in the rate constant,  $k$  (which is actually a constant only when the temperature remains constant). An increase in temperature generally results in an increase in  $k$ , which results in a faster rate. In 1889, Swedish chemist Svante Arrhenius wrote a paper quantifying the temperature dependence of the rate constant. The modern form of the **Arrhenius equation** shows the relationship between the rate constant ( $k$ ) and the temperature in kelvin ( $T$ ):

$$k = A e^{\frac{-E_a}{RT}}$$

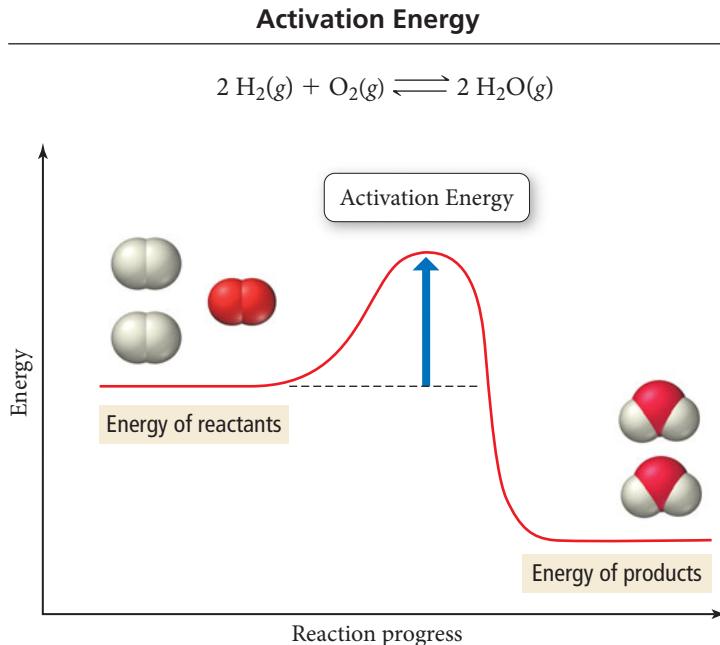
Activation energy  
 Frequency factor      Exponential factor

[13.24]

In this equation,  $R$  is the gas constant (8.314 J/mol · K),  $A$  is a constant called the *frequency factor* (or the *pre-exponential factor*), and  $E_a$  is the *activation energy* (or *activation barrier*).

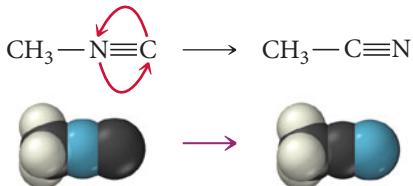
**► FIGURE 13.12 The Activation Energy**

**Barrier** Even though the reaction is energetically favorable (the energy of the products is lower than that of the reactants), an input of energy is needed for the reaction to take place.



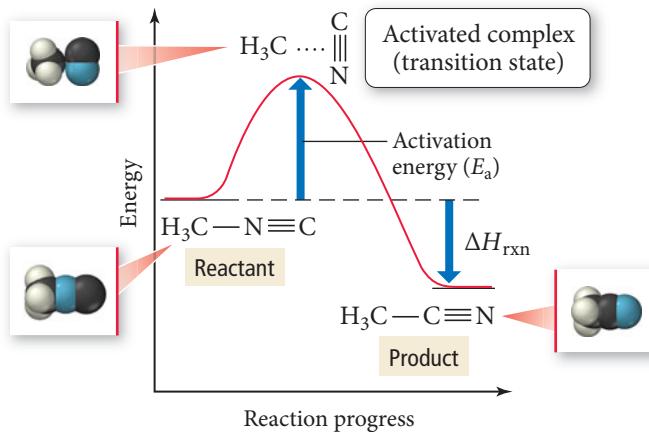
The **activation energy** ( $E_a$ ) is an energy barrier or hump that must be surmounted for the reactants to be transformed into products (Figure 13.12 ▲). We examine the frequency factor more closely in the next section; for now, we can think of the **frequency factor** ( $A$ ) as the number of times that the reactants approach the activation barrier per unit time.

To understand each of these quantities better, consider the simple reaction in which  $\text{CH}_3\text{NC}$  (methyl isonitrile) rearranges to form  $\text{CH}_3\text{C}\equiv\text{N}$  (acetonitrile):



Let's examine the physical meaning of the activation energy, frequency factor, and exponential factor for this reaction.

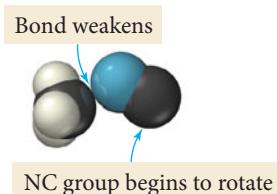
**The Activation Energy** Figure 13.13 ▼ shows the energy of a molecule as the reaction proceeds. The  $x$ -axis represents the progress of the reaction from left (reactant) to right (product). To get from the reactant to the product, the molecule must go through a high-energy intermediate state called the **activated complex** or **transition state**. Even though the overall reaction is energetically downhill (exothermic), it must first go uphill to reach



**► FIGURE 13.13 The Activated**

**Complex** The reaction pathway includes a transitional state—the activated complex—that has a higher energy than either the reactant or the product.

the activated complex because energy is required to initially weaken the H<sub>3</sub>C—N bond and allow the NC group to begin to rotate:



The energy required to reach the activated complex is the *activation energy*. *The higher the activation energy, the slower the reaction rate (at a given temperature)*.

**The Frequency Factor** Recall that the frequency factor represents the number of approaches to the activation barrier per unit time. Any time that it begins to rotate, the NC group approaches the activation barrier. For this reaction, the frequency factor represents the rate at which the NC part of the molecule wags (vibrates side-to-side). With each wag, the reactant approaches the activation barrier. However, approaching the activation barrier is not equivalent to surmounting it. Most of the approaches do not have enough total energy to make it over the activation barrier.

**The Exponential Factor** The **exponential factor** is a number between 0 and 1 that represents the fraction of molecules that have enough energy to make it over the activation barrier on a given approach. The exponential factor is the fraction of approaches that are actually successful and result in the product. For example, if the frequency factor is 10% and the exponential factor is 10<sup>-7</sup> at a certain temperature, then the overall rate constant at that temperature is 10% × 10<sup>-7</sup> = 10<sup>2</sup>/s. In this case, the CN group is wagging at a rate of 10%. With each wag, the activation barrier is approached. However, for a given wag only 1 in 10<sup>7</sup> molecules has sufficient energy to actually make it over the activation barrier.

The exponential factor depends on both the temperature ( $T$ ) and the activation energy ( $E_a$ ) of the reaction.

$$\text{Exponential factor} = e^{-E_a/RT}$$

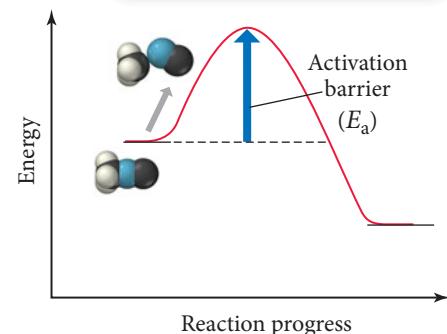
A low activation energy and a high temperature make the negative exponent small, so the exponential factor approaches one. For example, if the activation energy is zero, then the exponent is zero, and the exponential factor is exactly one ( $e^{-0} = 1$ )—every approach to the activation barrier is successful. By contrast, a large activation energy and a low temperature make the exponent a very large negative number, so the exponential factor becomes very small. For example, as the temperature approaches 0 K, the exponent approaches an infinitely large number, and the exponential factor approaches zero ( $e^{-\infty} = 0$ ).

As the temperature increases, the number of molecules having enough thermal energy to surmount the activation barrier increases. At any given temperature, a sample of molecules will have a distribution of energies, as shown in Figure 13.14 ►. Under common circumstances, only a small fraction of the molecules have enough energy to make it over the activation barrier. Because of the shape of the energy distribution curve, however, a small change in temperature results in a large difference in the number of molecules having enough energy to surmount the activation barrier. This explains the sensitivity of reaction rates to temperature.

### Summarizing Temperature and Reaction Rate:

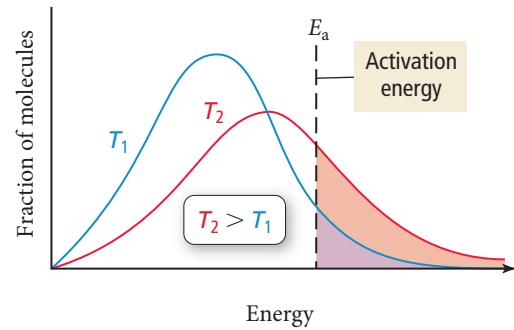
- The frequency factor is the number of times that the reactants approach the activation barrier per unit time.
- The exponential factor is the fraction of the approaches that are successful in surmounting the activation barrier and forming products.
- The exponential factor increases with increasing temperature but decreases with increasing activation energy.

Each wag is an approach to the activation barrier.



### Thermal Energy Distribution

As temperature increases, the fraction of molecules with enough energy to surmount the activation energy barrier also increases.



**▲ FIGURE 13.14 Thermal Energy Distribution** At any given temperature, the atoms or molecules in a gas sample have a range of energies. The higher the temperature, the wider the energy distribution and the greater the average energy. The fraction of molecules with enough energy to surmount the activation energy barrier and react (shaded regions) increases sharply as the temperature rises.

## Arrhenius Plots: Experimental Measurements of the Frequency Factor and the Activation Energy

The frequency factor and activation energy are important quantities in understanding the kinetics of any reaction. To see how we measure these factors in the laboratory, consider again Equation 13.24:  $k = Ae^{-E_a/RT}$ . Taking the natural log of both sides of this equation, we get the following result:

| Remember that  $\ln(AB) = \ln A + \ln B$ .

| Remember that  $\ln e^x = x$ .

In an Arrhenius analysis, the pre-exponential factor ( $A$ ) is assumed to be independent of temperature. Although the pre-exponential factor does depend on temperature to some degree, its temperature dependence is much less than that of the exponential factor and is often ignored.

$$\ln k = \ln(Ae^{-E_a/RT}) \quad [13.25]$$

$$\ln k = \ln A + \ln e^{-E_a/RT}$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A \quad [13.26]$$

$$y = mx + b$$

Equation 13.26 is in the form of a straight line. A plot of the natural log of the rate constant ( $\ln k$ ) versus the inverse of the temperature in kelvins ( $1/T$ ) yields a straight line with a slope of  $-E_a/R$  and a y-intercept of  $\ln A$ . Such a plot is called an **Arrhenius plot** and is commonly used in the analysis of kinetic data, as shown in Example 13.7.

### EXAMPLE 13.7 Using an Arrhenius Plot to Determine Kinetic Parameters

The decomposition of ozone shown here is important to many atmospheric reactions.



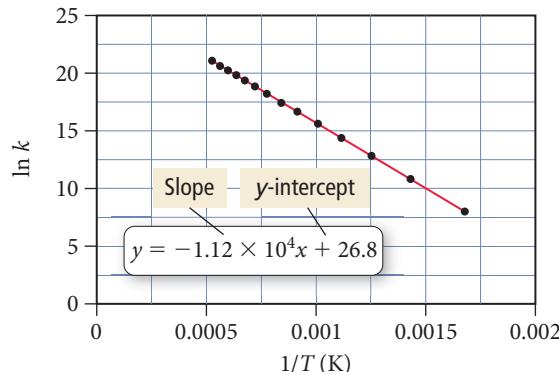
A study of the kinetics of the reaction results in the following data:

| Temperature (K) | Rate Constant ( $\text{M}^{-1} \cdot \text{s}^{-1}$ ) | Temperature (K) | Rate Constant ( $\text{M}^{-1} \cdot \text{s}^{-1}$ ) |
|-----------------|---|-----------------|---|
| 600             | $3.37 \times 10^3$                                    | 1300            | $7.83 \times 10^7$                                    |
| 700             | $4.85 \times 10^4$                                    | 1400            | $1.45 \times 10^8$                                    |
| 800             | $3.58 \times 10^5$                                    | 1500            | $2.46 \times 10^8$                                    |
| 900             | $1.70 \times 10^6$                                    | 1600            | $3.93 \times 10^8$                                    |
| 1000            | $5.90 \times 10^6$                                    | 1700            | $5.93 \times 10^8$                                    |
| 1100            | $1.63 \times 10^7$                                    | 1800            | $8.55 \times 10^8$                                    |
| 1200            | $3.81 \times 10^7$                                    | 1900            | $1.19 \times 10^9$                                    |

Determine the value of the frequency factor and activation energy for the reaction.

#### SOLUTION

To determine the frequency factor and activation energy, prepare a graph of the natural log of the rate constant ( $\ln k$ ) versus the inverse of the temperature ( $1/T$ ).



The plot is linear, as expected for Arrhenius behavior. The line that fits best has a slope of  $-1.12 \times 10^4 \text{ K}$  and a  $y$ -intercept of 26.8. Calculate the activation energy from the slope by setting the slope equal to  $-E_a/R$  and solving for  $E_a$ :

$$\begin{aligned} -1.12 \times 10^4 \text{ K} &= \frac{-E_a}{R} \\ E_a &= 1.12 \times 10^4 \text{ K} \left( 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) \\ &= 9.31 \times 10^4 \text{ J/mol} \\ &= 93.1 \text{ kJ/mol} \end{aligned}$$

Calculate the frequency factor ( $A$ ) by setting the intercept equal to  $\ln A$ .

$$\begin{aligned} 26.8 &= \ln A \\ A &= e^{26.8} \\ &= 4.36 \times 10^{11} \end{aligned}$$

Since the rate constants are measured in units of  $\text{M}^{-1} \cdot \text{s}^{-1}$ , the frequency factor is in the same units. Consequently, we can conclude that the reaction has an activation energy of 93.1 kJ/mol and a frequency factor of  $4.36 \times 10^{11} \text{ M}^{-1} \cdot \text{s}^{-1}$ .

### FOR PRACTICE 13.7

For the decomposition of ozone reaction in Example 13.7, use the results of the Arrhenius analysis to predict the rate constant at 298 K.

In some cases, when either data are limited or plotting capabilities are absent, we can calculate the activation energy if we know the rate constant at just two different temperatures. We can apply the Arrhenius expression in Equation 13.26 to the two different temperatures as follows:

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

We can then subtract  $\ln k_1$  from  $\ln k_2$ :

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

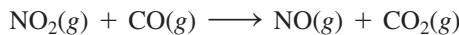
Rearranging, we get the two-point form of the Arrhenius equation:

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad [13.27]$$

Example 13.8 shows how you can use this equation to calculate the activation energy from experimental measurements of the rate constant at two different temperatures.

### EXAMPLE 13.8 Using the Two-Point Form of the Arrhenius Equation

Consider the reaction between nitrogen dioxide and carbon monoxide.



The rate constant at 701 K is measured as  $2.57 \text{ M}^{-1} \cdot \text{s}^{-1}$  and that at 895 K is measured as  $567 \text{ M}^{-1} \cdot \text{s}^{-1}$ . Find the activation energy for the reaction in kJ/mol.

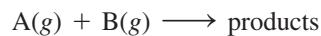
|   |  |
|---|--|
| <p><b>SORT</b> You are given the rate constant of a reaction at two different temperatures and asked to find the activation energy.</p>   | <p><b>GIVEN:</b> <math>T_1 = 701 \text{ K}</math>, <math>k_1 = 2.57 \text{ M}^{-1} \cdot \text{s}^{-1}</math><br/> <math>T_2 = 895 \text{ K}</math>, <math>k_2 = 567 \text{ M}^{-1} \cdot \text{s}^{-1}</math><br/> <b>FIND:</b> <math>E_a</math></p>  |
| <p><b>STRATEGIZE</b> Use the two-point form of the Arrhenius equation, which relates the activation energy to the given information and <math>R</math> (a constant).</p>                        | <p><b>EQUATION</b> <math>\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)</math></p>   |
| <p><b>SOLVE</b> Substitute the two rate constants and the two temperatures into the equation.</p> <p>Solve the equation for <math>E_a</math>, the activation energy, and convert to kJ/mol.</p> | <p><b>SOLUTION</b></p> $\ln \frac{567 \text{ M}^{-1} \cdot \text{s}^{-1}}{2.57 \text{ M}^{-1} \cdot \text{s}^{-1}} = \frac{E_a}{R} \left( \frac{1}{701 \text{ K}} - \frac{1}{895 \text{ K}} \right)$ $5.40 = \frac{E_a}{R} \left( \frac{3.09 \times 10^{-4}}{\text{K}} \right)$ $E_a = 5.40 \left( \frac{\text{K}}{3.09 \times 10^{-4}} \right) R$ $= 5.40 \left( \frac{\text{K}}{3.09 \times 10^{-4}} \right) 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}$ $= 1.45 \times 10^5 \text{ J/mol}$ $= 145 \text{ kJ/mol}$ |
| <p><b>CHECK</b> The magnitude of the answer is reasonable. Activation energies for most reactions range from tens to hundreds of kilojoules per mole.</p>                                       | <p><b>FOR PRACTICE 13.8</b><br/>Use the results from Example 13.8 and the given rate constant of the reaction at either of the two temperatures to predict the rate constant for this reaction at 525 K.</p>   |

## Conceptual Connection 13.5 Temperature Dependence of Reaction Rate

Reaction A and reaction B have identical frequency factors. However, reaction B has a higher activation energy than reaction A. Which reaction has a greater rate constant at room temperature?

### The Collision Model: A Closer Look at the Frequency Factor

We saw previously that the frequency factor in the Arrhenius equation represents the number of approaches to the activation barrier per unit time. Let's now refine that idea for a reaction involving two gas-phase reactants:

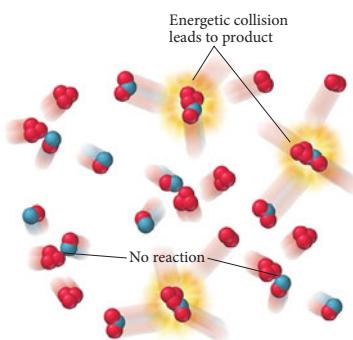


In the **collision model**, a chemical reaction occurs after a sufficiently energetic collision between two reactant molecules (Figure 13.15). In collision theory, therefore, each approach to the activation barrier is a collision between the reactant molecules. Consequently, the value of the frequency factor should simply be the number of collisions that occur per second. However, the frequency factors of most (though not all) gas-phase chemical reactions tend to be smaller than the number of collisions that occur per second. Why?

In the collision model, we can separate the frequency factor into two distinct parts, as shown in the following equations:

$$k = Ae^{\frac{-E_a}{RT}} = pze^{\frac{-E_a}{RT}}$$

Orientation factor      Collision frequency

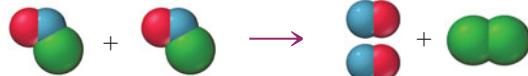


▲ FIGURE 13.15 The Collision Model

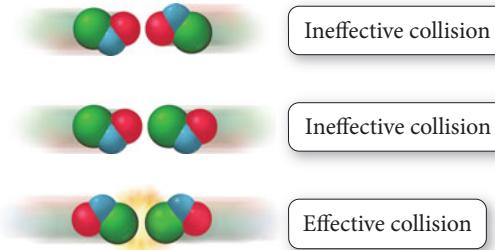
In the collision model, two molecules react after a sufficiently energetic collision with the correct orientation brings the reacting groups together.

where  $p$  is the **orientation factor** and  $z$  is the **collision frequency**. The collision frequency is the number of collisions that occur per unit time, which we can calculate for a gas-phase reaction from the pressure of the gases and the temperature of the reaction mixture. Under typical conditions, a single molecule undergoes on the order of  $10^9$  collisions every second. The orientation factor is a number, usually between 0 and 1, which represents the fraction of collisions with an orientation that allows the reaction to occur.

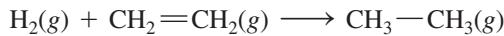
To better understand the orientation factor, consider the reaction represented by the following equation:



In order for the reaction to occur, two NOCl molecules must collide with sufficient energy. However, not all collisions with sufficient energy will lead to products, because the reactant molecules must also be properly oriented. Consider the three possible collision orientations of the reactant molecules shown below. The first two collisions, even if they occur with sufficient energy, will not result in a reaction, because the reactant molecules are not oriented in a way that allows the chlorine atoms to bond. In other words, if two molecules are to react with each other, they must collide in such a way that allows the necessary bonds to break and form. For the reaction of  $\text{NOCl}(g)$ , the orientation factor is  $p = 0.16$ . This means that only 16 out of 100 sufficiently energetic collisions are actually successful in forming the products.

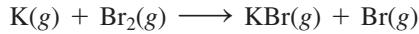


Some reactions have orientation factors that are much smaller than one. Consider the reaction between hydrogen and ethene:



The orientation factor for this reaction is  $1.7 \times 10^{-6}$ , which means that fewer than two out of each million sufficiently energetic collisions actually form products. The small orientation factor indicates that the orientational requirements for this reaction are very stringent—the molecules must be aligned in a *very specific way* for the reaction to occur.

Reactions between *individual atoms* usually have orientation factors of approximately 1 because atoms are spherically symmetric and thus any orientation can lead to the formation of products. A few reactions have orientation factors greater than one. Consider the reaction between potassium and bromine:



This reaction has an orientation factor of  $p = 4.8$ . In other words, there are more reactions than collisions—the reactants do not even have to collide to react! Apparently, through a process dubbed *the harpoon mechanism*, a potassium atom can actually transfer an electron to a bromine molecule without a collision. The resulting positive charge on the potassium and the negative charge on the bromine cause the two species to attract each other and form a bond. The potassium atom essentially *harpoons* a passing bromine molecule with an electron and *reels it in* through the coulombic attraction between unlike charges.

We can picture a sample of reactive gases as a frenzy of collisions between the reacting atoms or molecules. At normal temperatures, the vast majority of these collisions do not have sufficient energy to overcome the activation barrier, and the atoms or molecules simply bounce off one another. Of the collisions having sufficient energy to overcome

the activation barrier, most do not have the proper orientation for the reaction to occur (for the majority of common reactions). When two molecules with sufficient energy *and* the correct orientation collide, something extraordinary happens. The electrons on one of the atoms or molecules are attracted to the nuclei of the other; some bonds begin to weaken while other bonds begin to form and, if all goes well, the reactants go through the transition state and are transformed into the products. This is how a chemical reaction occurs.

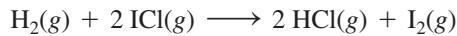
### Conceptual Connection 13.6 Collision Theory

Which reaction would you expect to have the smallest orientation factor?

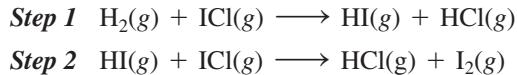
- (a)  $\text{H}(g) + \text{I}(g) \longrightarrow \text{HI}(g)$
- (b)  $\text{H}_2(g) + \text{I}_2(g) \longrightarrow 2 \text{ HI}(g)$
- (c)  $\text{HCl}(g) + \text{HCl}(g) \longrightarrow \text{H}_2(g) + \text{Cl}_2(g)$

## 13.6 Reaction Mechanisms

Most chemical reactions do not occur in a single step, but over the course of several steps. When we write a chemical equation to represent a chemical reaction, *we usually represent the overall reaction, not the series of individual steps by which the reaction occurs*. Consider the reaction in which hydrogen gas reacts with iodine monochloride:



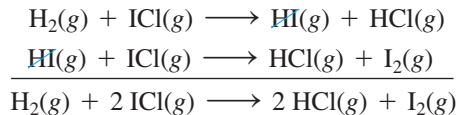
The overall equation just shows the substances present at the beginning of the reaction and the substances formed by the reaction—it does not show the intermediate steps. The **reaction mechanism** is the series of individual chemical steps by which an overall chemical reaction occurs. For example, the proposed mechanism for the reaction between hydrogen and iodine monochloride contains two steps:



An elementary step represents an actual interaction between the reactant molecules in the step. An overall reaction equation shows only the starting substances and the ending substances, not the path between them.

In the first step, an  $\text{H}_2$  molecule collides with an  $\text{ICl}$  molecule and forms an  $\text{HI}$  molecule and an  $\text{HCl}$  molecule. In the second step, the  $\text{HI}$  molecule formed in the first step collides with a second  $\text{ICl}$  molecule to form another  $\text{HCl}$  molecule and an  $\text{I}_2$  molecule. Each step in a reaction mechanism is an **elementary step**. Elementary steps cannot be broken down into simpler steps—they occur as they are written (they represent the exact species that are colliding in the reaction).

One of the requirements for a valid reaction mechanism is that the individual steps in the mechanism add to the overall reaction. For example, the mechanism just shown sums to the overall reaction as shown here:



Notice that the  $\text{HI}$  molecule appears in the reaction mechanism but not in the overall reaction equation. We call species such as  $\text{HI}$  *reaction intermediates*. A **reaction intermediate** forms in one elementary step and is consumed in another. The reaction mechanism is a complete, detailed description of the reaction at the molecular level—it specifies the individual collisions and reactions that result in the overall reaction. As such, reaction mechanisms are highly sought-after pieces of chemical knowledge.

How do we determine reaction mechanisms? Recall from the opening section of this chapter that chemical kinetics are not only practically important (because they allow us

to control the rate of a particular reaction), but also theoretically important because they can help us determine the mechanism of the reaction. We can piece together possible reaction mechanisms by measuring the kinetics of the overall reaction and working backward to write a mechanism consistent with the measured kinetics.

## Rate Laws for Elementary Steps

We characterize elementary steps by their **molecularity**, the number of reactant particles involved in the step. The most common molecularities are unimolecular and bimolecular:

|   |                     |
|---|---------------------|
| $A \longrightarrow \text{products}$     | <b>Unimolecular</b> |
| $A + A \longrightarrow \text{products}$ | <b>Bimolecular</b>  |
| $A + B \longrightarrow \text{products}$ | <b>Bimolecular</b>  |

Elementary steps in which three reactant particles collide, called **termolecular** steps, are very rare because the probability of three particles simultaneously colliding is small.

Although we cannot deduce the rate law for an *overall chemical reaction* from the balanced chemical equation, we can deduce the rate law for an *elementary step* from its equation. Since we know that an elementary step occurs through the collision of the reactant particles, the rate is proportional to the product of the concentrations of those particles. For example, the rate for the bimolecular elementary step in which A reacts with B is proportional to the concentration of A multiplied by the concentration of B:



Similarly, the rate law for the bimolecular step in which A reacts with A is proportional to the square of the concentration of A:

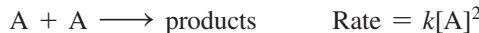


Table 13.3 summarizes the rate laws for the common elementary steps, as well as those for the rare termolecular step. Notice that the molecularity of the elementary step is equal to the overall order of the step.

**TABLE 13.3 Rate Laws for Elementary Steps**

| Elementary Step                             | Molecularity | Rate Law                   |
|---|--------------|----------------------------|
| $A \longrightarrow \text{products}$         | 1            | $\text{Rate} = k[A]$       |
| $A + A \longrightarrow \text{products}$     | 2            | $\text{Rate} = k[A]^2$     |
| $A + B \longrightarrow \text{products}$     | 2            | $\text{Rate} = k[A][B]$    |
| $A + A + A \longrightarrow \text{products}$ | 3 (rare)     | $\text{Rate} = k[A]^3$     |
| $A + A + B \longrightarrow \text{products}$ | 3 (rare)     | $\text{Rate} = k[A]^2[B]$  |
| $A + B + C \longrightarrow \text{products}$ | 3 (rare)     | $\text{Rate} = k[A][B][C]$ |

## Rate-Determining Steps and Overall Reaction Rate Laws

In most chemical reactions, one of the elementary steps—called the **rate-determining step**—is much slower than the others. The rate-determining step in a chemical reaction is analogous to the narrowest section on a freeway. If a section of a freeway narrows from four lanes to two lanes, for even a short distance, the rate at which cars travel along the freeway is limited by the rate at which they can travel through the narrow section (even though the rate might be much faster along the four-lane section). Similarly, the rate-determining step in a reaction mechanism limits the overall rate of the reaction (even though the other steps occur much faster) and therefore determines *the rate law for the overall reaction*.

► The rate-limiting step in a reaction mechanism limits the overall rate of the reaction just as the narrowest section of a highway limits the rate at which traffic can pass.



As an example, consider the reaction between nitrogen dioxide gas and carbon monoxide gas:



The experimentally determined rate law for this reaction is Rate =  $k[\text{NO}_2]^2$ . We can see from this rate law that the reaction must not be a single-step reaction—otherwise the rate law would be Rate =  $k[\text{NO}_2][\text{CO}]$ . A possible mechanism for this reaction involves two steps:

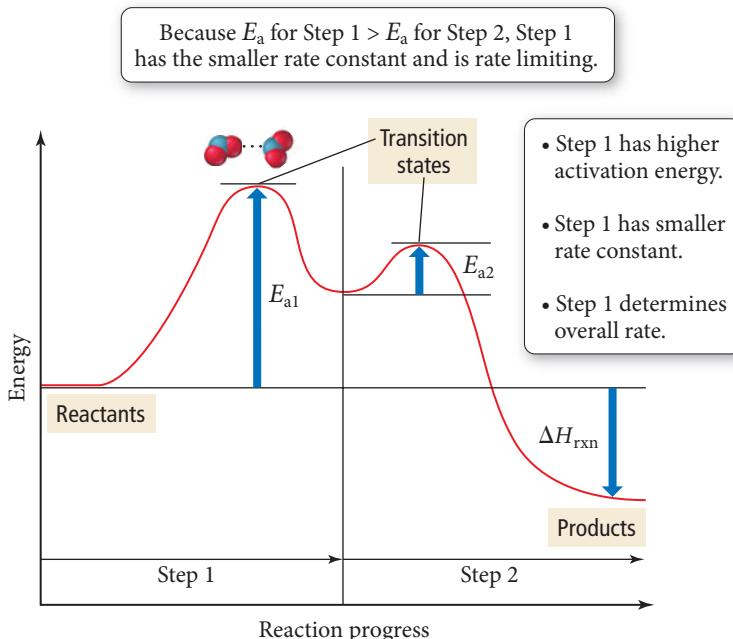


Figure 13.16 ▼ shows the energy diagram for this mechanism. The first step has a much larger activation energy than the second step. This greater activation energy results in a much smaller rate constant for the first step compared to the second step. The first step determines the overall rate of the reaction, and the predicted *overall* rate law is therefore Rate =  $k[\text{NO}_2]^2$ , which is consistent with the observed experimental rate law.

For a proposed reaction mechanism, such as the one shown here for  $\text{NO}_2$  and CO, to be *valid* (mechanisms can only be validated, not proven), two conditions must be met:

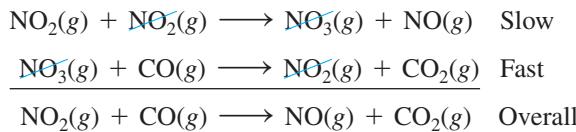
- 1. The elementary steps in the mechanism must sum to the overall reaction.**
- 2. The rate law predicted by the mechanism must be consistent with the experimentally observed rate law.**

### Energy Diagram for a Two-Step Mechanism



► FIGURE 13.16 Energy Diagram for a Two-Step Mechanism

We have already seen that the rate law predicted by the earlier mechanism is consistent with the experimentally observed rate law. We can check whether the elementary steps sum to the overall reaction by adding them together:

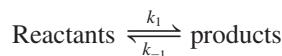


The mechanism fulfills both of the given requirements and is therefore valid. A valid mechanism is not a *proven* mechanism (because other mechanisms may also fulfill both of the given requirements). We can only say that a given mechanism is consistent with kinetic observations of the reaction and therefore possible. Other types of data—such as the experimental evidence for a proposed intermediate—are necessary to further strengthen the validity of a proposed mechanism.

## Mechanisms with a Fast Initial Step

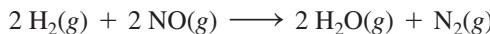
When the proposed mechanism for a reaction has a slow initial step—like the one shown previously for the reaction between  $\text{NO}_2$  and CO—the rate law predicted by the mechanism normally contains only reactants involved in the overall reaction. However, when a mechanism begins with a fast initial step, some other subsequent step in the mechanism is the rate-limiting step. In these cases, the rate law predicted by the rate-limiting step may contain reaction intermediates. Since reaction intermediates do not appear in the overall reaction equation, a rate law containing intermediates cannot generally correspond to the experimental rate law. Fortunately, however, we can often express the concentration of intermediates in terms of the concentrations of the reactants of the overall reaction.

In a multistep mechanism where the first step is fast, the products of the first step may build up, because the rate at which they are consumed is limited by some slower step further down the line. As those products build up, they can begin to react with one another to re-form the reactants. As long as the first step is fast enough compared to the rate-limiting step, the first-step reaction will reach equilibrium. We indicate equilibrium as follows:

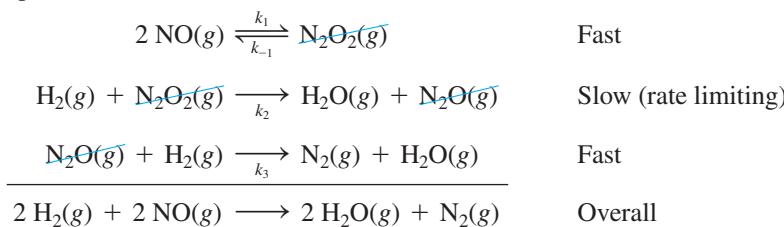


The double arrows indicate that both the forward reaction and the reverse reaction occur. If equilibrium is reached, then the rate of the forward reaction equals the rate of the reverse reaction.

As an example, consider the reaction by which hydrogen reacts with nitrogen monoxide to form water and nitrogen gas:



The experimentally observed rate law is Rate =  $k[\text{H}_2][\text{NO}]^2$ . The reaction is first order in hydrogen and second order in nitrogen monoxide. The proposed mechanism has a slow second step:



To determine whether the mechanism is valid, we must determine whether the two conditions described previously are met. As you can see, the steps do indeed sum to the overall reaction, so the first condition is met.

The second condition is that the rate law predicted by the mechanism must be consistent with the experimentally observed rate law. Since the second step is rate limiting, we write the following expression for the rate law:

$$\text{Rate} = k_2[\text{H}_2][\text{N}_2\text{O}_2] \quad [13.28]$$

This rate law contains an intermediate ( $\text{N}_2\text{O}_2$ ) and can therefore not be consistent with the experimentally observed rate law (which does not contain intermediates). Because of the equilibrium in the first step, however, *we can express the concentration of the intermediate in terms of the reactants of the overall equation*. Since the first step reaches equilibrium, the rate of the forward reaction in the first step equals the rate of the reverse reaction:

$$\text{Rate (forward)} = \text{Rate (reverse)}$$

The rate of the forward reaction is given by the rate law:

$$\text{Rate} = k_1[\text{NO}]^2$$

The rate of the reverse reaction is given by the rate law:

$$\text{Rate} = k_{-1}[\text{N}_2\text{O}_2]$$

Since these two rates are equal at equilibrium, we write the expression:

$$k_1[\text{NO}]^2 = k_{-1}[\text{N}_2\text{O}_2]$$

Rearranging, we get:

$$[\text{N}_2\text{O}_2] = \frac{k_1}{k_{-1}}[\text{NO}]^2$$

We can now substitute this expression into Equation 13.28, the rate law obtained from the slow step:

$$\text{Rate} = k_2[\text{H}_2][\text{N}_2\text{O}_2]$$

$$= k_2[\text{H}_2] \frac{k_1}{k_{-1}}[\text{NO}]^2$$

$$= \frac{k_2 k_1}{k_{-1}} [\text{H}_2][\text{NO}]^2$$

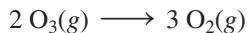
If we combine the individual rate constants into one overall rate constant, we get the predicted rate law:

$$\text{Rate} = k[\text{H}_2][\text{NO}]^2 \quad [13.29]$$

Since this rate law is consistent with the experimentally observed rate law, condition 2 is met and the proposed mechanism is valid.

### EXAMPLE 13.9 Reaction Mechanisms

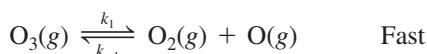
Ozone naturally decomposes to oxygen by this reaction:



The experimentally observed rate law for this reaction is:

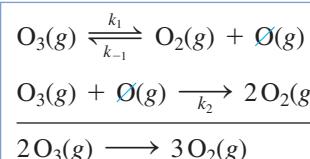
$$\text{Rate} = k[\text{O}_3]^2[\text{O}_2]^{-1}$$

Show that this proposed mechanism is consistent with the experimentally observed rate law.



**SOLUTION**

To determine whether the mechanism is valid, you must first determine whether the steps sum to the overall reaction. Since the steps do indeed sum to the overall reaction, the first condition is met.



The second condition is that the rate law predicted by the mechanism must be consistent with the experimentally observed rate law. Because the second step is rate limiting, write the rate law based on the second step.

Because the rate law contains an intermediate (O), you must express the concentration of the intermediate in terms of the concentrations of the reactants of the overall reaction. To do this, set the rates of the forward reaction and the reverse reaction of the first step equal to each other. Solve the expression from the previous step for [O], the concentration of the intermediate.

Finally, substitute [O] into the rate law predicted by the slow step.

$$\text{Rate} = k_2[\text{O}_3][\text{O}]$$

$$\text{Rate (forward)} = \text{Rate (backward)}$$

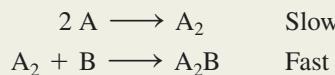
$$k_1[\text{O}_3] = k_{-1}[\text{O}_2][\text{O}]$$

$$[\text{O}] = \frac{k_1[\text{O}_3]}{k_{-1}[\text{O}_2]}$$

**CHECK** Because the two steps in the proposed mechanism sum to the overall reaction, and because the rate law obtained from the proposed mechanism is consistent with the experimentally observed rate law, the proposed mechanism is valid. The  $-1$  reaction order with respect to  $[\text{O}_2]$  indicates that the rate slows down as the concentration of oxygen increases—oxygen inhibits, or slows down, the reaction.

**FOR PRACTICE 13.9**

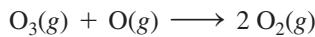
Predict the overall reaction and rate law that results from the following two-step mechanism.



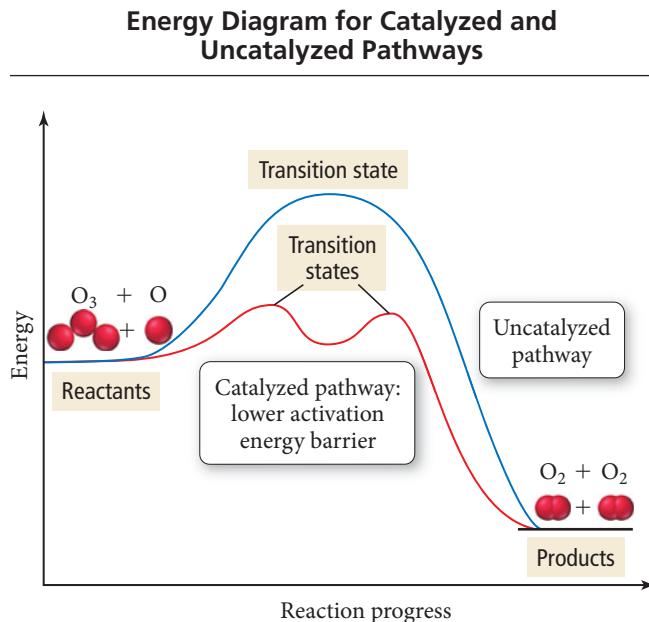
## 13.7 Catalysis

Throughout this chapter, we have learned about ways to control the rates of chemical reactions. We can speed up the rate of a reaction by increasing the concentration of the reactants or by increasing the temperature. However, these approaches are not always feasible. There are limits to how concentrated we can make a reaction mixture, and increases in temperature may allow unwanted reactions—such as the decomposition of a reactant—to occur.

Alternatively, reaction rates can be increased by using a **catalyst**, a substance that increases the rate of a chemical reaction but is not consumed by the reaction. A catalyst works by providing an alternative mechanism for the reaction—one in which the rate-determining step has a lower activation energy. For example, consider the noncatalytic destruction of ozone in the upper atmosphere, discussed in Section 6.10, which happens according to this reaction:

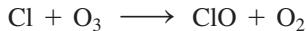


**► FIGURE 13.17** Catalyzed and Uncatalyzed Decomposition of Ozone  
In the catalytic destruction of ozone (red), the activation barrier for the rate-limiting step is much lower than in the uncatalyzed process (blue).



Photodissociation means *light-induced* dissociation. The energy from a photon of light can break chemical bonds and therefore dissociate, or break apart, a molecule.

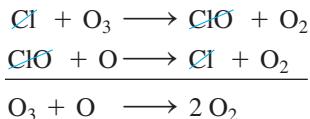
In this reaction, an ozone molecule collides with an oxygen atom to form two oxygen molecules in a single elementary step. The reason that Earth has a protective ozone layer in the upper atmosphere is that the activation energy for this reaction is fairly high and the reaction, therefore, proceeds at a fairly slow rate; the ozone layer does not rapidly decompose into  $O_2$ . However, the addition of Cl atoms (which come from the photodissociation of man-made chlorofluorocarbons) to the upper atmosphere makes available another pathway by which  $O_3$  can be destroyed. The first step in this pathway—called the catalytic destruction of ozone—is the reaction of Cl with  $O_3$  to form  $ClO$  and  $O_2$ :



This is followed by a second step in which  $ClO$  reacts with O, regenerating Cl:

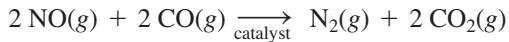


If we add the two reactions, the overall reaction is identical to the noncatalytic reaction:

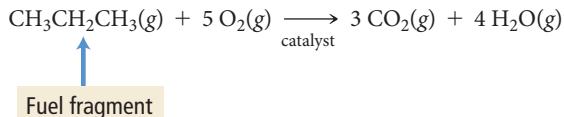


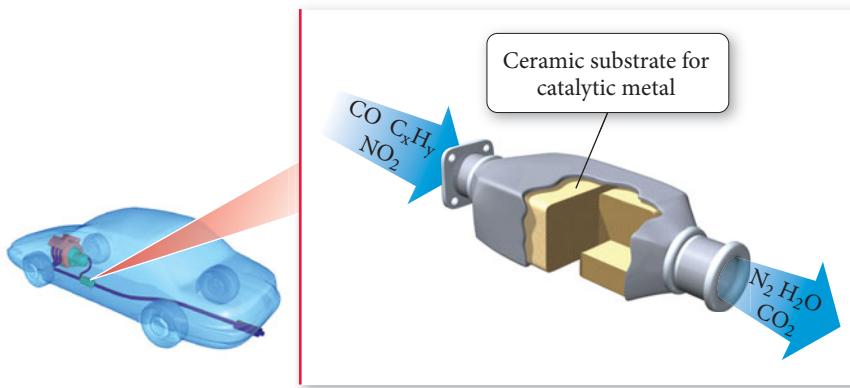
However, the activation energy for the rate-limiting step in this pathway is much smaller than for the first, uncatalyzed pathway (as shown in Figure 13.17 ▲), and therefore the reaction occurs at a much faster rate. Note that the Cl is not consumed in the overall reaction—this is characteristic of a catalyst.

In the case of the catalytic destruction of ozone, the catalyst speeds up a reaction that we *do not* want to happen. Most of the time, however, catalysts are used to speed up reactions that we *do* want to happen. For example, your car most likely has a catalytic converter in its exhaust system. The catalytic converter contains solid catalysts, such as platinum, rhodium, or palladium, dispersed on an underlying high-surface-area ceramic structure. These catalysts convert exhaust pollutants such as nitrogen monoxide and carbon monoxide into less harmful substances:



The catalytic converter also promotes the complete combustion of any fuel fragments present in the exhaust:





► The catalytic converter in the exhaust system of a car helps eliminate pollutants in the exhaust.

Fuel fragments in exhaust are harmful because they lead to the formation of ozone. Recall from Section 6.10 that although ozone is a natural part of our *upper* atmosphere that protects us from excess exposure to ultraviolet light, it is a pollutant in the *lower* atmosphere, interfering with cardiovascular function and acting as an eye and lung irritant. The use of catalytic converters in motor vehicles has resulted in lower levels of these pollutants over most U.S. cities in the last 30 years even though the number of cars on the roadways has dramatically increased (see Table 13.4).

**TABLE 13.4 Change in Pollutant Levels**

| Pollutant | Change 1980–2010 |
|-----------|------------------|
| $NO_2$    | -52%             |
| $O_3$     | -28%             |
| CO        | -82%             |

Source: U.S. Environmental Protection Agency, *Our Nation's Air: Status and Trends through 2010*.

## Homogeneous and Heterogeneous Catalysis

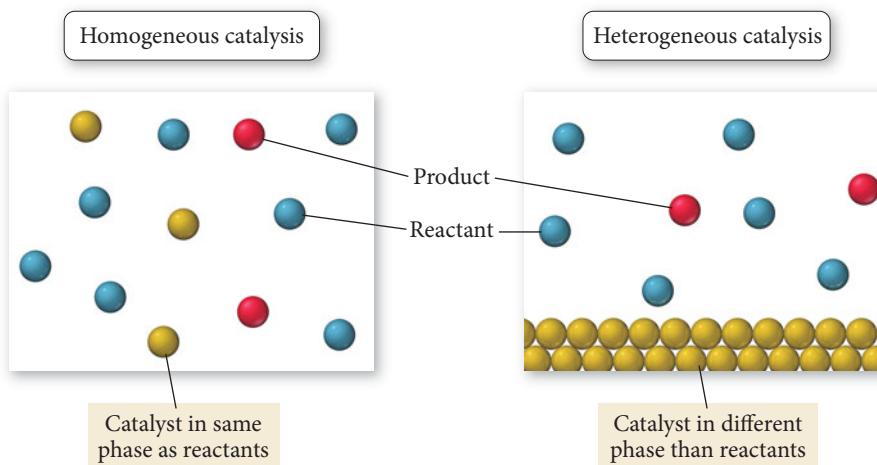
Catalysis can be categorized into two types: homogeneous and heterogeneous (Figure 13.18 ▼). In **homogeneous catalysis**, the catalyst exists in the same phase (or state) as the reactants. The catalytic destruction of ozone by Cl is an example of homogeneous catalysis—the chlorine atoms exist in the gas phase with the gas-phase reactants. In **heterogeneous catalysis**, the catalyst exists in a different phase than the reactants. The solid catalysts used in catalytic converters are examples of heterogeneous catalysts—they are solids while the reactants are gases. The use of solid catalysts with gas-phase or solution-phase reactants is the most common type of heterogeneous catalysis.

Research has shown that heterogeneous catalysis is most likely responsible for the annual formation of an ozone hole over Antarctica. After the discovery of the Antarctic ozone hole in 1985, scientists wondered why there was such a dramatic drop in ozone over Antarctica but not over the rest of the planet. After all, the chlorine from chlorofluorocarbons that catalyzes ozone destruction is evenly distributed throughout the entire atmosphere.

As it turns out, most of the chlorine that enters the atmosphere from chlorofluorocarbons gets bound up in chlorine reservoirs, substances such as  $ClONO_2$  that hold chlorine and prevent it from catalyzing ozone destruction. The unique conditions over Antarctica—especially the cold isolated air mass that exists during the long dark winter—result in clouds that contain solid ice particles. These unique clouds are called



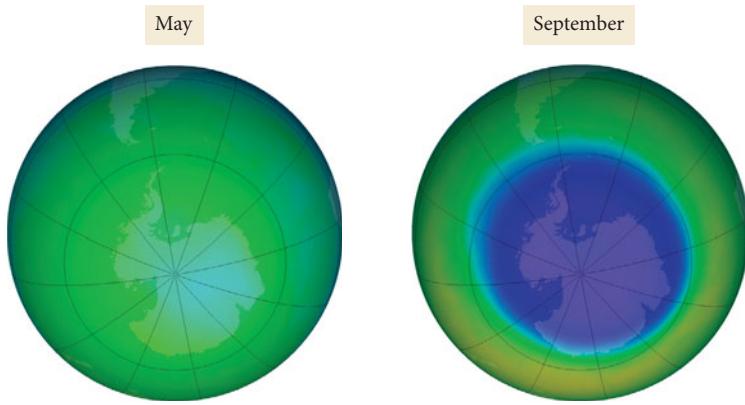
► Polar stratospheric clouds contain ice particles that catalyze reactions by which chlorine is released from its atmospheric chemical reservoirs.



**FIGURE 13.18** Homogeneous and Heterogeneous Catalysis

A homogeneous catalyst exists in the same phase as the reactants. A heterogeneous catalyst exists in a different phase than the reactants. Often a heterogeneous catalyst provides a solid surface on which the reaction can take place.

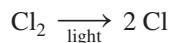
**► FIGURE 13.19 Ozone Depletion in the Antarctic Spring** The concentration of ozone over Antarctica drops sharply during the months of September and October due to the catalyzed destruction of ozone by chlorine. The image at the left shows the average ozone levels in May 2011 while the image at the right shows the average levels from September 2011. (The lowest ozone levels are represented in purple.) Source: NASA Ozone Watch, OMI instrument (KNMI/NASA) onboard the Aura satellite.



polar stratospheric clouds (or PSCs), and the surfaces of the ice particles within these clouds appear to catalyze the release of chlorine from their reservoirs:

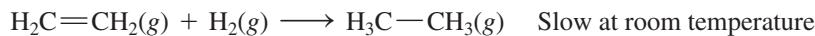


When the sun rises in the Antarctic spring, the sunlight dissociates the chlorine molecules into chlorine atoms:

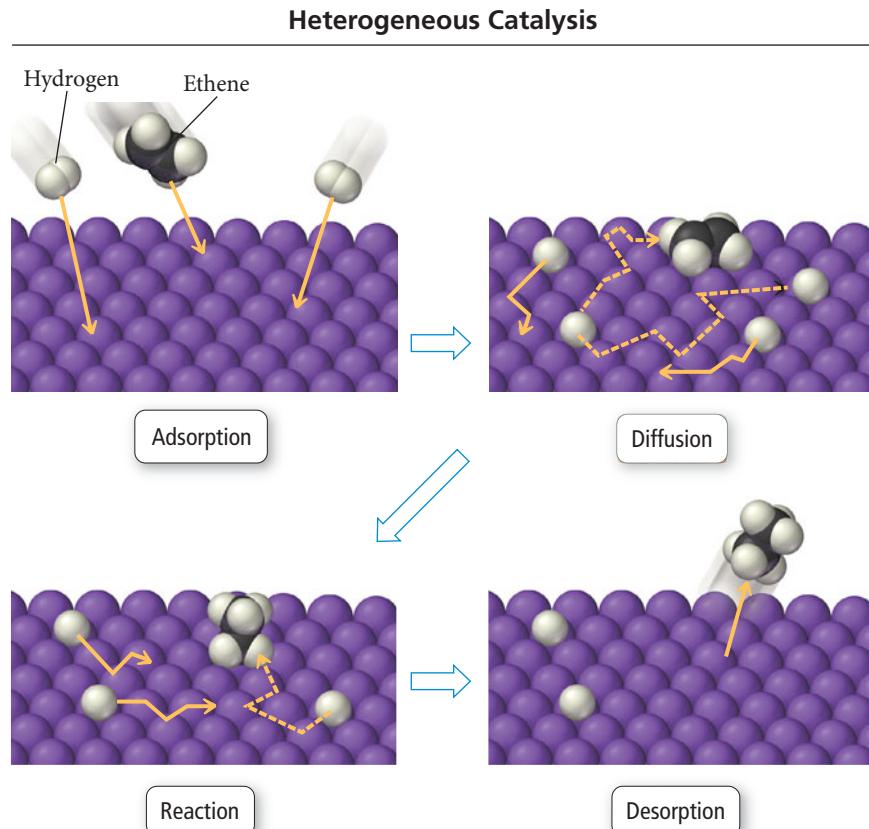


The chlorine atoms then catalyze the destruction of ozone by the mechanism discussed previously. This continues until the sun melts the stratospheric clouds, allowing chlorine atoms to be reincorporated into their reservoirs. The result is an ozone hole that forms every spring and lasts about 6–8 weeks (Figure 13.19 ▲).

A second example of heterogeneous catalysis involves the **hydrogenation** of double bonds within alkenes. Consider the reaction between ethene and hydrogen, which is relatively slow at normal temperatures:



However, in the presence of finely divided platinum, palladium, or nickel, the reaction happens rapidly. The catalysis occurs by the four-step process depicted in Figure 13.20 ▼.



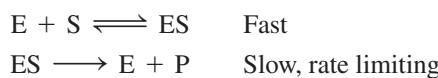
**► FIGURE 13.20** Catalytic Hydrogenation of Ethene

1. Adsorption: the reactants are adsorbed onto the metal surface.
2. Diffusion: the reactants diffuse on the surface until they approach each other.
3. Reaction: the reactants react to form the products.
4. Desorption: the products desorb from the surface into the gas phase.

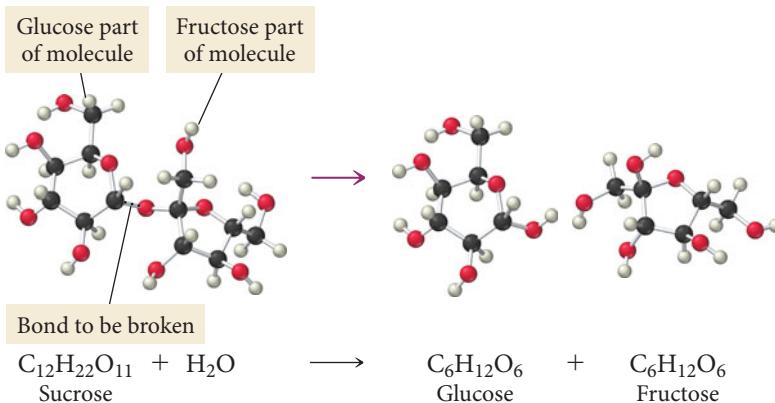
The large activation energy of the hydrogenation reaction—due primarily to the strength of the hydrogen–hydrogen bond in H<sub>2</sub>—is greatly lowered when the reactants adsorb onto the surface.

## Enzymes: Biological Catalysts

We find perhaps the best example of chemical catalysis in living organisms. Most of the thousands of reactions that must occur for an organism to survive are too slow at normal temperatures. So living organisms rely on **enzymes**, biological catalysts that increase the rates of biochemical reactions. Enzymes are usually large protein molecules with complex three-dimensional structures. Within each enzyme's structure is a specific area called the **active site**. The properties and shape of the active site are just right to bind the reactant molecule, usually called the **substrate**. The substrate fits into the active site in a manner that is analogous to a key fitting into a lock (Figure 13.21 ▶). When the substrate binds to the active site of the enzyme—through intermolecular forces such as hydrogen bonding and dispersion forces, or even covalent bonds—the activation energy of the reaction is greatly lowered, allowing the reaction to occur at a much faster rate. The general mechanism by which an enzyme (E) binds a substrate (S) and then reacts to form the products (P) is:

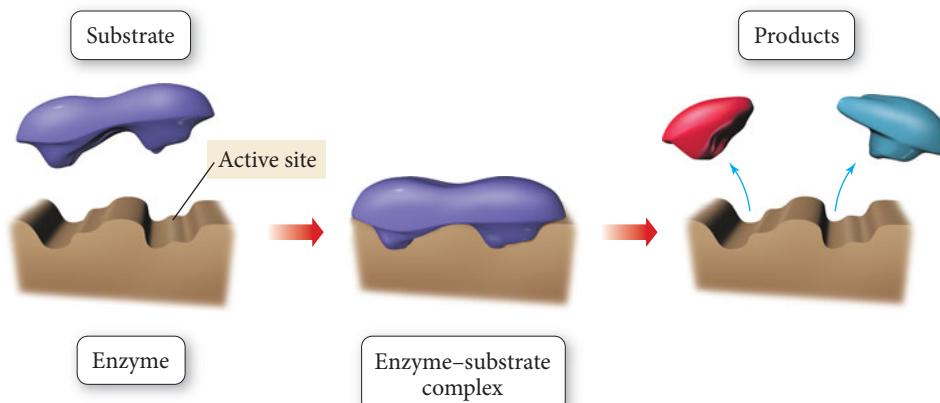


Sucrase is an enzyme that catalyzes the breaking up of sucrose (table sugar) into glucose and fructose within the body. At body temperature, sucrose does not break into glucose and fructose because the activation energy is high, resulting in a slow reaction rate. However,

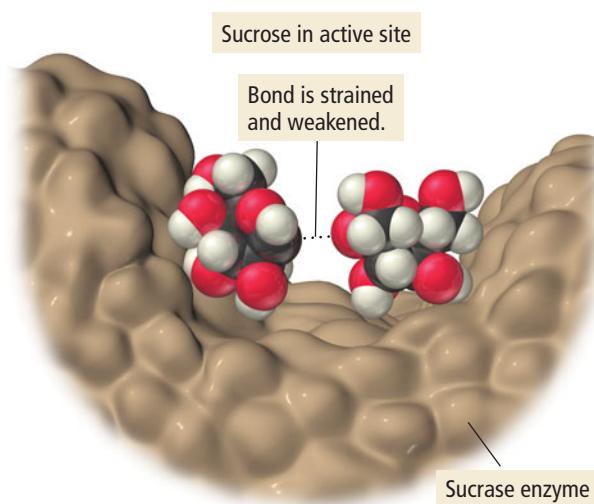


The strategies used to speed up chemical reactions in the laboratory—high temperatures, high pressures, strongly acidic or alkaline conditions—are not available to living organisms, since they would be fatal to cells.

## Enzyme–Substrate Binding



◀ **FIGURE 13.21** Enzyme–Substrate Binding A substrate (or reactant) fits into the active site of an enzyme much as a key fits into a lock. It is held in place by intermolecular forces and forms an enzyme–substrate complex. (Sometimes temporary covalent bonding may also be involved.) After the reaction occurs, the products are released from the active site.



**▲ FIGURE 13.22** An Enzyme-Catalyzed Reaction Sucrase catalyzes the conversion of sucrose into glucose and fructose by weakening the bond that joins the two rings.

when a sucrose molecule binds to the active site within sucrase, the bond between the glucose and fructose units weakens because glucose is forced into a geometry that stresses the bond (Figure 13.22 ▲). Weakening of this bond lowers the activation energy for the reaction, increasing the reaction rate. The reaction can then proceed toward equilibrium—which favors the products—at a much lower temperature.

By allowing otherwise slow reactions to occur at reasonable rates, enzymes give living organisms tremendous control over which reactions occur and when they occur. Enzymes are extremely specific (each enzyme catalyzes only a single reaction) and efficient, speeding up reaction rates by factors of as much as a billion. To turn a particular reaction on, a living organism produces or activates the correct enzyme to catalyze that reaction. Because organisms are so dependent on the reactions enzymes catalyze, many substances that inhibit the action of enzymes are highly toxic. Locking up a single enzyme molecule can stop the reaction of billions of substrates, much as one motorist stalled at a tollbooth can paralyze an entire highway full of cars. (For another example of enzyme action, see the *Chemistry and Medicine* box on the role of chymotrypsin in digestion.)

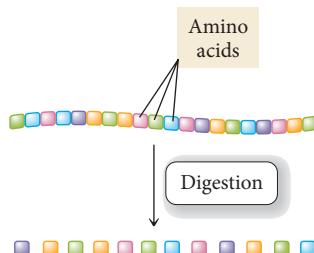


## Chemistry and Medicine

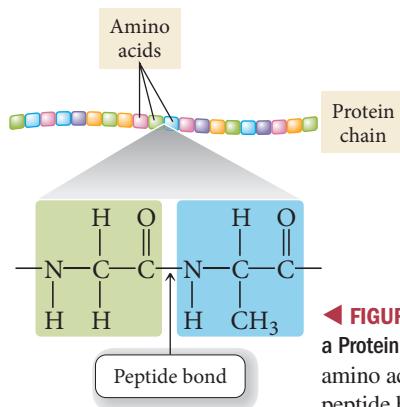
### Enzyme Catalysis and the Role of Chymotrypsin in Digestion

When we eat foods containing proteins—such as meats, eggs, beans, and nuts—the proteins must be digested. Proteins are large biological molecules composed of individual units called amino acids. (We will discuss the structure of proteins and other biologically important molecules more fully in Chapter 21.) The amino acids in proteins are linked together via peptide bonds, as shown in Figure 13.23 ▼. During digestion, the protein must be broken up into individual amino acids (Figure 13.24 ▶), which can pass through the walls of the small intestine and into the bloodstream. However, the peptide bonds that link amino acids together are relatively stable, and under ordinary conditions the reaction is slow.

The pancreas secretes an enzyme called chymotrypsin (Figure 13.25 ▶) into the small intestine. Like many enzymes, chymotrypsin is highly selective in its action—it operates

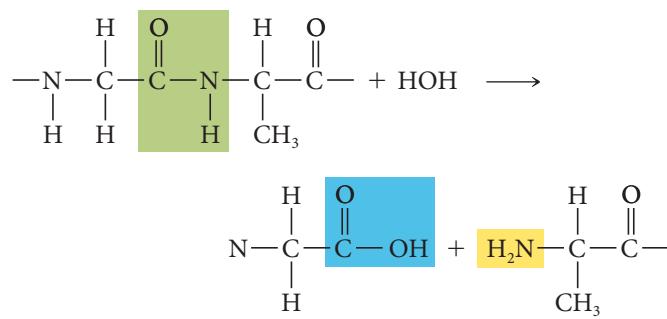


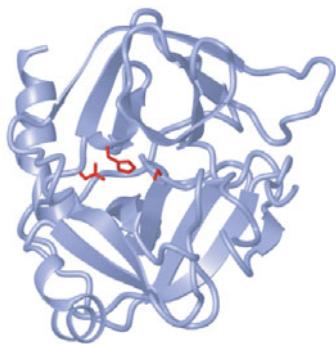
**◀ FIGURE 13.24** Protein Digestion During digestion, a protein is broken down into its component amino acids.



**◀ FIGURE 13.23** The Structure of a Protein Proteins are chains of amino acids linked together by peptide bonds.

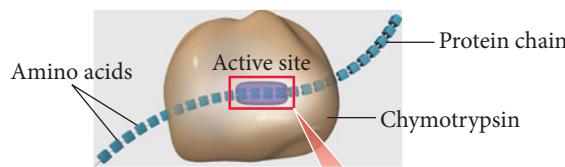
only on peptide bonds between certain kinds of amino acids. When a protein molecule containing such a pair of amino acids is attached to the active site of chymotrypsin, the peptide bond between them is weakened as the chymotrypsin forms a covalent bond with the carbon in the peptide bond. A water molecule can then come in and cleave the bond, with an —OH from the water binding to the carbon atom and the remaining —H bonding to the nitrogen (Figure 13.26 ▶).





**▲ FIGURE 13.25 Chymotrypsin, a Digestive Enzyme** This model of chymotrypsin shows a section of a protein substrate in the active site.

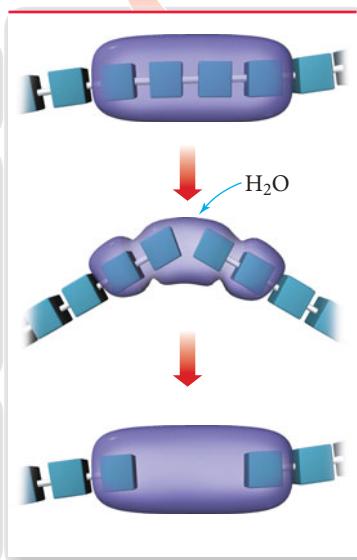
The amino acid chain is thus clipped at the peptide bond. The products of the reaction leave the active site, another protein binds to the chymotrypsin, and the process is repeated. Other digestive enzymes cleave protein chains between other pairs of amino acids. Together, these enzymes eventually reduce the entire protein to its constituent amino acids.



Protein fits into enzyme's active site.

Enzyme changes shape, straining and weakening peptide bond between adjacent amino acids and exposing them to water.

Peptide bond breaks. Enzyme releases two halves of protein chain and returns to original shape.

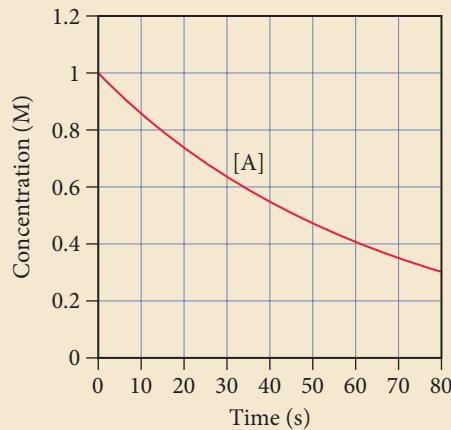


**▲ FIGURE 13.26 The Action of Chymotrypsin**

## CHAPTER IN REVIEW

### Self Assessment Quiz

- Q1.** This graph shows the concentration of the reactant A in the reaction  $A \rightarrow B$ . Determine the average rate of the reaction between 0 and 10 seconds.



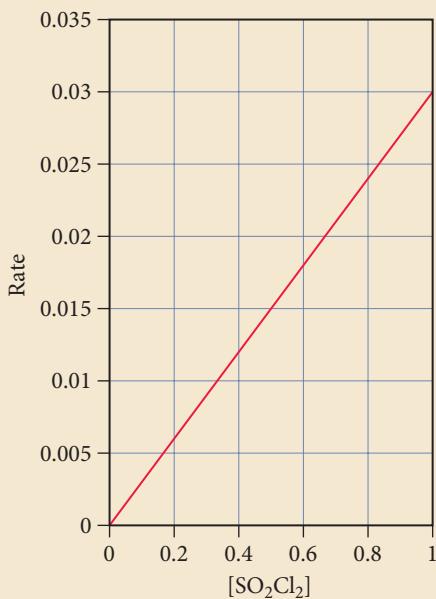
- a) 0.07 M/s      b) 0.007 M/s  
 c) 0.86 M/s      d) 0.014 M/s

- Q2.** Dinitrogen monoxide decomposes into nitrogen and oxygen when heated. The initial rate of the reaction is 0.022 M/s. What is the initial rate of change of the concentration of  $N_2O$  (that is,  $\Delta[N_2O]/\Delta t$ )?



- a)  $-0.022 \text{ M/s}$   
 b)  $-0.011 \text{ M/s}$   
 c)  $-0.044 \text{ M/s}$   
 d)  $+0.022 \text{ M/s}$

- Q3.** This plot shows the rate of the decomposition of  $\text{SO}_2\text{Cl}_2$  into  $\text{SO}_2$  and  $\text{Cl}_2$  as a function of the concentration of  $\text{SO}_2\text{Cl}_2$ . What is the order of the reaction?



- a) first order
- b) second order
- c) zero order
- d) Order cannot be determined without more information.

- Q4.** For the reaction  $2\text{A} + \text{B} \rightarrow \text{C}$ , the initial rate was measured at several different reactant concentrations. From the tabulated data, determine the rate law for the reaction.

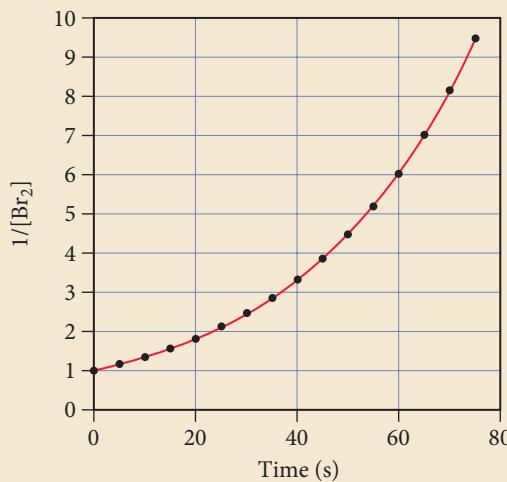
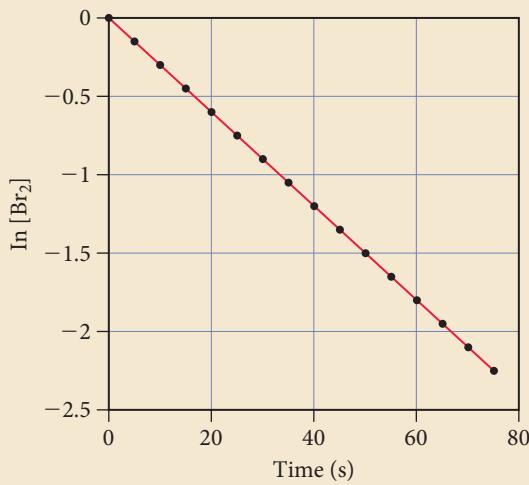
| [A] (M) | [B] (M) | Initial Rate (M/s) |
|---------|---------|--------------------|
| 0.05    | 0.05    | 0.035              |
| 0.10    | 0.05    | 0.070              |
| 0.20    | 0.10    | 0.56               |

- a) Rate =  $k[\text{A}][\text{B}]$
- b) Rate =  $k[\text{A}]^2[\text{B}]$
- c) Rate =  $k[\text{A}][\text{B}]^2$
- d) Rate =  $k[\text{A}]^2[\text{B}]^2$

- Q5.** What is the rate constant for the reaction in Question 4?

- a)  $2.8 \times 10^2 \text{ M}^{-2} \cdot \text{s}^{-1}$
- b)  $14 \text{ M}^{-2} \cdot \text{s}^{-1}$
- c)  $1.4 \times 10^2 \text{ M}^{-2} \cdot \text{s}^{-1}$
- d)  $1.4 \times 10^3 \text{ M}^{-2} \cdot \text{s}^{-1}$

- Q6.** The decomposition of  $\text{Br}_2$  was followed as a function of time; two different plots of the data are shown here. Determine the order and rate constant for the reaction.



- a) first order;  $0.030 \text{ s}^{-1}$
- b) first order;  $33.3 \text{ s}^{-1}$
- c) second order;  $0.045 \text{ M}^{-1} \cdot \text{s}^{-1}$
- d) second order;  $22.2 \text{ M}^{-1} \cdot \text{s}^{-1}$

- Q7.** The reaction  $\text{X} \rightarrow \text{products}$  is second order in  $\text{X}$  and has a rate constant of  $0.035 \text{ M}^{-1}\text{s}^{-1}$ . If a reaction mixture is initially  $0.45 \text{ M}$  in  $\text{X}$ , what is the concentration of  $\text{X}$  after 155 seconds?

- a)  $7.6 \text{ M}$
- b)  $2.0 \times 10^{-3} \text{ M}$
- c)  $0.13 \text{ M}$
- d)  $0.00 \text{ M}$

- Q8.** A decomposition reaction has a half-life that does not depend on the initial concentration of the reactant. What is the order of the reaction?

- a) zero order
- b) first order
- c) second order
- d) Order cannot be determined without more information.

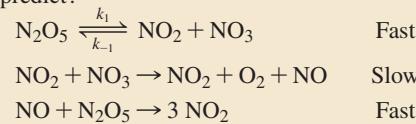
- Q9.** The rate constant of a reaction is measured at different temperatures. A plot of the natural log of the rate constant as a function of the inverse of the temperature (in kelvins) yields a straight line with a slope of  $-8.55 \times 10^3 \text{ K}^{-1}$ . What is the activation energy ( $E_a$ ) for the reaction?

- a)  $-71 \text{ kJ}$
- b)  $71 \text{ kJ}$
- c)  $1.0 \text{ kJ}$
- d)  $-1.0 \text{ kJ}$

- Q10.** The rate constant for a reaction at  $25.0^\circ\text{C}$  is  $0.010 \text{ s}^{-1}$ , and its activation energy is  $35.8 \text{ kJ}$ . Find the rate constant at  $50.0^\circ\text{C}$ .

- a)  $0.021 \text{ s}^{-1}$
- b)  $0.010 \text{ s}^{-1}$
- c)  $0.0033 \text{ s}^{-1}$
- d)  $0.031 \text{ s}^{-1}$

- Q11.** The mechanism shown here is proposed for the gas phase reaction,  $2 \text{ N}_2\text{O}_5 \rightarrow 2 \text{ NO}_2 + \text{ O}_2$ . What rate law does the mechanism predict?

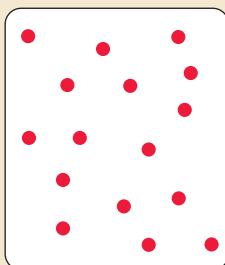


- a) Rate =  $k[\text{N}_2\text{O}_5]$
- b) Rate =  $k[\text{N}_2\text{O}_5]^2$
- c) Rate =  $k[\text{N}_2\text{O}_5]^0$
- d) Rate =  $k[\text{NO}_2][\text{NO}_3]$

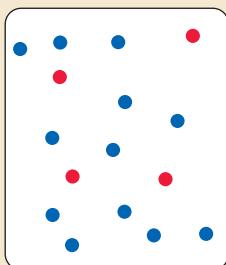
- Q12.** Which statement is true regarding the function of a catalyst in a chemical reaction?

- a) A catalyst increases the rate of a reaction.
- b) A catalyst provides an alternate mechanism for the reaction.
- c) A catalyst is not consumed by the reaction.
- d) All of the above are true.

- Q13.** These images represent the first order reaction  $A \rightarrow B$  initially and at some later time. The rate law for the reaction is  $\text{Rate} = 0.010 \text{ s}^{-1} [\text{A}]$ . How much time has passed between the two images?



Initial

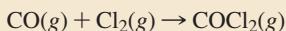
 $t = ?$ A  
B

- a) 69 s      b) 139 s  
c) 60 s      d) 12.5 s

- Q14.** Pick the single-step reaction that, according to collision theory, has the smallest orientation factor.

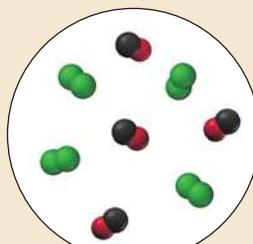
- a)  $\text{H} + \text{H} \rightarrow \text{H}_2$   
b)  $\text{I} + \text{HI} \rightarrow \text{I}_2 + \text{H}$   
c)  $\text{H}_2 + \text{H}_2\text{C}=\text{CH}_2 \rightarrow \text{H}_3\text{C}-\text{CH}_3$   
d) All of these reactions have the same orientation factor.

- Q15.** Carbon monoxide and chlorine gas react to form phosgene ( $\text{COCl}_2$ ) according to the equation:

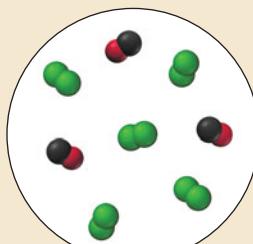


Answers: 1. (d) 2. (c) 3. (a) 4. (c) 5. (a) 6. (a) 7. (c) 8. (b) 9. (b) 10. (d) 11. (a) 12. (d) 13. (b) 14. (c) 15. (b)

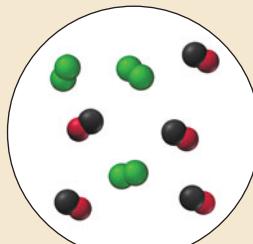
The rate law for the reaction is  $\text{rate} = k[\text{Cl}_2]^{3/2}[\text{CO}]$ . Which mixture of chlorine gas and carbon monoxide gas has the fastest initial rate?



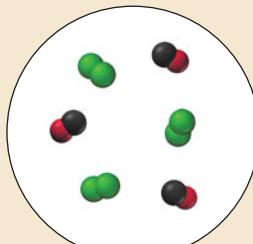
(a)



(b)



(c)



(d)

## Key Terms

### Section 13.3

rate law (603)  
rate constant ( $k$ ) (603)  
reaction order ( $n$ ) (603)  
overall order (606)

### Section 13.4

integrated rate law (608)  
half-life ( $t_{1/2}$ ) (612)

### Section 13.5

Arrhenius equation (615)  
activation energy ( $E_a$ ) (616)  
frequency factor ( $A$ ) (616)  
activated complex (transition state) (616)  
exponential factor (617)  
Arrhenius plot (618)  
collision model (620)  
orientation factor (621)  
collision frequency (621)

### Section 13.6

reaction mechanism (622)  
elementary step (622)  
reaction intermediates (622)  
molecularity (623)  
unimolecular (623)  
bimolecular (623)  
termolecular (623)  
rate-determining step (623)

### Section 13.7

catalyst (627)  
homogeneous catalysis (629)  
heterogeneous catalysis (629)  
hydrogenation (630)  
enzyme (631)  
active site (631)  
substrate (631)

## Key Concepts

### Reaction Rates, Orders, and Rate Laws (13.1–13.3)

- The rate of a chemical reaction is a measure of how fast a reaction occurs. The rate reflects the change in the concentration of a reactant or product per unit time and is usually reported in units of M/s.
- Reaction rates generally depend on the concentration of the reactants. The rate of a first-order reaction is directly proportional to the concentration of the reactant, the rate of a second-order reaction is proportional to the square of the concentration of the reactant, and the rate of a zero-order reaction is independent of the concentration of the reactant.
- For a reaction with more than one reactant, the order with respect to each reactant is, in general, independent of the order with respect to other reactants. The rate law shows the relationship between the rate and the concentrations of each reactant and must be determined experimentally.

### Integrated Rate Laws and Half-Life (13.4)

- The rate law for a reaction describes the relationship between the rate of the reaction and the concentrations of the reactants.
- The integrated rate law for a reaction describes the relationship between the concentration of a reactant and time.
- The integrated rate law for a zero-order reaction shows that the concentration of the reactant varies linearly with time. For a first-order reaction, the *natural log* of the concentration of the reactant varies linearly with time, and for a second-order reaction, the *inverse* of the concentration of the reactant varies linearly with time.
- The half-life of a reaction can be derived from the integrated rate law and represents the time required for the concentration of a reactant to fall to one-half of its initial value. The half-life of a first-order reaction is *independent* of initial concentration of the reactant. The half-life of a zero-order or second-order reaction *depends* on the initial concentration of reactant.

## The Effect of Temperature on Reaction Rate (13.5)

- The rate constant of a reaction generally depends on temperature and can be expressed by the Arrhenius equation, which consists of a frequency factor and an exponential factor.
- The frequency factor represents the number of times that the reactants approach the activation barrier per unit time. The exponential factor is the fraction of approaches that are successful in surmounting the activation barrier and forming products.
- The exponential factor depends on both the temperature and the activation energy, a barrier that the reactants must overcome to become products. The exponential factor increases with increasing temperature but decreases with increasing activation energy.
- We can determine the frequency factor and activation energy for a reaction by measuring the rate constant at different temperatures and constructing an Arrhenius plot.
- For reactions in the gas phase, Arrhenius behavior can be modeled with the collision model. In this model, reactions occur as a result of sufficiently energetic collisions. The colliding molecules must be oriented in such a way that the reaction can occur. The frequency factor contains two terms:  $p$ , which represents the fraction of collisions that have the proper orientation, and  $z$ , which represents the number of collisions per unit time.

## Reaction Mechanisms (13.6)

- Most chemical reactions occur not in a single step, but in several steps. The series of individual steps by which a reaction occurs is the reaction mechanism.
- In order for a proposed reaction mechanism to be valid, it must fulfill two conditions: (a) the steps must sum to the overall reaction, and (b) the mechanism must predict the experimentally observed rate law.
- For mechanisms with a slow initial step, we derive the rate law from the slow step.
- For mechanisms with a fast initial step, we first write the rate law based on the slow step but then assume that the fast steps reach equilibrium, so we can write concentrations of intermediates in terms of the reactants.

## Catalysis (13.7)

- A catalyst is a substance that increases the rate of a chemical reaction by providing an alternative mechanism that has a lower activation energy for the rate-determining step.
- Catalysts can be homogeneous or heterogeneous. A homogeneous catalyst exists in the same phase as the reactants and forms a homogeneous mixture with them. A heterogeneous catalyst generally exists in a different phase than the reactants.
- Enzymes are biological catalysts capable of increasing the rate of specific biochemical reactions by many orders of magnitude.

## Key Equations and Relationships

### The Rate of Reaction (13.2)

For a reaction,  $aA + bB \longrightarrow cC + dD$ , the rate is defined as

$$\text{Rate} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = +\frac{1}{c} \frac{\Delta[C]}{\Delta t} = +\frac{1}{d} \frac{\Delta[D]}{\Delta t}$$

### The Rate Law (13.3)

$$\begin{aligned}\text{Rate} &= k[A]^n && (\text{single reactant}) \\ \text{Rate} &= k[A]^m[B]^n && (\text{multiple reactants})\end{aligned}$$

### Integrated Rate Laws and Half-Life (13.4)

| Reaction Order | Integrated Rate Law                      | Units of $k$                        | Half-Life Expression         |
|----------------|--|-------------------------------------|------------------------------|
| 0              | $[A]_t = -kt + [A]_0$                    | $\text{M} \cdot \text{s}^{-1}$      | $t_{1/2} = \frac{[A]_0}{2k}$ |
| 1              | $\ln[A]_t = -kt + \ln[A]_0$              | $\text{s}^{-1}$                     | $t_{1/2} = \frac{0.693}{k}$  |
| 2              | $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$ | $\text{M}^{-1} \cdot \text{s}^{-1}$ | $t_{1/2} = \frac{1}{k[A]_0}$ |

### Arrhenius Equation (13.5)

$$\begin{aligned}k &= Ae^{-E_a/RT} \\ \ln k &= -\frac{E_a}{R} \left( \frac{1}{T} \right) + \ln A && (\text{linearized form}) \\ \ln \frac{k_2}{k_1} &= \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) && (\text{two-point form}) \\ k &= pze^{-E_a/RT} && (\text{collision theory})\end{aligned}$$

### Rate Laws for Elementary Steps (13.6)

| Elementary Step                             | Molecularity | Rate Law                   |
|---|--------------|----------------------------|
| $A \longrightarrow \text{products}$         | 1            | $\text{Rate} = k[A]$       |
| $A + A \longrightarrow \text{products}$     | 2            | $\text{Rate} = k[A]^2$     |
| $A + B \longrightarrow \text{products}$     | 2            | $\text{Rate} = k[A][B]$    |
| $A + A + A \longrightarrow \text{products}$ | 3 (rare)     | $\text{Rate} = k[A]^3$     |
| $A + A + B \longrightarrow \text{products}$ | 3 (rare)     | $\text{Rate} = k[A]^2[B]$  |
| $A + B + C \longrightarrow \text{products}$ | 3 (rare)     | $\text{Rate} = k[A][B][C]$ |

## Key Learning Outcomes

### Chapter Objectives

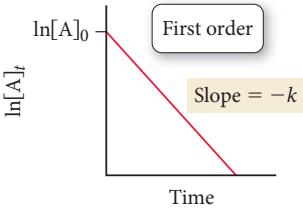
#### Expressing Reaction Rates (13.2)



### Assessment

#### Example 13.1 For Practice 13.1 Exercises 25–34

## Key Learning Outcomes, continued

|   |   |
|---|---|
| Determining the Order, Rate Law, and Rate Constant of a Reaction (13.3)                         | Example 13.2 For Practice 13.2 Exercises 41–44              |
| Using Graphical Analysis of Reaction Data to Determine Reaction Order and Rate Constants (13.4) | Examples 13.3, 13.5 For Practice 13.3, 13.5 Exercises 47–52 |
| Determining the Concentration of a Reactant at a Given Time (13.4)                              | Example 13.4 For Practice 13.4 Exercises 51–54              |
|                |   |
| Working with the Half-Life of a Reaction (13.4)   | Example 13.6 For Practice 13.6 Exercises 53–56              |
| Using the Arrhenius Equation to Determine Kinetic Parameters (13.5)                             | Examples 13.7, 13.8 For Practice 13.7, 13.8 Exercises 59–70 |
| Determining whether a Reaction Mechanism Is Valid (13.6)  | Example 13.9 For Practice 13.9 Exercises 73–76              |

## EXERCISES

### Review Questions

- Explain why lizards become sluggish in cold weather. How is this phenomenon related to chemistry?
- Why are reaction rates important (both practically and theoretically)?
- What units are typically used to express the rate of a reaction?
- Why is the reaction rate for reactants defined as the *negative* of the change in reactant concentration with respect to time, whereas for products it is defined as the change in reactant concentration with respect to time (with a positive sign)?
- Explain the difference between the average rate of reaction and the instantaneous rate of reaction.
- Consider a simple reaction in which a reactant A forms products:  

$$A \longrightarrow \text{products}$$

What is the rate law if the reaction is zero order with respect to A? First order? Second order? For each case, explain how a doubling of the concentration of A would affect the rate of reaction.
- How is the order of a reaction generally determined?
- For a reaction with multiple reactants, how is the overall order of the reaction defined?
- Explain the difference between the rate law for a reaction and the integrated rate law for a reaction. What relationship does each kind of rate law express?
- Write integrated rate laws for zero-order, first-order, and second-order reactions of the form  $A \longrightarrow \text{products}$ .
- What does the term *half-life* mean? Write the expressions for the half-lives of zero-order, first-order, and second-order reactions.
- How do reaction rates typically depend on temperature? What part of the rate law is temperature dependent?
- Explain the meaning of each term within the Arrhenius equation: activation energy, frequency factor, and exponential factor. Use these terms and the Arrhenius equation to explain why small changes in temperature can result in large changes in reaction rates.
- What is an Arrhenius plot? Explain the significance of the slope and intercept of an Arrhenius plot.
- Explain how a chemical reaction occurs according to the collision model. Explain the meaning of the orientation factor in this model.
- Explain the difference between a normal chemical equation for a chemical reaction and the mechanism of that reaction.
- In a reaction mechanism, what is an elementary step? Write down the three most common elementary steps and the corresponding rate law for each one.
- What are the two requirements for a proposed mechanism to be valid for a given reaction?
- What is an intermediate within a reaction mechanism?
- What is a catalyst? How does a catalyst increase the rate of a chemical reaction?
- Explain the difference between homogeneous catalysis and heterogeneous catalysis.
- What are the four basic steps involved in heterogeneous catalysis?
- What are enzymes? What is the active site of an enzyme? What is a substrate?
- What is the general two-step mechanism by which most enzymes work?

## Problems by Topic

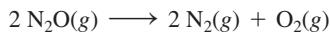
### Reaction Rates

25. Consider the reaction:



- a. Express the rate of the reaction in terms of the change in concentration of each of the reactants and products.
- b. In the first 25.0 s of this reaction, the concentration of HBr dropped from 0.600 M to 0.512 M. Calculate the average rate of the reaction during this time interval.
- c. If the volume of the reaction vessel in part b was 1.50 L, what amount of Br<sub>2</sub> (in moles) was formed during the first 15.0 s of the reaction?

26. Consider the reaction:

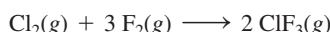


- a. Express the rate of the reaction in terms of the change in concentration of each of the reactants and products.
- b. In the first 15.0 s of the reaction, 0.015 mol of O<sub>2</sub> is produced in a reaction vessel with a volume of 0.500 L. What is the average rate of the reaction during this time interval?
- c. Predict the rate of change in the concentration of N<sub>2</sub>O during this time interval. In other words, what is  $\Delta[\text{N}_2\text{O}]/\Delta t$ ?

27. For the reaction 2 A(g) + B(g)  $\longrightarrow$  3 C(g),

- a. determine the expression for the rate of the reaction in terms of the change in concentration of each of the reactants and products.
- b. when A is decreasing at a rate of 0.100 M/s, how fast is B decreasing? How fast is C increasing?
- 28. For the reaction A(g) +  $\frac{1}{2}$  B(g)  $\longrightarrow$  2 C(g),
  - a. determine the expression for the rate of the reaction in terms of the change in concentration of each of the reactants and products.
  - b. when C is increasing at a rate of 0.025 M/s, how fast is B decreasing? How fast is A decreasing?

29. Consider the reaction:



Complete the table.

| $\Delta[\text{Cl}_2]/\Delta t$ | $\Delta[\text{F}_2]/\Delta t$ | $\Delta[\text{ClF}_3]/\Delta t$ | Rate |
|--------------------------------|-------------------------------|---------------------------------|------|
| -0.012 M/s                     |                               |                                 |      |

30. Consider the reaction:



Complete the table.

| $\Delta[\text{H}_2\text{S}]/\Delta t$ | $\Delta[\text{O}_2]/\Delta t$ | $\Delta[\text{H}_2\text{O}]/\Delta t$ | $\Delta[\text{S}_8]/\Delta t$ | Rate |
|---------------------------------------|-------------------------------|---------------------------------------|-------------------------------|------|
| -0.080 M/s                            |                               |                                       |                               |      |

31. Consider the reaction:



The tabulated data were collected for the concentration of C<sub>4</sub>H<sub>8</sub> as a function of time:

| Time (s) | [C <sub>4</sub> H <sub>8</sub> ] (M) |
|----------|--------------------------------------|
| 0        | 1.000                                |
| 10       | 0.913                                |
| 20       | 0.835                                |
| 30       | 0.763                                |
| 40       | 0.697                                |
| 50       | 0.637                                |

- a. What is the average rate of the reaction between 0 and 10 s? Between 40 and 50 s?
- b. What is the rate of formation of C<sub>2</sub>H<sub>4</sub> between 20 and 30 s?

32. Consider the reaction:

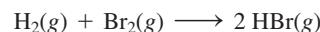


The tabulated data were collected for the concentration of NO<sub>2</sub> as a function of time:

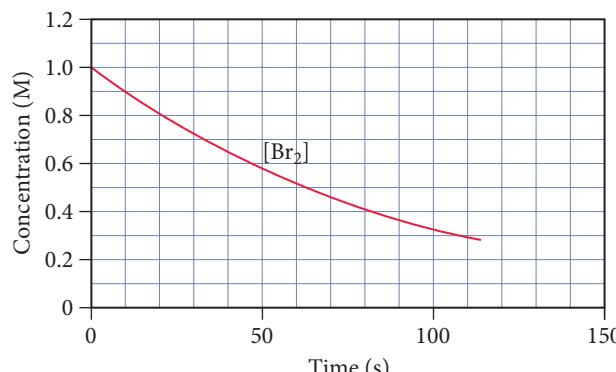
| Time (s) | [NO <sub>2</sub> ] (M) |
|----------|------------------------|
| 0        | 1.000                  |
| 10       | 0.951                  |
| 20       | 0.904                  |
| 30       | 0.860                  |
| 40       | 0.818                  |
| 50       | 0.778                  |
| 60       | 0.740                  |
| 70       | 0.704                  |
| 80       | 0.670                  |
| 90       | 0.637                  |
| 100      | 0.606                  |

- a. What is the average rate of the reaction between 10 and 20 s? Between 50 and 60 s?
- b. What is the rate of formation of O<sub>2</sub> between 50 and 60 s?

33. Consider the reaction:

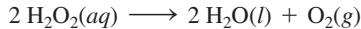


The graph shows the concentration of Br<sub>2</sub> as a function of time.

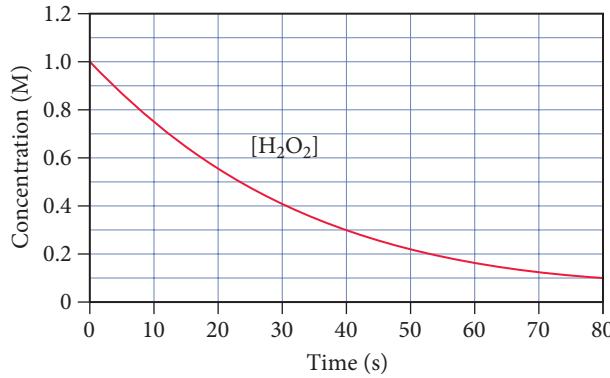


- a. Use the graph to calculate each quantity:
- the average rate of the reaction between 0 and 25 s
  - the instantaneous rate of the reaction at 25 s
  - the instantaneous rate of formation of HBr at 50 s
- b. Make a rough sketch of a curve representing the concentration of HBr as a function of time. Assume that the initial concentration of HBr is zero.

34. Consider the reaction:



The graph below shows the concentration of  $\text{H}_2\text{O}_2$  as a function of time.

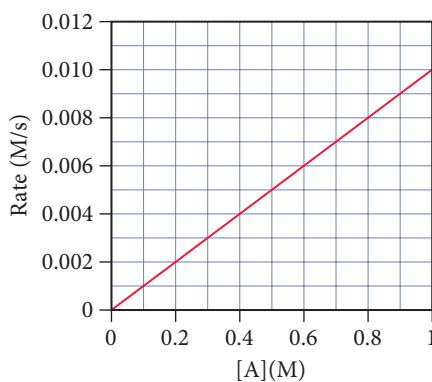


Use the graph to calculate each quantity:

- the average rate of the reaction between 10 and 20 s
- the instantaneous rate of the reaction at 30 s
- the instantaneous rate of formation of  $\text{O}_2$  at 50 s
- If the initial volume of the  $\text{H}_2\text{O}_2$  is 1.5 L, what total amount of  $\text{O}_2$  (in moles) is formed in the first 50 s of reaction?

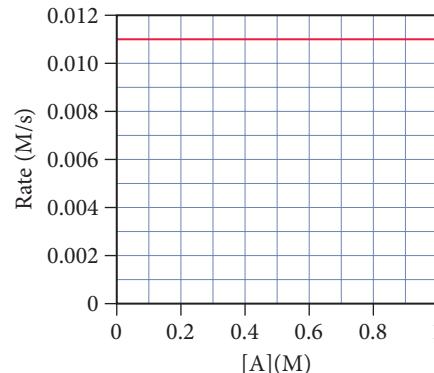
## The Rate Law and Reaction Orders

35. This graph shows a plot of the rate of a reaction versus the concentration of the reactant A for the reaction  $\text{A} \longrightarrow \text{products}$ .



- What is the order of the reaction with respect to A?
- Make a rough sketch of a plot of [A] versus time.
- Write a rate law for the reaction including an estimate for the value of  $k$ .

36. This graph shows a plot of the rate of a reaction versus the concentration of the reactant.



- a. What is the order of the reaction with respect to A?

- Make a rough sketch of a plot of [A] versus time.
- Write a rate law for the reaction including the value of  $k$ .

37. What are the units of  $k$  for each type of reaction?

- first-order reaction
- second-order reaction
- zero-order reaction

38. This reaction is first order in  $\text{N}_2\text{O}_5$ :



The rate constant for the reaction at a certain temperature is  $0.053/\text{s}$ .

- Calculate the rate of the reaction when  $[\text{N}_2\text{O}_5] = 0.055 \text{ M}$ .
- What would the rate of the reaction be at the concentration indicated in part a if the reaction were second order? Zero order? (Assume the same *numerical* value for the rate constant with the appropriate units.)

39. A reaction in which A, B, and C react to form products is first order in A, second order in B, and zero order in C.

- Write a rate law for the reaction.
- What is the overall order of the reaction?
- By what factor does the reaction rate change if [A] is doubled (and the other reactant concentrations are held constant)?
- By what factor does the reaction rate change if [B] is doubled (and the other reactant concentrations are held constant)?
- By what factor does the reaction rate change if [C] is doubled (and the other reactant concentrations are held constant)?
- By what factor does the reaction rate change if the concentrations of all three reactants are doubled?

40. A reaction in which A, B, and C react to form products is zero order in A, one-half order in B, and second order in C.

- Write a rate law for the reaction.
- What is the overall order of the reaction?
- By what factor does the reaction rate change if [A] is doubled (and the other reactant concentrations are held constant)?
- By what factor does the reaction rate change if [B] is doubled (and the other reactant concentrations are held constant)?
- By what factor does the reaction rate change if [C] is doubled (and the other reactant concentrations are held constant)?
- By what factor does the reaction rate change if the concentrations of all three reactants are doubled?

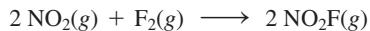
41. Consider the data showing the initial rate of a reaction ( $A \rightarrow$  products) at several different concentrations of A. What is the order of the reaction? Write a rate law for the reaction including the value of the rate constant,  $k$ .

| [A] (M) | Initial Rate (M/s) |
|---------|--------------------|
| 0.100   | 0.053              |
| 0.200   | 0.210              |
| 0.300   | 0.473              |

42. Consider the data showing the initial rate of a reaction ( $A \rightarrow$  products) at several different concentrations of A. What is the order of the reaction? Write a rate law for the reaction including the value of the rate constant,  $k$ .

| [A] (M) | Initial Rate (M/s) |
|---------|--------------------|
| 0.15    | 0.008              |
| 0.30    | 0.016              |
| 0.60    | 0.032              |

43. The tabulated data were collected for this reaction:



| [NO <sub>2</sub> ] (M) | [F <sub>2</sub> ] (M) | Initial Rate (M/s) |
|------------------------|-----------------------|--------------------|
| 0.100                  | 0.100                 | 0.026              |
| 0.200                  | 0.100                 | 0.051              |
| 0.200                  | 0.200                 | 0.103              |
| 0.400                  | 0.400                 | 0.411              |

Write an expression for the reaction rate law and calculate the value of the rate constant,  $k$ . What is the overall order of the reaction?

44. The tabulated data were collected for this reaction:



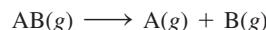
| [CH <sub>3</sub> Cl] (M) | [Cl <sub>2</sub> ] (M) | Initial Rate (M/s) |
|--------------------------|------------------------|--------------------|
| 0.050                    | 0.050                  | 0.014              |
| 0.100                    | 0.050                  | 0.029              |
| 0.100                    | 0.100                  | 0.041              |
| 0.200                    | 0.200                  | 0.115              |

Write an expression for the reaction rate law and calculate the value of the rate constant,  $k$ . What is the overall order of the reaction?

### The Integrated Rate Law and Half-Life

45. Indicate the order of reaction consistent with each observation.
- A plot of the concentration of the reactant versus time yields a straight line.
  - The reaction has a half-life that is independent of initial concentration.
  - A plot of the inverse of the concentration versus time yields a straight line.
46. Indicate the order of reaction consistent with each observation.
- The half-life of the reaction gets shorter as the initial concentration is increased.
  - A plot of the natural log of the concentration of the reactant versus time yields a straight line.
  - The half-life of the reaction gets longer as the initial concentration is increased.

47. The tabulated data show the concentration of AB versus time for this reaction:



| Time (s) | [AB] (M) |
|----------|----------|
| 0        | 0.950    |
| 50       | 0.459    |
| 100      | 0.302    |
| 150      | 0.225    |
| 200      | 0.180    |
| 250      | 0.149    |
| 300      | 0.128    |
| 350      | 0.112    |
| 400      | 0.0994   |
| 450      | 0.0894   |
| 500      | 0.0812   |

Determine the order of the reaction and the value of the rate constant. Predict the concentration of AB at 25 s.

48. The tabulated data show the concentration of N<sub>2</sub>O<sub>5</sub> versus time for this reaction:



| Time (s) | [N <sub>2</sub> O <sub>5</sub> ] (M) |
|----------|--------------------------------------|
| 0        | 1.000                                |
| 25       | 0.822                                |
| 50       | 0.677                                |
| 75       | 0.557                                |
| 100      | 0.458                                |
| 125      | 0.377                                |
| 150      | 0.310                                |
| 175      | 0.255                                |
| 200      | 0.210                                |

Determine the order of the reaction and the value of the rate constant. Predict the concentration of N<sub>2</sub>O<sub>5</sub> at 250 s.

49. The tabulated data show the concentration of cyclobutane (C<sub>4</sub>H<sub>8</sub>) versus time for this reaction:



| Time (s) | [C <sub>4</sub> H <sub>8</sub> ] (M) |
|----------|--------------------------------------|
| 0        | 1.000                                |
| 10       | 0.894                                |
| 20       | 0.799                                |
| 30       | 0.714                                |
| 40       | 0.638                                |
| 50       | 0.571                                |
| 60       | 0.510                                |
| 70       | 0.456                                |
| 80       | 0.408                                |
| 90       | 0.364                                |
| 100      | 0.326                                |

Determine the order of the reaction and the value of the rate constant. What is the rate of reaction when [C<sub>4</sub>H<sub>8</sub>] = 0.25 M?

50. A reaction in which  $A \longrightarrow$  products was monitored as a function of time. The results are shown here.

| Time (s) | [A] (M) |
|----------|---------|
| 0        | 1.000   |
| 25       | 0.914   |
| 50       | 0.829   |
| 75       | 0.744   |
| 100      | 0.659   |
| 125      | 0.573   |
| 150      | 0.488   |
| 175      | 0.403   |
| 200      | 0.318   |

Determine the order of the reaction and the value of the rate constant. What is the rate of reaction when  $[A] = 0.10\text{ M}$ ?

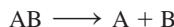
51. This reaction was monitored as a function of time:



A plot of  $\ln[A]$  versus time yields a straight line with slope  $-0.0045/\text{s}$ .

- What is the value of the rate constant ( $k$ ) for this reaction at this temperature?
- Write the rate law for the reaction.
- What is the half-life?
- If the initial concentration of A is  $0.250\text{ M}$ , what is the concentration after  $225\text{ s}$ ?

52. This reaction was monitored as a function of time:



A plot of  $1/[AB]$  versus time yields a straight line with a slope of  $+0.55/\text{M} \cdot \text{s}$ .

- What is the value of the rate constant ( $k$ ) for this reaction at this temperature?
- Write the rate law for the reaction.
- What is the half-life when the initial concentration is  $0.55\text{ M}$ ?
- If the initial concentration of AB is  $0.250\text{ M}$ , and the reaction mixture initially contains no products, what are the concentrations of A and B after  $75\text{ s}$ ?

53. The decomposition of  $\text{SO}_2\text{Cl}_2$  is first order in  $\text{SO}_2\text{Cl}_2$  and has a rate constant of  $1.42 \times 10^{-4}\text{s}^{-1}$  at a certain temperature.

- What is the half-life for this reaction?
- How long will it take for the concentration of  $\text{SO}_2\text{Cl}_2$  to decrease to 25% of its initial concentration?
- If the initial concentration of  $\text{SO}_2\text{Cl}_2$  is  $1.00\text{ M}$ , how long will it take for the concentration to decrease to  $0.78\text{ M}$ ?
- If the initial concentration of  $\text{SO}_2\text{Cl}_2$  is  $0.150\text{ M}$ , what is the concentration of  $\text{SO}_2\text{Cl}_2$  after  $2.00 \times 10^2\text{ s}$ ? After  $5.00 \times 10^2\text{ s}$ ?

54. The decomposition of XY is second order in XY and has a rate constant of  $7.02 \times 10^{-3}\text{M}^{-1} \cdot \text{s}^{-1}$  at a certain temperature.

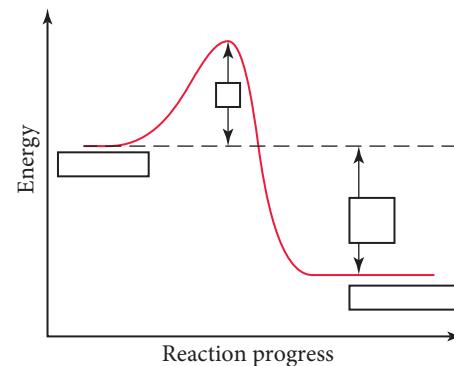
- What is the half-life for this reaction at an initial concentration of  $0.100\text{ M}$ ?
- How long will it take for the concentration of XY to decrease to 12.5% of its initial concentration when the initial concentration is  $0.100\text{ M}$ ? When the initial concentration is  $0.200\text{ M}$ ?

- If the initial concentration of XY is  $0.150\text{ M}$ , how long will it take for the concentration to decrease to  $0.062\text{ M}$ ?
- If the initial concentration of XY is  $0.050\text{ M}$ , what is the concentration of XY after  $5.0 \times 10^1\text{ s}$ ? After  $5.50 \times 10^2\text{ s}$ ?

55. The half-life for the radioactive decay of U-238 is 4.5 billion years and is independent of initial concentration. How long will it take for 10% of the U-238 atoms in a sample of U-238 to decay? If a sample of U-238 initially contained  $1.5 \times 10^{18}\text{ atoms}$  when the universe was formed 13.8 billion years ago, how many U-238 atoms does it contain today?
56. The half-life for the radioactive decay of C-14 is 5730 years and is independent of the initial concentration. How long does it take for 25% of the C-14 atoms in a sample of C-14 to decay? If a sample of C-14 initially contains 1.5 mmol of C-14, how many millimoles are left after 2255 years?

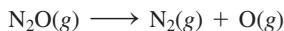
### The Effect of Temperature and the Collision Model

57. The diagram shows the energy of a reaction as the reaction progresses. Label each blank box in the diagram.



- reactants
  - products
  - activation energy ( $E_a$ )
  - enthalpy of reaction ( $\Delta H_{rxn}$ )
58. A chemical reaction is endothermic and has an activation energy that is twice the value of the enthalpy change of the reaction. Draw a diagram depicting the energy of the reaction as it progresses. Label the position of the reactants and products and indicate the activation energy and enthalpy of reaction.
59. The activation energy of a reaction is  $56.8\text{ kJ/mol}$  and the frequency factor is  $1.5 \times 10^{11}/\text{s}$ . Calculate the rate constant of the reaction at  $25^\circ\text{C}$ .
60. The rate constant of a reaction at  $32^\circ\text{C}$  is  $0.055/\text{s}$ . If the frequency factor is  $1.2 \times 10^{13}/\text{s}$ , what is the activation barrier?
61. The rate constant ( $k$ ) for a reaction was measured as a function of temperature. A plot of  $\ln k$  versus  $1/T$  (in K) is linear and has a slope of  $-7445\text{ K}$ . Calculate the activation energy for the reaction.
62. The rate constant ( $k$ ) for a reaction was measured as a function of temperature. A plot of  $\ln k$  versus  $1/T$  (in K) is linear and has a slope of  $-1.01 \times 10^4\text{ K}$ . Calculate the activation energy for the reaction.

63. The data shown here were collected for the first-order reaction:



Use an Arrhenius plot to determine the activation barrier and frequency factor for the reaction.

| Temperature (K) | Rate Constant (1/s)   |
|-----------------|-----------------------|
| 800             | $3.24 \times 10^{-5}$ |
| 900             | 0.00214               |
| 1000            | 0.0614                |
| 1100            | 0.955                 |

64. The tabulated data show the rate constant of a reaction measured at several different temperatures. Use an Arrhenius plot to determine the activation barrier and frequency factor for the reaction.

| Temperature (K) | Rate Constant (1/s) |
|-----------------|---------------------|
| 300             | 0.0134              |
| 310             | 0.0407              |
| 320             | 0.114               |
| 330             | 0.303               |
| 340             | 0.757               |

65. The tabulated data were collected for the second-order reaction:



Use an Arrhenius plot to determine the activation barrier and frequency factor for the reaction.

| Temperature (K) | Rate Constant (L/mol · s) |
|-----------------|---------------------------|
| 90              | 0.00357                   |
| 100             | 0.0773                    |
| 110             | 0.956                     |
| 120             | 7.781                     |

66. The tabulated data show the rate constant of a reaction measured at several different temperatures. Use an Arrhenius plot to determine the activation barrier and frequency factor for the reaction.

| Temperature (K) | Rate Constant (1/s) |
|-----------------|---------------------|
| 310             | 0.00434             |
| 320             | 0.0140              |
| 330             | 0.0421              |
| 340             | 0.118               |
| 350             | 0.316               |

67. A reaction has a rate constant of 0.0117/s at 400.0 K and 0.689/s at 450.0 K.

- a. Determine the activation barrier for the reaction.  
b. What is the value of the rate constant at 425 K?

68. A reaction has a rate constant of 0.000122/s at 27 °C and 0.228/s at 77 °C.

- a. Determine the activation barrier for the reaction.  
b. What is the value of the rate constant at 17 °C?

69. If a temperature increase from 10.0 °C to 20.0 °C doubles the rate constant for a reaction, what is the value of the activation barrier for the reaction?

70. If a temperature increase from 20.0 °C to 35.0 °C triples the rate constant for a reaction, what is the value of the activation barrier for the reaction?

71. Consider these two gas-phase reactions:

- a. AA(g) + BB(g)  $\longrightarrow$  2 AB(g)  
b. AB(g) + CD(g)  $\longrightarrow$  AC(g) + BD(g)

If the reactions have identical activation barriers and are carried out under the same conditions, which one would you expect to have the faster rate?

72. Which of these two reactions would you expect to have the smaller orientation factor? Explain.

- a. O(g) + N<sub>2</sub>(g)  $\longrightarrow$  NO(g) + N(g)  
b. NO(g) + Cl<sub>2</sub>(g)  $\longrightarrow$  NOCl(g) + Cl(g)

## Reaction Mechanisms

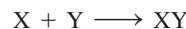
73. Consider this overall reaction, which is experimentally observed to be second order in AB and zero order in C:



Is the following mechanism valid for this reaction?



74. Consider this overall reaction, which is experimentally observed to be second order in X and first order in Y:



- a. Does the reaction occur in a single step in which X and Y collide?  
b. Is this two-step mechanism valid?



75. Consider this three-step mechanism for a reaction:



- a. What is the overall reaction?  
b. Identify the intermediates in the mechanism.  
c. What is the predicted rate law?

76. Consider this two-step mechanism for a reaction:



- a. What is the overall reaction?  
b. Identify the intermediates in the mechanism.  
c. What is the predicted rate law?

## Catalysis

77. Many heterogeneous catalysts are deposited on high surface-area supports. Why?

78. Suppose that the reaction A  $\longrightarrow$  products is exothermic and has an activation barrier of 75 kJ/mol. Sketch an energy diagram showing the energy of the reaction as a function of the progress of the reaction. Draw a second energy curve showing the effect of a catalyst.

- 79.** Suppose that a catalyst lowers the activation barrier of a reaction from 125 kJ/mol to 55 kJ/mol. By what factor would you expect the reaction rate to increase at 25 °C? (Assume that the frequency factors for the catalyzed and uncatalyzed reactions are identical.)
- 80.** The activation barrier for the hydrolysis of sucrose into glucose and fructose is 108 kJ/mol. If an enzyme increases the rate of the hydrolysis reaction by a factor of 1 million, how much lower must the activation barrier be when sucrose is in the active site of the enzyme? (Assume that the frequency factors for the catalyzed and uncatalyzed reactions are identical and a temperature of 25 °C.)

## Cumulative Problems

- 81.** The tabulated data were collected for this reaction at 500 °C:



| Time (h) | [CH <sub>3</sub> CN] (M) |
|----------|--------------------------|
| 0.0      | 1.000                    |
| 5.0      | 0.794                    |
| 10.0     | 0.631                    |
| 15.0     | 0.501                    |
| 20.0     | 0.398                    |
| 25.0     | 0.316                    |

- a. Determine the order of the reaction and the value of the rate constant at this temperature.
  - b. What is the half-life for this reaction (at the initial concentration)?
  - c. How long will it take for 90% of the CH<sub>3</sub>CN to convert to CH<sub>3</sub>NC?
- 82.** The tabulated data were collected for this reaction at a certain temperature:



| Time (h) | [X <sub>2</sub> Y] (M) |
|----------|------------------------|
| 0.0      | 0.100                  |
| 1.0      | 0.0856                 |
| 2.0      | 0.0748                 |
| 3.0      | 0.0664                 |
| 4.0      | 0.0598                 |
| 5.0      | 0.0543                 |

- a. Determine the order of the reaction and the value of the rate constant at this temperature.
- b. What is the half-life for this reaction (at the initial concentration)?
- c. What is the concentration of X after 10.0 hours?

- 83.** Consider the reaction:



The rate law for this reaction is:

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

Suppose the rate of the reaction at certain initial concentrations of A, B, and C is 0.0115 M/s. What is the rate of the reaction if the concentrations of A and C are doubled and the concentration of B is tripled?

- 84.** Consider the reaction:

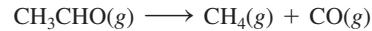


The rate law for this reaction is:

$$\text{Rate} = k \frac{[\text{O}_3]^2}{[\text{O}_2]}$$

Suppose that a 1.0 L reaction vessel initially contains 1.0 mol of O<sub>3</sub> and 1.0 mol of O<sub>2</sub>. What fraction of the O<sub>3</sub> will have reacted when the rate falls to one-half of its initial value?

- 85.** At 700 K acetaldehyde decomposes in the gas phase to methane and carbon monoxide. The reaction is:



A sample of CH<sub>3</sub>CHO is heated to 700 K and the pressure is measured as 0.22 atm before any reaction takes place. The kinetics of the reaction are followed by measurements of total pressure and these data are obtained:

| t (s)                    | 0    | 1000 | 3000 | 7000 |
|--------------------------|------|------|------|------|
| P <sub>Total</sub> (atm) | 0.22 | 0.24 | 0.27 | 0.31 |

Find the rate law, the rate constant and the total pressure after 2.00 × 10<sup>4</sup> s.

- 86.** At 400 K oxalic acid decomposes according to the reaction:



In three separate experiments, the initial pressure of oxalic acid and final total pressure after 20,000 s are measured.

| Experiment  | 1    | 2    | 3   |
|---|------|------|-----|
| P <sub>H<sub>2</sub>C<sub>2</sub>O<sub>4</sub></sub> at t = 0 | 65.8 | 92.1 | 111 |
| P <sub>Total</sub> at t = 20,000 s                            | 94.6 | 132  | 160 |

Find the rate law of the reaction and its specific rate constant.

- 87.** Dinitrogen pentoxide decomposes in the gas phase to form nitrogen dioxide and oxygen gas. The reaction is first order in dinitrogen pentoxide and has a half-life of 2.81 h at 25 °C. If a 1.5 L reaction vessel initially contains 745 torr of N<sub>2</sub>O<sub>5</sub> at 25 °C, what partial pressure of O<sub>2</sub> is present in the vessel after 215 minutes?

- 88.** Cyclopropane (C<sub>3</sub>H<sub>6</sub>) reacts to form propene (C<sub>3</sub>H<sub>6</sub>) in the gas phase. The reaction is first order in cyclopropane and has a rate constant of 5.87 × 10<sup>-4</sup>/s at 485 °C. If a 2.5 L reaction vessel initially contains 722 torr of cyclopropane at 485 °C, how long will it take for the partial pressure of cyclopropane to drop to below 1.00 × 10<sup>2</sup> torr?

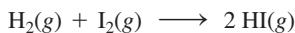
- 89.** Iodine atoms combine to form I<sub>2</sub> in liquid hexane solvent with a rate constant of 1.5 × 10<sup>10</sup> L/mol · s. The reaction is second order in I. Since the reaction occurs so quickly, the only way to study the reaction is to create iodine atoms almost instantaneously, usually by photochemical decomposition of I<sub>2</sub>. Suppose a flash of light creates an initial [I] concentration of 0.0100 M. How long will it take for 95% of the newly created iodine atoms to recombine to form I<sub>2</sub>?

90. The hydrolysis of sucrose ( $C_{12}H_{22}O_{11}$ ) into glucose and fructose in acidic water has a rate constant of  $1.8 \times 10^{-4} \text{ s}^{-1}$  at  $25^\circ\text{C}$ . Assuming the reaction is first order in sucrose, determine the mass of sucrose that is hydrolyzed when 2.55 L of a 0.150 M sucrose solution is allowed to react for 195 minutes.
91. The reaction  $\text{AB}(aq) \longrightarrow \text{A}(g) + \text{B}(g)$  is second order in AB and has a rate constant of  $0.0118 \text{ M}^{-1} \cdot \text{s}^{-1}$  at  $25.0^\circ\text{C}$ . A reaction vessel initially contains 250.0 mL of 0.100 M AB that is allowed to react to form the gaseous product. The product is collected over water at  $25.0^\circ\text{C}$ . How much time is required to produce 200.0 mL of the products at a barometric pressure of 755.1 mmHg? (The vapor pressure of water at this temperature is 23.8 mmHg.)
92. The reaction  $2 \text{H}_2\text{O}_2(aq) \longrightarrow 2 \text{H}_2\text{O}(l) + \text{O}_2(g)$  is first order in  $\text{H}_2\text{O}_2$  and under certain conditions has a rate constant of  $0.00752 \text{ s}^{-1}$  at  $20.0^\circ\text{C}$ . A reaction vessel initially contains 150.0 mL of 30.0%  $\text{H}_2\text{O}_2$  by mass solution (the density of the solution is 1.11 g/mL). The gaseous oxygen is collected over water at  $20.0^\circ\text{C}$  as it forms. What volume of  $\text{O}_2$  forms in 85.0 seconds at a barometric pressure of 742.5 mmHg? (The vapor pressure of water at this temperature is 17.5 mmHg.)
93. Consider this energy diagram:
- 
- a. How many elementary steps are involved in this reaction?  
b. Label the reactants, products, and intermediates.  
c. Which step is rate limiting?  
d. Is the overall reaction endothermic or exothermic?
94. Consider the reaction in which HCl adds across the double bond of ethene:
- $$\text{HCl} + \text{H}_2\text{C}=\text{CH}_2 \longrightarrow \text{H}_3\text{C}-\text{CH}_2\text{Cl}$$
- The following mechanism, with the accompanying energy diagram, has been suggested for this reaction:
- Step 1**  $\text{HCl} + \text{H}_2\text{C}=\text{CH}_2 \longrightarrow \text{H}_3\text{C}=\text{CH}_2^+ + \text{Cl}^-$
- Step 2**  $\text{H}_3\text{C}=\text{CH}_2^+ + \text{Cl}^- \longrightarrow \text{H}_3\text{C}-\text{CH}_2\text{Cl}$
- 
- a. Based on the energy diagram, determine which step is rate limiting.  
b. What is the expected order of the reaction based on the proposed mechanism?  
c. Is the overall reaction exothermic or endothermic?
95. The desorption of a single molecular layer of *n*-butane from a single crystal of aluminum oxide is found to be first order with a rate constant of  $0.128/\text{s}$  at  $150\text{ K}$ .
- a. What is the half-life of the desorption reaction?  
b. If the surface is initially completely covered with *n*-butane at  $150\text{ K}$ , how long will it take for 25% of the molecules to desorb? For 50% to desorb?  
c. If the surface is initially completely covered, what fraction will remain covered after 10 s? After 20 s?
96. The evaporation of a 120 nm film of *n*-pentane from a single crystal of aluminum oxide is zero order with a rate constant of  $1.92 \times 10^{13} \text{ molecules/cm}^2 \cdot \text{s}$  at  $120\text{ K}$ .
- a. If the initial surface coverage is  $8.9 \times 10^{16} \text{ molecules/cm}^2$ , how long will it take for one-half of the film to evaporate?  
b. What fraction of the film is left after 10 s? Assume the same initial coverage as in part a.
97. The kinetics of this reaction were studied as a function of temperature. (The reaction is first order in each reactant and second order overall.)
- $$\text{C}_2\text{H}_5\text{Br}(aq) + \text{OH}^-(aq) \longrightarrow \text{C}_2\text{H}_5\text{OH}(l) + \text{Br}^-(aq)$$
- | Temperature ( $^\circ\text{C}$ ) | $k(\text{L/mol} \cdot \text{s})$ |
|----------------------------------|----------------------------------|
| 25                               | $8.81 \times 10^{-5}$            |
| 35                               | 0.000285                         |
| 45                               | 0.000854                         |
| 55                               | 0.00239                          |
| 65                               | 0.00633                          |
- a. Determine the activation energy and frequency factor for the reaction.  
b. Determine the rate constant at  $15^\circ\text{C}$ .  
c. If a reaction mixture is 0.155 M in  $\text{C}_2\text{H}_5\text{Br}$  and 0.250 M in  $\text{OH}^-$ , what is the initial rate of the reaction at  $75^\circ\text{C}$ ?
98. The reaction  $2 \text{N}_2\text{O}_5 \longrightarrow 2 \text{N}_2\text{O}_4 + \text{O}_2$  takes place at around room temperature in solvents such as  $\text{CCl}_4$ . The rate constant at  $293\text{ K}$  is found to be  $2.35 \times 10^{-4} \text{ s}^{-1}$ , and at  $303\text{ K}$  the rate constant is found to be  $9.15 \times 10^{-4} \text{ s}^{-1}$ . Calculate the frequency factor for the reaction.
99. This reaction has an activation energy of zero in the gas phase:
- $$\text{CH}_3 + \text{CH}_3 \longrightarrow \text{C}_2\text{H}_6$$
- a. Would you expect the rate of this reaction to change very much with temperature?  
b. Why might the activation energy be zero?  
c. What other types of reactions would you expect to have little or no activation energy?
100. Consider the two reactions:
- $$\text{O} + \text{N}_2 \longrightarrow \text{NO} + \text{N} \quad E_a = 315 \text{ kJ/mol}$$
- $$\text{Cl} + \text{H}_2 \longrightarrow \text{HCl} + \text{H} \quad E_a = 23 \text{ kJ/mol}$$
- a. Why is the activation barrier for the first reaction so much higher than that for the second?  
b. The frequency factors for these two reactions are very close to each other in value. Assuming that they are the same, calculate the ratio of the reaction rate constants for these two reactions at  $25^\circ\text{C}$ .

- 101.** Anthropologists can estimate the age of a bone or other sample of organic matter by its carbon-14 content. The carbon-14 in a living organism is constant until the organism dies, after which carbon-14 decays with first-order kinetics and a half-life of 5730 years. Suppose a bone from an ancient human contains 19.5% of the C-14 found in living organisms. How old is the bone?

- 102.** Geologists can estimate the age of rocks by their uranium-238 content. The uranium is incorporated in the rock as it hardens and then decays with first-order kinetics and a half-life of 4.5 billion years. A rock contains 83.2% of the amount of uranium-238 that it contained when it was formed. (The amount that the rock contained when it was formed can be deduced from the presence of the decay products of U-238.) How old is the rock?

- 103.** Consider the gas-phase reaction:

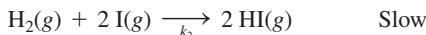


The reaction was experimentally determined to be first order in  $\text{H}_2$  and first order in  $\text{I}_2$ . Consider the proposed mechanisms.

Proposed mechanism I:

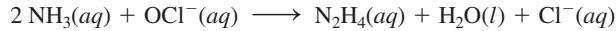


Proposed mechanism II:

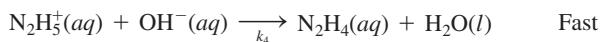
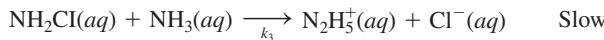


- a. Show that both of the proposed mechanisms are valid.
- b. What kind of experimental evidence might lead you to favor mechanism II over mechanism I?

- 104.** Consider the reaction:

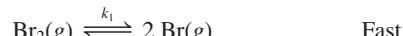


This three-step mechanism is proposed:



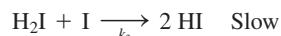
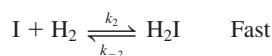
- a. Show that the mechanism sums to the overall reaction.
- b. What is the rate law predicted by this mechanism?

- 105.** The proposed mechanism for the formation of hydrogen bromide can be written in a simplified form as:



What rate law corresponds to this mechanism?

- 106.** A proposed mechanism for the formation of hydrogen iodide can be written in simplified form as



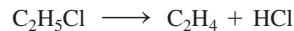
What rate law corresponds to this mechanism?

- 107.** A certain substance X decomposes. Fifty percent of X remains after 100 minutes. How much X remains after 200 minutes if the reaction order with respect to X is (a) zero order, (b) first order, (c) second order?

- 108.** The half-life for radioactive decay (a first-order process) of plutonium-239 is 24,000 years. How many years does it take for one mole of this radioactive material to decay until just one atom remains?

- 109.** The energy of activation for the decomposition of 2 mol of HI to  $\text{H}_2$  and  $\text{I}_2$  in the gas phase is 185 kJ. The heat of formation of  $\text{HI}(g)$  from  $\text{H}_2(g)$  and  $\text{I}_2(g)$  is  $-5.65 \text{ kJ/mol}$ . Find the energy of activation for the reaction of 1 mol of  $\text{H}_2$  and 1 mol of  $\text{I}_2$  to form 2 mol of HI in the gas phase.

- 110.** Ethyl chloride vapor decomposes by the first-order reaction:



The activation energy is 249 kJ/mol, and the frequency factor is  $1.6 \times 10^{14} \text{ s}^{-1}$ . Find the value of the specific rate constant at 710 K. What fraction of the ethyl chloride decomposes in 15 minutes at this temperature? Find the temperature at which the rate of the reaction would be twice as fast.

## Challenge Problems

- 111.** In this chapter we have seen a number of reactions in which a single reactant forms products. For example, consider the following first-order reaction:



However, we also learned that gas-phase reactions occur through collisions.

- a. One possible explanation is that two molecules of  $\text{CH}_3\text{NC}$  collide with each other and form two molecules of the product in a single elementary step. If that were the case, what reaction order would you expect?

- b. Another possibility is that the reaction occurs through more than one step. For example, a possible mechanism involves one step in which the two  $\text{CH}_3\text{NC}$  molecules collide, resulting in the “activation” of one of them. In a second step, the activated molecule goes on to form the product. Write down this mechanism and determine which step must be rate determining in order for the kinetics of the reaction to be first order. Show explicitly how the mechanism predicts first-order kinetics.

- 112.** The first-order *integrated* rate law for a reaction  $A \longrightarrow$  products is derived from the rate law using calculus:

$$\text{Rate} = k[A] \text{ (first-order rate law)}$$

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

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

The equation just given is a first-order, separable differential equation that can be solved by separating the variables and integrating:

$$\frac{d[A]}{[A]} = -kdt$$

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

In the integral just given,  $[A]_0$  is the initial concentration of A. We then evaluate the integral:

$$[\ln[A]]_{[A]_0}^{[A]} = -kt'_0$$

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

$$\ln[A] = -kt + \ln[A]_0 \text{ (integrated rate law)}$$

- a. Use a procedure similar to the one just to derive an integrated rate law for a reaction  $A \longrightarrow$  products, which is one-half order in the concentration of A (that is, Rate =  $k[A]^{1/2}$ ).
  - b. Use the result from part a to derive an expression for the half-life of a one-half-order reaction.
- 113.** The previous exercise shows how the first-order integrated rate law is derived from the first-order differential rate law. Begin with the second-order differential rate law and derive the second-order integrated rate law.

- 114.** The rate constant for the first-order decomposition of  $\text{N}_2\text{O}_5(g)$  to  $\text{NO}_2(g)$  and  $\text{O}_2(g)$  is  $7.48 \times 10^{-3} \text{ s}^{-1}$  at a given temperature.

- a. Find the length of time required for the total pressure in a system containing  $\text{N}_2\text{O}_5$  at an initial pressure of 0.100 atm to rise to 0.145 atm.

- b. To 0.200 atm.

- c. Find the total pressure after 100 s of reaction.

- 115.** Phosgene ( $\text{Cl}_2\text{CO}$ ), a poison gas used in World War I, is formed by the reaction of  $\text{Cl}_2$  and CO. The proposed mechanism for the reaction is:



What rate law is consistent with this mechanism?

- 116.** The rate of decomposition of  $\text{N}_2\text{O}_3(g)$  to  $\text{NO}_2(g)$  and  $\text{NO}(g)$  is followed by measuring  $[\text{NO}_2]$  at different times. The following data are obtained.

|                               |   |       |       |       |        |
|-------------------------------|---|-------|-------|-------|--------|
| $[\text{NO}_2](\text{mol/L})$ | 0 | 0.193 | 0.316 | 0.427 | 0.784  |
| t (s)                         | 0 | 884   | 1610  | 2460  | 50,000 |

The reaction follows a first-order rate law. Calculate the rate constant. Assume that after 50,000 s all the  $\text{N}_2\text{O}_3(g)$  had decomposed.

- 117.** At 473 K, for the elementary reaction  $2 \text{ NOCl}(g) \xrightleftharpoons[k_{-1}]{k_1} 2 \text{ NO}(g) + \text{Cl}_2(g)$

$$k_1 = 7.8 \times 10^{-2} \text{ L/mol s} \quad \text{and}$$

$$k_{-1} = 4.7 \times 10^2 \text{ L}^2/\text{mol}^2 \text{ s}$$

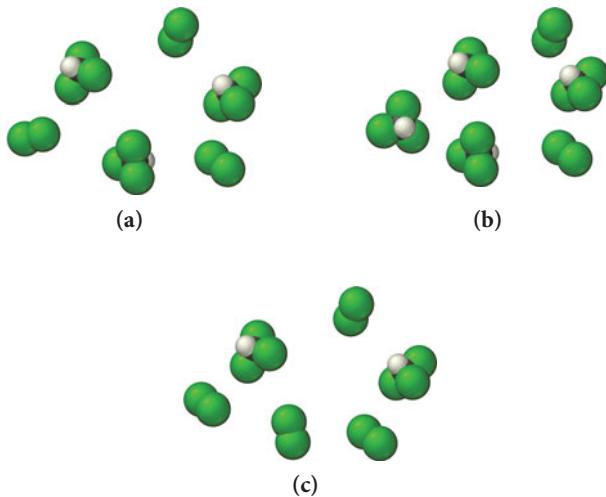
A sample of  $\text{NOCl}$  is placed in a container and heated to 473 K. When the system comes to equilibrium,  $[\text{NOCl}]$  is found to be 0.12 mol/L. What are the concentrations of NO and  $\text{Cl}_2$ ?

## Conceptual Problems

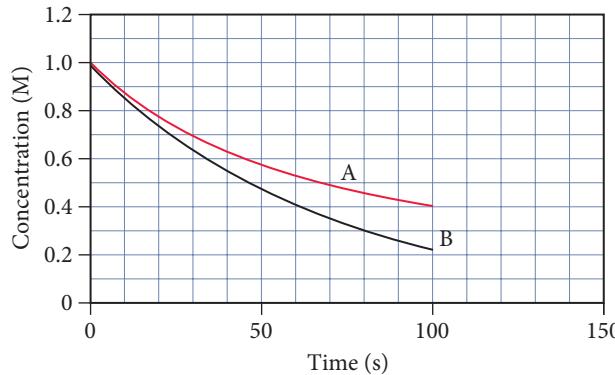
- 118.** Consider the reaction:



The reaction is first order in  $\text{CHCl}_3$  and one-half order in  $\text{Cl}_2$ . Which reaction mixture would you expect to have the fastest initial rate?



- 119.** The accompanying graph shows the concentration of a reactant as a function of time for two different reactions. One of the reactions is first order and the other is second order. Which of the two reactions is first order? Second order? How would you change each plot to make it linear?



- 120.** A particular reaction,  $A \longrightarrow$  products, has a rate that slows down as the reaction proceeds. The half-life of the reaction is found to depend on the initial concentration of A. Determine whether each statement is likely to be true or false for this reaction.
- A doubling of the concentration of A doubles the rate of the reaction.
  - A plot of  $1/[A]$  versus time is linear.
  - The half-life of the reaction gets longer as the initial concentration of A increases.
  - A plot of the concentration of A versus time has a constant slope.

## Answers to Conceptual Connections

### Reaction Rates

- 13.1** (c) The rate at which B changes is twice the rate of the reaction because its coefficient is 2, and it is negative because B is a reactant.

### Order of Reaction

- 13.2** (d) Since the reaction is second order, increasing the concentration of A by a factor of 5 causes the rate to increase by  $5^2$  or 25.

### Rate and Concentration

- 13.3** All three mixtures have the same total number of molecules, but mixture (c) has the greatest number of NO molecules. Since the reaction is second order in NO and only first order in O<sub>2</sub>, mixture (c) has the fastest initial rate.

### Rate Law and Integrated Rate Law

- 13.4** (c) The reaction is most likely second order because its rate depends on the concentration (therefore it cannot be zero order), and its half-life depends on the initial concentration

(therefore it cannot be first order). For a second-order reaction, a doubling of the initial concentration results in the quadrupling of the rate.

### Temperature Dependence of Reaction Rate

- 13.5** Reaction A has a faster rate because it has a lower activation energy; therefore, the exponential factor is larger at a given temperature, making the rate constant larger. (With a larger rate constant and the same initial concentration, the rate will be faster).

### Collision Theory

- 13.6** (c) Since the reactants in part (a) are atoms, the orientation factor should be about one. The reactants in parts (b) and (c) are both molecules, so we expect orientation factors of less than one. Since the reactants in (b) are symmetrical, we would not expect the collision to have as specific an orientation requirement as in (c), where the reactants are asymmetrical and must therefore collide in such way that a hydrogen atom is in close proximity to another hydrogen atom. Therefore, we expect (c) to have the smallest orientation factor.

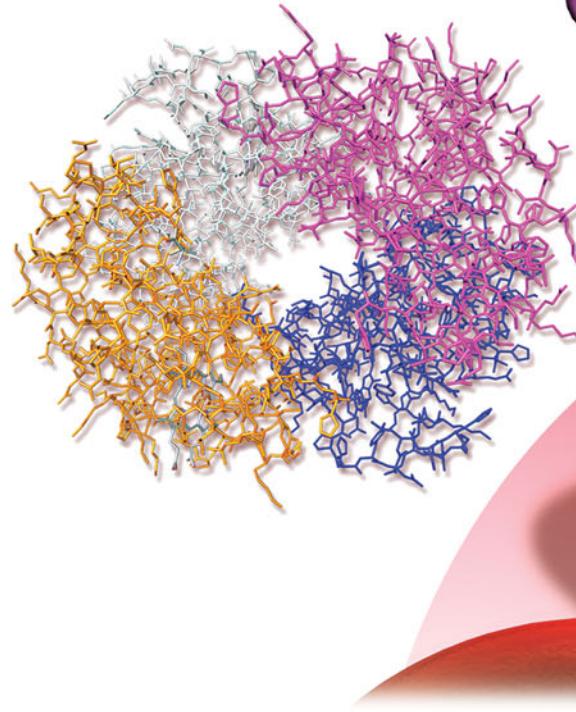
# 14

# Chemical Equilibrium

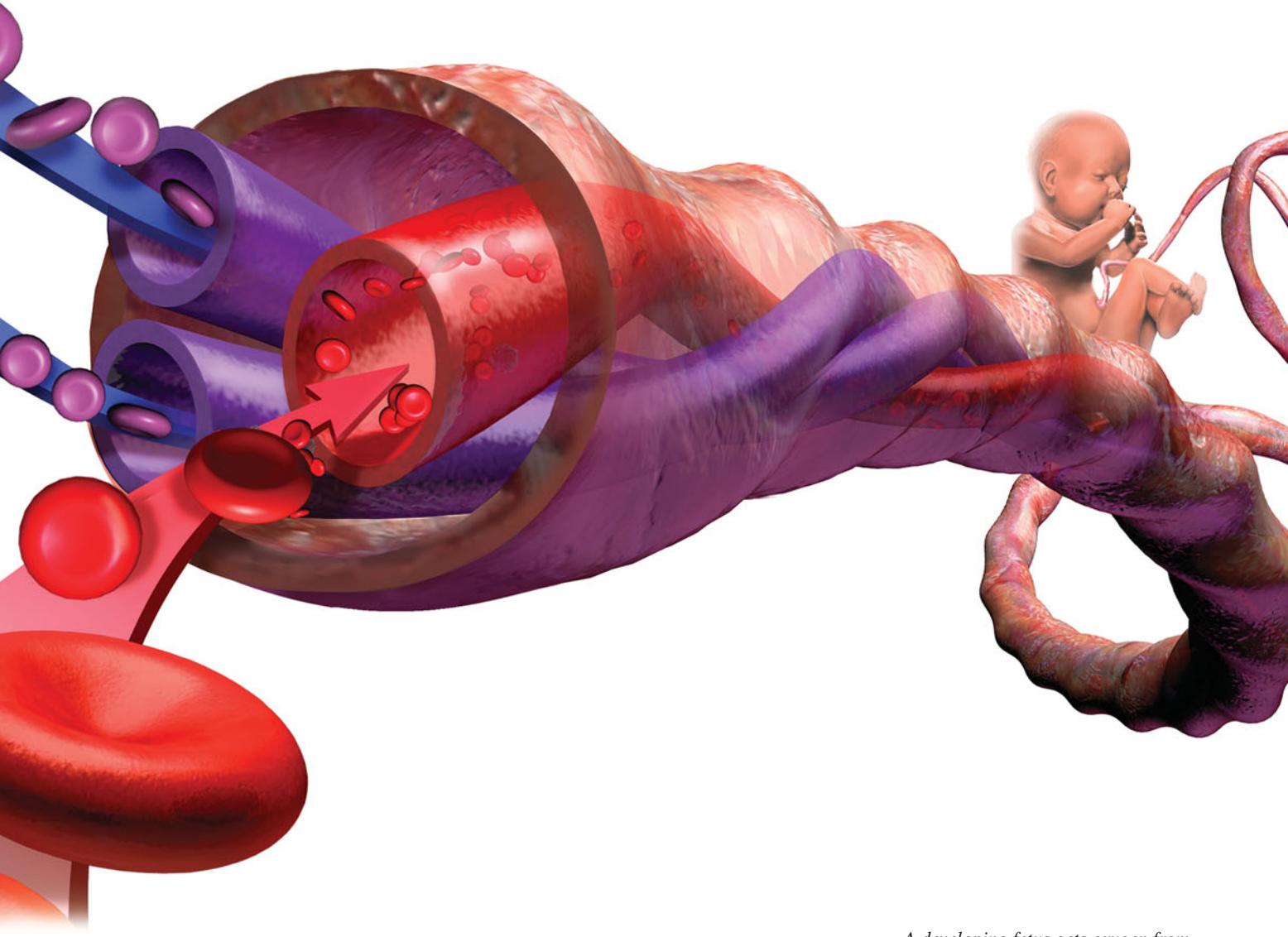
*Every system in chemical equilibrium, under the influence of a change of any one of the factors of equilibrium, undergoes a transformation . . . [that produces a change] . . . in the opposite direction of the factor in question.*

—Henri Le Châtelier (1850–1936)

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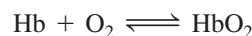
In Chapter 13, we examined *how fast* a chemical reaction occurs. In this chapter we examine *how far* a chemical reaction goes. The *speed* of a chemical reaction is determined by kinetics. The *extent* of a chemical reaction is determined by thermodynamics. In this chapter, we focus on describing and quantifying how far a chemical reaction goes based on an experimentally measurable quantity called *the equilibrium constant*. A reaction with a large equilibrium constant proceeds nearly to completion—nearly all the reactants react to form products. A reaction with a small equilibrium constant barely proceeds at all—nearly all the reactants remain as reactants, hardly forming any products. In this chapter we simply accept the equilibrium constant as an experimentally measurable quantity and learn how to use it to predict and quantify the extent of a reaction. In Chapter 17, we will explore the reasons underlying the magnitude of equilibrium constants.



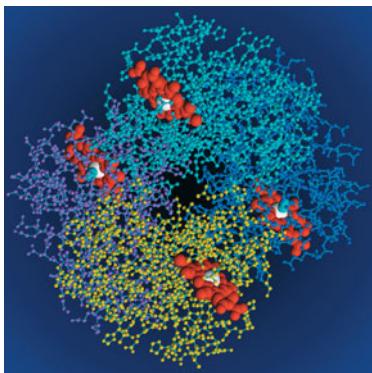
A developing fetus gets oxygen from the mother's blood because the reaction between oxygen and fetal hemoglobin has a larger equilibrium constant than the reaction between oxygen and maternal hemoglobin.

## 14.1 Fetal Hemoglobin and Equilibrium

Have you ever wondered how a baby in the womb gets oxygen? Unlike you and me, a fetus does not breathe air. Yet, like you and me, a fetus needs oxygen. Where does that oxygen come from? After we are born, we inhale air into our lungs and that air diffuses into capillaries, where it comes into contact with our blood. Within our red blood cells, a protein called hemoglobin (Hb) reacts with oxygen according to the chemical equation:



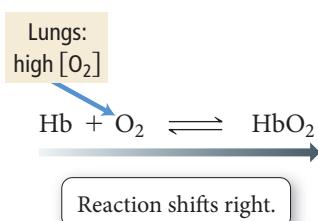
The double arrows in this equation indicate that the reaction can occur in both the forward and reverse directions and can reach chemical *equilibrium*. We encountered this term in Chapters 11 and 12, and we define it more carefully in the next section.



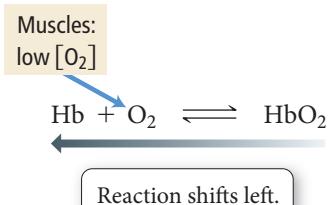
▲ Hemoglobin is the oxygen-carrying protein in red blood cells. Oxygen binds to iron atoms, which are depicted here in white.

For now, understand that the concentrations of the reactants and products in a reaction at equilibrium are described by the *equilibrium constant*,  $K$ . A large value of  $K$  means that the reaction lies far to the right at equilibrium—a high concentration of products and a low concentration of reactants. A small value of  $K$  means that the reaction lies far to the left at equilibrium—a high concentration of reactants and a low concentration of products. In other words, the value of  $K$  is a measure of how far a reaction proceeds—the larger the value of  $K$ , the more the reaction proceeds toward the products.

The equilibrium constant for the reaction between hemoglobin and oxygen is such that hemoglobin efficiently binds oxygen at typical lung oxygen concentrations, but it can also release oxygen under the appropriate conditions. Any system at equilibrium, including the hemoglobin–oxygen system, responds to changes in ways that maintain equilibrium. If any of the concentrations of the reactants or products change, the reaction shifts to counteract that change. For the hemoglobin system, as blood flows through the lungs where oxygen concentrations are high, the equilibrium shifts to the right—hemoglobin binds oxygen:

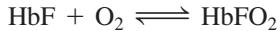


As blood flows out of the lungs and into muscles and organs where oxygen concentrations have been depleted (because muscles and organs use oxygen), the equilibrium shifts to the left—hemoglobin releases oxygen:

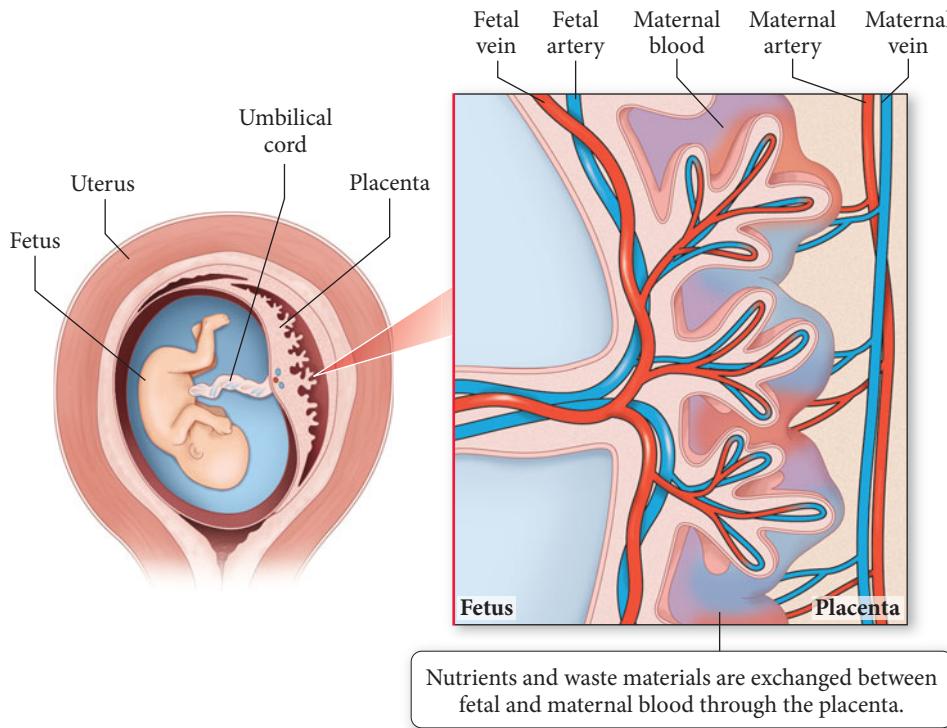


In other words, in order to maintain equilibrium, *hemoglobin binds oxygen when the surrounding oxygen concentration is high, but it releases oxygen when the surrounding oxygen concentration is low*. In this way, hemoglobin transports oxygen from the lungs to all parts of the body that use oxygen.

A fetus has its own circulatory system. The mother's blood never flows into the fetus's body, and the fetus cannot get any air in the womb. How, then, does the fetus get oxygen? The answer lies in the properties of fetal hemoglobin (HbF), which is slightly different from adult hemoglobin. Like adult hemoglobin, fetal hemoglobin is in equilibrium with oxygen:



However, the equilibrium constant for fetal hemoglobin is larger than the equilibrium constant for adult hemoglobin, meaning that the reaction tends to go farther in the direction of the product. Consequently, fetal hemoglobin loads oxygen at a lower oxygen concentration than does adult hemoglobin. In the placenta, fetal blood flows in close proximity to maternal blood. Although the two never mix, because of the different equilibrium constants, the maternal hemoglobin releases oxygen that the fetal hemoglobin then binds and carries into its own circulatory system (Figure 14.1 ►). Nature has evolved a chemical system through which the mother's hemoglobin can in effect *hand off* oxygen to the hemoglobin of the fetus.

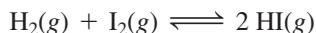


◀ FIGURE 14.1 Oxygen Exchange between the Maternal and Fetal Circulation

In the placenta, the blood of the fetus comes into close proximity with that of the mother, although the two do not mix directly. Because the reaction of fetal hemoglobin with oxygen has a larger equilibrium constant than the reaction of maternal hemoglobin with oxygen, the fetus receives oxygen from the mother's blood.

## 14.2 The Concept of Dynamic Equilibrium

Recall from the previous chapter that reaction rates generally increase with increasing concentration of the reactants (unless the reaction order is zero) and decrease with decreasing concentration of the reactants. With this in mind, consider the reaction between hydrogen and iodine:



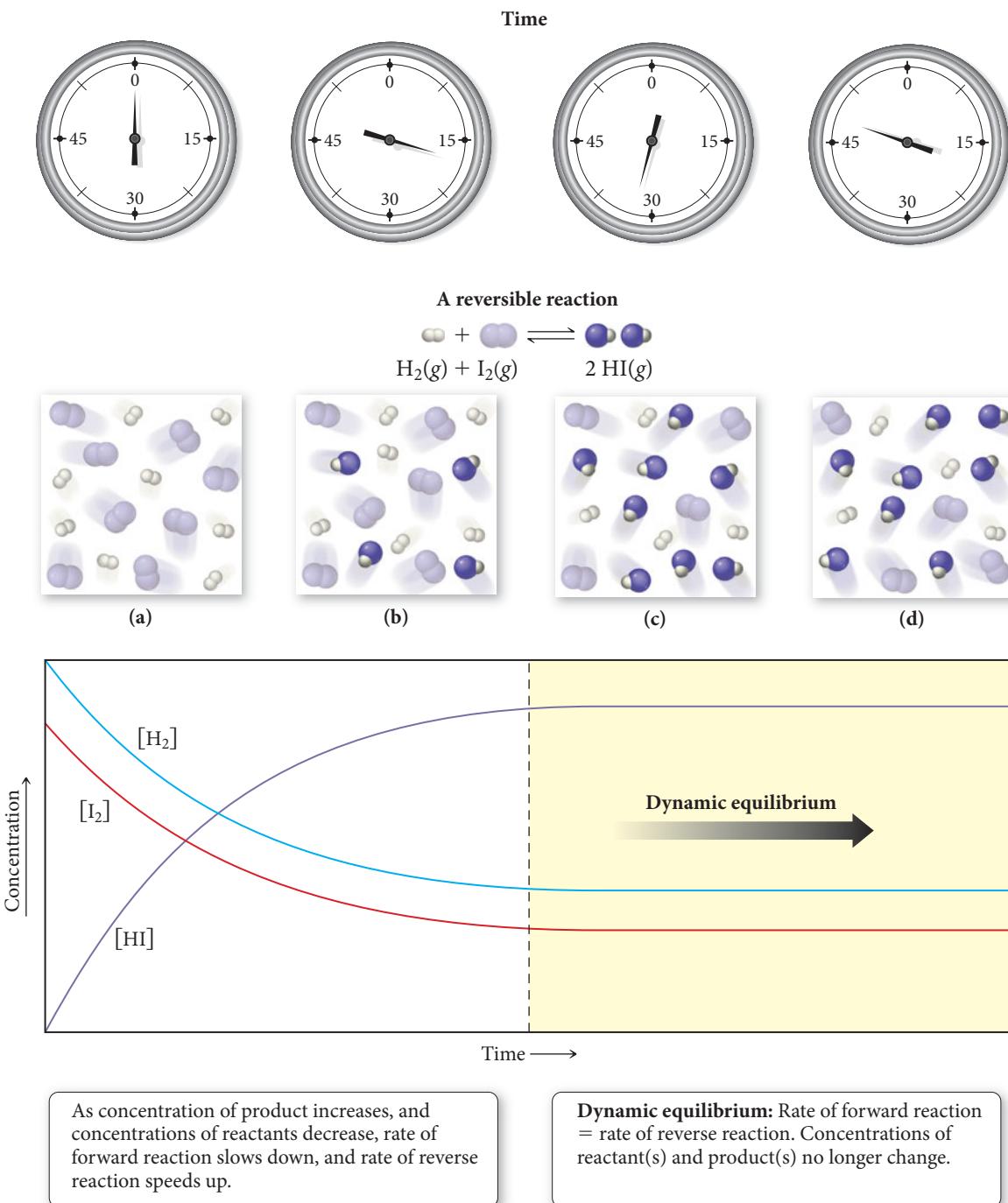
In this reaction,  $\text{H}_2$  and  $\text{I}_2$  react to form 2 HI molecules, but the 2 HI molecules can also react to re-form  $\text{H}_2$  and  $\text{I}_2$ . A reaction such as this one—that can proceed in both the forward and reverse directions—is said to be **reversible**. Suppose we begin with only  $\text{H}_2$  and  $\text{I}_2$  in a container (Figure 14.2a ▶). What happens? Initially  $\text{H}_2$  and  $\text{I}_2$  begin to react to form HI (Figure 14.2b). However, as  $\text{H}_2$  and  $\text{I}_2$  react, their concentrations decrease, which in turn *decreases the rate of the forward reaction*. At the same time, HI begins to form. As the concentration of HI increases, the reverse reaction begins to occur at a faster and faster rate. Eventually the rate of the reverse reaction (which has been increasing) equals the rate of the forward reaction (which has been decreasing). At that point, **dynamic equilibrium** is reached (Figure 14.2c, d).

**Dynamic equilibrium for a chemical reaction is the condition in which the rate of the forward reaction equals the rate of the reverse reaction.**

Dynamic equilibrium is called “dynamic” because the forward and reverse reactions are still occurring; however, they are occurring at the same rate. When dynamic equilibrium is reached, the concentrations of  $\text{H}_2$ ,  $\text{I}_2$ , and HI no longer change. They remain constant because the reactants and products form at the same rate that they are depleted. Note that just because the concentrations of reactants and products no longer change at equilibrium *does not mean that the concentrations of reactants and products are equal to one another* at equilibrium. Some reactions reach equilibrium only after most of the reactants have formed products. Others reach equilibrium when only a small fraction of the reactants have formed products. It depends on the reaction.

Nearly all chemical reactions are at least theoretically reversible. In many cases, however, the reversibility is so small that it can be ignored.

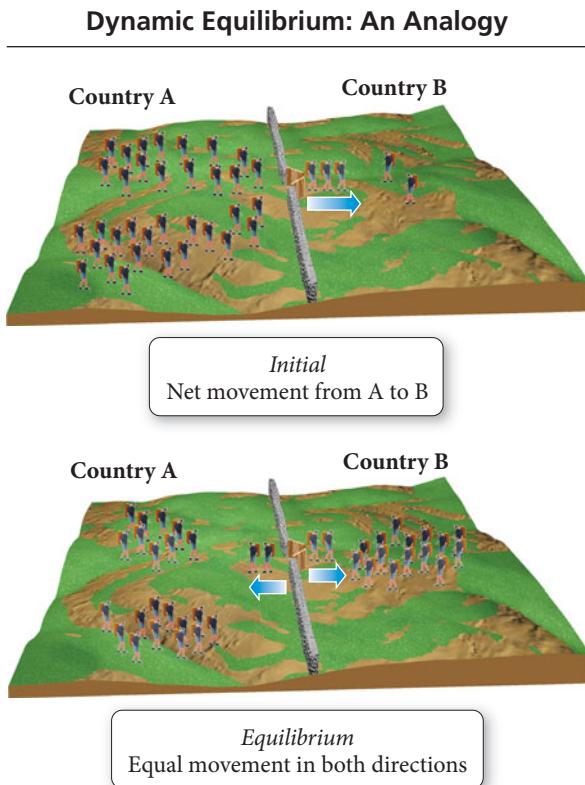
## Dynamic Equilibrium



**▲ FIGURE 14.2 Dynamic Equilibrium** Equilibrium is reached in a chemical reaction when the concentrations of the reactants and products no longer change. The molecular images depict the progress of the reaction  $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2 \text{HI}(g)$ . The graph shows the concentrations of  $\text{H}_2$ ,  $\text{I}_2$ , and  $\text{HI}$  as a function of time. When equilibrium is reached, both the forward and reverse reactions continue, but at equal rates, so the concentrations of the reactants and products remain constant.

We can better understand dynamic equilibrium with a simple analogy. Imagine two neighboring countries (A and B) with a closed border between them (Figure 14.3 ▶). Country A is overpopulated and Country B is underpopulated. One day, the border between the two countries opens, and people immediately begin to leave Country A for Country B.

Country A → Country B



◀ **FIGURE 14.3** A Population Analogy for Chemical Equilibrium Because Country A is initially overpopulated, people migrate from Country A to Country B. As the population of Country A falls and that of Country B rises, the rate of migration from Country A to Country B decreases and the rate of migration from Country B to Country A increases. Eventually the two rates become equal. Equilibrium has been reached.

The population of Country A goes down as the population of Country B goes up. As people leave Country A, however, the *rate* at which they leave slows down, because as Country A becomes less populated, the pool of potential emigrants gets smaller. (In other words, the rate of emigration is directly proportional to the population—as the population decreases, the emigration rate goes down.) On the other hand, as people move into Country B, it gets more crowded and some people begin to move from Country B to Country A.



As the population of Country B continues to grow, the rate of people moving out of Country B gets faster. Eventually the *rate* of people moving out of Country A (which has been slowing down as people leave) equals the *rate* of people moving out of Country B (which has been increasing as Country B gets more crowded). Dynamic equilibrium has been reached.



Notice that when the two countries reach dynamic equilibrium, their populations no longer change, because the number of people moving out of either country equals the number of people moving in. However, one country—because of its charm or the availability of good jobs or lower taxes, or for whatever other reason—may have a higher population than the other country, even when dynamic equilibrium is reached.

Similarly, when a chemical reaction reaches dynamic equilibrium, the rate of the forward reaction equals the rate of the reverse reaction, and the relative concentrations of reactants and products become *constant*. But the concentrations of reactants and products will not necessarily be *equal* at equilibrium, just as the populations of the two countries are not necessarily equal at equilibrium.

## 14.3 The Equilibrium Constant ( $K$ )

We have just seen that the *concentrations of reactants and products* are not equal at equilibrium—rather, the *rates of the forward and reverse reactions* are equal. So what about the concentrations? The *equilibrium constant* is a way to quantify the concentrations of the reactants and products at equilibrium.

We distinguish between the equilibrium constant ( $K$ ) and the Kelvin unit of temperature (K) by italicizing the equilibrium constant.

Consider the general chemical equation:



where A and B are reactants, C and D are products, and  $a$ ,  $b$ ,  $c$ , and  $d$  are the respective stoichiometric coefficients in the chemical equation. The **equilibrium constant ( $K$ )** for the reaction is defined as the ratio—*at equilibrium*—of the concentrations of the products raised to their stoichiometric coefficients divided by the concentrations of the reactants raised to their stoichiometric coefficients.

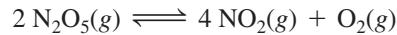
### Law of Mass Action

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

In this notation,  $[A]$  represents the molar concentration of A. The equilibrium constant quantifies the relative concentrations of reactants and products *at equilibrium*. The relationship between the balanced chemical equation and the expression of the equilibrium constant is known as the **law of mass action**.

### Expressing Equilibrium Constants for Chemical Reactions

To express an equilibrium constant for a chemical reaction, we examine the balanced chemical equation and apply the law of mass action. For example, suppose we want to express the equilibrium constant for the reaction:



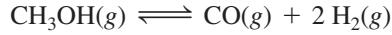
The equilibrium constant is  $[\text{NO}_2]$  raised to the fourth power multiplied by  $[\text{O}_2]$  raised to the first power divided by  $[\text{N}_2\text{O}_5]$  raised to the second power:

$$K = \frac{[\text{NO}_2]^4[\text{O}_2]}{[\text{N}_2\text{O}_5]^2}$$

Notice that the *coefficients* in the chemical equation become the *exponents* in the expression of the equilibrium constant.

#### EXAMPLE 14.1 Expressing Equilibrium Constants for Chemical Equations

Express the equilibrium constant for the chemical equation:



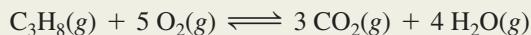
#### SOLUTION

The equilibrium constant is the equilibrium concentrations of the products raised to their stoichiometric coefficients divided by the equilibrium concentrations of the reactants raised to their stoichiometric coefficients.

$$K = \frac{[\text{CO}][\text{H}_2]^2}{[\text{CH}_3\text{OH}]}$$

#### FOR PRACTICE 14.1

Express the equilibrium constant for the combustion of propane as shown by the balanced chemical equation:

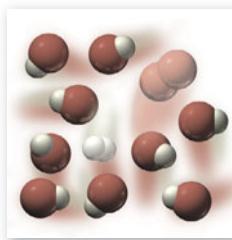
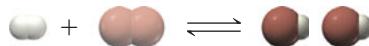
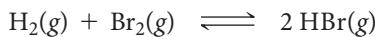


## The Significance of the Equilibrium Constant

You now know how to express the equilibrium constant, but what does it mean? What, for example, does a large equilibrium constant ( $K \gg 1$ ) imply about a reaction? A large equilibrium constant indicates that the numerator (which specifies the amounts of products at equilibrium) is larger than the denominator (which specifies the amounts of reactants at equilibrium). Therefore, when the equilibrium constant is large, the forward reaction is favored. For example, consider the reaction:



The equilibrium constant is large, indicating that the equilibrium point for the reaction lies far to the right—high concentrations of products, low concentrations of reactants (Figure 14.4 ▶). Remember that the equilibrium constant says nothing about *how fast* a reaction reaches equilibrium, only *how far* the reaction has proceeded once equilibrium is reached. A reaction with a large equilibrium constant may be kinetically very slow and take a long time to reach equilibrium.



$$K = \frac{[\text{HBr}]^2}{[\text{H}_2][\text{Br}_2]} = \text{large number}$$

**◀ FIGURE 14.4 The Meaning of a Large Equilibrium Constant** If the equilibrium constant for a reaction is large, the equilibrium point of the reaction lies far to the right—the concentration of products is large and the concentration of reactants is small.

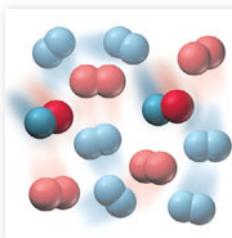
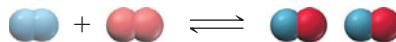
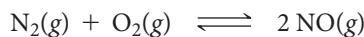
Conversely, what does a *small* equilibrium constant ( $K \ll 1$ ) mean? It indicates that the reverse reaction is favored and that there will be more reactants than products when equilibrium is reached. For example, consider the reaction:



The equilibrium constant is very small, indicating that the equilibrium point for the reaction lies far to the left—high concentrations of reactants, low concentrations of products (Figure 14.5 ▶). This is fortunate because  $\text{N}_2$  and  $\text{O}_2$  are the main components of air. If this equilibrium constant were large, much of the  $\text{N}_2$  and  $\text{O}_2$  in air would react to form NO, a toxic gas.

### Summarizing the Significance of the Equilibrium Constant:

- ▶  $K \ll 1$  Reverse reaction is favored; forward reaction does not proceed very far.
- ▶  $K \approx 1$  Neither direction is favored; forward reaction proceeds about halfway.
- ▶  $K \gg 1$  Forward reaction is favored; forward reaction proceeds essentially to completion.



$$K = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = \text{small number}$$

**◀ FIGURE 14.5 The Meaning of a Small Equilibrium Constant** If the equilibrium constant for a reaction is small, the equilibrium point of the reaction lies far to the left—the concentration of products is small and the concentration of reactants is large.

## Conceptual Connection 14.1 Equilibrium Constants

The equilibrium constant for the reaction  $A(g) \rightleftharpoons B(g)$  is 10. A reaction mixture initially contains  $[A] = 1.1\text{ M}$  and  $[B] = 0.0\text{ M}$ . Which statement is true at equilibrium?

- (a) The reaction mixture will contain  $[A] = 1.0\text{ M}$  and  $[B] = 0.1\text{ M}$ .
- (b) The reaction mixture will contain  $[A] = 0.1\text{ M}$  and  $[B] = 1.0\text{ M}$ .
- (c) The reaction mixture will contain equal concentrations of A and B.

### Relationships between the Equilibrium Constant and the Chemical Equation

If a chemical equation is modified in some way, then the equilibrium constant for the equation changes because of the modification. The three modifications discussed here are common.

- If you reverse the equation, invert the equilibrium constant.** For example, consider this equilibrium equation:



The expression for the equilibrium constant of this reaction is:

$$K_{\text{forward}} = \frac{[C]^3}{[A][B]^2}$$



## Chemistry and Medicine

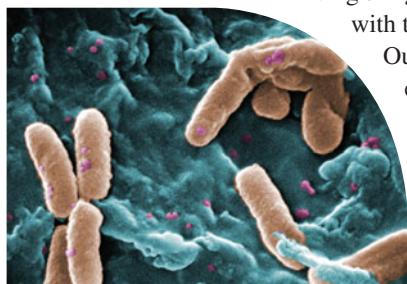
### Life and Equilibrium

Have you ever tried to define life? If you have, you probably know that a definition is elusive. How are living things different from nonliving things? You may try to define living things as those things that can move. But of course many living things do not move (most plants, for example), and some nonliving things, such as glaciers and Earth itself, do move. So motion is neither unique to nor definitive of life. You may try to define living things as those things that can reproduce. But again, many living things, such as mules or sterile humans, cannot reproduce; yet they are alive. In addition, some nonliving things, such as crystals, for example, reproduce (in some sense). So what is unique about living things?

One definition of life involves the concept of equilibrium—living things *are not* in equilibrium with their surroundings.

Our body temperature, for example, is not the same as the temperature of our surroundings. If we jump into a

◀ What makes these cells alive?

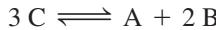


swimming pool, the acidity of our blood does not become the same as the acidity of the surrounding water. Living things, even the simplest ones, maintain some measure of *disequilibrium* with their environment.

We must add one more concept, however, to complete our definition of life with respect to equilibrium. A cup of hot water is in disequilibrium with its environment with respect to temperature, yet it is not alive. The cup of hot water has no control over its disequilibrium, however, and will slowly come to equilibrium with its environment. In contrast, living things—as long as they are alive—maintain and *control* their disequilibrium. Your body temperature, for example, is not *only* in disequilibrium with your surroundings—it is in *controlled disequilibrium*. Your body maintains your temperature within a specific range that is not in equilibrium with the surrounding temperature.

So, one criterion for life is that living things are in *controlled disequilibrium* with their environment. Maintaining disequilibrium is a main activity of living organisms, requiring energy obtained from their environment. Plants derive that energy from sunlight; animals eat plants (or other animals that have eaten plants), and thus they too ultimately derive their energy from the sun. A living thing comes into equilibrium with its surroundings only after it dies.

If we reverse the equation:



then, according to the law of mass action, the expression for the equilibrium constant becomes:

$$K_{\text{reverse}} = \frac{[\text{A}][\text{B}]^2}{[\text{C}]^3} = \frac{1}{K_{\text{forward}}}$$

- 2. If you multiply the coefficients in the equation by a factor, raise the equilibrium constant to the same factor.** Consider again this chemical equation and corresponding expression for the equilibrium constant:



If we multiply the equation by  $n$ , we get:



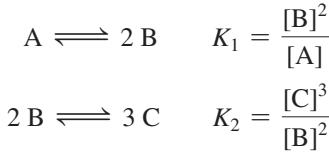
Applying the law of mass action, the expression for the equilibrium constant becomes:

$$K' = \frac{[\text{C}]^{3n}}{[\text{A}]^n[\text{B}]^{2n}} = \left( \frac{[\text{C}]^3}{[\text{A}][\text{B}]^2} \right)^n = K^n$$

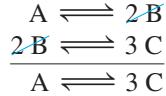
If  $n$  is a fractional quantity, raise  $K$  to the same fractional quantity.

Remember that  $(x^a)^b = x^{ab}$ .

- 3. If you add two or more individual chemical equations to obtain an overall equation, multiply the corresponding equilibrium constants by each other to obtain the overall equilibrium constant.** Consider these two chemical equations and their corresponding equilibrium constant expressions:



The two equations sum as follows:



According to the law of mass action, the equilibrium constant for this overall equation is then:

$$K_{\text{overall}} = \frac{[\text{C}]^3}{[\text{A}]}$$

Notice that  $K_{\text{overall}}$  is the product of  $K_1$  and  $K_2$ :

$$\begin{aligned} K_{\text{overall}} &= K_1 \times K_2 \\ &= \frac{[\text{B}]^2}{[\text{A}]} \times \frac{[\text{C}]^3}{[\text{B}]^2} \\ &= \frac{[\text{C}]^3}{[\text{A}]} \end{aligned}$$

### Conceptual Connection 14.2 The Equilibrium Constant and the Chemical Equation

The reaction  $\text{A}(g) \rightleftharpoons 2 \text{ B}(g)$  has an equilibrium constant of  $K = 0.010$ . What is the equilibrium constant for the reaction  $\text{B}(g) \rightleftharpoons \frac{1}{2} \text{ A}(g)$ ?

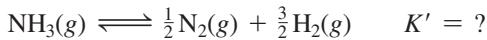
- (a) 1      (b) 10      (c) 100      (d) 0.0010

**EXAMPLE 14.2** Manipulating the Equilibrium Constant to Reflect Changes in the Chemical Equation

Consider the chemical equation and equilibrium constant for the synthesis of ammonia at 25 °C:

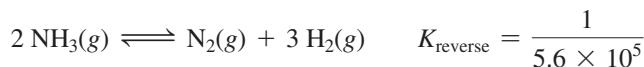


Calculate the equilibrium constant for the following reaction at 25 °C:

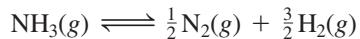

**SOLUTION**

You want to manipulate the given reaction and value of  $K$  to obtain the desired reaction and value of  $K$ . You can see that the given reaction is the reverse of the desired reaction, and its coefficients are twice those of the desired reaction.

Begin by reversing the given reaction and taking the inverse of the value of  $K$ .



Next, multiply the reaction by  $\frac{1}{2}$  and raise the equilibrium constant to the  $\frac{1}{2}$  power.



$$K' = K_{\text{reverse}}^{1/2} = \left( \frac{1}{5.6 \times 10^5} \right)^{1/2}$$

Calculate the value of  $K'$ .

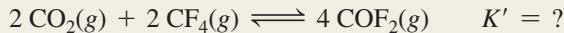
$$K' = 1.3 \times 10^{-3}$$

**FOR PRACTICE 14.2**

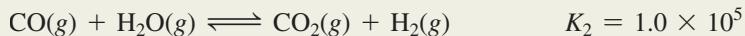
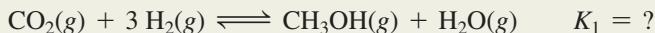
Consider the following chemical equation and equilibrium constant at 25 °C:



Calculate the equilibrium constant for the following reaction at 25 °C:


**FOR MORE PRACTICE 14.2**

Predict the equilibrium constant for the first reaction shown here given the equilibrium constants for the second and third reactions:



## 14.4 Expressing the Equilibrium Constant in Terms of Pressure

So far, we have expressed the equilibrium constant only in terms of the *concentrations* of the reactants and products. For gaseous reactions, the partial pressure of a particular gas is proportional to its concentration. Therefore, we can also express the equilibrium constant in terms of the *partial pressures* of the reactants and products. Consider the gaseous reaction:



From this point on, we designate  $K_c$  as the equilibrium constant with respect to concentration in molarity. For the reaction just given,  $K_c$  is expressed using the law of mass action:

$$K_c = \frac{[\text{SO}_2]^2 [\text{O}_2]}{[\text{SO}_3]^2}$$

We now designate  $K_p$  as the equilibrium constant with respect to partial pressures in atmospheres. *The expression for  $K_p$  takes the form of the expression for  $K_c$ , except that we use the partial pressure of each gas in place of its concentration.* For the  $\text{SO}_3$  reaction, we write  $K_p$  as:

$$K_p = \frac{(P_{\text{SO}_2})^2 P_{\text{O}_2}}{(P_{\text{SO}_3})^2}$$

where  $P_A$  is simply the partial pressure of gas A in units of atmospheres.

Since the partial pressure of a gas in atmospheres is not the same as its concentration in molarity, the value of  $K_p$  for a reaction is not necessarily equal to the value of  $K_c$ . However, as long as the gases are behaving ideally, we can derive a relationship between the two constants. The concentration of an ideal gas A is the number of moles of A ( $n_A$ ) divided by its volume (V) in liters:

$$[A] = \frac{n_A}{V}$$

From the ideal gas law, we can relate the quantity  $n_A/V$  to the partial pressure of A as follows:

$$P_A V = n_A R T$$

$$P_A = \frac{n_A}{V} R T$$

Since  $[A] = n_A/V$ , we can write:

$$P_A = [A] R T \quad \text{or} \quad [A] = \frac{P_A}{R T} \quad [14.1]$$

Now consider the following general equilibrium chemical equation:



According to the law of mass action, we write  $K_c$  as follows:

$$K_c = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

Substituting  $[X] = P_X/RT$  for each concentration term, we get:

$$\begin{aligned} K_c &= \frac{\left(\frac{P_{\text{C}}}{RT}\right)^c \left(\frac{P_{\text{D}}}{RT}\right)^d}{\left(\frac{P_{\text{A}}}{RT}\right)^a \left(\frac{P_{\text{B}}}{RT}\right)^b} = \frac{P_{\text{C}}^c P_{\text{D}}^d \left(\frac{1}{RT}\right)^{c+d}}{P_{\text{A}}^a P_{\text{B}}^b \left(\frac{1}{RT}\right)^{a+b}} = \frac{P_{\text{C}}^c P_{\text{D}}^d \left(\frac{1}{RT}\right)^{c+d-(a+b)}}{P_{\text{A}}^a P_{\text{B}}^b \left(\frac{1}{RT}\right)^{a+b}} \\ &= K_p \left(\frac{1}{RT}\right)^{c+d-(a+b)} \end{aligned}$$

Rearranging,

$$K_p = K_c (RT)^{c+d-(a+b)}$$

Finally, if we let  $\Delta n = c + d - (a + b)$ , which is the sum of the stoichiometric coefficients of the gaseous products minus the sum of the stoichiometric coefficients of the gaseous reactants, we get the following general result:

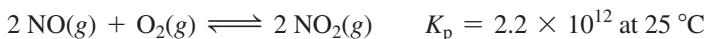
$$K_p = K_c (RT)^{\Delta n} \quad [14.2]$$

Notice that if the total number of moles of gas is the same after the reaction as before, then  $\Delta n = 0$ , and  $K_p$  is equal to  $K_c$ .

In the equation  $K_p = K_c (RT)^{\Delta n}$ , the quantity  $\Delta n$  represents the difference between the number of moles of gaseous products and gaseous reactants.

**EXAMPLE 14.3** Relating  $K_p$  and  $K_c$ 

Nitrogen monoxide, a pollutant in automobile exhaust, is oxidized to nitrogen dioxide in the atmosphere according to the equation:



Find  $K_c$  for this reaction.

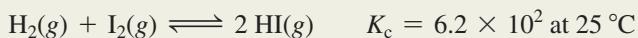
|  |   |
|--|---|
| <b>SORT</b> You are given $K_p$ for the reaction and asked to find $K_c$ . | <b>GIVEN:</b> $K_p = 2.2 \times 10^{12}$<br><b>FIND:</b> $K_c$  |
| <b>STRATEGIZE</b> Use Equation 14.2 to relate $K_p$ and $K_c$ .            | <b>EQUATION</b> $K_p = K_c (RT)^{\Delta n}$   |
| <b>SOLVE</b> Solve the equation for $K_c$ .                                | <b>SOLUTION</b><br>$K_c = \frac{K_p}{(RT)^{\Delta n}}$ $\Delta n = 2 - 3 = -1$ $K_c = \frac{2.2 \times 10^{12}}{\left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 298 \text{ K}\right)^{-1}}$ $= 5.4 \times 10^{13}$ |

**CHECK** The easiest way to check this answer is to substitute it back into Equation 14.2 and confirm that you get the original value for  $K_p$ .

$$\begin{aligned} K_p &= K_c (RT)^{\Delta n} \\ &= 5.4 \times 10^{13} \left( 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 298 \text{ K} \right)^{-1} \\ &= 2.2 \times 10^{12} \end{aligned}$$

**FOR PRACTICE 14.3**

Consider the following reaction and corresponding value of  $K_c$ :



What is the value of  $K_p$  at this temperature?

**Units of  $K$** 

Throughout this book, we express concentrations and partial pressures within the equilibrium constant expression in units of molarity and atmospheres, respectively. When expressing the value of the equilibrium constant, however, we have not included the units. Formally, the values of concentration or partial pressure that we substitute into the equilibrium constant expression are ratios of the concentration or pressure to a reference concentration (exactly 1 M) or a reference pressure (exactly 1 atm). For example, within the equilibrium constant expression, a pressure of 1.5 atm becomes

$$\frac{1.5 \text{ atm}}{1 \text{ atm}} = 1.5$$

Similarly, a concentration of 1.5 M becomes

$$\frac{1.5 \text{ M}}{1 \text{ M}} = 1.5$$

As long as concentration units are expressed in molarity for  $K_c$  and pressure units are expressed in atmospheres for  $K_p$ , we can skip this formality and enter the quantities directly into the equilibrium expression, dropping their corresponding units.



### Conceptual Connection 14.3 The Relationship between $K_p$ and $K_c$

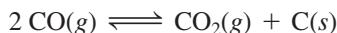
Under which circumstances are  $K_p$  and  $K_c$  equal for the reaction  $aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$ ?

- (a) If  $a + b = c + d$ .
- (b) If the reaction is reversible.
- (c) If the equilibrium constant is small.

## 14.5 Heterogeneous Equilibria: Reactions Involving Solids and Liquids

Many chemical reactions involve pure solids or pure liquids as reactants or products.

Consider, for example, the reaction:



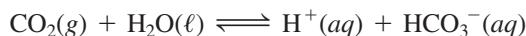
We might expect the expression for the equilibrium constant to be:

$$K_c = \frac{[\text{CO}_2][\text{C}]}{[\text{CO}]^2} \quad (\text{incorrect})$$

However, since carbon is a solid, its concentration is constant (if you double the amount of carbon its *concentration* remains the same). The concentration of a solid does not change, because a solid does not expand to fill its container. Its concentration, therefore, depends only on its density, which is constant as long as *some* solid is present (Figure 14.6 ▶). Consequently, pure solids—those reactants or products labeled in the chemical equation with an (s)—are not included in the equilibrium expression (because their constant value is incorporated into the value of  $K$ ). The correct equilibrium expression for this reaction is therefore:

$$K_c = \frac{[\text{CO}_2]}{[\text{CO}]^2}$$

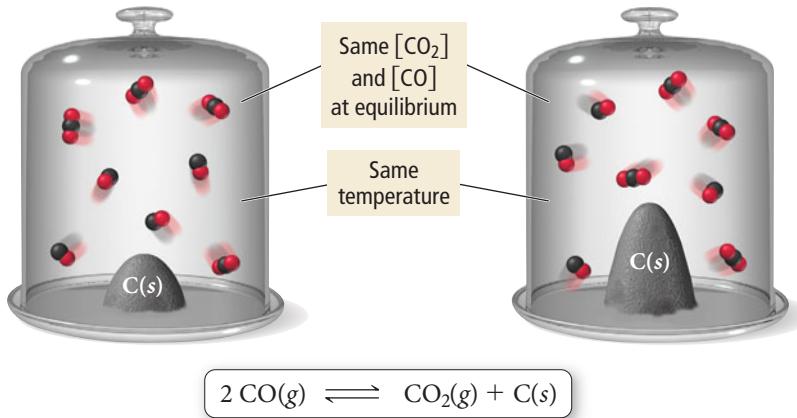
Similarly, the concentration of a pure liquid does not change. So, pure liquids—reactants or products labeled in the chemical equation with an (l)—are also excluded from the equilibrium expression. For example, consider the equilibrium expression for the reaction between carbon dioxide and water:



Since  $\text{H}_2\text{O}(l)$  is pure liquid, it is omitted from the equilibrium expression:

$$K_c = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]}$$

### A Heterogeneous Equilibrium



**◀ FIGURE 14.6** Heterogeneous Equilibrium The concentration of solid carbon (the number of atoms per unit volume) is constant as long as some solid carbon is present. The same is true for pure liquids. For this reason, the concentrations of solids and pure liquids are not included in equilibrium constant expressions.

### EXAMPLE 14.4 Writing Equilibrium Expressions for Reactions Involving a Solid or a Liquid

Write an expression for the equilibrium constant ( $K_c$ ) for this chemical equation:



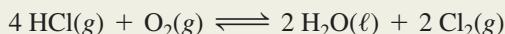
#### SOLUTION

Since  $\text{CaCO}_3(s)$  and  $\text{CaO}(s)$  are both solids, omit them from the equilibrium expression.

$$K_c = [\text{CO}_2]$$

#### FOR PRACTICE 14.4

Write an equilibrium expression ( $K_c$ ) for the equation:



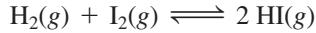
### Conceptual Connection 14.4 Heterogeneous Equilibria, $K_p$ and $K_c$

For which reaction does  $K_p = K_c$ ?

- (a)  $2 \text{ Na}_2\text{O}_2(s) + 2 \text{ CO}_2(g) \rightleftharpoons 2 \text{ Na}_2\text{CO}_3(s) + \text{O}_2(g)$
- (b)  $\text{Fe}_2\text{O}_3(s) + 3 \text{ CO}(g) \rightleftharpoons 2 \text{ Fe}(s) + 3 \text{ CO}_2(g)$
- (c)  $\text{NH}_4\text{NO}_3(s) \rightleftharpoons \text{N}_2\text{O}(g) + 2 \text{ H}_2\text{O}(g)$

## 14.6 Calculating the Equilibrium Constant from Measured Equilibrium Concentrations

The most direct way to obtain an experimental value for the equilibrium constant of a reaction is to measure the concentrations of the reactants and products in a reaction mixture at equilibrium. Consider the following reaction:



Suppose a mixture of  $\text{H}_2$  and  $\text{I}_2$  is allowed to come to equilibrium at 445 °C. The measured equilibrium concentrations are  $[\text{H}_2] = 0.11 \text{ M}$ ,  $[\text{I}_2] = 0.11 \text{ M}$ , and  $[\text{HI}] = 0.78 \text{ M}$ . What is the value of the equilibrium constant at this temperature? We can write the expression for  $K_c$  from the balanced equation:

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

To calculate the value of  $K_c$ , we substitute the correct equilibrium concentrations into the expression for  $K_c$ :

$$\begin{aligned} K_c &= \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} \\ &= \frac{(0.78)^2}{(0.11)(0.11)} \\ &= 5.0 \times 10^1 \end{aligned}$$

The concentrations within  $K_c$  should always be written in moles per liter (M); however, as noted in Section 14.4, we do not normally include the units when expressing the value of the equilibrium constant, so  $K_c$  is unitless.

For any reaction, the equilibrium *concentrations* of the reactants and products depend on the initial concentrations (and in general vary from one set of initial concentrations to another). However, the equilibrium *constant* is always the same at a given temperature, regardless of the initial concentrations. For example, Table 14.1

Since equilibrium constants depend on temperature, many equilibrium problems state the temperature even though it has no formal part in the calculation.

**TABLE 14.1 Initial and Equilibrium Concentrations for the Reaction  
 $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{ HI}(\text{g})$  at 445 °C**

| Initial Concentrations |                   |      | Equilibrium Concentrations |                   |       | Equilibrium Constant                                   |
|------------------------|-------------------|------|----------------------------|-------------------|-------|--|
| [H <sub>2</sub> ]      | [I <sub>2</sub> ] | [HI] | [H <sub>2</sub> ]          | [I <sub>2</sub> ] | [HI]  | $K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$ |
| 0.50                   | 0.50              | 0.0  | 0.11                       | 0.11              | 0.78  | $\frac{(0.78)^2}{(0.11)(0.11)} = 50$                   |
| 0.0                    | 0.0               | 0.50 | 0.055                      | 0.055             | 0.39  | $\frac{(0.39)^2}{(0.055)(0.055)} = 50$                 |
| 0.50                   | 0.50              | 0.50 | 0.165                      | 0.165             | 1.17  | $\frac{(1.17)^2}{(0.165)(0.165)} = 50$                 |
| 1.0                    | 0.50              | 0.0  | 0.53                       | 0.033             | 0.934 | $\frac{(0.934)^2}{(0.53)(0.033)} = 50$                 |
| 0.50                   | 1.0               | 0.0  | 0.033                      | 0.53              | 0.934 | $\frac{(0.934)^2}{(0.033)(0.53)} = 50$                 |

shows several different equilibrium concentrations of H<sub>2</sub>, I<sub>2</sub>, and HI, each from a different set of initial concentrations. Notice that the equilibrium constant is always the same, regardless of the initial concentrations. Whether you start with only reactants or only products, the reaction reaches equilibrium concentrations at which the equilibrium constant is the same. No matter what the initial concentrations are, the reaction always goes in a direction that ensures that the equilibrium concentrations—when substituted into the equilibrium expression—give the same constant, K.

So far, we have calculated equilibrium constants from values of the equilibrium concentrations of all the reactants and products. In most cases, however, we need only know the initial concentrations of the reactant(s) and the equilibrium concentration of any *one* reactant or product. We can deduce the other equilibrium concentrations from the stoichiometry of the reaction. For example, consider the simple reaction:



Suppose that we have a reaction mixture in which the initial concentration of A is 1.00 M and the initial concentration of B is 0.00 M. When equilibrium is reached, the concentration of A is 0.75 M. Since [A] has changed by  $-0.25 \text{ M}$ , we can deduce (based on the stoichiometry) that [B] must have changed by  $2 \times (+0.25 \text{ M})$  or  $+0.50 \text{ M}$ . We summarize the initial conditions, the changes, and the equilibrium conditions in the following table:

|             | [A]     | [B]     |
|-------------|---------|---------|
| Initial     | 1.00    | 0.00    |
| Change      | $-0.25$ | $+0.50$ |
| Equilibrium | 0.75    | 0.50    |

This type of table is often referred to as an ICE table (I = initial, C = change, E = equilibrium). To calculate the equilibrium constant, we use the balanced equation to write an expression for the equilibrium constant and then substitute the equilibrium concentrations from the ICE table:

$$K = \frac{[\text{B}]^2}{[\text{A}]} = \frac{(0.50)^2}{(0.75)} = 0.33$$

In Example 14.5 and 14.6, we show the general procedure for solving these kinds of equilibrium problems in the left column and work two examples exemplifying the procedure in the center and right columns.

**PROCEDURE FOR...****Finding Equilibrium Constants from Experimental Concentration Measurements**

To solve these types of problems, follow the given procedure.

- Using the balanced equation as a guide, prepare an ICE table showing the known initial concentrations and equilibrium concentrations of the reactants and products.** Leave space in the middle of the table for determining the changes in concentration that occur during the reaction.

- For the reactant or product whose concentration is known both initially and at equilibrium, calculate the change in concentration that occurs.**

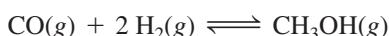
- Use the change calculated in step 2 and the stoichiometric relationships from the balanced chemical equation to determine the changes in concentration of all other reactants and products.** Since reactants are consumed during the reaction, the changes in their concentrations are negative. Since products are formed, the changes in their concentrations are positive.

- Sum each column for each reactant and product to determine the equilibrium concentrations.**

- Use the balanced equation to write an expression for the equilibrium constant and substitute the equilibrium concentrations to calculate  $K$ .**

**EXAMPLE 14.5****Finding Equilibrium Constants from Experimental Concentration Measurements**

Consider the following reaction:



A reaction mixture at 780 °C initially contains  $[\text{CO}] = 0.500 \text{ M}$  and  $[\text{H}_2] = 1.00 \text{ M}$ . At equilibrium, the CO concentration is found to be 0.15 M. What is the value of the equilibrium constant?

| $\text{CO}(g) + 2 \text{H}_2(g) \rightleftharpoons \text{CH}_3\text{OH}(g)$ |       |                   |                      |
|---|-------|-------------------|----------------------|
|   | [CO]  | [H <sub>2</sub> ] | [CH <sub>3</sub> OH] |
| Initial   | 0.500 | 1.00              | 0.00                 |
| Change  |       |                   |                      |
| Equil   | 0.15  |                   |                      |

**EXAMPLE 14.6****Finding Equilibrium Constants from Experimental Concentration Measurements**

Consider the following reaction:



A reaction mixture at 1700 °C initially contains  $[\text{CH}_4] = 0.115 \text{ M}$ . At equilibrium, the mixture contains  $[\text{C}_2\text{H}_2] = 0.035 \text{ M}$ . What is the value of the equilibrium constant?

| $2 \text{CH}_4(g) \rightleftharpoons \text{C}_2\text{H}_2(g) + 3 \text{H}_2(g)$ |                    |                                  |                   |
|---|--------------------|----------------------------------|-------------------|
|   | [CH <sub>4</sub> ] | [C <sub>2</sub> H <sub>2</sub> ] | [H <sub>2</sub> ] |
| Initial   | 0.115              | 0.00                             | 0.00              |
| Change  |                    | +0.035                           |                   |
| Equil   |                    | 0.035                            |                   |

| $2 \text{CH}_4(g) \rightleftharpoons \text{C}_2\text{H}_2(g) + 3 \text{H}_2(g)$ |                    |                                  |                   |
|---|--------------------|----------------------------------|-------------------|
|   | [CH <sub>4</sub> ] | [C <sub>2</sub> H <sub>2</sub> ] | [H <sub>2</sub> ] |
| Initial   | 0.115              | 0.00                             | 0.00              |
| Change  | -0.070             | +0.035                           | +0.105            |
| Equil   |                    | 0.035                            |                   |

|         | [CO]  | [H <sub>2</sub> ] | [CH <sub>3</sub> OH] |
|---------|-------|-------------------|----------------------|
| Initial | 0.500 | 1.00              | 0.00                 |
| Change  | -0.35 | -0.70             | +0.35                |
| Equil   | 0.15  | 0.30              | 0.35                 |

$$\begin{aligned} K_c &= \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2} \\ &= \frac{0.35}{(0.15)(0.30)^2} \\ &= 26 \end{aligned}$$

$$\begin{aligned} K_c &= \frac{[\text{C}_2\text{H}_2][\text{H}_2]^3}{[\text{CH}_4]^2} \\ &= \frac{(0.035)(0.105)^3}{(0.045)^2} \\ &= 0.020 \end{aligned}$$

**FOR PRACTICE 14.5**

The reaction in Example 14.5 between CO and H<sub>2</sub> is carried out at a different temperature with initial concentrations of [CO] = 0.27 M and [H<sub>2</sub>] = 0.49 M. At equilibrium, the concentration of CH<sub>3</sub>OH is 0.11 M. Find the equilibrium constant at this temperature.

**FOR PRACTICE 14.6**

The reaction of CH<sub>4</sub> in Example 14.6 is carried out at a different temperature with an initial concentration of [CH<sub>4</sub>] = 0.087 M. At equilibrium, the concentration of H<sub>2</sub> is 0.012 M. Find the equilibrium constant at this temperature.

## 14.7 The Reaction Quotient: Predicting the Direction of Change

When the reactants of a chemical reaction mix, they generally react to form products—we say that the reaction proceeds to the right (toward the products). The amount of products formed when equilibrium is reached depends on the magnitude of the equilibrium constant, as we have seen. However, what if a reaction mixture not at equilibrium contains both reactants *and products*? Can we predict the direction of change for such a mixture?

To gauge the progress of a reaction relative to equilibrium, we use a quantity called the *reaction quotient*. The definition of the reaction quotient takes the same form as the definition of the equilibrium constant, except that the reaction need not be at equilibrium. So, for the general reaction:



we define the **reaction quotient** ( $Q_c$ ) as the ratio—at any point in the reaction—of the concentrations of the products raised to their stoichiometric coefficients divided by the concentrations of the reactants raised to their stoichiometric coefficients. For gases with amounts measured in atmospheres, the reaction quotient uses the partial pressures in place of concentrations and is called  $Q_p$ :

$$Q_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad Q_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

The difference between the reaction quotient and the equilibrium constant is that, at a given temperature, the equilibrium constant has only one value and it specifies the relative amounts of reactants and products *at equilibrium*. The reaction quotient, by contrast, depends on the current state of the reaction and has many different values as the reaction proceeds. For example, in a reaction mixture containing only reactants, the reaction quotient is zero ( $Q_c = 0$ ):

$$Q_c = \frac{[0]^c[0]^d}{[A]^a[B]^b} = 0$$

In a reaction mixture containing only products, the reaction quotient is infinite ( $Q_c = \infty$ ):

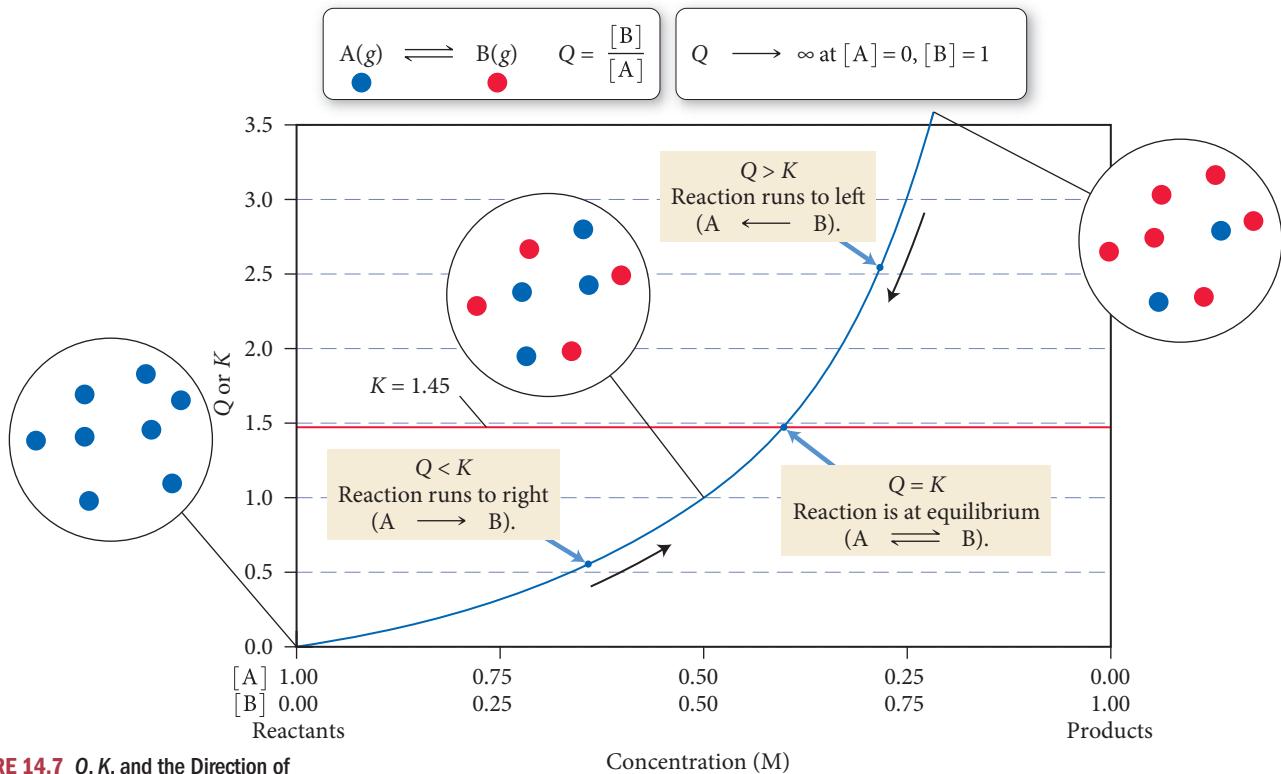
$$Q_c = \frac{[C]^c[D]^d}{[0]^a[0]^b} = \infty$$

In a reaction mixture containing both reactants and products, each at a concentration of 1 M, the reaction quotient is one ( $Q_c = 1$ ):

$$Q_c = \frac{(1)^c(1)^d}{(1)^a(1)^b} = 1$$

The reaction quotient is useful because *the value of Q relative to K is a measure of the progress of the reaction toward equilibrium. At equilibrium, the reaction quotient*

### *Q, K, and the Direction of a Reaction*



▲ FIGURE 14.7 *Q, K, and the Direction of a Reaction*

**a Reaction** The graph shows a plot of  $Q$  as a function of the concentrations of the reactants and products in a simple reaction  $A \rightleftharpoons B$ , in which  $K = 1.45$  and the sum of the reactant and product concentrations is 1 M.

The far left of the graph represents pure reactant and the far right represents pure product. The midpoint of the graph represents an equal mixture of A and B. When  $Q$  is less than  $K$ , the reaction moves in the forward direction ( $A \rightarrow B$ ). When  $Q$  is greater than  $K$ , the reaction moves in the reverse direction ( $A \leftarrow B$ ). When  $Q$  is equal to  $K$ , the reaction is at equilibrium.

is equal to the equilibrium constant. Figure 14.7 ▲ shows a plot of  $Q$  as a function of the concentrations of A and B for the simple reaction  $A(g) \rightleftharpoons B(g)$ , which has an equilibrium constant of  $K = 1.45$ . The following points are representative of three possible conditions:

| <b>Q</b> | <b>K</b> | <b>Predicted Direction of Reaction</b> |
|----------|----------|--|
| 0.55     | 1.45     | To the right (toward products)         |
| 2.55     | 1.45     | To the left (toward reactants)         |
| 1.45     | 1.45     | No change (at equilibrium)             |

For the first set of values in the table,  $Q$  is less than  $K$  and must therefore get larger as the reaction proceeds toward equilibrium.  $Q$  becomes larger as the reactant concentration decreases and the product concentration increases—the reaction proceeds to the right. For the second set of values,  $Q$  is greater than  $K$  and must therefore get smaller as the reaction proceeds toward equilibrium.  $Q$  gets smaller as the reactant concentration increases and the product concentration decreases—the reaction proceeds to the left. In the third set of values,  $Q = K$ , implying that the reaction is at equilibrium—the reaction will not proceed in either direction.

#### *Summarizing Direction of Change Predictions:*

The reaction quotient ( $Q$ ) relative to the equilibrium constant ( $K$ ) is a measure of the progress of a reaction toward equilibrium.

- ▶  $Q < K$  Reaction goes to the right (toward products).
- ▶  $Q > K$  Reaction goes to the left (toward reactants).
- ▶  $Q = K$  Reaction is at equilibrium.

### EXAMPLE 14.7 Predicting the Direction of a Reaction by Comparing $Q$ and $K$

Consider the reaction and its equilibrium constant:



A reaction mixture contains  $P_{I_2} = 0.114$  atm,  $P_{Cl_2} = 0.102$  atm, and  $P_{ICl} = 0.355$  atm. Is the reaction mixture at equilibrium? If not, in which direction will the reaction proceed?

#### SOLUTION

To determine the progress of the reaction relative to the equilibrium state, first calculate  $Q$ .

$$\begin{aligned} Q_p &= \left( \frac{P_{ICl}^2}{P_{I_2} P_{Cl_2}} \right) \\ &= \frac{(0.355)^2}{(0.114)(0.102)} \\ &= 10.8 \end{aligned}$$

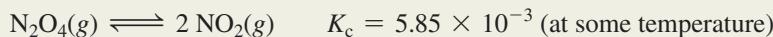
Compare  $Q$  to  $K$ .

$$Q_p = 10.8; K_p = 81.9$$

Since  $Q_p < K_p$ , the reaction is not at equilibrium and will proceed to the right.

#### FOR PRACTICE 14.7

Consider the reaction and its equilibrium constant:



A reaction mixture contains  $[NO_2] = 0.0255$  M and  $[N_2O_4] = 0.0331$  M. Calculate  $Q_c$  and determine the direction in which the reaction will proceed.

### Conceptual Connection 14.5 $Q$ and $K$

For the reaction  $N_2O_4(g) \rightleftharpoons 2 NO_2(g)$ , a reaction mixture at a certain temperature initially contains both  $N_2O_4$  and  $NO_2$  in their standard states (see the definition of standard state in Section 6.9). If  $K_p = 0.15$ , which statement is true of the reaction mixture before any reaction occurs?

- (a)  $Q = K$ ; the reaction is at equilibrium.
- (b)  $Q < K$ ; the reaction will proceed to the right.
- (c)  $Q > K$ ; the reaction will proceed to the left.

## 14.8 Finding Equilibrium Concentrations

In Section 14.6, we discussed how to calculate an equilibrium constant from the equilibrium concentrations of the reactants and products. Just as commonly we will want to calculate equilibrium concentrations of reactants or products from the equilibrium constant. These kinds of calculations are important because they allow us to calculate the amount of a reactant or product at equilibrium. For example, in a synthesis reaction, we might want to know how much of the product forms when the reaction reaches equilibrium. Or for the hemoglobin–oxygen equilibrium discussed in Section 14.1, we might want to know the concentration of oxygenated hemoglobin present under certain oxygen concentrations within the lungs or muscles.

We can divide these types of problems into two categories: (1) finding equilibrium concentrations when we know the equilibrium constant and all but one of the equilibrium concentrations of the reactants and products, and (2) finding equilibrium

concentrations when we know the equilibrium constant and only initial concentrations. The second category of problem is more difficult than the first. Let's examine each separately.

### Finding Equilibrium Concentrations from the Equilibrium Constant and All but One of the Equilibrium Concentrations of the Reactants and Products

We can use the equilibrium constant to calculate the equilibrium concentration of one of the reactants or products, given the equilibrium concentrations of the others. To solve this type of problem, we can follow our general problem-solving procedure.

#### EXAMPLE 14.8

#### Finding Equilibrium Concentrations When You Know the Equilibrium Constant and All but One of the Equilibrium Concentrations of the Reactants and Products

Consider the following reaction:



In an equilibrium mixture, the concentration of  $\text{COF}_2$  is 0.255 M and the concentration of  $\text{CF}_4$  is 0.118 M. What is the equilibrium concentration of  $\text{CO}_2$ ?

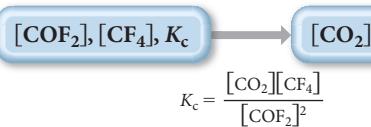
**SORT** You are given the equilibrium constant of a chemical reaction, together with the equilibrium concentrations of the reactant and one product. You are asked to find the equilibrium concentration of the other product.

**GIVEN:**  $[\text{COF}_2] = 0.255 \text{ M}$   
 $[\text{CF}_4] = 0.118 \text{ M}$   
 $K_c = 2.00$

**FIND:**  $[\text{CO}_2]$

**STRATEGIZE** You can calculate the concentration of the product using the given quantities and the expression for  $K_c$ .

#### CONCEPTUAL PLAN



**SOLVE** Solve the equilibrium expression for  $[\text{CO}_2]$  and then substitute in the appropriate values to calculate it.

#### SOLUTION

$$[\text{CO}_2] = K_c \frac{[\text{COF}_2]^2}{[\text{CF}_4]}$$

$$[\text{CO}_2] = 2.00 \left( \frac{(0.255)^2}{0.118} \right) = 1.10 \text{ M}$$

**CHECK** Check your answer by mentally substituting the given values of  $[\text{COF}_2]$  and  $[\text{CF}_4]$  as well as your calculated value for  $\text{CO}_2$  back into the equilibrium expression.

$$K_c = \frac{[\text{CO}_2][\text{CF}_4]}{[\text{COF}_2]^2}$$

$[\text{CO}_2]$  was found to be roughly equal to 1.  $[\text{COF}_2]^2 \approx 0.06$  and  $[\text{CF}_4] \approx 0.12$ . Therefore  $K_c$  is approximately 2, as given in the problem.

#### FOR PRACTICE 14.8

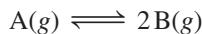
Diatomeric iodine  $[\text{I}_2]$  decomposes at high temperature to form I atoms according to the reaction:



In an equilibrium mixture, the concentration of  $\text{I}_2$  is 0.10 M. What is the equilibrium concentration of I?

## Finding Equilibrium Concentrations from the Equilibrium Constant and Initial Concentrations or Pressures

More commonly, we know the equilibrium constant and only initial concentrations of reactants and need to find the *equilibrium concentrations* of the reactants or products. These kinds of problems are generally more involved than those we just examined and require a specific procedure to solve them. The procedure has some similarities to the one used in Example 14.5 and 14.6 in that we set up an ICE table showing the initial conditions, the changes, and the equilibrium conditions. However, unlike Example 14.5 and 14.6, here the changes in concentration are not known and are represented with the variable  $x$ . For example, consider again the simple reaction:



Suppose that, as before (see Section 14.6), we have a reaction mixture in which the initial concentration of A is 1.0 M and the initial concentration of B is 0.00 M. However, now we know the equilibrium constant,  $K = 0.33$ , and want to find the equilibrium concentrations. We set up the ICE table with the given initial concentrations and then *represent the unknown change in [A] with the variable  $x$*  as follows:

|         | [A]       | [B]   |   |
|---------|-----------|-------|---|
| Initial | 1.0       | 0.00  |   |
| Change  | $-x$      | $+2x$ | Represent changes from initial conditions with the variable $x$ . |
| Equil   | $1.0 - x$ | $2x$  |   |

Notice that, due to the stoichiometry of the reaction, the change in [B] must be  $+2x$ . As before, each *equilibrium* concentration is the sum of the two entries above it in the ICE table. In order to find the equilibrium concentrations of A and B, we must find the value of the variable  $x$ . Since we know the value of the equilibrium constant, we can use the equilibrium constant expression to set up an equation in which  $x$  is the only variable:

$$K = \frac{[B]^2}{[A]} = \frac{(2x)^2}{1.0 - x} = 0.33$$

or more simply:

$$\frac{4x^2}{1.0 - x} = 0.33$$

This equation is a *quadratic* equation—it contains the variable  $x$  raised to the second power. In general, we can solve quadratic equations with the quadratic formula (see Appendix IC), which we introduce in Example 14.10. If the quadratic equation is a perfect square, however, we can solve it by simpler means, as shown in Example 14.9. For both of these examples, we give the general procedure in the left column and apply the procedure to the two different example problems in the center and right columns. Later in this section, we see that quadratic equations can often be simplified by making some approximations based on our chemical knowledge.

**PROCEDURE FOR...****Finding Equilibrium Concentrations from Initial Concentrations and the Equilibrium Constant**

To solve these types of problems, follow the given procedure.

- Using the balanced equation as a guide, prepare a table showing the known initial concentrations of the reactants and products. Leave room in the table for the changes in concentrations and for the equilibrium concentrations.**

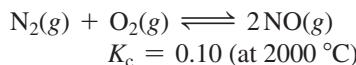
- Use the initial concentrations to calculate the reaction quotient ( $Q$ ) for the initial concentrations. Compare  $Q$  to  $K$  to predict the direction in which the reaction will proceed.**

- Represent the change in the concentration of one of the reactants or products with the variable  $x$ . Define the changes in the concentrations of the other reactants or products in terms of  $x$ . It is usually most convenient to let  $x$  represent the change in concentration of the reactant or product with the smallest stoichiometric coefficient.**

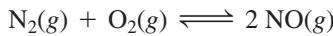
- Sum each column for each reactant and each product to determine the equilibrium concentrations in terms of the initial concentrations and the variable  $x$ .**

**EXAMPLE 14.9****Finding Equilibrium Concentrations from Initial Concentrations and the Equilibrium Constant**

Consider the reaction:



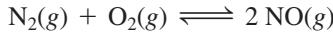
A reaction mixture at 2000 °C initially contains  $[\text{N}_2] = 0.200 \text{ M}$  and  $[\text{O}_2] = 0.200 \text{ M}$ . Find the equilibrium concentrations of the reactants and product at this temperature.



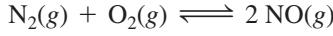
|         | [N <sub>2</sub> ] | [O <sub>2</sub> ] | [NO] |
|---------|-------------------|-------------------|------|
| Initial | 0.200             | 0.200             | 0.00 |
| Change  |                   |                   |      |
| Equil   |                   |                   |      |

$$Q_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = \frac{(0.00)^2}{(0.200)(0.200)} = 0$$

$Q < K$ ; therefore, the reaction will proceed to the right.



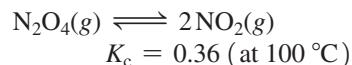
|         | [N <sub>2</sub> ] | [O <sub>2</sub> ] | [NO] |
|---------|-------------------|-------------------|------|
| Initial | 0.200             | 0.200             | 0.00 |
| Change  | -x                | -x                | +2x  |
| Equil   |                   |                   |      |



|         | [N <sub>2</sub> ] | [O <sub>2</sub> ] | [NO] |
|---------|-------------------|-------------------|------|
| Initial | 0.200             | 0.200             | 0.00 |
| Change  | -x                | -x                | +2x  |
| Equil   | 0.200-x           | 0.200-x           | 2x   |

**EXAMPLE 14.10****Finding Equilibrium Concentrations from Initial Concentrations and the Equilibrium Constant**

Consider the reaction:



A reaction mixture at 100 °C initially contains  $[\text{NO}_2] = 0.100 \text{ M}$ . Find the equilibrium concentrations of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  at this temperature.



|         | [N <sub>2</sub> O <sub>4</sub> ] | [NO <sub>2</sub> ] |
|---------|----------------------------------|--------------------|
| Initial | 0.00                             | 0.100              |
| Change  |                                  |                    |
| Equil   |                                  |                    |

$$Q_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{(0.100)^2}{0.00} = \infty$$

$Q > K$ ; therefore, the reaction will proceed to the left.



|         | [N <sub>2</sub> O <sub>4</sub> ] | [NO <sub>2</sub> ] |
|---------|----------------------------------|--------------------|
| Initial | 0.00                             | 0.100              |
| Change  | +x                               | -2x                |
| Equil   |                                  |                    |



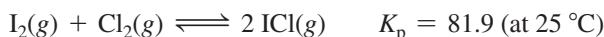
|         | [N <sub>2</sub> O <sub>4</sub> ] | [NO <sub>2</sub> ] |
|---------|----------------------------------|--------------------|
| Initial | 0.00                             | 0.100              |
| Change  | +x                               | -2x                |
| Equil   | x                                | 0.100 - 2x         |

|   |  |  |
|---|--|--|
| <p><b>5.</b> Substitute the expressions for the equilibrium concentrations (from step 4) into the expression for the equilibrium constant. Using the given value of the equilibrium constant, solve the expression for the variable <math>x</math>. In some cases, such as Example 14.9, you can take the square root of both sides of the expression to solve for <math>x</math>. In other cases, such as Example 14.10, you must solve a quadratic equation to find <math>x</math>.</p> <p>Remember the quadratic formula:</p> $ax^2 + bx + c = 0$ $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$ | $K_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}$ $= \frac{(2x)^2}{(0.200 - x)(0.200 - x)}$ $0.10 = \frac{(2x)^2}{(0.200 - x)^2}$ $\sqrt{0.10} = \frac{2x}{0.200 - x}$ $\sqrt{0.10}(0.200 - x) = 2x$ $\sqrt{0.10}(0.200) - \sqrt{0.10}x = 2x$ $0.063 = 2x + \sqrt{0.10}x$ $0.063 = 2.3x$ $x = 0.027$  | $K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$ $= \frac{(0.100 - 2x)^2}{x}$ $0.36 = \frac{0.0100 - 0.400x + 4x^2}{x}$ $0.36x = 0.0100 - 0.400x + 4x^2$ $4x^2 - 0.76x + 0.0100 = 0 \text{ (quadratic)}$ $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$ $= \frac{-(-0.76) \pm \sqrt{(-0.76)^2 - 4(4)(0.0100)}}{2(4)}$ $= \frac{0.76 \pm 0.65}{8}$ $x = 0.176 \text{ or } x = 0.014$  |
| <p><b>6.</b> Substitute <math>x</math> into the expressions for the equilibrium concentrations of the reactants and products (from step 4) and calculate the concentrations. In cases where you solved a quadratic and have two values for <math>x</math>, choose the value for <math>x</math> that gives a physically realistic answer. For example, reject the value of <math>x</math> that results in any negative concentrations.</p>   | $[\text{N}_2] = 0.200 - 0.027$ $= 0.173 \text{ M}$ $[\text{O}_2] = 0.200 - 0.027$ $= 0.173 \text{ M}$ $[\text{NO}] = 2(0.027)$ $= 0.054 \text{ M}$   | <p>We reject the root <math>x = 0.176</math> because it gives a negative concentration for <math>\text{NO}_2</math>. Using <math>x = 0.014</math>, we get the following concentrations:</p> $[\text{NO}_2] = 0.100 - 2x$ $= 0.100 - 2(0.014) = 0.072 \text{ M}$ $[\text{N}_2\text{O}_4] = x$ $= 0.014 \text{ M}$   |
| <p><b>7.</b> Check your answer by substituting the calculated equilibrium values into the equilibrium expression. The calculated value of <math>K</math> should match the given value of <math>K</math>. Note that rounding errors could cause a difference in the least significant digit when comparing values of the equilibrium constant.</p>   | $K_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}$ $= \frac{(0.054)^2}{(0.173)(0.173)} = 0.097$ <p>Since the calculated value of <math>K_c</math> matches the given value (to within one digit in the least significant figure), the answer is valid.</p> <p><b>FOR PRACTICE 14.9</b></p> <p>The reaction in Example 14.9 is carried out at a different temperature at which <math>K_c = 0.055</math>. This time, however, the reaction mixture starts with only the product, <math>[\text{NO}] = 0.0100 \text{ M}</math>, and no reactants. Find the equilibrium concentrations of <math>\text{N}_2</math>, <math>\text{O}_2</math>, and <math>\text{NO}</math> at equilibrium.</p> | $K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{(0.072)^2}{0.014}$ $= 0.37$ <p>Since the calculated value of <math>K_c</math> matches the given value (to within one digit in the least significant figure), the answer is valid.</p> <p><b>FOR PRACTICE 14.10</b></p> <p>The reaction in Example 14.10 is carried out at the same temperature, but this time the reaction mixture initially contains only the reactant, <math>[\text{N}_2\text{O}_4] = 0.0250 \text{ M}</math>, and no <math>\text{NO}_2</math>. Find the equilibrium concentrations of <math>\text{N}_2\text{O}_4</math> and <math>\text{NO}_2</math>.</p> |

When the initial conditions are given in terms of partial pressures (instead of concentrations) and the equilibrium constant is given as  $K_p$  instead of  $K_c$ , use the same procedure, but substitute partial pressures for concentrations, as shown in Example 14.11.

### EXAMPLE 14.11 Finding Equilibrium Partial Pressures When You Are Given the Equilibrium Constant and Initial Partial Pressures

Consider the reaction:

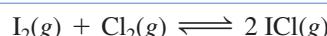


A reaction mixture at 25 °C initially contains  $P_{I_2} = 0.100 \text{ atm}$ ,  $P_{Cl_2} = 0.100 \text{ atm}$ , and  $P_{ICl} = 0.100 \text{ atm}$ . Find the equilibrium partial pressures of  $I_2$ ,  $Cl_2$ , and  $ICl$  at this temperature.

#### SOLUTION

Follow the procedure used in Example 14.5 and 14.6 (using partial pressures in place of concentrations) to solve the problem.

1. Using the balanced equation as a guide, prepare a table showing the known initial partial pressures of the reactants and products.



|         | $P_{I_2}$ (atm) | $P_{Cl_2}$ (atm) | $P_{ICl}$ (atm) |
|---------|-----------------|------------------|-----------------|
| Initial | 0.100           | 0.100            | 0.100           |
| Change  |                 |                  |                 |
| Equil   |                 |                  |                 |

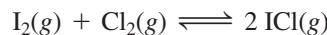
2. Use the initial partial pressures to calculate the reaction quotient ( $Q$ ). Compare  $Q$  to  $K$  to predict the direction in which the reaction will proceed.

$$Q_p = \frac{(P_{ICl})^2}{P_{I_2}P_{Cl_2}} = \frac{(0.100)^2}{(0.100)(0.100)} = 1$$

$$K_p = 81.9 \text{ (given)}$$

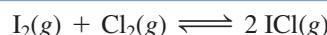
$Q < K$ ; therefore, the reaction will proceed to the right.

3. Represent the change in the partial pressure of one of the reactants or products with the variable  $x$ . Define the changes in the partial pressures of the other reactants or products in terms of  $x$ .



|         | $P_{I_2}$ (atm) | $P_{Cl_2}$ (atm) | $P_{ICl}$ (atm) |
|---------|-----------------|------------------|-----------------|
| Initial | 0.100           | 0.100            | 0.100           |
| Change  | $-x$            | $-x$             | $+2x$           |
| Equil   |                 |                  |                 |

4. Sum each column for each reactant and product to determine the equilibrium partial pressures in terms of the initial partial pressures and the variable  $x$ .



|         | $P_{I_2}$ (atm) | $P_{Cl_2}$ (atm) | $P_{ICl}$ (atm) |
|---------|-----------------|------------------|-----------------|
| Initial | 0.100           | 0.100            | 0.100           |
| Change  | $-x$            | $-x$             | $+2x$           |
| Equil   | $0.100 - x$     | $0.100 - x$      | $0.100 + 2x$    |

5. Substitute the expressions for the equilibrium partial pressures (from step 4) into the expression for the equilibrium constant. Use the given value of the equilibrium constant to solve the expression for the variable  $x$ .

$$K_p = \frac{(P_{ICl})^2}{P_{I_2}P_{Cl_2}} = \frac{(0.100 + 2x)^2}{(0.100 - x)(0.100 - x)}$$

$$81.9 = \frac{(0.100 + 2x)^2}{(0.100 - x)^2} \quad (\text{perfect square})$$

$$\sqrt{81.9} = \frac{(0.100 + 2x)}{(0.100 - x)}$$

$$\sqrt{81.9}(0.100 - x) = 0.100 + 2x$$

$$\sqrt{81.9}(0.100) - \sqrt{81.9}x = 0.100 + 2x$$

$$\sqrt{81.9}(0.100) - 0.100 = 2x + \sqrt{81.9}x$$

$$0.805 = 11.05x$$

$$x = 0.0729$$

6. Substitute  $x$  into the expressions for the equilibrium partial pressures of the reactants and products (from step 4) and calculate the partial pressures.

$$P_{I_2} = 0.100 - 0.0729 = 0.027 \text{ atm}$$

$$P_{Cl_2} = 0.100 - 0.0729 = 0.027 \text{ atm}$$

$$P_{ICl} = 0.100 + 2(0.0729) = 0.246 \text{ atm}$$

7. Check your answer by substituting the calculated equilibrium partial pressures into the equilibrium expression. The calculated value of  $K$  should match the given value of  $K$ .

$$K_p = \frac{(P_{\text{ICl}})^2}{P_{\text{I}_2} P_{\text{Cl}_2}} = \frac{(0.246)^2}{(0.027)(0.027)} = 83$$

Since the calculated value of  $K_p$  matches the given value (within the uncertainty indicated by the significant figures), the answer is valid.

### FOR PRACTICE 14.11

The reaction between  $\text{I}_2$  and  $\text{Cl}_2$  in Example 14.11 is carried out at the same temperature, but with these initial partial pressures:  $P_{\text{I}_2} = 0.150 \text{ atm}$ ,  $P_{\text{Cl}_2} = 0.150 \text{ atm}$ ,  $P_{\text{ICl}} = 0.00 \text{ atm}$ . Find the equilibrium partial pressures of all three substances.

## Simplifying Approximations in Working Equilibrium Problems

For some equilibrium problems of the type shown in Example 14.9, 14.10, and 14.11, we can make an approximation that simplifies the calculations without any significant loss of accuracy. For example, if the equilibrium constant is relatively small, the reaction will not proceed very far to the right. Therefore, if the initial reactant concentration is relatively large, we can make the assumption that  $x$  is small relative to the initial concentration of reactant. To see how this approximation works, consider again the simple reaction  $\text{A} \rightleftharpoons 2 \text{B}$ . Suppose that, as before, we have a reaction mixture in which the initial concentration of  $\text{A}$  is 1.0 M and the initial concentration of  $\text{B}$  is 0.0 M and that we want to find the equilibrium concentrations. However, suppose that in this case the equilibrium constant is much smaller, say  $K = 3.3 \times 10^{-5}$ . The ICE table is identical to the one we set up previously:

|         | [A]       | [B]   |
|---------|-----------|-------|
| Initial | 1.0       | 0.0   |
| Change  | $-x$      | $+2x$ |
| Equil   | $1.0 - x$ | $2x$  |

Except for the value of  $K$ , we end up with the exact quadratic equation that we had before:

$$K = \frac{[\text{B}]^2}{[\text{A}]} = \frac{(2x)^2}{1.0 - x} = 3.3 \times 10^{-5}$$

or more simply:

$$\frac{4x^2}{1.0 - x} = 3.3 \times 10^{-5}$$

We can rearrange this quadratic equation into standard form and solve it using the quadratic formula. But since  $K$  is small, the reaction will not proceed very far toward products and, therefore,  $x$  will also be small. If  $x$  is much smaller than 1.0, then  $(1.0 - x)$  (the quantity in the denominator) can be approximated by (1.0):

$$\frac{4x^2}{(1.0 - x)} = 3.3 \times 10^{-5}$$

This approximation greatly simplifies the equation, which we can then solve for  $x$  as follows:

$$\begin{aligned} \frac{4x^2}{1.0} &= 3.3 \times 10^{-5} \\ 4x^2 &= 3.3 \times 10^{-5} \\ x &= \sqrt{\frac{3.3 \times 10^{-5}}{4}} = 0.0029 \end{aligned}$$

We can check the validity of this approximation by comparing the calculated value of  $x$  to the number it was subtracted from. The ratio of  $x$  to the number it is subtracted from should be less than 0.05 (or 5%) for the approximation to be valid. In this case,  $x$  was subtracted from 1.0, and therefore the ratio of the value of  $x$  to 1.0 is calculated as follows:

$$\frac{0.0029}{1.0} \times 100\% = 0.29\%$$

The approximation is therefore valid. In Example 14.12 and 14.13, we treat two nearly identical problems—the only difference is the initial concentration of the reactant. In Example 14.12, the initial concentration of the reactant is relatively large, the equilibrium constant is small, and the  $x$  is *small* approximation works well. In Example 14.13, however, the initial concentration of the reactant is much smaller, and even though the equilibrium constant is the same, the  $x$  is *small* approximation does not work (because the initial concentration is also small). In cases such as this, we have a couple of options to solve the problem. We can either solve the equation exactly (using the quadratic formula, for example), or we can use the *method of successive approximations*, which is introduced in Example 14.13. In this method, we essentially solve for  $x$  as if it were small, and then substitute the value obtained back into the equation (where  $x$  was initially neglected) to solve for  $x$  again. This can be repeated until the calculated value of  $x$  stops changing with each iteration, an indication that we have arrived at an acceptable value for  $x$ .

Note that the  $x$  is *small* approximation does not imply that  $x$  is *zero*. If that were the case, the reactant and product concentrations would not change from their initial values. The  $x$  is *small* approximation just means that when  $x$  is added or subtracted to another number, it does not change that number by very much. For example, we can calculate the value of the difference  $1.0 - x$  when  $x = 3.0 \times 10^{-4}$ :

$$1.0 - x = 1.0 - 3.0 \times 10^{-4} = 0.9997 = 1.0$$

Since the value of 1.0 is known only to two significant figures, subtracting the small  $x$  does not change the value at all. This situation is similar to weighing yourself on a bathroom scale with and without a penny in your pocket. Unless your scale is unusually precise, removing the penny from your pocket will not change the reading on the scale. This does not imply that the penny is weightless, only that its weight is small when compared to your body weight. You can neglect the weight of the penny in reading your weight with no detectable loss in accuracy.

### PROCEDURE FOR...

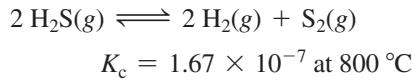
#### Finding Equilibrium Concentrations from Initial Concentrations in Cases with a Small Equilibrium Constant

To solve these types of problems, follow the given procedure.

### EXAMPLE 14.12

#### Finding Equilibrium Concentrations from Initial Concentrations in Cases with a Small Equilibrium Constant

Consider the reaction for the decomposition of hydrogen disulfide:

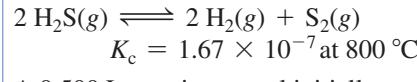


A 0.500 L reaction vessel initially contains 0.0125 mol of  $\text{H}_2\text{S}$  at  $800^\circ\text{C}$ . Find the equilibrium concentrations of  $\text{H}_2$  and  $\text{S}_2$ .

### EXAMPLE 14.13

#### Finding Equilibrium Concentrations from Initial Concentrations in Cases with a Small Equilibrium Constant

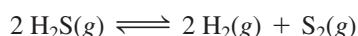
Consider the reaction for the decomposition of hydrogen disulfide:



A 0.500 L reaction vessel initially contains  $1.25 \times 10^{-4}$  mol of  $\text{H}_2\text{S}$  at  $800^\circ\text{C}$ . Find the equilibrium concentrations of  $\text{H}_2$  and  $\text{S}_2$ .

- Using the balanced equation as a guide, prepare a table showing the known initial concentrations of the reactants and products. (In these examples, you must first calculate the concentration of  $\text{H}_2\text{S}$  from the given number of moles and volume.)

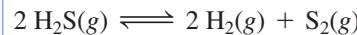
$$[\text{H}_2\text{S}] = \frac{0.0125 \text{ mol}}{0.500 \text{ L}} = 0.0250 \text{ M}$$



|         | [H <sub>2</sub> S] | [H <sub>2</sub> ] | [S <sub>2</sub> ] |
|---------|--------------------|-------------------|-------------------|
| Initial | 0.0250             | 0.00              | 0.00              |
| Change  |                    |                   |                   |
| Equil   |                    |                   |                   |

$$[\text{H}_2\text{S}] = \frac{1.25 \times 10^{-4} \text{ mol}}{0.500 \text{ L}}$$

$$= 2.50 \times 10^{-4} \text{ M}$$



|         | [H <sub>2</sub> S]    | [H <sub>2</sub> ] | [S <sub>2</sub> ] |
|---------|-----------------------|-------------------|-------------------|
| Initial | $2.50 \times 10^{-4}$ | 0.00              | 0.00              |
| Change  |                       |                   |                   |
| Equil   |                       |                   |                   |

| <p><b>2.</b> Use the initial concentrations to calculate the reaction quotient (<math>Q</math>). Compare <math>Q</math> to <math>K</math> to predict the direction in which the reaction will proceed.</p>   | <p>By inspection, <math>Q = 0</math>; the reaction will proceed to the right.</p>   | <p>By inspection, <math>Q = 0</math>; the reaction will proceed to the right.</p>   |                    |                   |                   |         |        |      |      |        |     |     |    |       |               |      |     |   |  |                    |                   |                   |         |                       |      |      |        |     |     |    |       |                            |      |     |
|--|---|---|--------------------|-------------------|-------------------|---------|--------|------|------|--------|-----|-----|----|-------|---------------|------|-----|---|--|--------------------|-------------------|-------------------|---------|-----------------------|------|------|--------|-----|-----|----|-------|----------------------------|------|-----|
| <p><b>3.</b> Represent the change in the concentration of one of the reactants or products with the variable <math>x</math>. Define the changes in the concentrations of the other reactants or products with respect to <math>x</math>.</p>   | $2 \text{H}_2\text{S}(g) \rightleftharpoons 2 \text{H}_2(g) + \text{S}_2(g)$ <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th></th> <th>[H<sub>2</sub>S]</th> <th>[H<sub>2</sub>]</th> <th>[S<sub>2</sub>]</th> </tr> </thead> <tbody> <tr> <td>Initial</td> <td>0.0250</td> <td>0.00</td> <td>0.00</td> </tr> <tr> <td>Change</td> <td>-2x</td> <td>+2x</td> <td>+x</td> </tr> <tr> <td>Equil</td> <td></td> <td></td> <td></td> </tr> </tbody> </table>   |   | [H <sub>2</sub> S] | [H <sub>2</sub> ] | [S <sub>2</sub> ] | Initial | 0.0250 | 0.00 | 0.00 | Change | -2x | +2x | +x | Equil |               |      |     | $2 \text{H}_2\text{S}(g) \rightleftharpoons 2 \text{H}_2(g) + \text{S}_2(g)$ <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th></th> <th>[H<sub>2</sub>S]</th> <th>[H<sub>2</sub>]</th> <th>[S<sub>2</sub>]</th> </tr> </thead> <tbody> <tr> <td>Initial</td> <td><math>2.50 \times 10^{-4}</math></td> <td>0.00</td> <td>0.00</td> </tr> <tr> <td>Change</td> <td>-2x</td> <td>+2x</td> <td>+x</td> </tr> <tr> <td>Equil</td> <td></td> <td></td> <td></td> </tr> </tbody> </table>   |  | [H <sub>2</sub> S] | [H <sub>2</sub> ] | [S <sub>2</sub> ] | Initial | $2.50 \times 10^{-4}$ | 0.00 | 0.00 | Change | -2x | +2x | +x | Equil |                            |      |     |
|  | [H <sub>2</sub> S]  | [H <sub>2</sub> ]   | [S <sub>2</sub> ]  |                   |                   |         |        |      |      |        |     |     |    |       |               |      |     |   |  |                    |                   |                   |         |                       |      |      |        |     |     |    |       |                            |      |     |
| Initial  | 0.0250  | 0.00  | 0.00               |                   |                   |         |        |      |      |        |     |     |    |       |               |      |     |   |  |                    |                   |                   |         |                       |      |      |        |     |     |    |       |                            |      |     |
| Change   | -2x   | +2x   | +x                 |                   |                   |         |        |      |      |        |     |     |    |       |               |      |     |   |  |                    |                   |                   |         |                       |      |      |        |     |     |    |       |                            |      |     |
| Equil  |   |   |                    |                   |                   |         |        |      |      |        |     |     |    |       |               |      |     |   |  |                    |                   |                   |         |                       |      |      |        |     |     |    |       |                            |      |     |
|  | [H <sub>2</sub> S]  | [H <sub>2</sub> ]   | [S <sub>2</sub> ]  |                   |                   |         |        |      |      |        |     |     |    |       |               |      |     |   |  |                    |                   |                   |         |                       |      |      |        |     |     |    |       |                            |      |     |
| Initial  | $2.50 \times 10^{-4}$   | 0.00  | 0.00               |                   |                   |         |        |      |      |        |     |     |    |       |               |      |     |   |  |                    |                   |                   |         |                       |      |      |        |     |     |    |       |                            |      |     |
| Change   | -2x   | +2x   | +x                 |                   |                   |         |        |      |      |        |     |     |    |       |               |      |     |   |  |                    |                   |                   |         |                       |      |      |        |     |     |    |       |                            |      |     |
| Equil  |   |   |                    |                   |                   |         |        |      |      |        |     |     |    |       |               |      |     |   |  |                    |                   |                   |         |                       |      |      |        |     |     |    |       |                            |      |     |
| <p><b>4.</b> Sum each column for each reactant and product to determine the equilibrium concentrations in terms of the initial concentrations and the variable <math>x</math>.</p>   | $2 \text{H}_2\text{S}(g) \rightleftharpoons 2 \text{H}_2(g) + \text{S}_2(g)$ <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th></th> <th>[H<sub>2</sub>S]</th> <th>[H<sub>2</sub>]</th> <th>[S<sub>2</sub>]</th> </tr> </thead> <tbody> <tr> <td>Initial</td> <td>0.0250</td> <td>0.00</td> <td>0.00</td> </tr> <tr> <td>Change</td> <td>-2x</td> <td>+2x</td> <td>+x</td> </tr> <tr> <td>Equil</td> <td><math>0.0250 - 2x</math></td> <td><math>2x</math></td> <td><math>x</math></td> </tr> </tbody> </table>  |   | [H <sub>2</sub> S] | [H <sub>2</sub> ] | [S <sub>2</sub> ] | Initial | 0.0250 | 0.00 | 0.00 | Change | -2x | +2x | +x | Equil | $0.0250 - 2x$ | $2x$ | $x$ | $2 \text{H}_2\text{S}(g) \rightleftharpoons 2 \text{H}_2(g) + \text{S}_2(g)$ <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th></th> <th>[H<sub>2</sub>S]</th> <th>[H<sub>2</sub>]</th> <th>[S<sub>2</sub>]</th> </tr> </thead> <tbody> <tr> <td>Initial</td> <td><math>2.50 \times 10^{-4}</math></td> <td>0.00</td> <td>0.00</td> </tr> <tr> <td>Change</td> <td>-2x</td> <td>+2x</td> <td>+x</td> </tr> <tr> <td>Equil</td> <td><math>2.50 \times 10^{-4} - 2x</math></td> <td><math>2x</math></td> <td><math>x</math></td> </tr> </tbody> </table> |  | [H <sub>2</sub> S] | [H <sub>2</sub> ] | [S <sub>2</sub> ] | Initial | $2.50 \times 10^{-4}$ | 0.00 | 0.00 | Change | -2x | +2x | +x | Equil | $2.50 \times 10^{-4} - 2x$ | $2x$ | $x$ |
|  | [H <sub>2</sub> S]  | [H <sub>2</sub> ]   | [S <sub>2</sub> ]  |                   |                   |         |        |      |      |        |     |     |    |       |               |      |     |   |  |                    |                   |                   |         |                       |      |      |        |     |     |    |       |                            |      |     |
| Initial  | 0.0250  | 0.00  | 0.00               |                   |                   |         |        |      |      |        |     |     |    |       |               |      |     |   |  |                    |                   |                   |         |                       |      |      |        |     |     |    |       |                            |      |     |
| Change   | -2x   | +2x   | +x                 |                   |                   |         |        |      |      |        |     |     |    |       |               |      |     |   |  |                    |                   |                   |         |                       |      |      |        |     |     |    |       |                            |      |     |
| Equil  | $0.0250 - 2x$   | $2x$  | $x$                |                   |                   |         |        |      |      |        |     |     |    |       |               |      |     |   |  |                    |                   |                   |         |                       |      |      |        |     |     |    |       |                            |      |     |
|  | [H <sub>2</sub> S]  | [H <sub>2</sub> ]   | [S <sub>2</sub> ]  |                   |                   |         |        |      |      |        |     |     |    |       |               |      |     |   |  |                    |                   |                   |         |                       |      |      |        |     |     |    |       |                            |      |     |
| Initial  | $2.50 \times 10^{-4}$   | 0.00  | 0.00               |                   |                   |         |        |      |      |        |     |     |    |       |               |      |     |   |  |                    |                   |                   |         |                       |      |      |        |     |     |    |       |                            |      |     |
| Change   | -2x   | +2x   | +x                 |                   |                   |         |        |      |      |        |     |     |    |       |               |      |     |   |  |                    |                   |                   |         |                       |      |      |        |     |     |    |       |                            |      |     |
| Equil  | $2.50 \times 10^{-4} - 2x$  | $2x$  | $x$                |                   |                   |         |        |      |      |        |     |     |    |       |               |      |     |   |  |                    |                   |                   |         |                       |      |      |        |     |     |    |       |                            |      |     |
| <p><b>5.</b> Substitute the expressions for the equilibrium concentrations (from step 4) into the expression for the equilibrium constant. Use the given value of the equilibrium constant to solve the resulting equation for the variable <math>x</math>.</p> <p>In this case, the resulting equation is cubic in <math>x</math>. Although cubic equations can be solved, the solutions are not usually simple. However, since the equilibrium constant is small, we know that the reaction does not proceed very far to the right. Therefore, <math>x</math> will be a small number and can be dropped from any quantities in which it is added to or subtracted from another number (as long as the number itself is not too small).</p> <p>Check whether your approximation was valid by comparing the calculated value of <math>x</math> to the number it was added to or subtracted from. The ratio of the two numbers should be less than 0.05 (or 5%) for the approximation to be valid. If approximation is not valid, proceed to step 5a.</p> | $K_c = \frac{[\text{H}_2]^2[\text{S}_2]}{[\text{H}_2\text{S}]^2}$ $= \frac{(2x)^2x}{(0.0250 - 2x)^2}$ $1.67 \times 10^{-7} = \frac{4x^3}{(0.0250 - 2x)^2}$ $1.67 \times 10^{-7} = \frac{4x^3}{(0.0250 - 2x)^2} \quad x \text{ is small.}$ $1.67 \times 10^{-7} = \frac{4x^3}{6.25 \times 10^{-4}}$ $6.25 \times 10^{-4}(1.67 \times 10^{-7}) = 4x^3$ $x^3 = \frac{6.25 \times 10^{-4}(1.67 \times 10^{-7})}{4}$ $x = 2.97 \times 10^{-4}$ <p>Checking the <math>x</math> is small approximation:</p> $\frac{2.97 \times 10^{-4}}{0.0250} \times 100\% = 1.19\%$ <p>The <math>x</math> is small approximation is valid, proceed to step 6.</p> | $K_c = \frac{[\text{H}_2]^2[\text{S}_2]}{[\text{H}_2\text{S}]^2}$ $= \frac{(2x)^2x}{(2.50 \times 10^{-4} - 2x)^2}$ $1.67 \times 10^{-7} = \frac{4x^3}{(2.50 \times 10^{-4} - 2x)^2} \quad x \text{ is small.}$ $1.67 \times 10^{-7} = \frac{4x^3}{6.25 \times 10^{-8}}$ $6.25 \times 10^{-8}(1.67 \times 10^{-7}) = 4x^3$ $x^3 = \frac{6.25 \times 10^{-8}(1.67 \times 10^{-7})}{4}$ $x = 1.38 \times 10^{-5}$ <p>Checking the <math>x</math> is small approximation:</p> $\frac{1.38 \times 10^{-5}}{2.50 \times 10^{-4}} \times 100\% = 5.52\%$ <p>The approximation does not satisfy the &lt;5% rule (although it is close).</p> |                    |                   |                   |         |        |      |      |        |     |     |    |       |               |      |     |   |  |                    |                   |                   |         |                       |      |      |        |     |     |    |       |                            |      |     |

- 5a.** If the approximation is not valid, you can either solve the equation exactly (by hand or with your calculator), or use the method of successive approximations. In this case, we use the method of successive approximations.

Substitute the value obtained for  $x$  in step 5 back into the original cubic equation, but only at the exact spot where  $x$  was assumed to be negligible, and then solve the equation for  $x$  again. Continue this procedure until the value of  $x$  obtained from solving the equation is the same as the one that is substituted into the equation.

- 6.** Substitute  $x$  into the expressions for the equilibrium concentrations of the reactants and products (from step 4) and calculate the concentrations.

- 7.** Check your answer by substituting the calculated equilibrium values into the equilibrium expression. The calculated value of  $K$  should match the given value of  $K$ . Note that the approximation method and rounding errors could cause a difference of up to about 5% when comparing values of the equilibrium constant.

$$\begin{aligned} [\text{H}_2\text{S}] &= 0.0250 - 2(2.97 \times 10^{-4}) \\ &= 0.0244 \text{ M} \\ [\text{H}_2] &= 2(2.97 \times 10^{-4}) \\ &= 5.94 \times 10^{-4} \text{ M} \\ [\text{S}_2] &= 2.97 \times 10^{-4} \text{ M} \end{aligned}$$

$$K_c = \frac{(5.94 \times 10^{-4})^2 (2.97 \times 10^{-4})}{(0.0244)^2} = 1.76 \times 10^{-7}$$

The calculated value of  $K$  is close enough to the given value when we consider the uncertainty introduced by the approximation. Therefore the answer is valid.

#### FOR PRACTICE 14.12

The reaction in Example 14.12 is carried out at the same temperature with the following initial concentrations:  $[\text{H}_2\text{S}] = 0.100 \text{ M}$ ,  $[\text{H}_2] = 0.100 \text{ M}$ , and  $[\text{S}_2] = 0.00 \text{ M}$ . Find the equilibrium concentration of  $[\text{S}_2]$ .

$$1.67 \times 10^{-7} = \frac{4x^3}{(2.50 \times 10^{-4} - 2x)^2}$$

$$x = 1.38 \times 10^{-5}$$

$$1.67 \times 10^{-7} = \frac{4x^3}{(2.50 \times 10^{-4} - 2.76 \times 10^{-5})^2}$$

$$x = 1.27 \times 10^{-5}$$

If we substitute this value of  $x$  back into the cubic equation and solve it, we get  $x = 1.28 \times 10^{-5}$ , which is nearly identical to  $1.27 \times 10^{-5}$ . Therefore, we have arrived at the best approximation for  $x$ .

$$\begin{aligned} [\text{H}_2\text{S}] &= 2.50 \times 10^{-4} - 2(1.28 \times 10^{-5}) \\ &= 2.24 \times 10^{-4} \text{ M} \\ [\text{H}_2] &= 2(1.28 \times 10^{-5}) \\ &= 2.56 \times 10^{-5} \text{ M} \\ [\text{S}_2] &= 1.28 \times 10^{-5} \text{ M} \end{aligned}$$

$$K_c = \frac{(2.56 \times 10^{-5})^2 (1.28 \times 10^{-5})}{(2.24 \times 10^{-4})^2} = 1.67 \times 10^{-7}$$

The calculated value of  $K$  is equal to the given value. Therefore the answer is valid.

#### FOR PRACTICE 14.13

The reaction in Example 14.13 is carried out at the same temperature with the following initial concentrations:  $[\text{H}_2\text{S}] = 1.00 \times 10^{-4} \text{ M}$ ,  $[\text{H}_2] = 0.00 \text{ M}$ , and  $[\text{S}_2] = 0.00 \text{ M}$ . Find the equilibrium concentration of  $[\text{S}_2]$ .



#### Conceptual Connection 14.6 The $x$ is small Approximation

For the generic reaction,  $\text{A}(g) \rightleftharpoons \text{B}(g)$ , consider each value of  $K$  and initial concentration of A. For which set will the  $x$  is small approximation most likely apply?

- (a)  $K = 1.0 \times 10^{-5}$ ;  $[\text{A}] = 0.250 \text{ M}$
- (b)  $K = 1.0 \times 10^{-2}$ ;  $[\text{A}] = 0.250 \text{ M}$
- (c)  $K = 1.0 \times 10^{-5}$ ;  $[\text{A}] = 0.00250 \text{ M}$
- (d)  $K = 1.0 \times 10^{-2}$ ;  $[\text{A}] = 0.00250 \text{ M}$

## 14.9 Le Châtelier's Principle: How a System at Equilibrium Responds to Disturbances

We have seen that a chemical system not in equilibrium tends to progress toward equilibrium and that the relative concentrations of the reactants and products at equilibrium are characterized by the equilibrium constant,  $K$ . What happens, however, when a chemical system already at equilibrium is disturbed? **Le Châtelier's principle** states that the chemical system responds to minimize the disturbance.

| Pronounced "Le-sha-te-lyay"

**Le Châtelier's principle:** When a chemical system at equilibrium is disturbed, the system shifts in a direction that minimizes the disturbance.

In other words, a system at equilibrium tends to maintain that equilibrium—it bounces back when disturbed.

We can understand Le Châtelier's principle by returning to our two neighboring countries analogy. Suppose the populations of Country A and Country B are at equilibrium. This means that the rate of people moving out of Country A and into Country B is equal to the rate of people moving into Country A and out of Country B, and the populations of the two countries are stable.

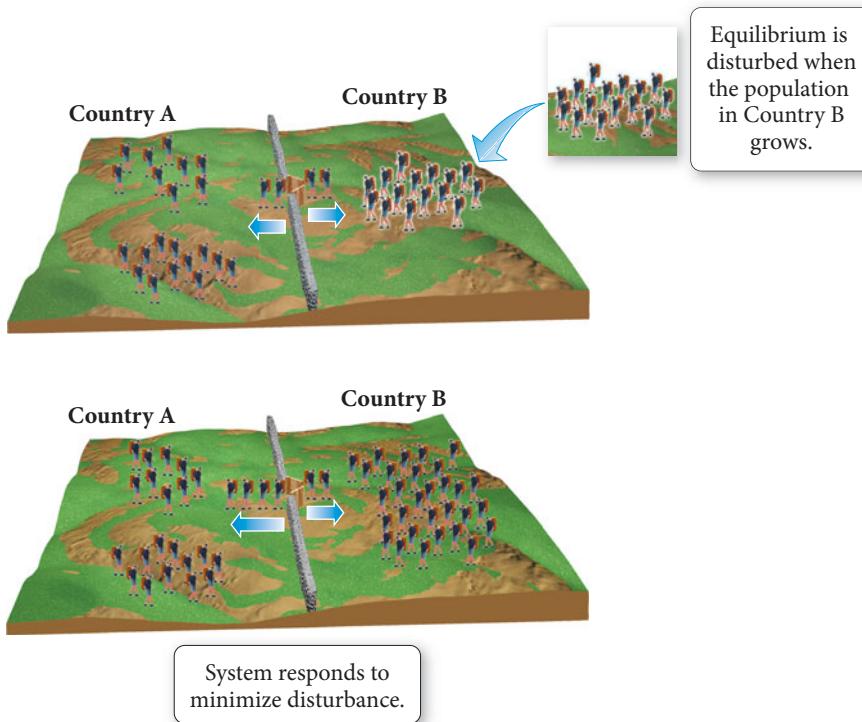


Now imagine disturbing the balance (Figure 14.8 ▶). Suppose there is a notable increase in the birthrate in Country B. What happens? After Country B becomes more crowded, the rate of people leaving Country B increases. The net flow of people is out of Country B and into Country A. Equilibrium is disturbed by the addition of more people to Country B, and people leave Country B in response. In effect, the system responded by shifting in the direction that minimized the disturbance.

On the other hand, what happens if there is a baby boom in Country A instead? As Country A gets more crowded, the rate of people leaving Country A increases. The net flow of people is out of Country A and into Country B. The number of people in Country A initially increases and the system responds; people move out of Country A. Chemical systems behave similarly: when their equilibrium is disturbed, they react to

The two-country analogy should help you see the effects of disturbing a system in equilibrium—it should not be taken as an exact parallel.

### Le Châtelier's Principle: An Analogy



◀ FIGURE 14.8 A Population Analogy for Le Châtelier's Principle A baby boom in Country B shifts the equilibrium to the left. People leave Country B (because it has become too crowded) and migrate to Country A until equilibrium is reestablished.

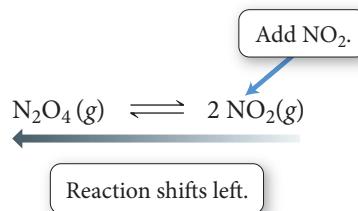
counter the disturbance. We can disturb a system in chemical equilibrium in several different ways, including changing the concentration of a reactant or product, changing the volume or pressure, and changing the temperature. We consider each of these separately.

## The Effect of a Concentration Change on Equilibrium

Consider the following reaction in chemical equilibrium:



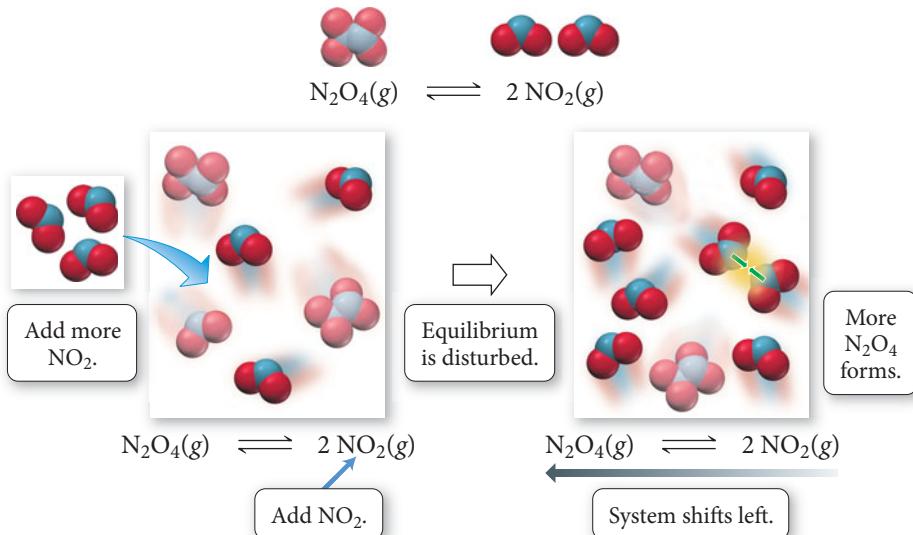
Suppose we disturb the equilibrium by adding  $\text{NO}_2$  to the equilibrium mixture (Figure 14.9 ▶). In other words, we increase the concentration of  $\text{NO}_2$ , the product. What happens? According to Le Châtelier's principle, the system shifts in a direction to minimize the disturbance. The reaction goes to the left (it proceeds in the reverse direction), consuming some of the added  $\text{NO}_2$  and thus bringing its concentration back down, as shown graphically in Figure 14.10a ▷.



The reaction shifts to the left because the value of  $Q$  changes as follows:

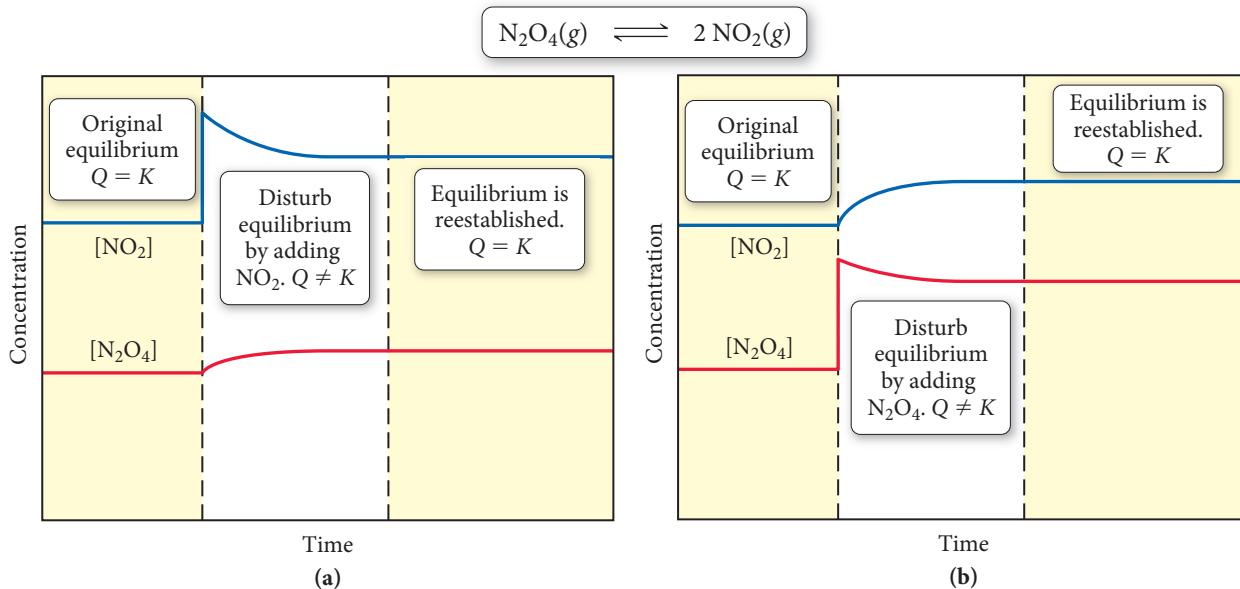
- Before addition of  $\text{NO}_2$ :  $Q = K$ .
- Immediately after addition of  $\text{NO}_2$ :  $Q > K$ .
- Reaction shifts to left to reestablish equilibrium.

### Le Châtelier's Principle: Changing Concentration

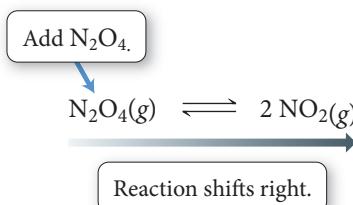


**▲ FIGURE 14.9** Le Châtelier's Principle: The Effect of a Concentration Change Adding  $\text{NO}_2$  causes the reaction to shift left, consuming some of the added  $\text{NO}_2$  and forming more  $\text{N}_2\text{O}_4$ .

### Le Châtelier's Principle: Graphical Representation



On the other hand, what happens if we add extra  $\text{N}_2\text{O}_4$  (the reactant), increasing its concentration? In this case, the reaction shifts to the right, consuming some of the added  $\text{N}_2\text{O}_4$  and bringing *its* concentration back down, as shown graphically in Figure 14.10b ▲.



**▲ FIGURE 14.10** Le Châtelier's Principle: Changing Concentration

The graph shows the concentrations of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  for the reaction  $\text{N}_2\text{O}_4(g) \rightleftharpoons 2 \text{NO}_2(g)$  as a function of time in three distinct stages of the reaction: initially at equilibrium (left), upon disturbance of the equilibrium by addition of more  $\text{NO}_2$  (a) or  $\text{N}_2\text{O}_4$  (b) to the reaction mixture (center), and upon reestablishment of equilibrium (right).

The reaction shifts to the right because the value of  $Q$  changes as follows:

- Before addition of  $\text{N}_2\text{O}_4$ :  $Q = K$ .
- Immediately after addition of  $\text{N}_2\text{O}_4$ :  $Q < K$ .
- Reaction shifts to right to reestablish equilibrium.

In both of these cases, the system shifts in a direction that minimizes the disturbance. Lowering the concentration of a reactant (which makes  $Q > K$ ) causes the system to shift in the direction of the reactants to minimize the disturbance. Lowering the concentration of a product (which makes  $Q < K$ ) causes the system to shift in the direction of products.

#### Summarizing the Effect of a Concentration Change on Equilibrium:

If a chemical system is at equilibrium:

- ▶ Increasing the concentration of one or more of the *reactants* (which makes  $Q < K$ ) causes the reaction to *shift to the right* (in the direction of the products).
- ▶ Increasing the concentration of one or more of the *products* (which makes  $Q > K$ ) causes the reaction to *shift to the left* (in the direction of the reactants).
- ▶ Decreasing the concentration of one or more of the *reactants* (which makes  $Q > K$ ) causes the reaction to *shift to the left* (in the direction of the reactants).
- ▶ Decreasing the concentration of one or more of the *products* (which makes  $Q < K$ ) causes the reaction to *shift to the right* (in the direction of the products).

### EXAMPLE 14.14 The Effect of a Concentration Change on Equilibrium

Consider the following reaction at equilibrium:



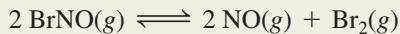
What is the effect of adding additional  $\text{CO}_2$  to the reaction mixture? What is the effect of adding additional  $\text{CaCO}_3$ ?

#### SOLUTION

Adding additional  $\text{CO}_2$  increases the concentration of  $\text{CO}_2$  and causes the reaction to shift to the left. Adding additional  $\text{CaCO}_3$ , however, does *not* increase the concentration of  $\text{CaCO}_3$  because  $\text{CaCO}_3$  is a solid and therefore has a constant concentration. Thus, adding additional  $\text{CaCO}_3$  has no effect on the position of the equilibrium. (Note that, as we saw in Section 14.5, solids are not included in the equilibrium expression.)

#### FOR PRACTICE 14.14

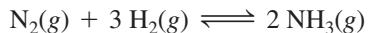
Consider the following reaction in chemical equilibrium:



What is the effect of adding additional  $\text{Br}_2$  to the reaction mixture? What is the effect of adding additional  $\text{BrNO}$ ?

## The Effect of a Volume (or Pressure) Change on Equilibrium

How does a system in chemical equilibrium respond to a volume change? Recall from Chapter 5 that changing the volume of a gas (or a gas mixture) results in a change in pressure. Remember also that pressure and volume are inversely related: a *decrease* in volume causes an *increase* in pressure, and an *increase* in volume causes a *decrease* in pressure. So, if the volume of a reaction mixture at chemical equilibrium is changed, the pressure changes and the system shifts in a direction to minimize that change. For example, consider the following reaction at equilibrium in a cylinder equipped with a moveable piston:



What happens if we push down on the piston, lowering the volume and raising the pressure (Figure 14.11 ►)? How can the chemical system respond to bring the pressure back down? Look carefully at the reaction coefficients. If the reaction shifts to the right, 4 mol of gas particles are converted to 2 mol of gas particles. From the ideal gas law ( $PV = nRT$ ), we know that decreasing the number of moles of a gas ( $n$ ) results in a lower pressure ( $P$ ). Therefore, the system shifts to the right, decreasing the number of gas molecules and bringing the pressure back down, minimizing the disturbance.

Consider the same reaction mixture at equilibrium again. What happens if, this time, we pull *up* on the piston, *increasing* the volume (Figure 14.11b)? The higher volume results in a lower pressure and the system responds to bring the pressure back up. It does this by shifting to the left, converting every 2 mol of gas particles into 4 mol of gas particles, increasing the pressure and minimizing the disturbance.

Consider again the same reaction mixture at equilibrium. What happens if, this time, we keep the volume the same but increase the pressure by *adding an inert gas* to the mixture? Although the overall pressure of the mixture increases, the partial pressures of the reactants and products do not change. Consequently, there is no effect and the reaction does not shift in either direction.

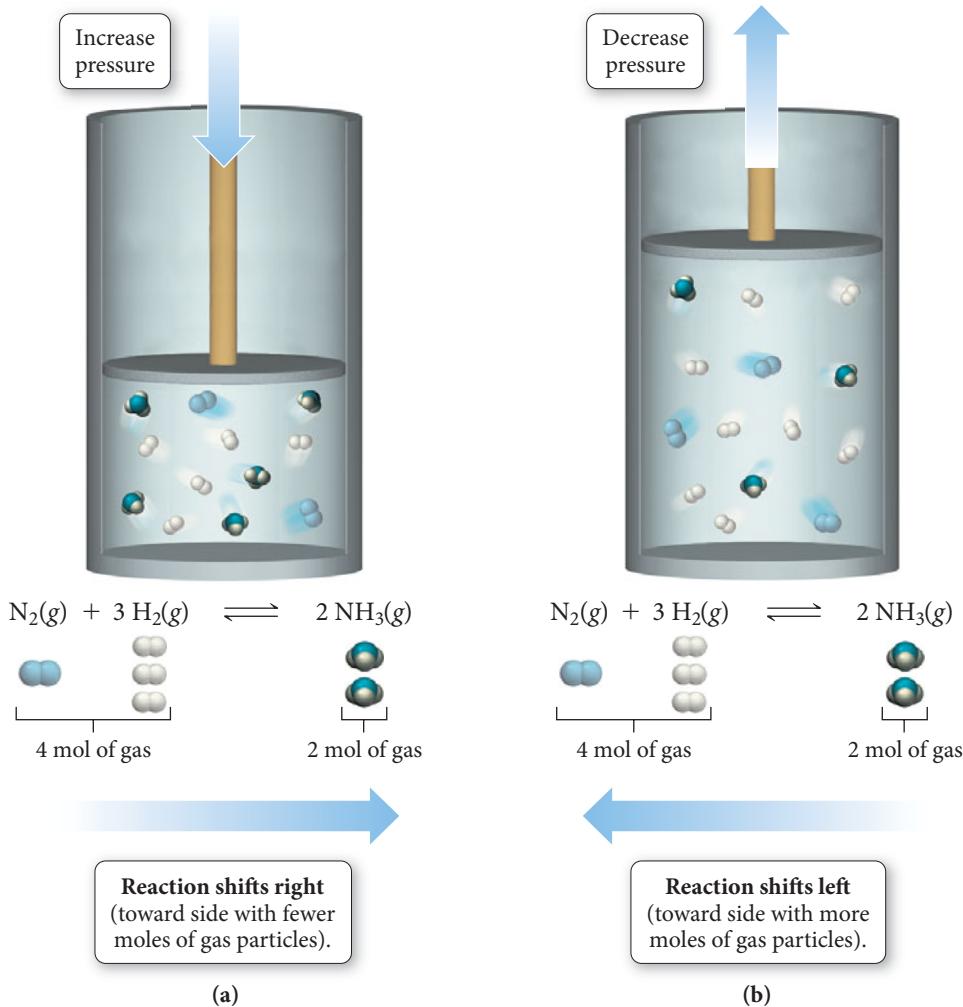
#### *Summarizing the Effect of Volume Change on Equilibrium:*

If a chemical system is at equilibrium:

- *Decreasing* the volume causes the reaction to shift in the direction that has *the fewer moles of gas particles*.
- *Increasing* the volume causes the reaction to shift in the direction that has *the greater number of moles of gas particles*.

In considering the effect of a change in volume, we are assuming that the change in volume is carried out at constant temperature.

### Le Châtelier's Principle: Changing Pressure



◀ FIGURE 14.11 Le Châtelier's Principle: The Effect of a Pressure Change

(a) Decreasing the volume increases the pressure, causing the reaction to shift to the right (fewer moles of gas, lower pressure). (b) Increasing the volume reduces the pressure, causing the reaction to shift to the left (more moles of gas, higher pressure).

### EXAMPLE 14.15 The Effect of a Volume Change on Equilibrium

Consider the following reaction at chemical equilibrium:



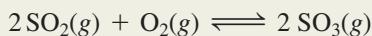
What is the effect of decreasing the volume of the reaction mixture? Increasing the volume of the reaction mixture? Adding an inert gas at constant volume?

#### SOLUTION

The chemical equation has 3 mol of gas on the right and zero moles of gas on the left. Decreasing the volume of the reaction mixture increases the pressure and causes the reaction to shift to the left (toward the side with fewer moles of gas particles). Increasing the volume of the reaction mixture decreases the pressure and causes the reaction to shift to the right (toward the side with more moles of gas particles.) Adding an inert gas has no effect.

#### FOR PRACTICE 14.15

Consider the following reaction at chemical equilibrium:



What is the effect of decreasing the volume of the reaction mixture? Increasing the volume of the reaction mixture?

## The Effect of a Temperature Change on Equilibrium

In considering the effect of a change in temperature, we are assuming that the heat is added (or removed) at constant pressure.

According to Le Châtelier's principle, if the temperature of a system at equilibrium is changed, the system will shift in a direction to counter that change. So, if the temperature is increased, the reaction will shift in the direction that tends to decrease the temperature and vice versa. Recall from Chapter 6 that an exothermic reaction (negative  $\Delta H$ ) emits heat:

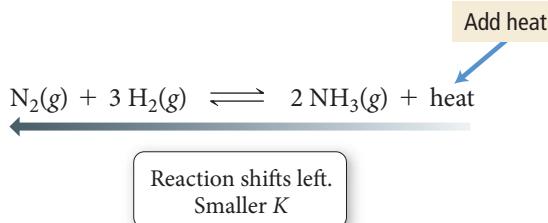


We can think of heat as a product in an exothermic reaction. In an endothermic reaction (positive  $\Delta H$ ), the reaction absorbs heat.



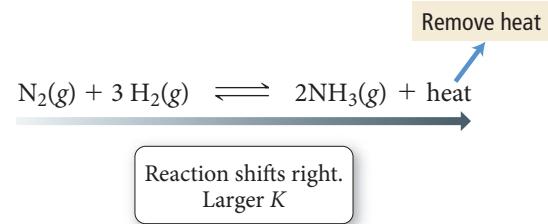
We can think of heat as a reactant in an endothermic reaction.

At constant pressure, raising the temperature of an *exothermic* reaction—think of this as adding heat—is similar to adding more product, causing the reaction to shift left. For example, the reaction of nitrogen with hydrogen to form ammonia is exothermic:

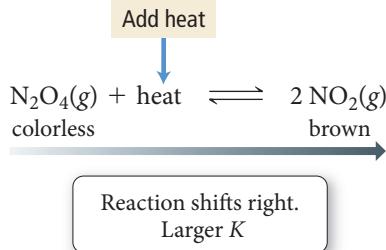


Raising the temperature of an equilibrium mixture of these three gases causes the reaction to shift left, absorbing some of the added heat and forming less products and more reactants. Note that, unlike adding additional  $\text{NH}_3$  to the reaction mixture (which does *not* change the value of the equilibrium constant), *changing the temperature does change the value of the equilibrium constant*. The new equilibrium mixture will have more reactants and fewer products and therefore a smaller value of  $K$ .

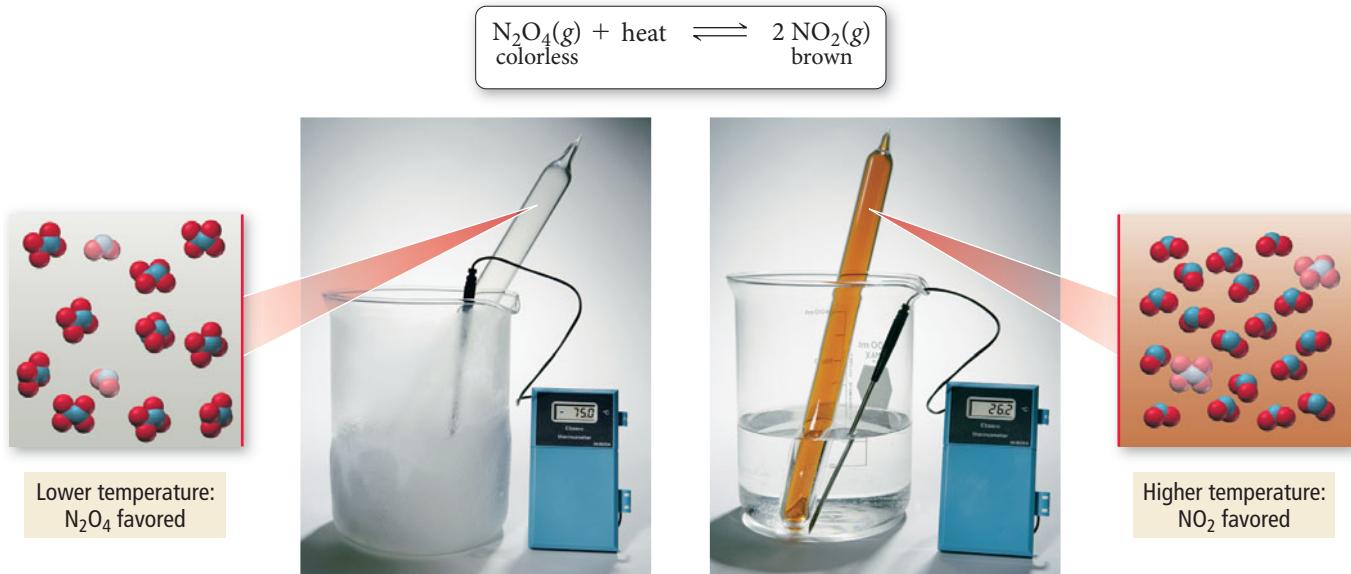
Conversely, lowering the temperature causes the reaction to shift right, releasing heat and producing more products because the value of  $K$  has increased:



In contrast, for an *endothermic* reaction, raising the temperature (adding heat) causes the reaction to shift right to absorb the added heat. For example, the following reaction is endothermic:

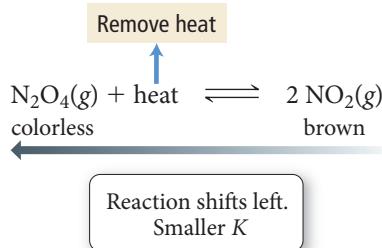


### Le Châtelier's Principle: Changing Temperature



**▲ FIGURE 14.12** Le Châtelier's Principle: The Effect of a Temperature Change Because the reaction is endothermic, raising the temperature causes a shift to the right, toward the formation of brown  $\text{NO}_2$ .

Raising the temperature of an equilibrium mixture of these two gases causes the reaction to shift right, absorbing some of the added heat and producing more products because the value of  $K$  has increased. Since  $\text{N}_2\text{O}_4$  is colorless and  $\text{NO}_2$  is brown, the effects of changing the temperature of this reaction are easily seen (Figure 14.12 ▲). On the other hand, lowering the temperature (removing heat) of a reaction mixture of these two gases causes the reaction to shift left, releasing heat, forming less products, and lowering the value of  $K$ :



#### *Summarizing the Effect of a Temperature Change on Equilibrium:*

In an *exothermic* chemical reaction, heat is a product.

- ▶ *Increasing* the temperature causes an exothermic reaction to *shift left* (in the direction of the reactants); the value of the equilibrium constant decreases.
- ▶ *Decreasing* the temperature causes an exothermic reaction to *shift right* (in the direction of the products); the value of the equilibrium constant increases.

In an *endothermic* chemical reaction, heat is a reactant.

- ▶ *Increasing* the temperature causes an endothermic reaction to *shift right* (in the direction of the products); the equilibrium constant increases.
- ▶ *Decreasing* the temperature causes an endothermic reaction to *shift left* (in the direction of the reactants); the equilibrium constant decreases.

Adding heat favors the endothermic direction. Removing heat favors the exothermic direction.

**EXAMPLE 14.16****The Effect of a Temperature Change on Equilibrium**

The following reaction is endothermic:



What is the effect of increasing the temperature of the reaction mixture? Decreasing the temperature?

**SOLUTION**

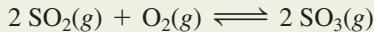
Since the reaction is endothermic, we can think of heat as a reactant:



Raising the temperature is equivalent to adding a reactant, causing the reaction to shift to the right. Lowering the temperature is equivalent to removing a reactant, causing the reaction to shift to the left.

**FOR PRACTICE 14.16**

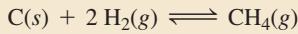
The following reaction is exothermic:



What is the effect of increasing the temperature of the reaction mixture? Decreasing the temperature?

**CHAPTER IN REVIEW****Self Assessment Quiz**

- Q1.** What is the correct expression for the equilibrium constant ( $K_c$ ) for the reaction between carbon and hydrogen gas to form methane shown here?



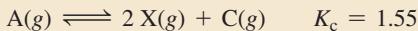
- a)  $K_c = \frac{[\text{CH}_4]}{[\text{H}_2]}$
- b)  $K_c = \frac{[\text{CH}_4]}{[\text{C}][\text{H}_2]}$
- c)  $K_c = \frac{[\text{CH}_4]}{[\text{C}][\text{H}_2]^2}$
- d)  $K_c = \frac{[\text{CH}_4]}{[\text{H}_2]^2}$

- Q2.** The equilibrium constant for the reaction shown here is  $K_c = 1.0 \times 10^3$ . A reaction mixture at equilibrium contains  $[\text{A}] = 1.0 \times 10^{-3}$  M. What is the concentration of B in the mixture?



- a)  $1.0 \times 10^{-3}$  M
- b) 1.0 M
- c) 2.0 M
- d)  $1.0 \times 10^3$  M

- Q3.** Use the data below to find the equilibrium constant ( $K_c$ ) for the reaction  $\text{A}(g) \rightleftharpoons 2 \text{B}(g) + \text{C}(g)$ .



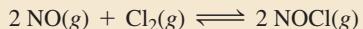
- a) 984
- b) 26.8
- c)  $6.10 \times 10^{-4}$
- d)  $2.44 \times 10^{-3}$

- Q4.** The reaction shown here has a  $K_p = 4.5 \times 10^2$  at 825 K. Find  $K_c$  for the reaction at this temperature.



- a) 0.098
- b)  $2.1 \times 10^6$
- c) 6.6
- d)  $4.5 \times 10^{-2}$

- Q5.** Consider the reaction between NO and  $\text{Cl}_2$  to form  $\text{NOCl}$ :



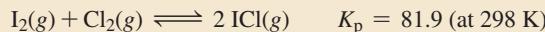
A reaction mixture at a certain temperature initially contains only  $[\text{NO}] = 0.50$  M and  $[\text{Cl}_2] = 0.50$  M. After the reaction comes to equilibrium, the concentration of  $\text{NOCl}$  is 0.30 M. Find the value of the equilibrium constant ( $K_c$ ) at this temperature.

- a) 11
- b) 4.3
- c) 6.4
- d) 0.22

- Q6.** For the reaction  $2 \text{A}(g) \rightleftharpoons \text{B}(g)$ , the equilibrium constant is  $K_p = 0.76$ . A reaction mixture initially contains 2.0 atm of each gas ( $P_{\text{A}} = 2.0$  atm and  $P_{\text{B}} = 2.0$  atm). Which statement is true of the reaction mixture?

- a) The reaction mixture is at equilibrium.
- b) The reaction mixture will proceed toward products.
- c) The reaction mixture will proceed toward reactants.
- d) It is not possible to determine from the information given the future direction of the reaction mixture.

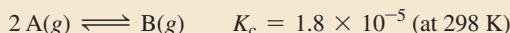
- Q7.** Consider the reaction between iodine gas and chlorine gas to form iodine monochloride:



A reaction mixture at 298 K initially contains  $P_{\text{I}_2} = 0.25$  atm and  $P_{\text{Cl}_2} = 0.25$  atm. What is the partial pressure of iodine monochloride when the reaction reaches equilibrium?

- a) 0.17 atm
- b) 0.64 atm
- c) 0.41 atm
- d) 2.3 atm

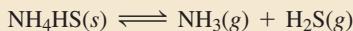
- Q8.** Consider the reaction of A to form B:



A reaction mixture at 298 K initially contains  $[\text{A}] = 0.50 \text{ M}$ . What is the concentration of B when the reaction reaches equilibrium?

- a)  $9.0 \times 10^{-6} \text{ M}$       b)  $0.060 \text{ M}$   
 c)  $0.030 \text{ M}$       d)  $4.5 \times 10^{-6} \text{ M}$

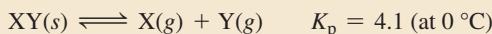
- Q9.** The decomposition of  $\text{NH}_4\text{HS}$  is endothermic:



Which change to an equilibrium mixture of this reaction results in the formation of more  $\text{H}_2\text{S}$ ?

- a) a decrease in the volume of the reaction vessel (at constant temperature)  
 b) an increase in the amount of  $\text{NH}_4\text{HS}$  in the reaction vessel  
 c) an increase in temperature  
 d) all of the above

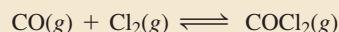
- Q10.** The solid XY decomposes into gaseous X and Y:



If the reaction is carried out in a 22.4 L container, which initial amounts of X and Y will result in the formation of solid XY?

- a) 5 mol X; 0.5 mol Y  
 b) 2.0 mol X; 2.0 mol Y  
 c) 1 mol X; 1 mol Y  
 d) none of the above

- Q11.** What is the effect of adding helium gas (at constant volume) to an equilibrium mixture of the reaction:



- a) The reaction shifts toward the products.  
 b) The reaction shifts toward the reactants.  
 c) The reaction does not shift in either direction.  
 d) The reaction slows down.

- Q12.** The reaction  $\text{X}_2(g) \rightleftharpoons 2 \text{X}(g)$  occurs in a closed reaction vessel at constant volume and temperature. Initially, the vessel contains only  $\text{X}_2$  at a pressure of 1.55 atm. After the reaction reaches equilibrium, the total pressure is 2.85 atm. What is the value of the equilibrium constant,  $K_p$ , for the reaction?

- a) 27  
 b) 10  
 c) 5.2  
 d) 32

Answers: 1. (d) 2. (b) 3. (d) 4. (a) 5. (c) 6. (c) 7. (c) 8. (d) 9. (c) 10. (d) 11. (c) 12. (a)

## Key Terms

### Section 14.2

reversible (651)  
 dynamic equilibrium (651)

### Section 14.3

equilibrium constant ( $K$ ) (654)  
 law of mass action (654)

### Section 14.7

reaction quotient ( $Q$ ) (665)

### Section 14.9

Le Châtelier's principle (677)

## Key Concepts

### The Equilibrium Constant (14.1)

- The relative concentrations of the reactants and the products at equilibrium are expressed by the equilibrium constant,  $K$ .
- The equilibrium constant measures how far a reaction proceeds toward products: a large  $K$  (much greater than 1) indicates a high concentration of products at equilibrium, and a small  $K$  (less than 1) indicates a low concentration of products at equilibrium.

### Dynamic Equilibrium (14.2)

- Most chemical reactions are reversible; they can proceed in either the forward or the reverse direction.
- When a chemical reaction is in dynamic equilibrium, the rate of the forward reaction equals the rate of the reverse reaction, so the net concentrations of reactants and products do not change. However, this does *not* imply that the concentrations of the reactants and the products are equal at equilibrium.

### The Equilibrium Constant Expression (14.3)

- The equilibrium constant expression is given by the law of mass action and is equal to the concentrations of the products, raised to their stoichiometric coefficients, divided by the concentrations of the reactants, raised to their stoichiometric coefficients.
- When the equation for a chemical reaction is reversed, multiplied, or added to another equation,  $K$  must be modified accordingly.

### The Equilibrium Constant, $K$ (14.4)

- The equilibrium constant can be expressed in terms of concentrations ( $K_c$ ) or in terms of partial pressures ( $K_p$ ). These two constants are related by Equation 14.2. Concentration must always be expressed in units of molarity for  $K_c$ . Partial pressures must always be expressed in units of atmospheres for  $K_p$ .

### States of Matter and the Equilibrium Constant (14.5)

- The equilibrium constant expression contains only partial pressures or concentrations of reactants and products that exist as gases or solutes dissolved in solution. Pure liquids and solids are not included in the expression for the equilibrium constant.

### Calculating K (14.6)

- We can calculate the equilibrium constant from equilibrium concentrations or partial pressures by substituting measured values into the expression for the equilibrium constant (as obtained from the law of mass action).
- In most cases, we can calculate the equilibrium concentrations of the reactants and products—and therefore the value of the equilibrium constant—from the initial concentrations of the reactants and products and the equilibrium concentration of *just one* reactant or product.

### The Reaction Quotient, Q (14.7)

- The reaction quotient,  $Q$ , is the ratio of the concentrations (or partial pressures) of products raised to their stoichiometric coefficients to the concentrations of reactants raised to their stoichiometric coefficients *at any point in the reaction*.

## Key Equations and Relationships

### Expression for the Equilibrium Constant, $K_c$ (14.3)

$$aA + bB \rightleftharpoons cC + dD$$

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad (\text{equilibrium concentrations only})$$

### Relationship between the Equilibrium Constant and the Chemical Equation (14.3)

- If you reverse the equation, invert the equilibrium constant.
- If you multiply the coefficients in the equation by a factor, raise the equilibrium constant to the same factor.
- If you add two or more individual chemical equations to obtain an overall equation, multiply the corresponding equilibrium constants by each other to obtain the overall equilibrium constant.

### Expression for the Equilibrium Constant, $K_p$ (14.4)

$$aA + bB \rightleftharpoons cC + dD$$

$$K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b} \quad (\text{equilibrium partial pressures only})$$

### Relationship between the Equilibrium Constants, $K_c$ and $K_p$ (14.4)

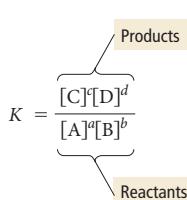
$$K_p = K_c (RT)^{\Delta n}$$

## Key Learning Outcomes

### Chapter Objectives

Expressing Equilibrium Constants for Chemical Equations (14.3)

### Law of Mass Action

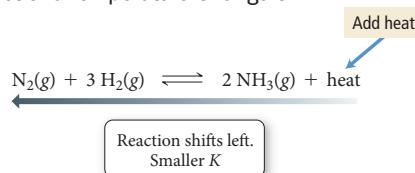


### Assessment

Example 14.1 For Practice 14.1 Exercises 21, 22

## Key Learning Outcomes, continued

|  |   |
|--|---|
| Manipulating the Equilibrium Constant to Reflect Changes in the Chemical Equation (14.3)                               | Example 14.2 For Practice 14.2 For More Practice 14.2 Exercises 27–30 |
| Relating $K_p$ and $K_c$ (14.4)  | Example 14.3 For Practice 14.3 Exercises 31, 32                       |
| Writing Equilibrium Expressions for Reactions Involving a Solid or a Liquid (14.5)                                     | Example 14.4 For Practice 14.4 Exercises 33, 34                       |
| Finding Equilibrium Constants from Experimental Concentration Measurements (14.6)                                      | Examples 14.5, 14.6 For Practice 14.5, 14.6 Exercises 35, 36, 43, 44  |
| Predicting the Direction of a Reaction by Comparing $Q$ and $K$ (14.7)   | Example 14.7 For Practice 14.7 Exercises 47–50                        |
| Calculating Equilibrium Concentrations from the Equilibrium Constant and One or More Equilibrium Concentrations (14.8) | Example 14.8 For Practice 14.8 Exercises 37–46                        |
| Finding Equilibrium Concentrations from Initial Concentrations and the Equilibrium Constant (14.8)                     | Examples 14.9, 14.10 For Practice 14.9, 14.10 Exercises 53–58         |
| Calculating Equilibrium Partial Pressures from the Equilibrium Constant and Initial Partial Pressures (14.8)           | Example 14.11 For Practice 14.11 Exercises 59, 60                     |
| Finding Equilibrium Concentrations from Initial Concentrations in Cases with a Small Equilibrium Constant (14.8)       | Examples 14.12, 14.13 For Practice 14.12, 14.13 Exercises 61, 62      |
| Determining the Effect of a Concentration Change on Equilibrium (14.9)   | Example 14.14 For Practice 14.14 Exercises 63–66                      |
| Determining the Effect of a Volume Change on Equilibrium (14.9)  | Example 14.15 For Practice 14.15 Exercises 67, 68                     |
| Determining the Effect of a Temperature Change on Equilibrium (14.9)   | Example 14.16 For Practice 14.16 Exercises 69, 70                     |



## EXERCISES

### Review Questions

- How does a developing fetus get oxygen in the womb?
- What is dynamic equilibrium? Why is it called *dynamic*?
- Give the general expression for the equilibrium constant of the following generic reaction:



- What is the significance of the equilibrium constant? What does a large equilibrium constant tell us about a reaction? A small one?

- What happens to the value of the equilibrium constant for a reaction if the reaction equation is reversed? Multiplied by a constant?
- If two reactions sum to an overall reaction, and the equilibrium constants for the two reactions are  $K_1$  and  $K_2$ , what is the equilibrium constant for the overall reaction?
- Explain the difference between  $K_c$  and  $K_p$ . For a given reaction, how are the two constants related?

8. What units should be used when expressing concentrations or partial pressures in the equilibrium constant? What are the units of  $K_p$  and  $K_c$ ? Explain.
9. Why are the concentrations of solids and liquids omitted from equilibrium expressions?
10. Does the value of the equilibrium constant depend on the initial concentrations of the reactants and products? Do the equilibrium concentrations of the reactants and products depend on their initial concentrations? Explain.
11. Explain how you might deduce the equilibrium constant for a reaction in which you know the initial concentrations of the reactants and products and the equilibrium concentration of only one reactant or product.
12. What is the definition of the reaction quotient ( $Q$ ) for a reaction? What does  $Q$  measure?
13. What is the value of  $Q$  when each reactant and product is in its standard state? (See Section 6.9 for the definition of standard states.)
14. In what direction will a reaction proceed for each condition: (a)  $Q < K$ ; (b)  $Q > K$ ; and (c)  $Q = K$ ?
15. Many equilibrium calculations involve finding the equilibrium concentrations of reactants and products given their initial concentrations and the equilibrium constant. Outline the general procedure used in solving these kinds of problems.
16. In equilibrium problems involving equilibrium constants that are small relative to the initial concentrations of reactants, we can often assume that the quantity  $x$  (which represents how far the reaction proceeds toward products) is small. When this assumption is made, we can ignore the quantity  $x$  when it is subtracted from a large number but not when it is multiplied by a large number. In other words,  $2.5 - x \approx 2.5$ , but  $2.5x \neq 2.5$ . Explain why we can ignore a small  $x$  in the first case, but not in the second.
17. What happens to a chemical system at equilibrium when that equilibrium is disturbed?
18. What is the effect of a change in concentration of a reactant or product on a chemical reaction initially at equilibrium?
19. What is the effect of a change in volume on a chemical reaction (that includes gaseous reactants or products) initially at equilibrium?
20. What is the effect of a temperature change on a chemical reaction initially at equilibrium? How does the effect differ for an exothermic reaction compared to an endothermic one?

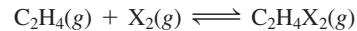
## Problems by Topic

### Equilibrium and the Equilibrium Constant Expression

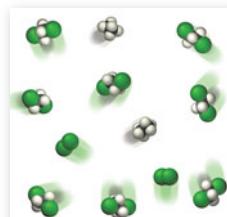
21. Write an expression for the equilibrium constant of each chemical equation.
  - $\text{SbCl}_5(g) \rightleftharpoons \text{SbCl}_3(g) + \text{Cl}_2(g)$
  - $2 \text{BrNO}(g) \rightleftharpoons 2 \text{NO}(g) + \text{Br}_2(g)$
  - $\text{CH}_4(g) + 2 \text{H}_2\text{S}(g) \rightleftharpoons \text{CS}_2(g) + 4 \text{H}_2(g)$
  - $2 \text{CO}(g) + \text{O}_2(g) \rightleftharpoons 2 \text{CO}_2(g)$
22. Find and fix each mistake in the equilibrium constant expressions.
  - $2 \text{H}_2\text{S}(g) \rightleftharpoons 2 \text{H}_2(g) + \text{S}_2(g) \quad K = \frac{[\text{H}_2][\text{S}_2]}{[\text{H}_2\text{S}]}$
  - $\text{CO}(g) + \text{Cl}_2(g) \rightleftharpoons \text{COCl}_2(g) \quad K = \frac{[\text{CO}][\text{Cl}_2]}{[\text{COCl}_2]}$
23. When this reaction comes to equilibrium, will the concentrations of the reactants or products be greater? Does the answer to this question depend on the initial concentrations of the reactants and products?



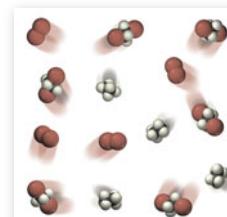
24. Ethene ( $\text{C}_2\text{H}_4$ ) can be halogenated by this reaction:



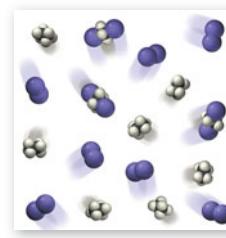
where  $\text{X}_2$  can be  $\text{Cl}_2$  (green),  $\text{Br}_2$  (brown), or  $\text{I}_2$  (purple). Examine the three figures representing equilibrium concentrations in this reaction at the same temperature for the three different halogens. Rank the equilibrium constants for the three reactions from largest to smallest.



(a)

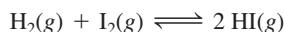


(b)



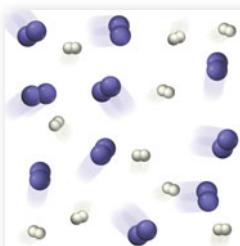
(c)

- 25.**  $\text{H}_2$  and  $\text{I}_2$  are combined in a flask and allowed to react according to the reaction:

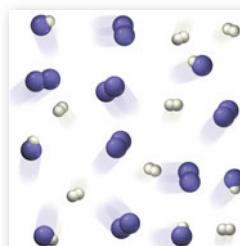


Examine the figures (sequential in time) and answer the questions:

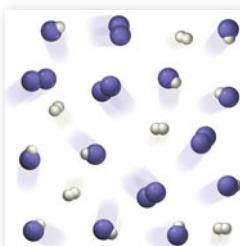
- Which figure represents the point at which equilibrium is reached?
- How would the series of figures change in the presence of a catalyst?
- Would there be different amounts of reactants and products in the final figure (vi) in the presence of a catalyst?



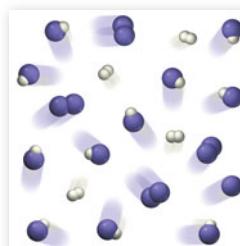
(i)



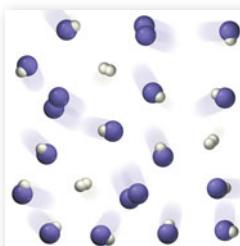
(ii)



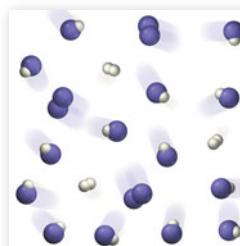
(iii)



(iv)



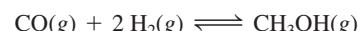
(v)



(vi)

- 26.** A chemist trying to synthesize a particular compound attempts two different synthesis reactions. The equilibrium constants for the two reactions are 23.3 and  $2.2 \times 10^4$  at room temperature. However, upon carrying out both reactions for 15 minutes, the chemist finds that the reaction with the smaller equilibrium constant produces more of the desired product. Explain how this might be possible.

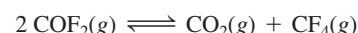
- 27.** This reaction has an equilibrium constant of  $K_p = 2.26 \times 10^4$  at 298 K.



Calculate  $K_p$  for each reaction and predict whether reactants or products will be favored at equilibrium.

- $\text{CH}_3\text{OH}(g) \rightleftharpoons \text{CO}(g) + 2 \text{H}_2(g)$
- $\frac{1}{2}\text{CO}(g) + \text{H}_2(g) \rightleftharpoons \frac{1}{2}\text{CH}_3\text{OH}(g)$
- $2 \text{CH}_3\text{OH}(g) \rightleftharpoons 2 \text{CO}(g) + 4 \text{H}_2(g)$

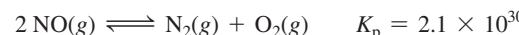
- 28.** This reaction has an equilibrium constant of  $K_p = 2.2 \times 10^6$  at 298 K.



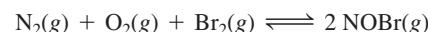
Calculate  $K_p$  for each reaction and predict whether reactants or products will be favored at equilibrium.

- $\text{COF}_2(g) \rightleftharpoons \frac{1}{2}\text{CO}_2(g) + \frac{1}{2}\text{CF}_4(g)$
- $6 \text{COF}_2(g) \rightleftharpoons 3 \text{CO}_2(g) + 3 \text{CF}_4(g)$
- $2 \text{CO}_2(g) + 2 \text{CF}_4(g) \rightleftharpoons 4 \text{COF}_2(g)$

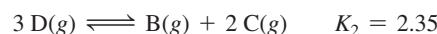
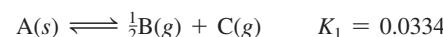
- 29.** Consider the reactions and their respective equilibrium constants:



Use these reactions and their equilibrium constants to predict the equilibrium constant for the following reaction:



- 30.** Use the following reactions and their equilibrium constants to predict the equilibrium constant for the reaction  $2 \text{A}(s) \rightleftharpoons 3 \text{D}(g)$ .



### $K_p$ , $K_c$ , and Heterogeneous Equilibria

- 31.** Calculate  $K_c$  for each reaction:

- $\text{I}_2(g) \rightleftharpoons 2 \text{I}(g) \quad K_p = 6.26 \times 10^{-22} \text{ (at 298 K)}$
  - $\text{CH}_4(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + 3 \text{H}_2(g) \quad K_p = 7.7 \times 10^{24} \text{ (at 298 K)}$
  - $\text{I}_2(g) + \text{Cl}_2(g) \rightleftharpoons 2 \text{ICl}(g) \quad K_p = 81.9 \text{ (at 298 K)}$
- $\text{N}_2\text{O}_4(g) \rightleftharpoons 2 \text{NO}_2(g) \quad K_c = 5.9 \times 10^{-3} \text{ (at 298 K)}$
  - $\text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g) \quad K_c = 3.7 \times 10^8 \text{ (at 298 K)}$
  - $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{NO}(g) \quad K_c = 4.10 \times 10^{-31} \text{ (at 298 K)}$

33. Write an equilibrium expression for each chemical equation involving one or more solid or liquid reactants or products.

- $\text{CO}_3^{2-}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCO}_3^-(aq) + \text{OH}^-(aq)$
- $2 \text{KClO}_3(s) \rightleftharpoons 2 \text{KCl}(s) + 3 \text{O}_2(g)$
- $\text{HF}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{F}^-(aq)$
- $\text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq)$

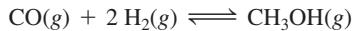
34. Find and fix the mistake in the equilibrium expression.



$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}$$

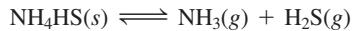
### Relating the Equilibrium Constant to Equilibrium Concentrations and Equilibrium Partial Pressures

35. Consider the reaction:



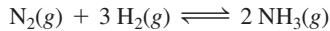
An equilibrium mixture of this reaction at a certain temperature has  $[\text{CO}] = 0.105 \text{ M}$ ,  $[\text{H}_2] = 0.114 \text{ M}$ , and  $[\text{CH}_3\text{OH}] = 0.185 \text{ M}$ . What is the value of the equilibrium constant ( $K_c$ ) at this temperature?

36. Consider the reaction:



An equilibrium mixture of this reaction at a certain temperature has  $[\text{NH}_3] = 0.278 \text{ M}$  and  $[\text{H}_2\text{S}] = 0.355 \text{ M}$ . What is the value of the equilibrium constant ( $K_c$ ) at this temperature?

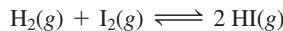
37. Consider the reaction:



Complete the table. Assume that all concentrations are equilibrium concentrations in M.

| T (K) | [N <sub>2</sub> ] | [H <sub>2</sub> ] | [NH <sub>3</sub> ] | K <sub>c</sub> |
|-------|-------------------|-------------------|--------------------|----------------|
| 500   | 0.115             | 0.105             | 0.439              | _____          |
| 575   | 0.110             | _____             | 0.128              | 9.6            |
| 775   | 0.120             | 0.140             | _____              | 0.0584         |

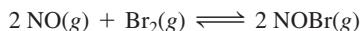
38. Consider the following reaction:



Complete the table. Assume that all concentrations are equilibrium concentrations in M.

| T (°C) | [H <sub>2</sub> ] | [I <sub>2</sub> ] | [HI]  | K <sub>c</sub> |
|--------|-------------------|-------------------|-------|----------------|
| 25     | 0.0355            | 0.0388            | 0.922 | _____          |
| 340    | _____             | 0.0455            | 0.387 | 9.6            |
| 445    | 0.0485            | 0.0468            | _____ | 50.2           |

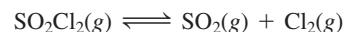
39. Consider the reaction:



$$K_p = 28.4 \text{ at } 298 \text{ K}$$

In a reaction mixture at equilibrium, the partial pressure of NO is 108 torr and that of Br<sub>2</sub> is 126 torr. What is the partial pressure of NOBr in this mixture?

40. Consider the reaction:



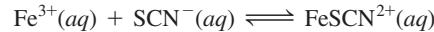
$$K_p = 2.91 \times 10^3 \text{ at } 298 \text{ K}$$

In a reaction at equilibrium, the partial pressure of SO<sub>2</sub> is 137 torr and that of Cl<sub>2</sub> is 285 torr. What is the partial pressure of SO<sub>2</sub>Cl<sub>2</sub> in this mixture?

41. For the reaction A(g)  $\rightleftharpoons$  2 B(g), a reaction vessel initially contains only A at a pressure of  $P_A = 1.32 \text{ atm}$ . At equilibrium,  $P_A = 0.25 \text{ atm}$ . Calculate the value of  $K_p$ . (Assume no changes in volume or temperature.)

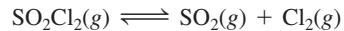
42. For the reaction 2 A(g)  $\rightleftharpoons$  B(g) + 2 C(g), a reaction vessel initially contains only A at a pressure of  $P_A = 255 \text{ mmHg}$ . At equilibrium,  $P_A = 55 \text{ mmHg}$ . Calculate the value of  $K_p$ . (Assume no changes in volume or temperature.)

43. Consider the reaction:



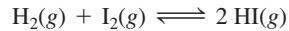
A solution is made containing an initial  $[\text{Fe}^{3+}]$  of  $1.0 \times 10^{-3} \text{ M}$  and an initial  $[\text{SCN}^-]$  of  $8.0 \times 10^{-4} \text{ M}$ . At equilibrium,  $[\text{FeSCN}^{2+}] = 1.7 \times 10^{-4} \text{ M}$ . Calculate the value of the equilibrium constant ( $K_c$ ).

44. Consider the reaction:



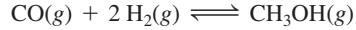
A reaction mixture is made containing an initial  $[\text{SO}_2\text{Cl}_2]$  of  $0.020 \text{ M}$ . At equilibrium,  $[\text{Cl}_2] = 1.2 \times 10^{-2} \text{ M}$ . Calculate the value of the equilibrium constant ( $K_c$ ).

45. Consider the reaction:



A reaction mixture in a 3.67 L flask at a certain temperature initially contains 0.763 g H<sub>2</sub> and 96.9 g I<sub>2</sub>. At equilibrium, the flask contains 90.4 g HI. Calculate the equilibrium constant ( $K_c$ ) for the reaction at this temperature.

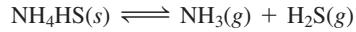
46. Consider the reaction:



A reaction mixture in a 5.19 L flask at a certain temperature contains 26.9 g CO and 2.34 g H<sub>2</sub>. At equilibrium, the flask contains 8.65 g CH<sub>3</sub>OH. Calculate the equilibrium constant ( $K_c$ ) for the reaction at this temperature.

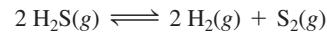
### The Reaction Quotient and Reaction Direction

47. Consider the reaction:



At a certain temperature,  $K_c = 8.5 \times 10^{-3}$ . A reaction mixture at this temperature containing solid NH<sub>4</sub>HS has  $[\text{NH}_3] = 0.166 \text{ M}$  and  $[\text{H}_2\text{S}] = 0.166 \text{ M}$ . Will more of the solid form or will some of the existing solid decompose as equilibrium is reached?

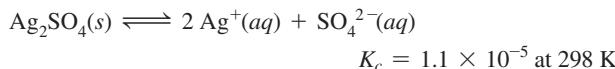
48. Consider the reaction:



$$K_p = 2.4 \times 10^{-4} \text{ at } 1073 \text{ K}$$

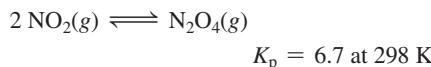
A reaction mixture contains 0.112 atm of H<sub>2</sub>, 0.055 atm of S<sub>2</sub>, and 0.445 atm of H<sub>2</sub>S. Is the reaction mixture at equilibrium? If not, in what direction will the reaction proceed?

- 49.** Silver sulfate dissolves in water according to the reaction:



A 1.5 L solution contains 6.55 g of dissolved silver sulfate. If additional solid silver sulfate is added to the solution, will it dissolve?

- 50.** Nitrogen dioxide dimerizes according to the reaction:



A 2.25 L container contains 0.055 mol of  $\text{NO}_2$  and 0.082 mol of  $\text{N}_2\text{O}_4$  at 298 K. Is the reaction at equilibrium? If not, in what direction will the reaction proceed?

### Finding Equilibrium Concentrations from Initial Concentrations and the Equilibrium Constant

- 51.** Consider the reaction and the associated equilibrium constant:



Find the equilibrium concentrations of A and B for each value of  $a$  and  $b$ . Assume that the initial concentration of A in each case is 1.0 M and that no B is present at the beginning of the reaction.

- a.  $a = 1; b = 1$
- b.  $a = 2; b = 2$
- c.  $a = 1; b = 2$

- 52.** Consider the reaction and the associated equilibrium constant:



Find the equilibrium concentrations of A, B, and C for each value of  $a$ ,  $b$ , and  $c$ . Assume that the initial concentrations of A and B are each 1.0 M and that no product is present at the beginning of the reaction.

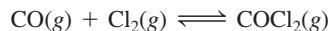
- a.  $a = 1; b = 1; c = 2$
- b.  $a = 1; b = 1; c = 1$
- c.  $a = 2; b = 1; c = 1$  (set up equation for  $x$ ; don't solve)

- 53.** For the reaction,  $K_c = 0.513$  at 500 K.



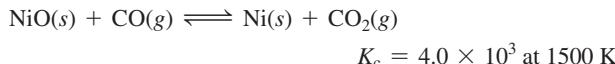
If a reaction vessel initially contains an  $\text{N}_2\text{O}_4$  concentration of 0.0500 M at 500 K, what are the equilibrium concentrations of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  at 500 K?

- 54.** For the reaction,  $K_c = 255$  at 1000 K.



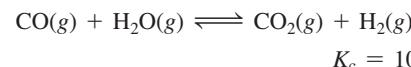
If a reaction mixture initially contains a CO concentration of 0.1500 M and a  $\text{Cl}_2$  concentration of 0.175 M at 1000 K, what are the equilibrium concentrations of CO,  $\text{Cl}_2$ , and  $\text{COCl}_2$  at 1000 K?

- 55.** Consider the reaction:



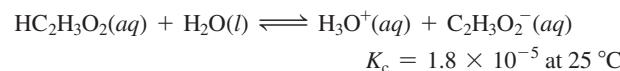
If a mixture of solid nickel(II) oxide and 0.20 M carbon monoxide comes to equilibrium at 1500 K, what is the equilibrium concentration of  $\text{CO}_2$ ?

- 56.** Consider the reaction:



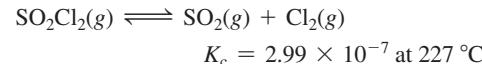
If a reaction mixture initially contains 0.110 M CO and 0.110 M  $\text{H}_2\text{O}$ , what will the equilibrium concentration of each of the reactants and products be?

- 57.** Consider the reaction:



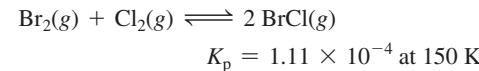
If a solution initially contains 0.210 M  $\text{HC}_2\text{H}_3\text{O}_2$ , what is the equilibrium concentration of  $\text{H}_3\text{O}^+$  at  $25^\circ\text{C}$ ?

- 58.** Consider the reaction:



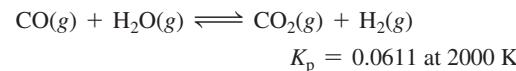
If a reaction mixture initially contains 0.175 M  $\text{SO}_2\text{Cl}_2$ , what is the equilibrium concentration of  $\text{Cl}_2$  at 227 °C?

- 59.** Consider the reaction:



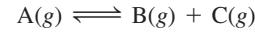
A reaction mixture initially contains a  $\text{Br}_2$  partial pressure of 755 torr and a  $\text{Cl}_2$  partial pressure of 735 torr at 150 K. Calculate the equilibrium partial pressure of  $\text{BrCl}$ .

- 60.** Consider the reaction:



A reaction mixture initially contains a CO partial pressure of 1344 torr and a  $\text{H}_2\text{O}$  partial pressure of 1766 torr at 2000 K. Calculate the equilibrium partial pressures of each of the products.

- 61.** Consider the reaction:



Find the equilibrium concentrations of A, B, and C for each value of  $K_c$ . Assume that the initial concentration of A in each case is 1.0 M and that the reaction mixture initially contains no products. Make any appropriate simplifying assumptions.

- a.  $K_c = 1.0$
- b.  $K_c = 0.010$
- c.  $K_c = 1.0 \times 10^{-5}$

- 62.** Consider the reaction:

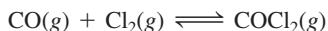


Find the equilibrium partial pressures of A and B for each value of  $K$ . Assume that the initial partial pressure of B in each case is 1.0 atm and that the initial partial pressure of A is 0.0 atm. Make any appropriate simplifying assumptions.

- a.  $K_c = 1.0$
- b.  $K_c = 1.0 \times 10^{-4}$
- c.  $K_c = 1.0 \times 10^5$

### Le Châtelier's Principle

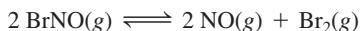
63. Consider this reaction at equilibrium:



Predict whether the reaction will shift left, shift right, or remain unchanged after each disturbance:

- a.  $\text{COCl}_2$  is added to the reaction mixture.
- b.  $\text{Cl}_2$  is added to the reaction mixture.
- c.  $\text{COCl}_2$  is removed from the reaction mixture.

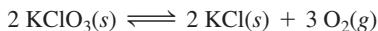
64. Consider this reaction at equilibrium:



Predict whether the reaction will shift left, shift right, or remain unchanged after each disturbance.

- a. NO is added to the reaction mixture.
- b. BrNO is added to the reaction mixture.
- c.  $\text{Br}_2$  is removed from the reaction mixture.

65. Consider this reaction at equilibrium:



Predict whether the reaction will shift left, shift right, or remain unchanged after each disturbance.

- a.  $\text{O}_2$  is removed from the reaction mixture.
- b. KCl is added to the reaction mixture.
- c.  $\text{KClO}_3$  is added to the reaction mixture.
- d. O<sub>2</sub> is added to the reaction mixture.

66. Consider this reaction at equilibrium:



Predict whether the reaction will shift left, shift right, or remain unchanged after each disturbance.

- a. C is added to the reaction mixture.
- b. H<sub>2</sub>O is condensed and removed from the reaction mixture.
- c. CO is added to the reaction mixture.
- d. H<sub>2</sub> is removed from the reaction mixture.

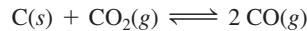
67. Each reaction is allowed to come to equilibrium and then the volume is changed as indicated. Predict the effect (shift right, shift left, or no effect) of the indicated volume change.

- a.  $\text{I}_2(g) \rightleftharpoons 2 \text{I}(g)$  (volume is increased)
- b.  $2 \text{H}_2\text{S}(g) \rightleftharpoons 2 \text{H}_2(g) + \text{S}_2(g)$  (volume is decreased)
- c.  $\text{I}_2(g) + \text{Cl}_2(g) \rightleftharpoons 2 \text{ICl}(g)$  (volume is decreased)

68. Each reaction is allowed to come to equilibrium and then the volume is changed as indicated. Predict the effect (shift right, shift left, or no effect) of the indicated volume change.

- a.  $\text{CO}(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g)$  (volume is decreased)
- b.  $\text{PCl}_3(g) + \text{Cl}_2(g) \rightleftharpoons \text{PCl}_5(g)$  (volume is increased)
- c.  $\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$  (volume is increased)

69. This reaction is endothermic.



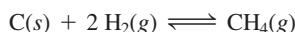
Predict the effect (shift right, shift left, or no effect) of increasing and decreasing the reaction temperature. How does the value of the equilibrium constant depend on temperature?

70. This reaction is exothermic.



Predict the effect (shift right, shift left, or no effect) of increasing and decreasing the reaction temperature. How does the value of the equilibrium constant depend on temperature?

71. Coal, which is primarily carbon, can be converted to natural gas, primarily CH<sub>4</sub>, by the exothermic reaction:



Which disturbance will favor CH<sub>4</sub> at equilibrium?

- a. adding more C to the reaction mixture
- b. adding more H<sub>2</sub> to the reaction mixture
- c. raising the temperature of the reaction mixture
- d. lowering the volume of the reaction mixture
- e. adding a catalyst to the reaction mixture
- f. adding neon gas to the reaction mixture

72. Coal can be used to generate hydrogen gas (a potential fuel) by the endothermic reaction:



If this reaction mixture is at equilibrium, predict whether each disturbance will result in the formation of additional hydrogen gas, the formation of less hydrogen gas, or have no effect on the quantity of hydrogen gas.

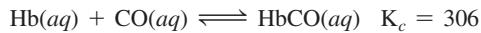
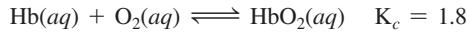
- a. adding more C to the reaction mixture
- b. adding more H<sub>2</sub>O to the reaction mixture
- c. raising the temperature of the reaction mixture
- d. increasing the volume of the reaction mixture
- e. adding a catalyst to the reaction mixture
- f. adding an inert gas to the reaction mixture

## Cumulative Problems

73. Carbon monoxide replaces oxygen in oxygenated hemoglobin according to the reaction:

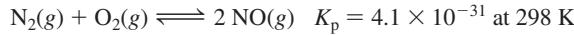


- a. Use the reactions and associated equilibrium constants at body temperature to find the equilibrium constant for the reaction just shown.



- b. Suppose that an air mixture becomes polluted with carbon monoxide at a level of 0.10%. Assuming the air contains 20.0% oxygen, and that the oxygen and carbon monoxide ratios that dissolve in the blood are identical to the ratios in the air, what is the ratio of HbCO to HbO<sub>2</sub> in the blood stream? Comment on the toxicity of carbon monoxide.

74. Nitrogen oxide is a pollutant in the lower atmosphere that irritates the eyes and lungs and leads to the formation of acid rain. Nitrogen oxide forms naturally in atmosphere according to the endothermic reaction:



Use the ideal gas law to calculate the concentrations of nitrogen and oxygen present in air at a pressure of 1.0 atm and a temperature of 298 K. Assume that nitrogen composes 78% of air by volume and that oxygen composes 21% of air. Find the “natural” equilibrium concentration of NO in air in units of molecules/cm<sup>3</sup>. How would you expect this concentration to change in an automobile engine in which combustion is occurring?

**75.** The reaction  $\text{CO}_2(g) + \text{C}(s) \rightleftharpoons 2 \text{CO}(g)$  has  $K_p = 5.78$  at 1200 K.

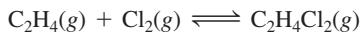
- Calculate the total pressure at equilibrium when 4.45 g of  $\text{CO}_2$  is introduced into a 10.0 L container and heated to 1200 K in the presence of 2.00 g of graphite.
- Repeat the calculation of part a in the presence of 0.50 g of graphite.

**76.** A mixture of water and graphite is heated to 600 K. When the system comes to equilibrium it contains 0.13 mol of  $\text{H}_2$ , 0.13 mol of CO, 0.43 mol of  $\text{H}_2\text{O}$ , and some graphite. Some  $\text{O}_2$  is added to the system and a spark is applied so that the  $\text{H}_2$  reacts completely with the  $\text{O}_2$ . Find the amount of CO in the flask when the system returns to equilibrium.

**77.** At 650 K, the reaction  $\text{MgCO}_3(s) \rightleftharpoons \text{MgO}(s) + \text{CO}_2(g)$  has  $K_p = 0.026$ . A 10.0 L container at 650 K has 1.0 g of  $\text{MgO}(s)$  and  $\text{CO}_2$  at  $P = 0.0260 \text{ atm}$ . The container is then compressed to a volume of 0.100 L. Find the mass of  $\text{MgCO}_3$  that is formed.

**78.** A system at equilibrium contains  $\text{I}_2(g)$  at a pressure of 0.21 atm and  $\text{I}(g)$  at a pressure of 0.23 atm. The system is then compressed to half its volume. Find the pressure of each gas when the system returns to equilibrium.

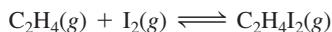
**79.** Consider the exothermic reaction:



If you were trying to maximize the amount of  $\text{C}_2\text{H}_4\text{Cl}_2$  produced, which tactic might you try? Assume that the reaction mixture reaches equilibrium.

- increasing the reaction volume
- removing  $\text{C}_2\text{H}_4\text{Cl}_2$  from the reaction mixture as it forms
- lowering the reaction temperature
- adding  $\text{Cl}_2$

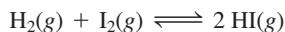
**80.** Consider the endothermic reaction:



If you were trying to maximize the amount of  $\text{C}_2\text{H}_4\text{I}_2$  produced, which tactic might you try? Assume that the reaction mixture reaches equilibrium.

- decreasing the reaction volume
- removing  $\text{I}_2$  from the reaction mixture
- raising the reaction temperature
- adding  $\text{C}_2\text{H}_4$  to the reaction mixture

**81.** Consider the reaction:



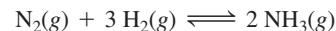
A reaction mixture at equilibrium at 175 K contains  $P_{\text{H}_2} = 0.958 \text{ atm}$ ,  $P_{\text{I}_2} = 0.877 \text{ atm}$ , and  $P_{\text{HI}} = 0.020 \text{ atm}$ . A second reaction mixture, also at 175 K, contains  $P_{\text{H}_2} = P_{\text{I}_2} = 0.621 \text{ atm}$  and  $P_{\text{HI}} = 0.101 \text{ atm}$ . Is the second reaction at equilibrium? If not, what will be the partial pressure of HI when the reaction reaches equilibrium at 175 K?

**82.** Consider the reaction:



A reaction mixture initially containing 0.500 M  $\text{H}_2\text{S}$  and 0.500 M  $\text{SO}_2$  contains 0.0011 M  $\text{H}_2\text{O}$  at a certain temperature. A second reaction mixture at the same temperature initially contains  $[\text{H}_2\text{S}] = 0.250 \text{ M}$  and  $[\text{SO}_2] = 0.325 \text{ M}$ . Calculate the equilibrium concentration of  $\text{H}_2\text{O}$  in the second mixture at this temperature.

**83.** Ammonia can be synthesized according to the reaction:



$$K_p = 5.3 \times 10^{-5} \text{ at } 725 \text{ K}$$

A 200.0 L reaction container initially contains 1.27 kg of  $\text{N}_2$  and 0.310 kg of  $\text{H}_2$  at 725 K. Assuming ideal gas behavior, calculate the mass of  $\text{NH}_3$  (in g) present in the reaction mixture at equilibrium. What is the percent yield of the reaction under these conditions?

**84.** Hydrogen can be extracted from natural gas according to the reaction:



$$K_p = 4.5 \times 10^2 \text{ at } 825 \text{ K}$$

An 85.0 L reaction container initially contains 22.3 kg of  $\text{CH}_4$  and 55.4 kg of  $\text{CO}_2$  at 825 K. Assuming ideal gas behavior, calculate the mass of  $\text{H}_2$  (in g) present in the reaction mixture at equilibrium. What is the percent yield of the reaction under these conditions?

**85.** The system described by the reaction:  $\text{CO}(g) + \text{Cl}_2(g) \rightleftharpoons \text{COCl}_2(g)$  is at equilibrium at a given temperature when  $P_{\text{CO}} = 0.30 \text{ atm}$ ,  $P_{\text{Cl}_2} = 0.10 \text{ atm}$ , and  $P_{\text{COCl}_2} = 0.60 \text{ atm}$ . An additional pressure of  $\text{Cl}_2(g) = 0.40 \text{ atm}$  is added. Find the pressure of CO when the system returns to equilibrium.

**86.** A reaction vessel at 27 °C contains a mixture of  $\text{SO}_2$  ( $P = 3.00 \text{ atm}$ ) and  $\text{O}_2$  ( $P = 1.00 \text{ atm}$ ). When a catalyst is added, this reaction takes place:  $2 \text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{SO}_3(g)$ .

At equilibrium, the total pressure is 3.75 atm. Find the value of  $K_c$ .

**87.** At 70 K,  $\text{CCl}_4$  decomposes to carbon and chlorine. The  $K_p$  for the decomposition is 0.76. Find the starting pressure of  $\text{CCl}_4$  at this temperature that will produce a total pressure of 1.0 atm at equilibrium.

**88.** The equilibrium constant for the reaction  $\text{SO}_2(g) + \text{NO}_2(g) \rightleftharpoons \text{SO}_3(g) + \text{NO}(g)$  is 3.0. Find the amount of  $\text{NO}_2$  that must be added to 2.4 mol of  $\text{SO}_2$  in order to form 1.2 mol of  $\text{SO}_3$  at equilibrium.

**89.** A sample of  $\text{CaCO}_3(s)$  is introduced into a sealed container of volume 0.654 L and heated to 1000 K until equilibrium is reached. The  $K_p$  for the reaction  $\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$  is  $3.9 \times 10^{-2}$  at this temperature. Calculate the mass of  $\text{CaO}(s)$  that is present at equilibrium.

**90.** An equilibrium mixture contains  $\text{N}_2\text{O}_4$ , ( $P = 0.28 \text{ atm}$ ) and  $\text{NO}_2$  ( $P = 1.1 \text{ atm}$ ) at 350 K. The volume of the container is doubled at constant temperature. Calculate the equilibrium pressures of the two gases when the system reaches a new equilibrium.

**91.** Carbon monoxide and chlorine gas react to form phosgene:

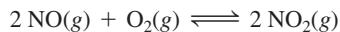


If a reaction mixture initially contains 215 torr of CO and 245 torr of  $\text{Cl}_2$ , what is the mole fraction of  $\text{COCl}_2$  when equilibrium is reached?

**92.** Solid carbon can react with gaseous water to form carbon monoxide gas and hydrogen gas. The equilibrium constant for the reaction at 700.0 K is  $K_p = 1.60 \times 10^{-3}$ . If a 1.55 L reaction vessel initially contains 145 torr of water at 700.0 K in contact with excess solid carbon, find the percent by mass of hydrogen gas of the gaseous reaction mixture at equilibrium.

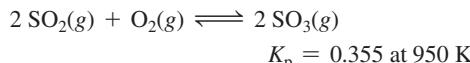
## Challenge Problems

**93.** Consider the reaction:



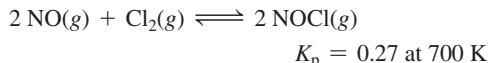
- a. A reaction mixture at 175 K initially contains 522 torr of NO and 421 torr of O<sub>2</sub>. At equilibrium, the total pressure in the reaction mixture is 748 torr. Calculate K<sub>p</sub> at this temperature.
- b. A second reaction mixture at 175 K initially contains 255 torr of NO and 185 torr of O<sub>2</sub>. What is the equilibrium partial pressure of NO<sub>2</sub> in this mixture?

**94.** Consider the reaction:



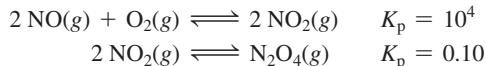
A 2.75 L reaction vessel at 950 K initially contains 0.100 mol of SO<sub>2</sub> and 0.100 mol of O<sub>2</sub>. Calculate the total pressure (in atmospheres) in the reaction vessel when equilibrium is reached.

**95.** Nitric oxide reacts with chlorine gas according to the reaction:



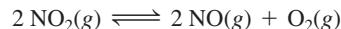
A reaction mixture initially contains equal partial pressures of NO and Cl<sub>2</sub>. At equilibrium, the partial pressure of NOCl is 115 torr. What were the initial partial pressures of NO and Cl<sub>2</sub>?

**96.** At a given temperature, a system containing O<sub>2</sub>(g) and some oxides of nitrogen can be described by these reactions:



A pressure of 1 atm of N<sub>2</sub>O<sub>4</sub>(g) is placed in a container at this temperature. Predict which, if any, component (other than N<sub>2</sub>O<sub>4</sub>) will be present at a pressure greater than 0.2 atm at equilibrium.

**97.** A sample of pure NO<sub>2</sub> is heated to 337 °C, at which temperature it partially dissociates according to the equation:



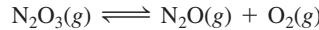
At equilibrium the density of the gas mixture is 0.520 g/L at 0.750 atm. Calculate K<sub>c</sub> for the reaction.

**98.** When N<sub>2</sub>O<sub>5</sub>(g) is heated it dissociates into N<sub>2</sub>O<sub>3</sub>(g) and O<sub>2</sub>(g) according to the reaction:



$$K_c = 7.75 \text{ at a given temperature}$$

The N<sub>2</sub>O<sub>3</sub>(g) dissociates to give N<sub>2</sub>O(g) and O<sub>2</sub>(g) according to the reaction:



$$K_c = 4.00 \text{ at the same temperature}$$

When 4.00 mol of N<sub>2</sub>O<sub>5</sub>(g) is heated in a 1.00 L reaction vessel to this temperature, the concentration of O<sub>2</sub>(g) at equilibrium is 4.50 mol/L. Find the concentrations of all the other species in the equilibrium system.

**99.** A sample of SO<sub>3</sub> is introduced into an evacuated sealed container and heated to 600 K. The following equilibrium is established:



The total pressure in the system is 3.0 atm and the mole fraction of O<sub>2</sub> is 0.12. Find K<sub>p</sub>.

## Conceptual Problems

**100.** A reaction A(g)  $\rightleftharpoons$  B(g) has an equilibrium constant of  $1.0 \times 10^{-4}$ . For which of the initial reaction mixtures is the *x is small* approximation most likely to apply?

- a. [A] = 0.0010 M; [B] = 0.00 M
- b. [A] = 0.00 M; [B] = 0.10 M
- c. [A] = 0.10 M; [B] = 0.10 M
- d. [A] = 0.10 M; [B] = 0.00 M

**101.** The reaction A(g)  $\rightleftharpoons$  2 B(g) has an equilibrium constant of K<sub>c</sub> = 1.0 at a given temperature. If a reaction vessel contains equal initial amounts (in moles) of A and B, will the direction in which the reaction proceeds depend on the volume of the reaction vessel? Explain.

**102.** A particular reaction has an equilibrium constant of K<sub>p</sub> = 0.50. A reaction mixture is prepared in which all the reactants and products are in their standard states. In which direction will the reaction proceed?

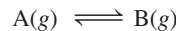
**103.** Consider the reaction:



Each of the entries in the following table represents equilibrium partial pressures of A and B under different initial conditions. What are the values of *a* and *b* in the reaction?

| P <sub>A</sub> (atm) | P <sub>B</sub> (atm) |
|----------------------|----------------------|
| 4.0                  | 2.0                  |
| 2.0                  | 1.4                  |
| 1.0                  | 1.0                  |
| 0.50                 | 0.71                 |
| 0.25                 | 0.50                 |

**104.** Consider the simple one-step reaction:



Since the reaction occurs in a single step, the forward reaction has a rate of k<sub>for</sub>[A] and the reverse reaction has a rate of k<sub>rev</sub>[B]. What happens to the rate of the forward reaction when we increase the concentration of A? How does this explain the reason behind Le Châtelier's principle?

## Answers to Conceptual Connections

### Equilibrium Constants

**14.1 (b)** The reaction mixture will contain  $[A] = 0.1 \text{ M}$  and  $[B] = 1.0 \text{ M}$  so that  $[B]/[A] = 10$ .

### The Equilibrium Constant and the Chemical Equation

**14.2 (b)** The reaction is reversed and divided through by two. Therefore, you invert the equilibrium constant and take the square root of the result.  $K = (1/0.010)^{1/2} = 10$ .

### The Relationship between $K_p$ and $K_c$

**14.3 (a)** When  $a + b = c + d$ , the quantity  $\Delta n$  is zero so that  $K_p = K_c (RT)^0$ . Since  $(RT)^0$  is equal to 1,  $K_p = K_c$ .

### Heterogeneous Equilibria, $K_p$ , and $K_c$

**14.4 (b)** Since  $\Delta n$  for gaseous reactants and products is zero,  $K_p$  equals  $K_c$ .

### $Q$ and $K$

**14.5 (c)** Because  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  are both in their standard states, they each have a partial pressure of 1.0 atm. Consequently,  $Q_p = 1$ . Since  $K_p = 0.15$ ,  $Q_p > K_p$ , and the reaction proceeds to the left.

### The $x$ Is Small Approximation

**14.6 (a)** The  $x$  is small approximation is most likely to apply to a reaction with a small equilibrium constant and an initial concentration of reactant that is not too small. The bigger the equilibrium constant and the smaller the initial concentration of reactant, the less likely that the  $x$  is small approximation will apply.

# 15

## Acids and Bases

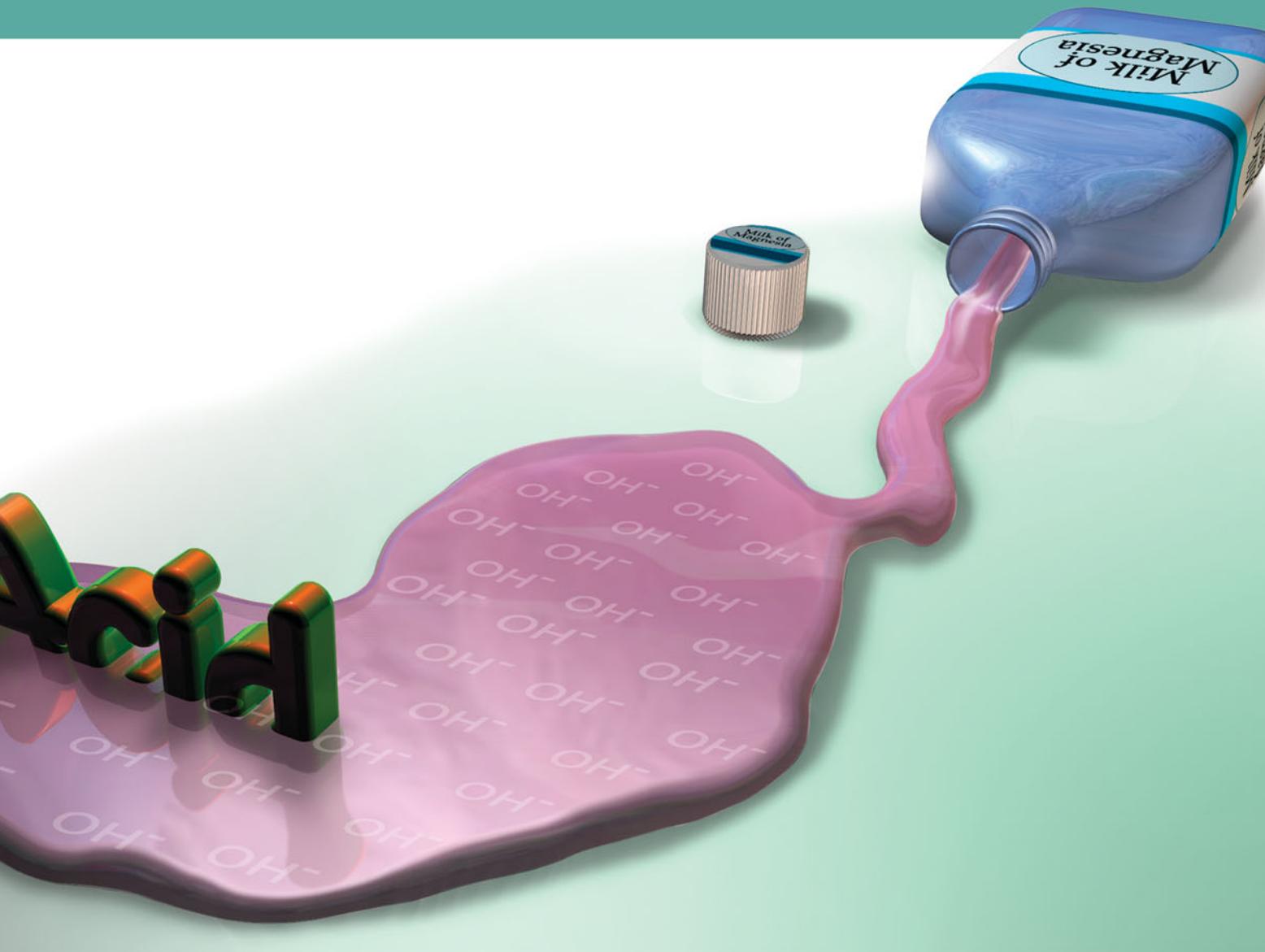
*The differences between the various acid–base concepts are not concerned with which is right, but which is most convenient to use in a particular situation.*

—James E. Huheey (1935–)

- 15.1** Heartburn 697
  - 15.2** The Nature of Acids and Bases 698
  - 15.3** Definitions of Acids and Bases 700
  - 15.4** Acid Strength and the Acid Ionization Constant ( $K_a$ ) 703
  - 15.5** Autoionization of Water and pH 706
  - 15.6** Finding the  $[H_3O^+]$  and pH of Strong and Weak Acid Solutions 711
  - 15.7** Base Solutions 720
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In **THIS CHAPTER**, we apply the equilibrium concepts learned in the previous chapter to acid–base phenomena. Acids are common in many foods, such as limes, lemons, and vinegar, and in a number of consumer products, such as toilet cleaners and batteries. Bases are less common in foods but are key ingredients in consumer products such as drain openers and antacids. We will examine three different models for acid–base behavior, all of which define that behavior differently. In spite of their differences, the three models coexist, each being useful at explaining a particular range of acid–base phenomena. We also examine how to calculate the acidity or basicity of solutions and define a useful scale, called the pH scale, to quantify acidity and basicity. These types of calculations often involve solving the kind of equilibrium problems that we explored in Chapter 14.





Milk of magnesia contains a base that can neutralize stomach acid and relieve heartburn.

## 15.1 Heartburn

Heartburn is a painful burning sensation in the esophagus (the tube that joins the throat to the stomach) just below the chest. The pain is caused by hydrochloric acid (HCl), which the stomach excretes to kill microorganisms and to activate enzymes that break down food. Hydrochloric acid sometimes backs up out of the stomach and into the esophagus, a phenomenon called *acid reflux*. Recall from Section 4.8 that acids are substances that—by one definition that we elaborate on shortly—produce H<sup>+</sup> ions in solution. When hydrochloric acid from the stomach comes in contact with the lining of the esophagus, the H<sup>+</sup> ions irritate the tissues, resulting in the burning sensation. Some of the acid can work its way into the lower throat and even the mouth, producing pain in the throat and a sour taste (characteristic of acids) in the mouth. Almost everyone experiences heartburn at some time, most commonly after a large meal when the stomach is full. Strenuous activity or lying in a horizontal position after a large meal increases the likelihood of stomach acid reflux and the resulting heartburn.

| Bases were first defined in Section 4.8.

| The concentration of stomach acid,  $[H_3O^+]$ , varies from about 0.01 to 0.1 M.

| For a review of acid naming, see Section 3.6.

| Litmus paper contains certain dyes that change color in the presence of acids and bases.

The simplest way to relieve mild heartburn is to swallow repeatedly. Saliva contains the bicarbonate ion ( $HCO_3^-$ ), which acts as a base and, when swallowed, neutralizes some of the acid in the esophagus. Later in this chapter, we will see how bicarbonate acts as a base. You can also treat heartburn with antacids such as Tums, milk of magnesia, or Mylanta. These over-the-counter medications contain more base than saliva and therefore are effective at neutralizing esophageal acid. We look at the bases in these medicines more carefully later (see the *Chemistry and Medicine* box in Section 15.7).

For some people, heartburn becomes a chronic problem. Gastroesophageal reflux disease (GERD) is the medical condition associated with chronic heartburn. In patients with GERD, the band of muscles (called the esophageal sphincter) at the bottom of the esophagus just above the stomach does not close tightly enough, allowing the stomach contents to leak back into the esophagus on a regular basis. Medical researchers have developed a wireless sensor to help diagnose and evaluate treatment of GERD. Using a tube that goes down through the throat, a physician attaches the sensor to tissues in the patient's esophagus. The sensor reads pH—a measure of acidity that we discuss in Section 15.5—and transmits the readings to a recorder worn on the patient's body. The patient goes about his or her normal business for the next few days while the recorder monitors esophageal pH. The physician then reads the record of esophageal pH to make a diagnosis or evaluate treatment.

In this chapter, we examine acid and base behavior. Acids and bases are not only important to our health (as we have just seen), but are also found in many household products, foods, medicines, and of course in nearly every chemistry laboratory. Acid–base chemistry is central to much of biochemistry and molecular biology. The building blocks of proteins, for example, are acids (called amino acids) and the molecules that carry the genetic code in DNA are bases.

## 15.2 The Nature of Acids and Bases

*Acids* have the following general properties: a sour taste, the ability to dissolve many metals, the ability to turn blue litmus paper red, and the ability to neutralize bases. Table 15.1 lists some common acids.

You can find hydrochloric acid in most chemistry laboratories. In industry, it is used to clean metals, to prepare and process some foods, and to refine metal ores. As we just discussed in Section 15.1, hydrochloric acid is also the main component of stomach acid.

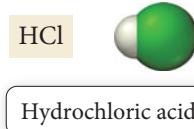
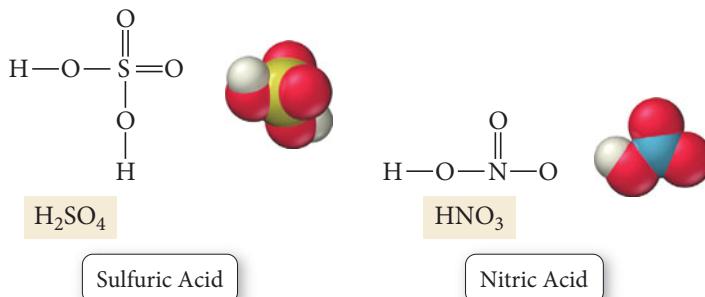


TABLE 15.1 Some Common Acids

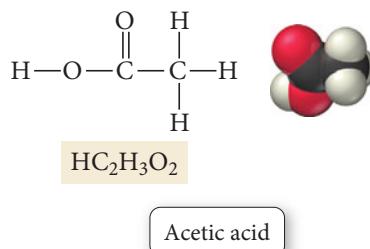
| Name                           | Occurrence/Uses  |
|--------------------------------|--|
| Hydrochloric acid (HCl)        | Metal cleaning; food preparation; ore refining; primary component of stomach acid                                |
| Sulfuric acid ( $H_2SO_4$ )    | Fertilizer and explosives manufacturing; dye and glue production; automobile batteries; electroplating of copper |
| Nitric acid ( $HNO_3$ )        | Fertilizer and explosives manufacturing; dye and glue production   |
| Acetic acid ( $HC_2H_3O_2$ )   | Plastic and rubber manufacturing; food preservative; active component of vinegar                                 |
| Citric acid ( $H_3C_6H_5O_7$ ) | Present in citrus fruits such as lemons and limes; used to adjust pH in foods and beverages                      |
| Carbonic acid ( $H_2CO_3$ )    | Found in carbonated beverages due to the reaction of carbon dioxide with water                                   |
| Hydrofluoric acid (HF)         | Metal cleaning; glass frosting and etching   |
| Phosphoric acid ( $H_3PO_4$ )  | Fertilizer manufacture; biological buffering; preservative in beverages  |

| The formula for acetic acid can also be written as  $CH_3COOH$ .

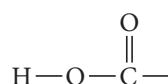
Sulfuric acid and nitric acid are also common in the laboratory. They play major roles in the manufacture of fertilizers, explosives, dyes, and glues. Sulfuric acid, produced in larger quantities than any other industrial chemical, is contained in most automobile batteries.



You can probably find acetic acid in your home—it is the active component of vinegar. It is also produced in improperly stored wines. The word *vinegar* originates from the French words *vin aigre*, which means “sour wine”. Wine experts consider the presence of vinegar in wines a serious fault, since it makes the wine taste like salad dressing.



Acetic acid is a **carboxylic acid**, an acid that contains the following grouping of atoms:

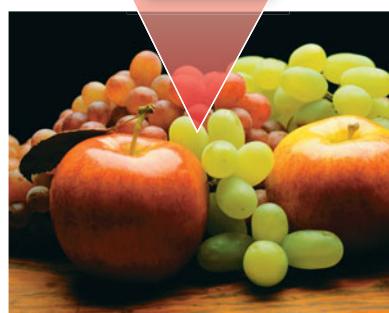
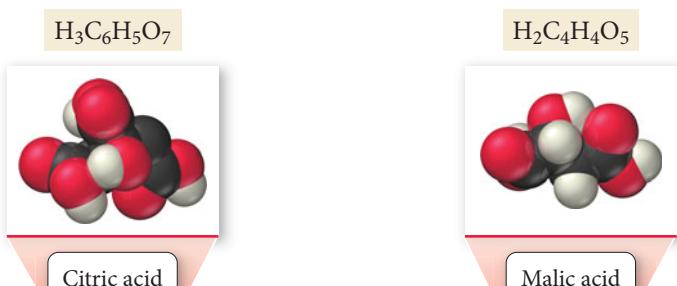


**Carboxylic acid group**

Carboxylic acids are often found in substances derived from living organisms. Other examples of carboxylic acids are citric acid, the main acid in lemons and limes, and malic acid, found in apples, grapes, and wine.



▲ Acetic acid makes vinegar taste sour.



◀ Citrus fruits, apples, and grapes all contain acids.



▲ Many common household products and remedies contain bases.

Coffee is acidic overall, but bases present in coffee—such as caffeine—and other compounds impart a bitter flavor.

**TABLE 15.2 Common Bases**

| Name  | Occurrence/Uses  |
|---|--|
| Sodium hydroxide (NaOH)                             | Petroleum processing; soap and plastic manufacturing                           |
| Potassium hydroxide (KOH)                           | Cotton processing; electroplating; soap production; batteries                  |
| Sodium bicarbonate (NaHCO <sub>3</sub> )            | Antacid; ingredient of baking soda; source of CO <sub>2</sub>                  |
| Sodium carbonate (Na <sub>2</sub> CO <sub>3</sub> ) | Manufacture of glass and soap; general cleanser; water softener                |
| Ammonia (NH <sub>3</sub> )                          | Detergent; fertilizer and explosives manufacturing; synthetic fiber production |

Bases have the following general properties: a bitter taste, a slippery feel, the ability to turn red litmus paper blue, and the ability to neutralize acids. Because of their bitterness, bases are less common in foods than are acids. Our aversion to the taste of bases is probably an evolutionary adaptation to warn us against **alkaloids**, organic bases found in plants that are often poisonous. (For example, the active component of hemlock—the poisonous plant that killed the Greek philosopher Socrates—is the alkaloid coniine.) Nonetheless, some foods, such as coffee and chocolate (especially dark chocolate), contain bitter flavors. Many people enjoy the bitterness, but only after acquiring the taste over time.

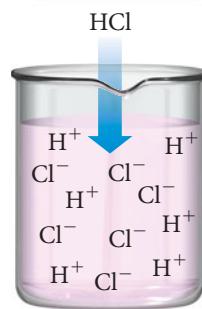
Bases feel slippery because they react with oils on the skin to form soap-like substances. Some household cleaning solutions, such as ammonia, are basic and have the characteristic slippery feel of a base. Bases turn red litmus paper blue; in the laboratory, litmus paper is routinely used to test the basicity of solutions.

Some common bases are listed in Table 15.2. You can find sodium hydroxide and potassium hydroxide in most chemistry laboratories. They are used in petroleum and cotton processing and in soap and plastic manufacturing. Sodium hydroxide is the active ingredient in products such as Drano that unclog drains. In many homes, you can find sodium bicarbonate in the medicine cabinet (it is an active ingredient in some antacids) as well as in the kitchen (labeled as baking soda).

## 15.3 Definitions of Acids and Bases

What are the main characteristics of the molecules and ions that exhibit acid and base behavior? In this chapter, we examine three different definitions: the Arrhenius definition, the Brønsted–Lowry definition, and the Lewis definition. Why three definitions, and which one is correct? As Huheey noted in the quotation that opens this chapter, no single definition is “correct.” Rather, each definition is useful in a given instance. We discuss the Lewis definition of acids and bases in Section 15.11; here we discuss the other two.

### Arrhenius Acid



### ▲ FIGURE 15.1 Arrhenius Acid

An Arrhenius acid produces H<sup>+</sup> ions in solution.

### The Arrhenius Definition

In the 1880s, Swedish chemist Svante Arrhenius proposed the following molecular definitions of acids and bases:

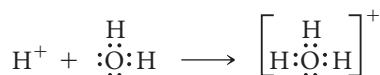
**Acid:** A substance that produces H<sup>+</sup> ions in aqueous solution.

**Base:** A substance that produces OH<sup>-</sup> ions in aqueous solution.

According to the **Arrhenius definition**, HCl is an acid because it produces H<sup>+</sup> ions in solution (Figure 15.1 ▲):



Hydrogen chloride (HCl) is a covalent compound and does not contain ions. However, in water it *ionizes* completely to form H<sup>+(aq)</sup> ions and Cl<sup>-(aq)</sup> ions. The H<sup>+</sup> ions are highly reactive. In aqueous solution, the ions bond to water to form H<sub>3</sub>O<sup>+</sup>:



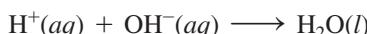
The  $\text{H}_3\text{O}^+$  ion is called the **hydronium ion**. In water,  $\text{H}^+$  ions *always* associate with  $\text{H}_2\text{O}$  molecules to form hydronium ions and other associated species with the general formula  $\text{H}(\text{H}_2\text{O})_n^+$ . For example, an  $\text{H}^+$  ion can associate with two water molecules to form  $\text{H}(\text{H}_2\text{O})_2^+$ , with three to form  $\text{H}(\text{H}_2\text{O})_3^+$ , and so on. Chemists often use  $\text{H}^+(\text{aq})$  and  $\text{H}_3\text{O}^+(\text{aq})$  interchangeably to mean the same thing—an  $\text{H}^+$  ion that has been solvated (or dissolved) in water.

According to the Arrhenius definition,  $\text{NaOH}$  is a base because it produces  $\text{OH}^-$  ions in solution (Figure 15.2 ▶):



$\text{NaOH}$  is an ionic compound and therefore contains  $\text{Na}^+$  and  $\text{OH}^-$  ions. When  $\text{NaOH}$  is added to water, it *dissociates* or breaks apart into its component ions.

Under the Arrhenius definition, acids and bases combine to form water, neutralizing each other in the process:



Arrhenius Base

 $\text{NaOH}$ 

▲ **FIGURE 15.2** Arrhenius Base An Arrhenius base produces  $\text{OH}^-$  ions in solution.

## The Brønsted-Lowry Definition

A second, more widely applicable definition of acids and bases, called the **Brønsted-Lowry definition**, was introduced in 1923. This definition focuses on the *transfer of  $\text{H}^+$  ions* in an acid–base reaction. Since an  $\text{H}^+$  ion is a proton—a hydrogen atom without its electron—this definition focuses on the idea of a proton donor and a proton acceptor:

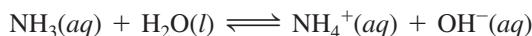
**Acid:** proton ( $\text{H}^+$  ion) *donor*

**Base:** proton ( $\text{H}^+$  ion) *acceptor*

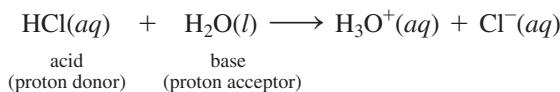
According to this definition,  $\text{HCl}$  is an acid because, in solution, it donates a proton to water:



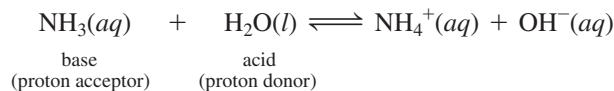
This definition clearly describes what happens to the  $\text{H}^+$  ion from an acid—it associates with a water molecule to form  $\text{H}_3\text{O}^+$  (a hydronium ion). The Brønsted-Lowry definition also applies nicely to bases (such as  $\text{NH}_3$ ) that do not inherently contain  $\text{OH}^-$  ions but still produce  $\text{OH}^-$  ions in solution. According to the Brønsted-Lowry definition,  $\text{NH}_3$  is a base because it accepts a proton from water:



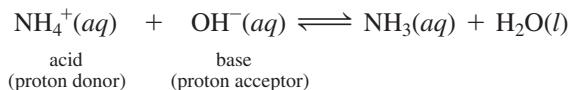
According to the Brønsted-Lowry definition, acids (proton donors) and bases (proton acceptors) always occur together in an acid–base reaction. In the reaction between  $\text{HCl}$  and  $\text{H}_2\text{O}$ ,  $\text{HCl}$  is the proton donor (acid) and  $\text{H}_2\text{O}$  is the proton acceptor (base).



In the reaction between  $\text{NH}_3$  and  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}$  is the proton donor (acid) and  $\text{NH}_3$  is the proton acceptor (base).



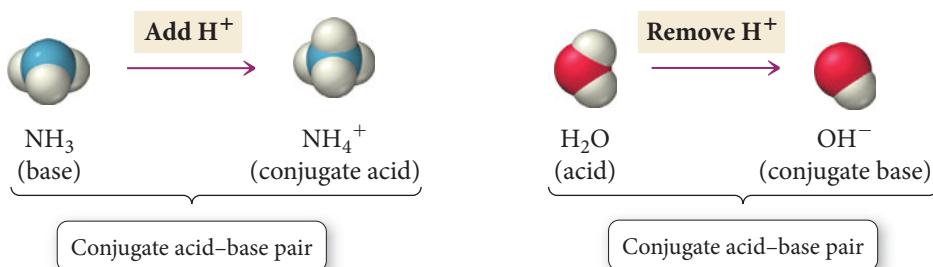
According to the Brønsted-Lowry definition, some substances—such as water in the previous two equations—can act as acids *or* bases. Substances that can act as acids or bases are **amphoteric**. Notice what happens when we reverse an equation representing a Brønsted-Lowry acid–base reaction.



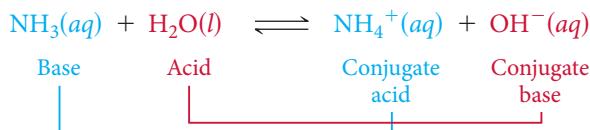
All Arrhenius acids and bases are acids and bases under the Brønsted-Lowry definition. However, some Brønsted-Lowry acids and bases cannot be classified as Arrhenius acids and bases.

► **FIGURE 15.3 Conjugate Acid–Base Pairs**

**Pairs** A conjugate acid–base pair consists of two substances related to each other by the transfer of a proton.



In this reaction,  $\text{NH}_4^+$  is the proton donor (acid) and  $\text{OH}^-$  is the proton acceptor (base). The substance that was the base ( $\text{NH}_3$ ) has become the acid ( $\text{NH}_4^+$ ) and vice versa.  $\text{NH}_4^+$  and  $\text{NH}_3$  are often referred to as a **conjugate acid–base pair**, two substances related to each other by the transfer of a proton (Figure 15.3 ▲). A **conjugate acid** is any base to which a proton has been added, and a **conjugate base** is any acid from which a proton has been removed. Going back to the original forward reaction, we can identify the conjugate acid–base pairs:



*Summarizing the Brønsted–Lowry Definition of Acids and Bases:*

- A base accepts a proton and becomes a conjugate acid.
- An acid donates a proton and becomes a conjugate base.

### EXAMPLE 15.1 Identifying Brønsted–Lowry Acids and Bases and Their Conjugates

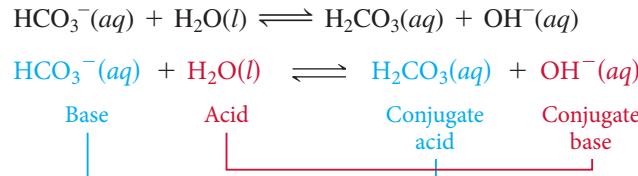
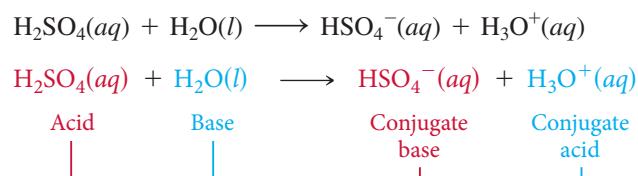
In each reaction, identify the Brønsted–Lowry acid, the Brønsted–Lowry base, the conjugate acid, and the conjugate base.

- (a)  $\text{H}_2\text{SO}_4(aq) + \text{H}_2\text{O}(l) \longrightarrow \text{HSO}_4^-(aq) + \text{H}_3\text{O}^+(aq)$   
 (b)  $\text{HCO}_3^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{CO}_3(aq) + \text{OH}^-(aq)$

#### SOLUTION

- (a) Because  $\text{H}_2\text{SO}_4$  donates a proton to  $\text{H}_2\text{O}$  in this reaction, it is the acid (proton donor). After  $\text{H}_2\text{SO}_4$  donates the proton, it becomes  $\text{HSO}_4^-$ , the conjugate base. Because  $\text{H}_2\text{O}$  accepts a proton, it is the base (proton acceptor). After  $\text{H}_2\text{O}$  accepts the proton, it becomes  $\text{H}_3\text{O}^+$ , the conjugate acid.

- (b) Because  $\text{H}_2\text{O}$  donates a proton to  $\text{HCO}_3^-$  in this reaction, it is the acid (proton donor). After  $\text{H}_2\text{O}$  donates the proton, it becomes  $\text{OH}^-$ , the conjugate base. Because  $\text{HCO}_3^-$  accepts a proton, it is the base (proton acceptor). After  $\text{HCO}_3^-$  accepts the proton, it becomes  $\text{H}_2\text{CO}_3$ , the conjugate acid.



#### FOR PRACTICE 15.1

In each reaction, identify the Brønsted–Lowry acid, the Brønsted–Lowry base, the conjugate acid, and the conjugate base.

- (a)  $\text{C}_5\text{H}_5\text{N}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{C}_5\text{H}_5\text{NH}^+(aq) + \text{OH}^-(aq)$   
 (b)  $\text{HNO}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{NO}_3^-(aq)$

**Conceptual Connection 15.1**
**Conjugate Acid–Base Pairs**

Which pair is not a conjugate acid–base pair?

- (a)  $(\text{CH}_3)_3\text{N}; (\text{CH}_3)_3\text{NH}^+$       (b)  $\text{H}_2\text{SO}_4; \text{H}_2\text{SO}_3$       (c)  $\text{HNO}_2; \text{NO}_2^-$

## 15.4 Acid Strength and the Acid Ionization Constant ( $K_a$ )

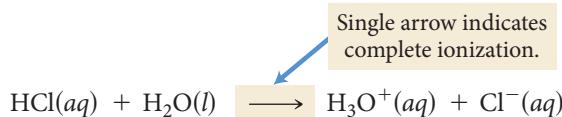
The strength of an electrolyte, first discussed in Section 4.5, depends on the extent of its dissociation into its component ions in solution. A **strong electrolyte** completely dissociates into ions in solution, whereas a **weak electrolyte** only partially dissociates. We define strong and weak acids accordingly. A **strong acid** completely ionizes in solution, whereas a **weak acid** only partially ionizes. In other words, the strength of an acid depends on the equilibrium:



In the preceding equation, HA is a generic formula for an acid. If the equilibrium lies far to the right, the acid is strong—it completely ionizes. If the equilibrium lies to the left, the acid is weak—only a small percentage of the acid molecules ionize. Of course, the range of acid strength is continuous, but for most purposes, the categories of strong and weak are useful.

### Strong Acids

Hydrochloric acid (HCl) is an example of a strong acid.



An HCl solution contains virtually no intact HCl; the HCl has essentially all ionized to form H<sub>3</sub>O<sup>+</sup>(aq) and Cl<sup>-</sup>(aq) (Figure 15.4 ▶). A 1.0 M HCl solution has an H<sub>3</sub>O<sup>+</sup> concentration of 1.0 M. Abbreviating the concentration of H<sub>3</sub>O<sup>+</sup> as [H<sub>3</sub>O<sup>+</sup>], we say that a 1.0 M HCl solution has [H<sub>3</sub>O<sup>+</sup>] = 1.0 M.

Table 15.3 lists the six important strong acids. The first five acids in the table are **monoprotic acids**, acids containing only one ionizable proton. Sulfuric acid is an example of a **diprotic acid**, an acid containing two ionizable protons.

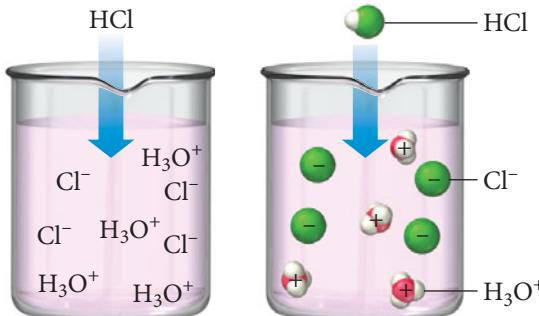
An ionizable proton is one that ionizes in solution. We discuss polyprotic acids in more detail in Section 15.9.

**TABLE 15.3 Strong Acids**

|                         |  |
|-------------------------|--|
| Hydrochloric acid (HCl) | Nitric acid (HNO <sub>3</sub> )                            |
| Hydrobromic acid (HBr)  | Perchloric acid (HClO <sub>4</sub> )                       |
| Hydriodic acid (HI)     | Sulfuric acid (H <sub>2</sub> SO <sub>4</sub> ) (diprotic) |

### A Strong Acid

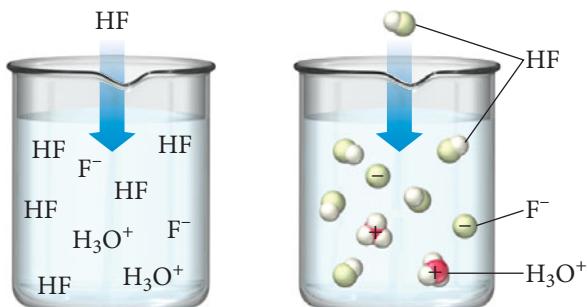
When HCl dissolves in water, it ionizes completely.



**◀ FIGURE 15.4 Ionization of a Strong Acid** When HCl dissolves in water, it completely ionizes to form H<sub>3</sub>O<sup>+</sup> and Cl<sup>-</sup>. The solution contains virtually no intact HCl.

## A Weak Acid

When HF dissolves in water, only a fraction of the molecules ionize.

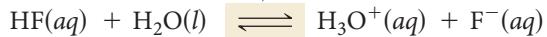


**▲ FIGURE 15.5 Ionization of a Weak Acid** When HF dissolves in water, only a fraction of the dissolved molecules ionize to form  $\text{H}_3\text{O}^+$  and  $\text{F}^-$ . The solution contains many intact HF molecules.

## Weak Acids

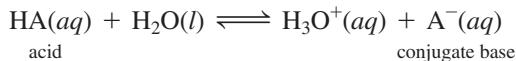
In contrast to HCl, HF is a weak acid, one that does not completely ionize in solution.

Equilibrium arrow indicates partial ionization.



An HF solution contains a large number of intact (or un-ionized) HF molecules; it also contains some  $\text{H}_3\text{O}^+(aq)$  and  $\text{F}^-(aq)$  (Figure 15.5 ▲). In other words, a 1.0 M HF solution has an  $[\text{H}_3\text{O}^+]$  that is much less than 1.0 M because only some of the HF molecules ionize to form  $\text{H}_3\text{O}^+$ .

The degree to which an acid is strong or weak depends on the attraction between the anion of the acid (the conjugate base) and the hydrogen ion, relative to the attractions of these ions to water. Recall that HA is a generic formula for an acid. The degree to which the following reaction proceeds in the forward direction depends on the strength of the attraction between  $\text{H}^+$  and  $\text{A}^-$ :

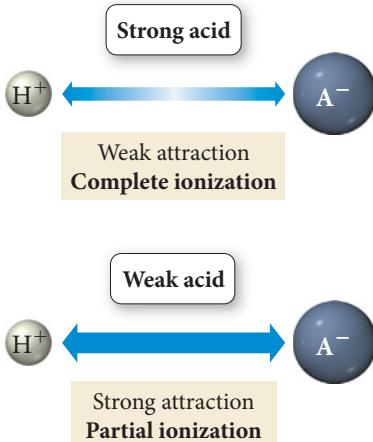


If the attraction between  $\text{H}^+$  and  $\text{A}^-$  is *weak*, then the reaction favors the forward direction and the acid is *strong*. If the attraction between  $\text{H}^+$  and  $\text{A}^-$  is *strong*, then the reaction favors the reverse direction and the acid is *weak*, as shown in Figure 15.6 ▲.

For example, in HCl, the conjugate base ( $\text{Cl}^-$ ) has a relatively weak attraction to  $\text{H}^+$ —the reverse reaction does not occur to any significant extent. In HF, on the other hand, the conjugate base ( $\text{F}^-$ ) has a greater attraction to  $\text{H}^+$ —the reverse reaction occurs to a significant degree. *In general, the stronger the acid, the weaker the conjugate base and vice versa.* If the forward reaction (that of the acid) has a high tendency to occur, then the reverse reaction (that of the conjugate base) has a low tendency to occur. Table 15.4 lists some common weak acids.

Notice that two of the weak acids in Table 15.4 are diprotic, meaning that they have two ionizable protons, and one is **triprotic** (three ionizable protons). We discuss polyprotic acids in more detail in Section 15.9.

The terms *strong* and *weak* acids are often confused with the terms *concentrated* and *dilute* acids. Can you articulate the difference between these terms?



**▲ FIGURE 15.6 Ionic Attraction and Acid Strength** In a strong acid, the attraction between  $\text{H}^+$  and  $\text{A}^-$  is weak, resulting in complete ionization. In a weak acid, the attraction between  $\text{H}^+$  and  $\text{A}^-$  is strong, resulting in only partial ionization.

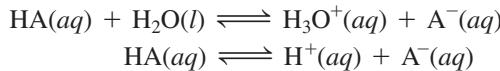
We can also write the formulas for acetic acid and formic acid as  $\text{CH}_3\text{COOH}$  and  $\text{HCOOH}$ , respectively, to indicate that in these compounds the only H that ionizes is the one attached to an oxygen atom.

**TABLE 15.4 Some Weak Acids**

|  |   |
|--|---|
| Hydrofluoric acid (HF)                         | Sulfurous acid ( $\text{H}_2\text{SO}_3$ ) (diprotic)   |
| Acetic acid ( $\text{H}_3\text{C}\text{OOH}$ ) | Carbonic acid ( $\text{H}_2\text{CO}_3$ ) (diprotic)    |
| Formic acid ( $\text{HCHO}_2$ )                | Phosphoric acid ( $\text{H}_3\text{PO}_4$ ) (triprotic) |

## The Acid Ionization Constant ( $K_a$ )

We quantify the relative strength of a weak acid with the **acid ionization constant ( $K_a$ )**, which is the equilibrium constant for the ionization reaction of the weak acid. As we saw in Section 14.3, for the two equivalent reactions:



the equilibrium constant is:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

Sometimes  $K_a$  is also referred to as the acid dissociation constant.

Recall from Chapter 14 that the concentrations of pure solids or pure liquids are not included in the expression for  $K_c$ ; therefore,  $\text{H}_2\text{O}(l)$  is not included in the expression for  $K_a$ .

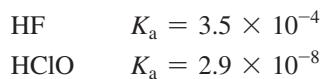
Since  $[\text{H}_3\text{O}^+]$  is equivalent to  $[\text{H}^+]$ , both forms of the expression are equal. Although the ionization constants for all weak acids are relatively small (otherwise the acid would not be a weak acid), they do vary in magnitude. The smaller the constant, the less the acid ionizes, and the weaker the acid. Table 15.5 lists the acid ionization constants for a number of common weak acids in order of decreasing acid strength.

**TABLE 15.5 Acid Ionization Constants ( $K_a$ ) for Some Monoprotic Weak Acids at 25 °C**

| Acid              | Formula                           | Structural Formula   | Ionization Reaction  | $K_a$                 |
|-------------------|-----------------------------------|--|--|-----------------------|
| Chlorous acid     | $\text{HClO}_2$                   | $\text{H}-\text{O}-\text{Cl}=\text{O}$   | $\text{HClO}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{ClO}_2^-(aq)$                                     | $1.1 \times 10^{-2}$  |
| Nitrous acid      | $\text{HNO}_2$                    | $\text{H}-\text{O}-\text{N}=\text{O}$  | $\text{HNO}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{NO}_2^-(aq)$                                       | $4.6 \times 10^{-4}$  |
| Hydrofluoric acid | $\text{HF}$                       | $\text{H}-\text{F}$  | $\text{HF}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{F}^-(aq)$   | $3.5 \times 10^{-4}$  |
| Formic acid       | $\text{HCHO}_2$                   | $\text{H}-\text{O}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{H}$  | $\text{HCHO}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CHO}_2^-(aq)$                                     | $1.8 \times 10^{-4}$  |
| Benzoic acid      | $\text{HC}_7\text{H}_5\text{O}_2$ | $\text{H}-\text{O}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{C}(\text{H})=\text{C}(\text{H})-\text{CH}_3$ | $\text{HC}_7\text{H}_5\text{O}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{C}_7\text{H}_5\text{O}_2^-(aq)$ | $6.5 \times 10^{-5}$  |
| Acetic acid       | $\text{HC}_2\text{H}_3\text{O}_2$ | $\text{H}-\text{O}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_3$                                       | $\text{HC}_2\text{H}_3\text{O}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{C}_2\text{H}_3\text{O}_2^-(aq)$ | $1.8 \times 10^{-5}$  |
| Hypochlorous acid | $\text{HClO}$                     | $\text{H}-\text{O}-\text{Cl}$  | $\text{HClO}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{ClO}^-(aq)$   | $2.9 \times 10^{-8}$  |
| Hydrocyanic acid  | $\text{HCN}$                      | $\text{H}-\text{C}\equiv\text{N}$  | $\text{HCN}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CN}^-(aq)$   | $4.9 \times 10^{-10}$ |
| Phenol            | $\text{HC}_6\text{H}_5\text{O}$   | $\text{HO}-\text{C}(\text{H})=\text{C}(\text{H})-\text{CH}_3$  | $\text{HC}_6\text{H}_5\text{O}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{C}_6\text{H}_5\text{O}^-(aq)$     | $1.3 \times 10^{-10}$ |

**Connection 15.2 Relative Strengths of Weak Acids**

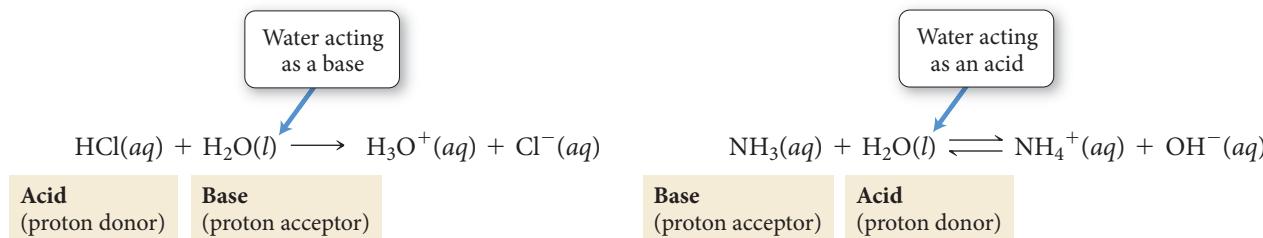
Consider these two acids and their  $K_a$  values:



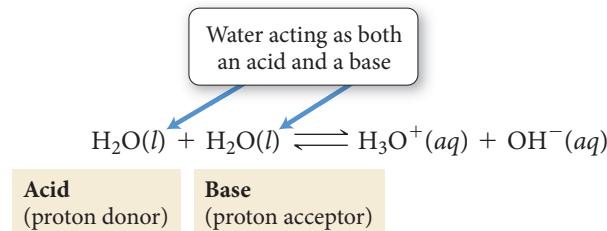
Which acid is stronger?

## 15.5 Autoionization of Water and pH

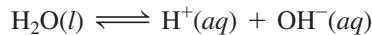
We saw previously that water acts as a base when it reacts with HCl and as an acid when it reacts with NH<sub>3</sub>:



Water is *amphoteric*; it can act as either an acid or a base. Even when pure, water acts as an acid and a base with itself, a process called **autoionization**:



We can write the autoionization reaction as:



The equilibrium constant for this reaction is the product of the concentration of the two ions:

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = [\text{H}^+][\text{OH}^-]$$

This equilibrium constant is called the **ion product constant for water ( $K_w$ )** (sometimes called the *dissociation constant for water*). At 25 °C,  $K_w = 1.0 \times 10^{-14}$ . In pure water, since H<sub>2</sub>O is the only source of these ions, the concentrations of H<sub>3</sub>O<sup>+</sup> and OH<sup>-</sup> are equal, and the solution is **neutral**. Since the concentrations are equal, we can easily calculate them from  $K_w$ .

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = \sqrt{K_w} = 1.0 \times 10^{-7} \quad (\text{in pure water at } 25^\circ\text{C})$$

As you can see, in pure water, the concentrations of H<sub>3</sub>O<sup>+</sup> and OH<sup>-</sup> are *very small* ( $1.0 \times 10^{-7}$  M) at room temperature.

An **acidic solution** contains an acid that creates additional H<sub>3</sub>O<sup>+</sup> ions, causing [H<sub>3</sub>O<sup>+</sup>] to increase. However, the *ion product constant still applies*:

$$[\text{H}_3\text{O}^+][\text{OH}^-] = K_w = 1.0 \times 10^{-14}$$

*The concentration of H<sub>3</sub>O<sup>+</sup> times the concentration of OH<sup>-</sup> is always  $1.0 \times 10^{-14}$  at 25 °C.* If [H<sub>3</sub>O<sup>+</sup>] increases, then [OH<sup>-</sup>] must decrease for the ion product constant to

remain  $1.0 \times 10^{-14}$ . For example, if  $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-3}$ , then we can find  $[\text{OH}^-]$  by solving the ion product constant expression for  $[\text{OH}^-]$ :

$$(1.0 \times 10^{-3})[\text{OH}^-] = 1.0 \times 10^{-14}$$

$$[\text{OH}^-] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-3}} = 1.0 \times 10^{-11} \text{ M}$$

In an acidic solution  $[\text{H}_3\text{O}^+] > [\text{OH}^-]$ .

A **basic solution** contains a base that creates additional  $\text{OH}^-$  ions, causing  $[\text{OH}^-]$  to increase and  $[\text{H}_3\text{O}^+]$  to decrease, but again the *ion product constant still applies*. Suppose  $[\text{OH}^-] = 1.0 \times 10^{-2}$ ; then we can find  $[\text{H}_3\text{O}^+]$  by solving the ion product constant expression for  $[\text{H}_3\text{O}^+]$ :

$$[\text{H}_3\text{O}^+](1.0 \times 10^{-2}) = 1.0 \times 10^{-14}$$

$$[\text{H}_3\text{O}^+] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-2}} = 1.0 \times 10^{-12} \text{ M}$$

In a basic solution  $[\text{OH}^-] > [\text{H}_3\text{O}^+]$ .

Notice that changing  $[\text{H}_3\text{O}^+]$  in an aqueous solution produces an inverse change in  $[\text{OH}^-]$  and vice versa.

### Summarizing $K_w$ :

- ▶ A *neutral solution* contains  $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$  (at 25 °C).
- ▶ An *acidic solution* contains  $[\text{H}_3\text{O}^+] > [\text{OH}^-]$ .
- ▶ A *basic solution* contains  $[\text{OH}^-] > [\text{H}_3\text{O}^+]$ .
- ▶ In *all aqueous solutions* both  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  are present, with  $[\text{H}_3\text{O}^+][\text{OH}^-] = K_w = 1.0 \times 10^{-14}$  (at 25 °C).

The ion product constant  $K_w$  depends on temperature. For all calculations in this book, assume 25 °C unless otherwise noted.

## EXAMPLE 15.2 Using $K_w$ in Calculations

Calculate  $[\text{OH}^-]$  at 25 °C for each solution and determine if the solution is acidic, basic, or neutral.

- (a)  $[\text{H}_3\text{O}^+] = 7.5 \times 10^{-5} \text{ M}$       (b)  $[\text{H}_3\text{O}^+] = 1.5 \times 10^{-9} \text{ M}$   
 (c)  $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-7} \text{ M}$

### SOLUTION

- (a) To find  $[\text{OH}^-]$  use the ion product constant. Substitute the given value for  $[\text{H}_3\text{O}^+]$  and solve the equation for  $[\text{OH}^-]$ .

Since  $[\text{H}_3\text{O}^+] > [\text{OH}^-]$ , the solution is acidic.

$$[\text{H}_3\text{O}^+][\text{OH}^-] = K_w = 1.0 \times 10^{-14}$$

$$(7.5 \times 10^{-5})[\text{OH}^-] = 1.0 \times 10^{-14}$$

$$[\text{OH}^-] = \frac{1.0 \times 10^{-14}}{7.5 \times 10^{-5}} = 1.3 \times 10^{-10} \text{ M}$$

Acidic solution

- (b) Substitute the given value for  $[\text{H}_3\text{O}^+]$  and solve the acid ionization equation for  $[\text{OH}^-]$ .

Since  $[\text{H}_3\text{O}^+] < [\text{OH}^-]$ , the solution is basic.

$$(1.5 \times 10^{-9})[\text{OH}^-] = 1.0 \times 10^{-14}$$

$$[\text{OH}^-] = \frac{1.0 \times 10^{-14}}{1.5 \times 10^{-9}} = 6.7 \times 10^{-6} \text{ M}$$

Basic solution

- (c) Substitute the given value for  $[\text{H}_3\text{O}^+]$  and solve the acid ionization equation for  $[\text{OH}^-]$ .

Since  $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-7}$  and  $[\text{OH}^-] = 1.0 \times 10^{-7}$ , the solution is neutral.

$$(1.0 \times 10^{-7})[\text{OH}^-] = 1.0 \times 10^{-14}$$

$$[\text{OH}^-] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-7}} = 1.0 \times 10^{-7} \text{ M}$$

Neutral solution

### FOR PRACTICE 15.2

Calculate  $[\text{H}_3\text{O}^+]$  at 25 °C for each solution and determine if the solution is acidic, basic, or neutral.

- (a)  $[\text{OH}^-] = 1.5 \times 10^{-2} \text{ M}$       (b)  $[\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$   
 (c)  $[\text{OH}^-] = 8.2 \times 10^{-10} \text{ M}$

The log of a number is the exponent to which 10 must be raised to obtain that number. Thus,  $\log 10^1 = 1$ ;  $\log 10^2 = 2$ ;  $\log 10^{-1} = -1$ ;  $\log 10^{-2} = -2$ , etc. (see Appendix I).

When you take the log of a quantity, the result should have the same number of decimal places as the number of significant figures in the original quantity.

Concentrated acid solutions can have negative pH. For example, if  $[\text{H}_3\text{O}^+] = 2.0 \text{ M}$ , the pH is  $-0.30$ .

**TABLE 15.6 The pH of Some Common Substances**

| Substance                        | pH        |
|----------------------------------|-----------|
| Gastric juice<br>(human stomach) | 1.0–3.0   |
| Limes                            | 1.8–2.0   |
| Lemons                           | 2.2–2.4   |
| Soft drinks                      | 2.0–4.0   |
| Plums                            | 2.8–3.0   |
| Wines                            | 2.8–3.8   |
| Apples                           | 2.9–3.3   |
| Peaches                          | 3.4–3.6   |
| Cherries                         | 3.2–4.0   |
| Beers                            | 4.0–5.0   |
| Rainwater (unpolluted)           | 5.6       |
| Human blood                      | 7.3–7.4   |
| Egg whites                       | 7.6–8.0   |
| Milk of magnesia                 | 10.5      |
| Household ammonia                | 10.5–11.5 |
| 4% NaOH solution                 | 14        |

## The pH Scale: A Way to Quantify Acidity and Basicity

The pH scale is a compact way to specify the acidity of a solution. We define **pH** as the negative of the log of the hydronium ion concentration:

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

A solution with  $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-3} \text{ M}$  (acidic) has a pH of:

$$\begin{aligned}\text{pH} &= -\log[\text{H}_3\text{O}^+] \\ &= -\log(1.0 \times 10^{-3}) \\ &= -(-3.00) \\ &= 3.00\end{aligned}$$

Notice that we report the pH to two *decimal places* here. This is because only the numbers to the right of the decimal point are significant in a logarithm. Because our original value for the concentration had two significant figures, the log of that number has two decimal places.

$$\log 1.0 \times 10^{-3} = 3.00$$

2 significant digits      2 decimal places

If the original number had three significant digits, the log would be reported to three decimal places.

$$\log 1.00 \times 10^{-3} = 3.000$$

3 significant digits      3 decimal places

A solution with  $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-7} \text{ M}$  (neutral at 25 °C) has a pH of:

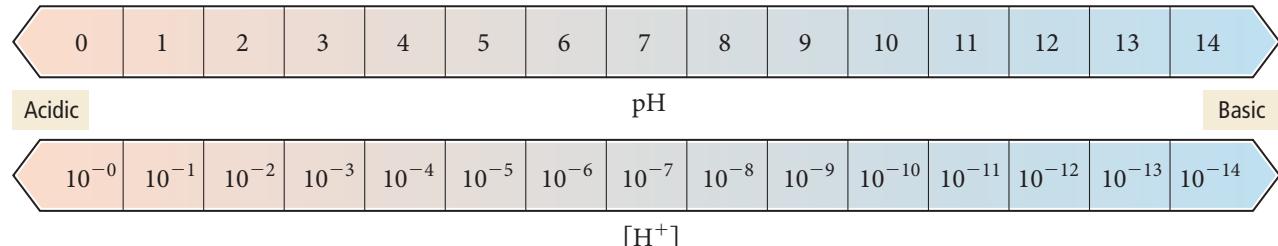
$$\begin{aligned}\text{pH} &= -\log[\text{H}_3\text{O}^+] \\ &= -\log(1.0 \times 10^{-7}) \\ &= -(-7.00) \\ &= 7.00\end{aligned}$$

In general, at 25 °C:

- pH < 7 The solution is *acidic*.
- pH > 7 The solution is *basic*.
- pH = 7 The solution is *neutral*.

Table 15.6 lists the pH of some common substances. As we discussed in Section 15.2, many foods, especially fruits, are acidic and have low pH values. Relatively few foods are basic. The foods with the lowest pH values are limes and lemons, and they are among the sourest. Because the pH scale is a *logarithmic scale*, a change of 1 pH unit corresponds to a 10-fold change in  $\text{H}_3\text{O}^+$  concentration (Figure 15.7 ▼). For example, a lime with a pH of

### The pH Scale



▲ **FIGURE 15.7** The pH Scale An increase of 1 on the pH scale corresponds to a factor of 10 decrease in  $[\text{H}_3\text{O}^+]$ .

2.0 is 10 times more acidic than a plum with a pH of 3.0 and 100 times more acidic than a cherry with a pH of 4.0.

### EXAMPLE 15.3 Calculating pH from $[H_3O^+]$ or $[OH^-]$

Calculate the pH of each solution at 25 °C and indicate whether the solution is acidic or basic.

(a)  $[H_3O^+] = 1.8 \times 10^{-4} \text{ M}$       (b)  $[OH^-] = 1.3 \times 10^{-2} \text{ M}$

#### SOLUTION

- (a) To calculate pH, substitute the given  $[H_3O^+]$  into the pH equation. Since  $pH < 7$ , this solution is acidic.

$$\begin{aligned} \text{pH} &= -\log[H_3O^+] \\ &= -\log(1.8 \times 10^{-4}) \\ &= -(−3.74) \\ &= 3.74 \text{ (acidic)} \end{aligned}$$

- (b) First use  $K_w$  to find  $[H_3O^+]$  from  $[OH^-]$ .

$$\begin{aligned} [H_3O^+][OH^-] &= K_w = 1.0 \times 10^{-14} \\ [H_3O^+](1.3 \times 10^{-2}) &= 1.0 \times 10^{-14} \\ [H_3O^+] &= \frac{1.0 \times 10^{-14}}{1.3 \times 10^{-2}} = 7.7 \times 10^{-13} \text{ M} \\ \text{pH} &= -\log[H_3O^+] \\ &= -\log(7.7 \times 10^{-13}) \\ &= -(−12.11) \\ &= 12.11 \text{ (basic)} \end{aligned}$$

Then substitute  $[H_3O^+]$  into the pH expression to find pH.

Since  $pH > 7$ , this solution is basic.

#### FOR PRACTICE 15.3

Calculate the pH of each solution and indicate whether the solution is acidic or basic.

(a)  $[H_3O^+] = 9.5 \times 10^{-9} \text{ M}$       (b)  $[OH^-] = 7.1 \times 10^{-3} \text{ M}$

### EXAMPLE 15.4 Calculating $[H_3O^+]$ from pH

Calculate the  $[H_3O^+]$  for a solution with a pH of 4.80.

#### SOLUTION

To find the  $[H_3O^+]$  from pH, start with the equation that defines pH. Substitute the given value of pH and then solve for  $[H_3O^+]$ . Since the given pH value was reported to two decimal places, the  $[H_3O^+]$  is written to two significant figures. (Remember that  $10^{\log x} = x$  (see Appendix I). Some calculators use an inv log key to represent this function.)

$$\begin{aligned} \text{pH} &= -\log[H_3O^+] \\ 4.80 &= -\log[H_3O^+] \\ -4.80 &= \log[H_3O^+] \\ 10^{-4.80} &= 10^{\log[H_3O^+]} \\ 10^{-4.80} &= [H_3O^+] \\ [H_3O^+] &= 1.6 \times 10^{-5} \text{ M} \end{aligned}$$

#### FOR PRACTICE 15.4

Calculate the  $[H_3O^+]$  for a solution with a pH of 8.37.

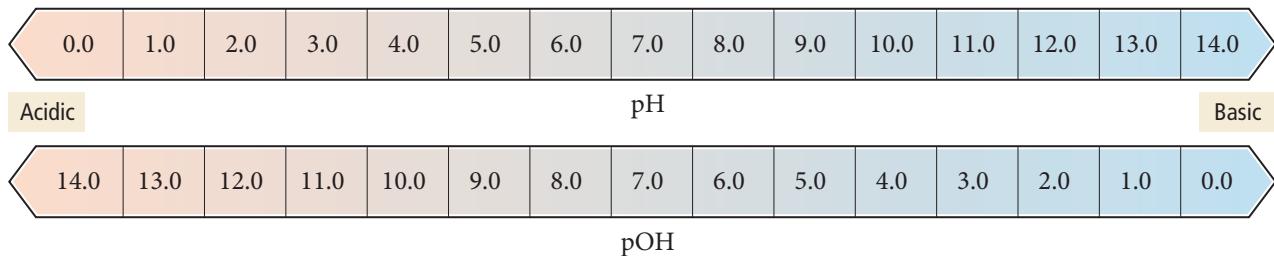
## pOH and Other p Scales

The pOH scale is analogous to the pH scale but is defined with respect to  $[OH^-]$  instead of  $[H_3O^+]$ .

$$\text{pOH} = -\log[OH^-]$$

A solution with an  $[OH^-]$  of  $1.0 \times 10^{-3} \text{ M}$  (basic) has a pOH of 3.00. On the pOH scale, a pOH less than 7 is basic and a pOH greater than 7 is acidic. A pOH of 7 is neutral

Notice that p is the mathematical operator  $-\log$ ; thus,  $pX = -\log X$ .



▲ FIGURE 15.8 pH and pOH

(Figure 15.8 ▲). We can derive a relationship between pH and pOH at 25 °C from the expression for  $K_w$ :

$$[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

Taking the log of both sides, we get:

$$\begin{aligned}\log([\text{H}_3\text{O}^+][\text{OH}^-]) &= \log(1.0 \times 10^{-14}) \\ \log[\text{H}_3\text{O}^+] + \log[\text{OH}^-] &= -14.00 \\ -\log[\text{H}_3\text{O}^+] - \log[\text{OH}^-] &= 14.00 \\ \text{pH} + \text{pOH} &= 14.00\end{aligned}$$

The sum of pH and pOH is always equal to 14.00 at 25 °C. Therefore, a solution with a pH of 3 has a pOH of 11.

Another common p scale is the  $\text{p}K_a$  scale defined as:

$$\text{p}K_a = -\log K_a$$

The  $\text{p}K_a$  of a weak acid is another way to quantify its strength. The smaller the  $\text{p}K_a$ , the stronger the acid. For example, chlorous acid, with a  $K_a$  of  $1.1 \times 10^{-2}$ , has a  $\text{p}K_a$  of 1.96; and formic acid, with a  $K_a$  of  $1.8 \times 10^{-4}$ , has a  $\text{p}K_a$  of 3.74.



## Chemistry and Medicine

### Ulcers

An ulcer is a lesion on the wall of the stomach or small intestine. Under normal circumstances, a thick layer of mucus lines the stomach wall and protects it from the hydrochloric acid and other gastric juices in the stomach. If that mucous layer is damaged, however, stomach juices come in direct contact with the stomach wall and begin to digest it, creating an ulcer. The main symptom of an ulcer is a burning or gnawing pain in the stomach.

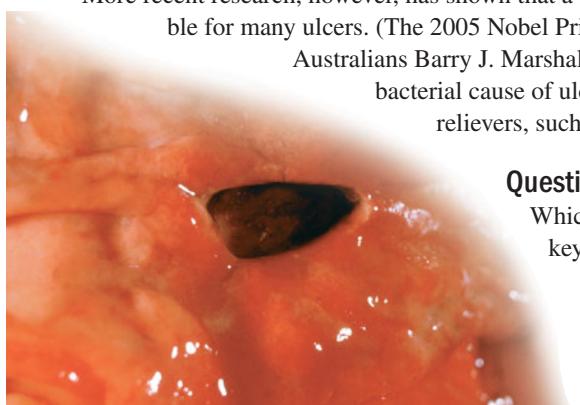
Acidic drugs, such as aspirin, and acidic foods, such as citrus fruits and pickling fluids, irritate ulcers. When consumed, these substances increase the acidity of the stomach juices, exacerbating the irritation to the stomach wall. On the other hand, antacids—which contain bases—relieve ulcers. Common antacids include Tums and milk of magnesia.

The causes of ulcers are manifold. For many years, a stressful lifestyle and a rich diet were blamed.

More recent research, however, has shown that a bacterial infection of the stomach lining is responsible for many ulcers. (The 2005 Nobel Prize in Physiology or Medicine was awarded to Australians Barry J. Marshall and J. Robin Warren, for their discovery of the bacterial cause of ulcers.) Long-term use of some over-the-counter pain relievers, such as aspirin, is also believed to produce ulcers.

### Question

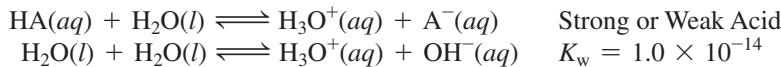
Which dessert would be less likely to irritate an ulcer, key lime pie or meringue (made of egg whites)?



◀ An ulcer is a lesion in the stomach wall.

## 15.6 Finding the $\text{H}_3\text{O}^+$ and pH of Strong and Weak Acid Solutions

A solution containing a strong or weak acid has two potential sources of  $\text{H}_3\text{O}^+$ : the ionization of the acid itself and the autoionization of water. If we let HA be a strong or weak acid, the ionization equations are:



Except in extremely dilute acid solutions, the autoionization of water contributes a negligibly small amount of  $\text{H}_3\text{O}^+$  compared to the ionization of the strong or weak acid. Recall from Section 15.5 that autoionization in pure water at 25 °C produces an  $\text{H}_3\text{O}^+$  concentration of  $1.0 \times 10^{-7}$  M. In a strong or weak acid solution, the additional  $\text{H}_3\text{O}^+$  from the acid causes the autoionization of water equilibrium to shift left (as described by Le Châtelier's principle). Consequently, in most strong or weak acid solutions, the autoionization of water produces even less  $\text{H}_3\text{O}^+$  than in pure water and can be ignored. Therefore we can focus exclusively on the amount of  $\text{H}_3\text{O}^+$  produced by the acid.

The only exceptions would be extremely dilute ( $< 10^{-5}$  M) strong acid solutions.

### Strong Acids

Because strong acids, by definition, completely ionize in solution, and because we can (in nearly all cases) ignore the contribution of the autoionization of water, *the concentration of  $\text{H}_3\text{O}^+$  in a strong acid solution is equal to the concentration of the strong acid*. For example, a 0.10 M HCl solution has an  $\text{H}_3\text{O}^+$  concentration of 0.10 M and a pH of 1.00.

$$0.10 \text{ M HCl} \Rightarrow [\text{H}_3\text{O}^+] = 0.10 \text{ M} \Rightarrow \text{pH} = -\log(0.10) = 1.00$$

### Weak Acids

Finding the pH of a weak acid solution is more complicated because the concentration of  $\text{H}_3\text{O}^+$  is *not equal* to the concentration of the weak acid. For example, if we make solutions of 0.10 M HCl (a strong acid) and 0.10 M acetic acid (a weak acid) in the laboratory and measure the pH of each, we get the following results:

|  |           |
|--|-----------|
| 0.10 M HCl                               | pH = 1.00 |
| 0.10 M $\text{HC}_2\text{H}_3\text{O}_2$ | pH = 2.87 |

The pH of the acetic acid solution is higher (it is less acidic) because acetic acid only partially ionizes. Calculating the  $[\text{H}_3\text{O}^+]$  formed by the ionization of a weak acid requires solving an equilibrium problem similar to those in Chapter 14. Consider, for example, a 0.10 M solution of the generic weak acid HA with an acid ionization constant  $K_a$ . Since we can ignore the contribution of the autoionization of water, we only have to determine the concentration of  $\text{H}_3\text{O}^+$  formed by the following equilibrium:



We can summarize the initial conditions, the changes, and the equilibrium conditions in the following ICE table:

|             | [HA]     | $[\text{H}_3\text{O}^+]$ | $[\text{A}^-]$ |
|-------------|----------|--------------------------|----------------|
| Initial     | 0.10     | ≈ 0.00                   | 0.00           |
| Change      | -x       | +x                       | +x             |
| Equilibrium | 0.10 - x | x                        | x              |

ICE tables were first introduced in Section 14.6. The reactant  $\text{H}_2\text{O}(l)$  is a pure liquid and is therefore not included in the equilibrium constant nor in the ICE table (see Section 14.5).

The initial  $\text{H}_3\text{O}^+$  concentration is listed as *approximately* zero because of the negligibly small contribution of  $\text{H}_3\text{O}^+$  due to the autoionization of water (discussed previously). The variable x represents the amount of HA that ionizes. As discussed in Chapter 14, each *equilibrium* concentration is the sum of the two entries above it in the ICE table.

In order to find the equilibrium concentration of  $\text{H}_3\text{O}^+$ , we must find the value of the variable  $x$ . We can use the equilibrium expression to set up an equation in which  $x$  is the only variable:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

$$= \frac{x^2}{0.10 - x}$$

As is often the case with equilibrium problems, we arrive at a quadratic equation in  $x$ , which we can solve using the quadratic formula (see Appendix IC). However, in many cases we can apply the  $x$  is small approximation (first discussed in Section 14.8). In Examples 15.5 and 15.6, we examine the general procedure for solving weak acid equilibrium problems. In both of these examples, the  $x$  is small approximation works well. In Example 15.7, we solve a problem in which the  $x$  is small approximation does not work. In such cases, we can solve the quadratic equation explicitly, or apply the method of successive approximations (also discussed in Section 14.8). Finally, in Example 15.8, we work a problem in which we find the equilibrium constant of a weak acid from its pH.

### PROCEDURE FOR...

#### Finding the pH (or $[\text{H}_3\text{O}^+]$ ) of a Weak Acid Solution

To solve these types of problems, follow the outlined procedure.

- Write the balanced equation for the ionization of the acid and use it as a guide to prepare an ICE table showing the given concentration of the weak acid as its initial concentration.** Leave room in the table for the changes in concentrations and for the equilibrium concentrations.

(Note that the  $[\text{H}_3\text{O}^+]$  is listed as approximately zero because the autoionization of water produces a negligibly small amount of  $\text{H}_3\text{O}^+$ ).

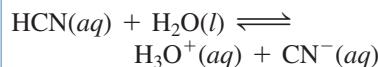
- Represent the change in the concentration of  $\text{H}_3\text{O}^+$  with the variable  $x$ . Define the changes in the concentrations of the other reactants and products in terms of  $x$ . Always keep in mind the stoichiometry of the reaction.**

- Sum each column to determine the equilibrium concentrations in terms of the initial concentrations and the variable  $x$ .**

### EXAMPLE 15.5

#### Finding the $[\text{H}_3\text{O}^+]$ of a Weak Acid Solution

Find the  $[\text{H}_3\text{O}^+]$  of a 0.100 M HCN solution.

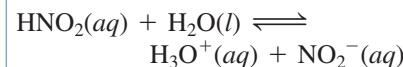


|         | [HCN] | $[\text{H}_3\text{O}^+]$ | $[\text{CN}^-]$ |
|---------|-------|--------------------------|-----------------|
| Initial | 0.100 | $\approx 0.00$           | 0.00            |
| Change  |       |                          |                 |
| Equil   |       |                          |                 |

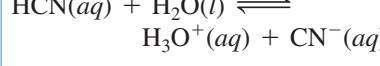
### EXAMPLE 15.6

#### Finding the pH of a Weak Acid Solution

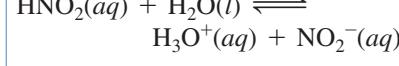
Find the pH of a 0.200 M  $\text{HNO}_2$  solution.



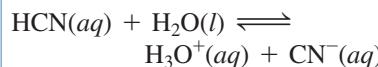
|         | [ $\text{HNO}_2$ ] | $[\text{H}_3\text{O}^+]$ | $[\text{NO}_2^-]$ |
|---------|--------------------|--------------------------|-------------------|
| Initial | 0.200              | $\approx 0.00$           | 0.00              |
| Change  |                    |                          |                   |
| Equil   |                    |                          |                   |



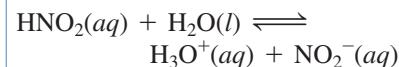
|         | [HCN] | $[\text{H}_3\text{O}^+]$ | $[\text{CN}^-]$ |
|---------|-------|--------------------------|-----------------|
| Initial | 0.100 | $\approx 0.00$           | 0.00            |
| Change  | $-x$  | $+x$                     | $+x$            |
| Equil   |       |                          |                 |



|         | [ $\text{HNO}_2$ ] | $[\text{H}_3\text{O}^+]$ | $[\text{NO}_2^-]$ |
|---------|--------------------|--------------------------|-------------------|
| Initial | 0.200              | $\approx 0.00$           | 0.00              |
| Change  | $-x$               | $+x$                     | $+x$              |
| Equil   |                    |                          |                   |



|         | [HCN]       | $[\text{H}_3\text{O}^+]$ | $[\text{CN}^-]$ |
|---------|-------------|--------------------------|-----------------|
| Initial | 0.100       | $\approx 0.00$           | 0.00            |
| Change  | $-x$        | $+x$                     | $+x$            |
| Equil   | $0.100 - x$ | $x$                      | $x$             |



|         | [ $\text{HNO}_2$ ] | $[\text{H}_3\text{O}^+]$ | $[\text{NO}_2^-]$ |
|---------|--------------------|--------------------------|-------------------|
| Initial | 0.200              | $\approx 0.00$           | 0.00              |
| Change  | $-x$               | $+x$                     | $+x$              |
| Equil   | $0.200 - x$        | $x$                      | $x$               |

**4. Substitute the expressions for the equilibrium concentrations (from step 3) into the expression for the acid ionization constant ( $K_a$ ).**

In many cases, you can make the approximation that  $x$  is small (as discussed in Section 14.8). **Substitute the value of the acid ionization constant (from Table 15.5) into the  $K_a$  expression and solve for  $x$ .**

Confirm that the  $x$  is small approximation is valid by calculating the ratio of  $x$  to the number it was subtracted from in the approximation. The ratio should be less than 0.05 (or 5%).

$$K_a = \frac{[H_3O^+][CN^-]}{[HCN]}$$

$$= \frac{x^2}{0.100 - x} \quad (x \text{ is small})$$

$$4.9 \times 10^{-10} = \frac{x^2}{0.100}$$

$$\sqrt{4.9 \times 10^{-10}} = \sqrt{\frac{x^2}{0.100}}$$

$$x = \sqrt{(0.100)(4.9 \times 10^{-10})}$$

$$= 7.0 \times 10^{-6}$$

$$\frac{7.0 \times 10^{-6}}{0.100} \times 100\% = 7.0 \times 10^{-3}\%$$

Therefore the approximation is valid.

$$K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]}$$

$$= \frac{x^2}{0.200 - x} \quad (x \text{ is small})$$

$$4.6 \times 10^{-4} = \frac{x^2}{0.200}$$

$$\sqrt{4.6 \times 10^{-4}} = \sqrt{\frac{x^2}{0.200}}$$

$$x = \sqrt{(0.200)(4.6 \times 10^{-4})}$$

$$= 9.6 \times 10^{-3}$$

$$\frac{9.6 \times 10^{-3}}{0.200} \times 100\% = 4.8\%$$

Therefore the approximation is valid (but barely so).

**5. Determine the  $[H_3O^+]$  from the calculated value of  $x$  and calculate the pH if necessary.**

$$[H_3O^+] = 7.0 \times 10^{-6} M$$

(pH was not asked for in this problem.)

$$[H_3O^+] = 9.6 \times 10^{-3} M$$

$$pH = -\log [H_3O^+]$$

$$= -\log (9.6 \times 10^{-3})$$

$$= 2.02$$

**6. Check your answer by substituting the computed equilibrium values into the acid ionization expression.** The calculated value of  $K_a$  should match the given value of  $K_a$ . Note that rounding errors and the  $x$  is small approximation could result in a difference in the least significant digit when comparing values of  $K_a$ .

$$K_a = \frac{[H_3O^+][CN^-]}{[HCN]} = \frac{(7.0 \times 10^{-6})^2}{0.100}$$

$$= 4.9 \times 10^{-10}$$

Since the calculated value of  $K_a$  matches the given value, the answer is valid.

$$K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]} = \frac{(9.6 \times 10^{-3})^2}{0.200}$$

$$= 4.6 \times 10^{-4}$$

Since the calculated value of  $K_a$  matches the given value, the answer is valid.

**FOR PRACTICE 15.5**

Find the  $H_3O^+$  concentration of a 0.250 M hydrofluoric acid solution.

**FOR PRACTICE 15.6**

Find the pH of a 0.0150 M acetic acid solution.

**EXAMPLE 15.7** Finding the pH of a Weak Acid Solution in Cases Where the  $x$  is small Approximation Does Not Work

Find the pH of a 0.100 M  $HClO_2$  solution.

**SOLUTION**

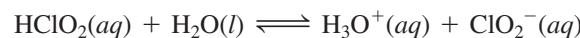
- 1.** Write the balanced equation for the ionization of the acid and use it as a guide to prepare an ICE table showing the given concentration of the weak acid as its initial concentration.

(Note that the  $H_3O^+$  concentration is listed as approximately zero. Although a little  $H_3O^+$  is present from the autoionization of water, this amount is negligibly small compared to the amount of  $HClO_2$  or  $H_3O^+$  formed by the acid.)



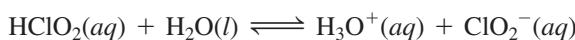
| $[HClO_2]$ | $[H_3O^+]$ | $[ClO_2^-]$    |
|------------|------------|----------------|
| Initial    | 0.100      | $\approx 0.00$ |
| Change     |            |                |
| Equil      |            |                |

- 2.** Represent the change in  $[H_3O^+]$  with the variable  $x$ . Define the changes in the concentrations of the other reactants and products in terms of  $x$ .



| $[HClO_2]$ | $[H_3O^+]$ | $[ClO_2^-]$    |
|------------|------------|----------------|
| Initial    | 0.100      | $\approx 0.00$ |
| Change     | $-x$       | $+x$           |
| Equil      |            |                |

- 3.** Sum each column to determine the equilibrium concentrations in terms of the initial concentrations and the variable  $x$ .



|         | [HClO <sub>2</sub> ] | [H <sub>3</sub> O <sup>+</sup> ] | [ClO <sub>2</sub> <sup>-</sup> ] |
|---------|----------------------|----------------------------------|----------------------------------|
| Initial | 0.100                | ≈ 0.00                           | 0.00                             |
| Change  | $-x$                 | $+x$                             | $+x$                             |
| Equil   | $0.100 - x$          | $x$                              | $x$                              |

- 4.** Substitute the expressions for the equilibrium concentrations (from step 3) into the expression for the acid ionization constant ( $K_a$ ). Make the  $x$  is small approximation and substitute the value of the acid ionization constant (from Table 15.5) into the  $K_a$  expression. Solve for  $x$ .

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{ClO}_2^-]}{[\text{HNO}_2]}$$

$$= \frac{x^2}{0.100 - x} \quad (x \text{ is small})$$

$$0.011 = \frac{x^2}{0.100}$$

$$\sqrt{0.011} = \sqrt{\frac{x^2}{0.100}}$$

$$x = \sqrt{(0.100)(0.011)}$$

$$= 0.033$$

Check to see if the  $x$  is small approximation is valid by calculating the ratio of  $x$  to the number it was subtracted from in the approximation. The ratio should be less than 0.05 (or 5%).

$$\frac{0.033}{0.100} \times 100\% = 33\%$$

Therefore, the  $x$  is small approximation is not valid.

- 4a.** If the  $x$  is small approximation is not valid, solve the quadratic equation explicitly or use the method of successive approximations to find  $x$ . In this case, we solve the quadratic equation.

$$0.011 = \frac{x^2}{0.100 - x}$$

$$0.011(0.100 - x) = x^2$$

$$0.0011 - 0.011x = x^2$$

$$x^2 + 0.011x - 0.0011 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$= \frac{-(0.011) \pm \sqrt{(0.011)^2 - 4(1)(-0.0011)}}{2(1)}$$

$$= \frac{-0.011 \pm 0.0672}{2}$$

$$x = -0.039 \quad \text{or} \quad x = 0.028$$

Since  $x$  represents the concentration of H<sub>3</sub>O<sup>+</sup>, and since concentrations cannot be negative, we reject the negative root.  
 $x = 0.028$

- 5.** Determine the H<sub>3</sub>O<sup>+</sup> concentration from the calculated value of  $x$  and calculate the pH (if necessary).

$$[\text{H}_3\text{O}^+] = 0.028 \text{ M}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

$$= -\log 0.028$$

$$= 1.55$$

- 6.** Check your answer by substituting the calculated equilibrium values into the acid ionization expression. The calculated value of  $K_a$  should match the given value of  $K_a$ . Note that rounding errors could result in a difference in the least significant digit when comparing values of  $K_a$ .

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{ClO}_2^-]}{[\text{HClO}_2]} = \frac{0.028^2}{0.100 - 0.028}$$

$$= 0.011$$

Since the calculated value of  $K_a$  matches the given value, the answer is valid.

### FOR PRACTICE 15.7

Find the pH of a 0.010 M HNO<sub>2</sub> solution.

**EXAMPLE 15.8** Finding the Equilibrium Constant from pH

A 0.100 M weak acid (HA) solution has a pH of 4.25. Find  $K_a$  for the acid.

**SOLUTION**

Use the given pH to find the equilibrium concentration of  $[H_3O^+]$ . Then write the balanced equation for the ionization of the acid and use it as a guide to prepare an ICE table showing all known concentrations.

$$pH = -\log[H_3O^+]$$

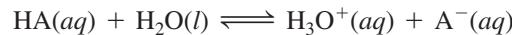
$$4.25 = -\log[H_3O^+]$$

$$[H_3O^+] = 5.6 \times 10^{-5} \text{ M}$$



| [HA]    | $[H_3O^+]$ | $[\text{A}^-]$       |
|---------|------------|----------------------|
| Initial | 0.100      | $\approx 0.00$       |
| Change  |            |                      |
| Equil   |            | $5.6 \times 10^{-5}$ |

Use the equilibrium concentration of  $H_3O^+$  and the stoichiometry of the reaction to predict the changes and equilibrium concentration for all species. For most weak acids, the initial and equilibrium concentrations of the weak acid (HA) are effectively equal because the amount that ionizes is usually very small compared to the initial concentration.



| [HA]    | $[H_3O^+]$  | $[\text{A}^-]$                               |
|---------|---|--|
| Initial | 0.100   | $\approx 0.00$                               |
| Change  | $-5.6 \times 10^{-5}$                             | $+5.6 \times 10^{-5}$                        |
| Equil   | $(0.100 - 5.6 \times 10^{-5})$<br>$\approx 0.100$ | $5.6 \times 10^{-5}$<br>$5.6 \times 10^{-5}$ |

Substitute the equilibrium concentrations into the expression for  $K_a$  and calculate its value.

$$\begin{aligned} K_a &= \frac{[H_3O^+][\text{A}^-]}{[\text{HA}]} \\ &= \frac{(5.6 \times 10^{-5})(5.6 \times 10^{-5})}{0.100} \\ &= 3.1 \times 10^{-8} \end{aligned}$$

**FOR PRACTICE 15.8**

A 0.175 M weak acid solution has a pH of 3.25. Find  $K_a$  for the acid.

**Connection 15.3** The  $x$  is small Approximation

The initial concentration and  $K_a$ 's of several weak acid (HA) solutions are listed here. For which of these is the  $x$  is small approximation least likely to work in finding the pH of the solution?

- (a) initial [HA] = 0.100 M;  $K_a = 1.0 \times 10^{-5}$
- (b) initial [HA] = 1.00 M;  $K_a = 1.0 \times 10^{-6}$
- (c) initial [HA] = 0.0100 M;  $K_a = 1.0 \times 10^{-3}$
- (d) initial [HA] = 1.0 M;  $K_a = 1.5 \times 10^{-3}$

**Connection 15.4** Strong and Weak Acids

Which solution is most acidic (that is, which one has the lowest pH)?

- (a) 0.10 M HCl
- (b) 0.10 M HF
- (c) 0.20 M HF

## Percent Ionization of a Weak Acid

We can quantify the ionization of a weak acid according to the percentage of acid molecules that actually ionizes. We define the **percent ionization** of a weak acid as the ratio of the ionized acid concentration to the initial acid concentration, multiplied by 100%:

$$\text{Percent ionization} = \frac{\text{concentration of ionized acid}}{\text{initial concentration of acid}} \times 100\% = \frac{[\text{H}_3\text{O}^+]_{\text{equil}}}{[\text{HA}]_{\text{init}}} \times 100\%$$

Since the concentration of ionized acid is equal to the  $\text{H}_3\text{O}^+$  concentration at equilibrium (for a monoprotic acid), we can use  $[\text{H}_3\text{O}^+]_{\text{equil}}$  and  $[\text{HA}]_{\text{init}}$  in the formula to calculate the percent ionization. For example, in Example 15.6, we found that a 0.200 M  $\text{HNO}_2$  solution contains  $9.6 \times 10^{-3}$  M  $\text{H}_3\text{O}^+$ . The 0.200 M  $\text{HNO}_2$  solution therefore has the following percent ionization:

$$\begin{aligned}\% \text{ ionization} &= \frac{[\text{H}_3\text{O}^+]_{\text{equil}}}{[\text{HA}]_{\text{init}}} \times 100\% \\ &= \frac{9.6 \times 10^{-3} \text{ M}}{0.200 \text{ M}} \times 100\% \\ &= 4.8\%\end{aligned}$$

As you can see, the percent ionization is relatively small. In this case, even though  $\text{HNO}_2$  has the second largest  $K_a$  in Table 15.5, fewer than 5 molecules out of 100 ionize. For most other weak acids (with smaller  $K_a$  values) the percent ionization is even less.

In Example 15.9, we calculate the percent ionization of a more concentrated  $\text{HNO}_2$  solution. In the example, notice that the calculated  $\text{H}_3\text{O}^+$  concentration is much greater (as we would expect for a more concentrated solution), but the *percent ionization* is actually smaller.

### EXAMPLE 15.9 Finding the Percent Ionization of a Weak Acid

Find the percent ionization of a 2.5 M  $\text{HNO}_2$  solution.

#### SOLUTION

To find the percent ionization, you must find the equilibrium concentration of  $\text{H}_3\text{O}^+$ . Follow the procedure in Example 15.5, shown in condensed form here.



|         | $[\text{HNO}_2]$ | $[\text{H}_3\text{O}^+]$ | $[\text{NO}_2^-]$ |
|---------|------------------|--------------------------|-------------------|
| Initial | 2.5              | $\approx 0.00$           | 0.00              |
| Change  | $-x$             | $+x$                     | $+x$              |
| Equil   | $2.5 - x$        | $x$                      | $x$               |

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NO}_2^-]}{[\text{HNO}_2]} = \frac{x^2}{2.5 - x} \quad (x \text{ is small})$$

$$4.6 \times 10^{-4} = \frac{x^2}{2.5}$$

$$x = 0.034$$

Therefore,  $[\text{H}_3\text{O}^+] = 0.034 \text{ M}$ .

Use the definition of percent ionization to calculate it. (Since the percent ionization is less than 5%, the *x is small* approximation is valid.)

$$\begin{aligned}\% \text{ ionization} &= \frac{[\text{H}_3\text{O}^+]_{\text{equil}}}{[\text{HA}]_{\text{init}}} \times 100\% \\ &= \frac{0.034 \text{ M}}{2.5 \text{ M}} \times 100\% \\ &= 1.4\%\end{aligned}$$

#### FOR PRACTICE 15.9

Find the percent ionization of a 0.250 M  $\text{HC}_2\text{H}_3\text{O}_2$  solution at 25 °C.

We can summarize the results of Examples 15.6 and 15.9:

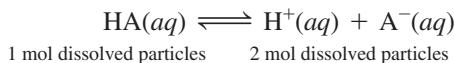
| $[\text{HNO}_2]$ | $[\text{H}_3\text{O}^+]$ | Percent Dissociation |
|------------------|--------------------------|----------------------|
| 0.200            | 0.0096                   | 4.8%                 |
| 2.5              | 0.034                    | 1.4%                 |

The trend you can see in the table applies to all weak acids.

- The equilibrium  $\text{H}_3\text{O}^+$  concentration of a weak acid increases with increasing initial concentration of the acid.
- The percent ionization of a weak acid decreases with increasing concentration of the acid.

In other words, as the concentration of a weak acid solution increases, the concentration of the hydronium ion also increases, but the increase is not linear. The  $\text{H}_3\text{O}^+$  concentration increases more slowly than the concentration of the acid because as the acid concentration increases, a smaller fraction of weak acid molecules ionize.

We can understand this behavior by analogy with Le Châtelier's principle. Consider the following weak acid ionization equilibrium:



If we dilute a weak acid solution initially at equilibrium, the system (according to Le Châtelier's principle) responds to minimize the disturbance. The equilibrium shifts to the right because the right side of the equation contains more particles in solution (2 mol versus 1 mol) than the left side. If the system shifts to the right, the percent ionization is greater in the more dilute solution, which is what we observe.

### Conceptual Connection 15.5 Percent Ionization

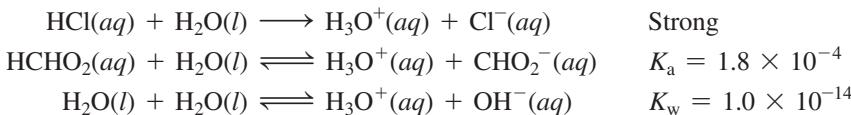
Which of these weak acid solutions has the greatest percent ionization? Which solution has the lowest (most acidic) pH?

- 0.100 M  $\text{HC}_2\text{H}_3\text{O}_2$
- 0.500 M  $\text{HC}_2\text{H}_3\text{O}_2$
- 0.0100 M  $\text{HC}_2\text{H}_3\text{O}_2$

### Mixtures of Acids

Finding the pH of a mixture of acids may seem difficult at first. However, in many cases, the relative strengths of the acids in the mixture allow us to neglect the weaker acid and focus only on the stronger one. Here, we consider two possible acid mixtures: a strong acid with a weak acid, and a weak acid with another weak acid.

**A Strong Acid and a Weak Acid** Consider a mixture that is 0.10 M in HCl and 0.10 M in  $\text{HCHO}_2$ . There are three sources of  $\text{H}_3\text{O}^+$  ions: the strong acid (HCl), the weak acid ( $\text{HCHO}_2$ ), and the autoionization of water.



Since HCl is strong, we know that it completely ionizes to produce a significant concentration of  $\text{H}_3\text{O}^+$  (0.10 M). The  $\text{H}_3\text{O}^+$  formed by HCl then suppresses the formation of additional  $\text{H}_3\text{O}^+$  formed by the ionization of  $\text{HCHO}_2$  or the autoionization of water. In other words, according to Le Châtelier's principle, the formation of  $\text{H}_3\text{O}^+$  by the strong acid causes the weak acid to ionize even less than it would in the absence of the strong acid. To see this clearly, let us calculate  $[\text{H}_3\text{O}^+]$  and  $[\text{CHO}_2^-]$  in this solution.

In an initial estimate of  $[\text{H}_3\text{O}^+]$ , we can neglect the contribution of  $\text{HCHO}_2$  and  $\text{H}_2\text{O}$ . The concentration of  $\text{H}_3\text{O}^+$  is then equal to the initial concentration of HCl.

$$[\text{H}_3\text{O}^+] = [\text{HCl}] = 0.10 \text{ M}$$

To find  $[\text{CHO}_2^-]$  we must solve an equilibrium problem. However, the initial concentration of  $\text{H}_3\text{O}^+$  in this case is not negligible (as it has been in all the other weak acid equilibrium problems that we have worked so far) because HCl has formed a significant amount of  $\text{H}_3\text{O}^+$ . The concentration of  $\text{H}_3\text{O}^+$  formed by HCl becomes the *initial* concentration of  $\text{H}_3\text{O}^+$  in the ICE table for  $\text{HCHO}_2$  as shown here:



|         | $[\text{HCHO}_2]$ | $[\text{H}_3\text{O}^+]$ | $[\text{CHO}_2^-]$ |
|---------|-------------------|--------------------------|--------------------|
| Initial | 0.10              | 0.10                     | 0.00               |
| Change  | $-x$              | $+x$                     | $+x$               |
| Equil   | $0.10 - x$        | $0.10 + x$               | $x$                |

We then use the equilibrium expression to set up an equation in which  $x$  is the only variable:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CHO}_2^-]}{[\text{HCHO}_2]}$$

$$= \frac{(0.10 + x)x}{0.10 - x}$$

Since the equilibrium constant is small relative to the initial concentration of the acid, we can make the  $x$  is *small* approximation:

$$K_a = \frac{(0.10 + x)x}{0.10 - x}$$

$$1.8 \times 10^{-4} = \frac{(0.10)x}{0.10}$$

$$x = 1.8 \times 10^{-4}$$

Checking the  $x$  is *small* approximation:

$$\frac{1.8 \times 10^{-4}}{0.10} \times 100\% = 0.18\%$$

We find that the approximation is valid. Therefore,  $[\text{CHO}_2^-] = 1.8 \times 10^{-4} \text{ M}$ . We can now see that we can completely ignore the ionization of the weak acid ( $\text{HCHO}_2$ ) in calculating  $[\text{H}_3\text{O}^+]$  for the mixture. The contribution to the concentration of  $\text{H}_3\text{O}^+$  by the weak acid must necessarily be equal to the concentration of  $\text{CHO}_2^-$  that we just calculated (because of the stoichiometry of the ionization reaction). Therefore, we have the following contributions to  $[\text{H}_3\text{O}^+]$ :

HCl contributes 0.10 M

$\text{HCHO}_2$  contributes  $1.8 \times 10^{-4} \text{ M}$  or 0.00018 M

Total  $[\text{H}_3\text{O}^+] = 0.10 \text{ M} + 0.00018 \text{ M} = 0.10 \text{ M}$

As we can see, since the significant figure rules for addition limit the answer to two decimal places, the amount of  $\text{H}_3\text{O}^+$  contributed by  $\text{HCHO}_2$  is completely negligible. The amount of  $\text{H}_3\text{O}^+$  contributed by the autoionization of water is even smaller and therefore similarly negligible.

**A Mixture of Two Weak Acids** When two weak acids are mixed, we again have three potential sources of  $\text{H}_3\text{O}^+$  to consider: each of the two weak acids and the autoionization of water. However, if the  $K_a$ 's of the two weak acids are sufficiently different in magnitude (if they differ by more than a factor of several hundred), then as long as the concentrations of the two acids are similar in magnitude (or the concentration of the stronger one is greater than that of the weaker), we can assume that the weaker acid will not make a significant contribution to

the concentration of  $\text{H}_3\text{O}^+$ . We make this assumption for the same reason that we made a similar assumption for a mixture of a strong acid and a weak one: the  $\text{H}_3\text{O}^+$  formed by the stronger acid suppresses the ionization of the weaker one, in accordance with Le Châtelier's principle. Example 15.10 shows how to calculate the concentration of  $\text{H}_3\text{O}^+$  in a mixture of two weak acids.

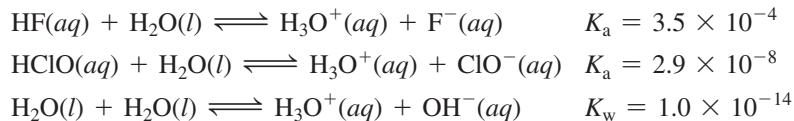
### EXAMPLE 15.10 Mixtures of Weak Acids

Find the pH of a mixture that is 0.150 M in HF and 0.100 M in HClO.

#### SOLUTION

The three possible sources of  $\text{H}_3\text{O}^+$  ions are HF, HClO, and  $\text{H}_2\text{O}$ . Write the ionization equations for the three sources and their corresponding equilibrium constants. Since the equilibrium constant for the ionization of HF is about 12,000 times larger than that for the ionization of HClO, the contribution of HF to  $[\text{H}_3\text{O}^+]$  is by far the greatest. You can therefore just calculate the  $[\text{H}_3\text{O}^+]$  formed by HF and neglect the other two potential sources of  $\text{H}_3\text{O}^+$ .

Write the balanced equation for the ionization of HF and use it as a guide to prepare an ICE table.



|         | [HF]        | $[\text{H}_3\text{O}^+]$ | $[\text{F}^-]$ |
|---------|-------------|--------------------------|----------------|
| Initial | 0.150       | $\approx 0.00$           | 0.00           |
| Change  | $-x$        | $+x$                     | $+x$           |
| Equil   | $0.150 - x$ | $x$                      | $x$            |

Substitute the expressions for the equilibrium concentrations into the expression for the acid ionization constant ( $K_a$ ). Since the equilibrium constant is small relative to the initial concentration of HF, you can make the  $x$  is small approximation. Substitute the value of the acid ionization constant (from Table 15.5) into the  $K_a$  expression and solve for  $x$ .

Confirm that the  $x$  is small approximation is valid by calculating the ratio of  $x$  to the number it was subtracted from in the approximation. The ratio should be less than 0.05 (or 5%).

Determine the  $\text{H}_3\text{O}^+$  concentration from the calculated value of  $x$  and find the pH.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} = \frac{x^2}{0.150 - x} \quad (x \text{ is small})$$

$$3.5 \times 10^{-4} = \frac{x^2}{0.150}$$

$$\sqrt{(0.150)(3.5 \times 10^{-4})} = \sqrt{x^2}$$

$$x = 7.2 \times 10^{-3}$$

$$\frac{7.2 \times 10^{-3}}{0.150} \times 100\% = 4.8\%$$

Therefore, the approximation is valid (though barely so).

$$\begin{aligned} [\text{H}_3\text{O}^+] &= 7.2 \times 10^{-3} \text{ M} \\ \text{pH} &= -\log(7.2 \times 10^{-3}) = 2.14 \end{aligned}$$

#### FOR PRACTICE 15.10

Find the  $\text{ClO}^-$  concentration of the above mixture of HF and HClO.

### Conceptual Connection 15.6 Judging Relative pH

Which solution is most acidic (that is, has the lowest pH)?

- (a) 1.0 M HCl
- (b) 2.0 M HF
- (c) A solution that is 1.0 M in HF and 1.0 M in HClO

## 15.7 Base Solutions

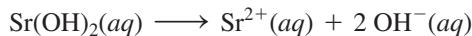
### Strong Bases

Just as we define a strong acid as one that completely ionizes in solution, analogously we define a **strong base** as a base that completely dissociates in solution. NaOH, for example, is a strong base:



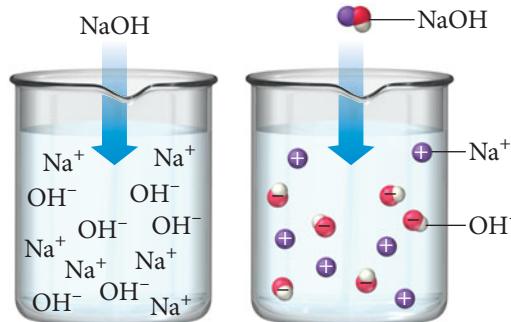
An NaOH solution contains no intact NaOH—it has all dissociated to form  $\text{Na}^+(aq)$  and  $\text{OH}^-(aq)$  (Figure 15.9 ▶). In other words, a 1.0 M NaOH solution has  $[\text{OH}^-] = 1.0 \text{ M}$  and  $[\text{Na}^+] = 1.0 \text{ M}$ . Table 15.7 lists the common strong bases.

As you can see, most strong bases are group 1A or group 2A metal hydroxides. The group 1A metal hydroxides are highly soluble in water and can form concentrated base solutions. The group 2A metal hydroxides, however, are only slightly soluble, a useful property for some applications (see the *Chemistry and Medicine* box in this section). Notice that the general formula for the group 2A metal hydroxides is  $\text{M(OH)}_2$ . When they dissolve in water, they produce 2 mol of  $\text{OH}^-$  per mole of the base. For example,  $\text{Sr(OH)}_2$  dissociates as follows:



Unlike diprotic acids, which ionize in two steps, bases containing two  $\text{OH}^-$  ions dissociate in one step.

#### A Strong Base



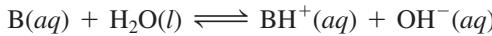
▲ FIGURE 15.9 Ionization of a Strong Base When NaOH dissolves in water, it dissociates completely into  $\text{Na}^+$  and  $\text{OH}^-$ . The solution contains virtually no intact NaOH.

TABLE 15.7 Strong Bases

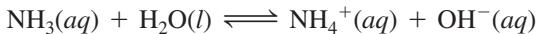
|                                      |  |
|--------------------------------------|--|
| Lithium hydroxide ( $\text{LiOH}$ )  | Strontium hydroxide [ $\text{Sr}(\text{OH})_2$ ] |
| Sodium hydroxide ( $\text{NaOH}$ )   | Calcium hydroxide [ $\text{Ca}(\text{OH})_2$ ]   |
| Potassium hydroxide ( $\text{KOH}$ ) | Baarium hydroxide [ $\text{Ba}(\text{OH})_2$ ]   |

### Weak Bases

A **weak base** is analogous to a weak acid. Unlike strong bases that contain  $\text{OH}^-$  and dissociate in water, the most common weak bases produce  $\text{OH}^-$  by accepting a proton from water, ionizing water to form  $\text{OH}^-$  according to the general equation:

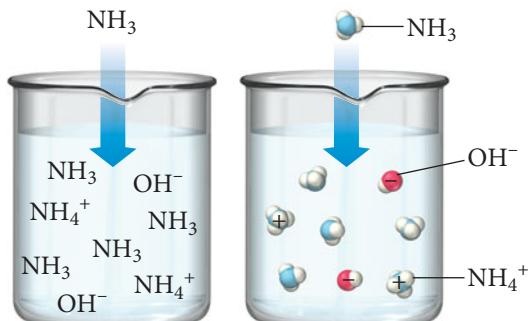


In this equation, B is a generic symbol for a weak base. Ammonia, for example, ionizes water as follows:



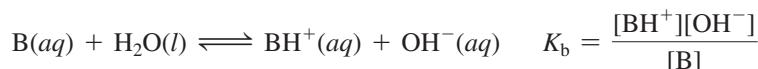
The double arrow indicates that the ionization is not complete. An  $\text{NH}_3$  solution contains mostly  $\text{NH}_3$  with only some  $\text{NH}_4^+$  and  $\text{OH}^-$  (Figure 15.10 ►). A 1.0 M  $\text{NH}_3$  solution will have  $[\text{OH}^-] < 1.0 \text{ M}$ .

### A Weak Base



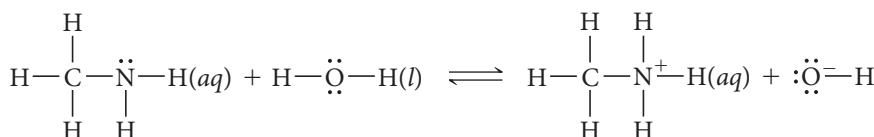
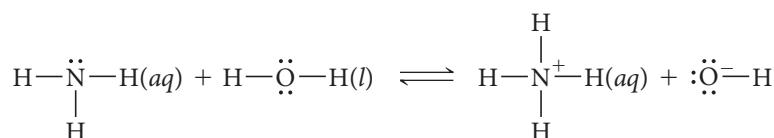
**▲ FIGURE 15.10** Ionization of a Weak Base When  $\text{NH}_3$  dissolves in water, it partially ionizes water to form  $\text{NH}_4^+$  and  $\text{OH}^-$ . Most of the  $\text{NH}_3$  molecules in solution remain as  $\text{NH}_3$ .

The extent of ionization of a weak base is quantified with the **base ionization constant**,  $K_b$ . For the general reaction in which a weak base ionizes water, we define  $K_b$  as follows:



By analogy with  $K_a$ , the smaller the value of  $K_b$ , the weaker the base. Table 15.8 lists some common weak bases, their ionization reactions, and values for  $K_b$ . The “p” scale can also be applied to  $K_b$ , so that  $pK_b = -\log K_b$ .

All but two of the weak bases listed in Table 15.8 are either ammonia or an amine, which we can think of as ammonia with one or more hydrocarbon groups substituted for one or more hydrogen atoms. All of these bases have a nitrogen atom with a lone pair (Figure 15.11 ▶). This lone pair acts as the proton acceptor that makes the substance a base, as shown in the reactions for ammonia and methylamine:



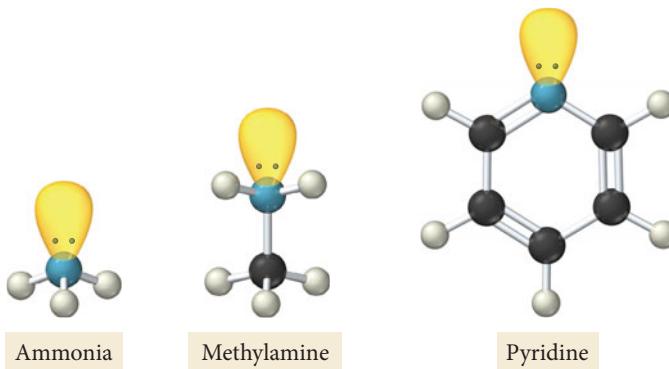
**TABLE 15.8** Some Common Weak Bases

| Weak Base  | Ionization Reaction  | $K_b$ (at 25 °C)      |
|--|--|-----------------------|
| Carbonate ion ( $\text{CO}_3^{2-}$ )*                            | $\text{CO}_3^{2-}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCO}_3^-(aq) + \text{OH}^-(aq)$                                   | $1.8 \times 10^{-4}$  |
| Methylamine ( $\text{CH}_3\text{NH}_2$ )                         | $\text{CH}_3\text{NH}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CH}_3\text{NH}_3^+(aq) + \text{OH}^-(aq)$                   | $4.4 \times 10^{-4}$  |
| Ethylamine ( $\text{C}_2\text{H}_5\text{NH}_2$ )                 | $\text{C}_2\text{H}_5\text{NH}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{C}_2\text{H}_5\text{NH}_3^+(aq) + \text{OH}^-(aq)$ | $5.6 \times 10^{-4}$  |
| Ammonia ( $\text{NH}_3$ )  | $\text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq)$   | $1.76 \times 10^{-5}$ |
| Bicarbonate ion ( $\text{HCO}_3^-$ )*<br>(or hydrogen carbonate) | $\text{HCO}_3^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{CO}_3(aq) + \text{OH}^-(aq)$                              | $2.3 \times 10^{-8}$  |
| Pyridine ( $\text{C}_5\text{H}_5\text{N}$ )                      | $\text{C}_5\text{H}_5\text{N}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{C}_5\text{H}_5\text{NH}^+(aq) + \text{OH}^-(aq)$      | $1.7 \times 10^{-9}$  |
| Aniline ( $\text{C}_6\text{H}_5\text{NH}_2$ )                    | $\text{C}_6\text{H}_5\text{NH}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+(aq) + \text{OH}^-(aq)$ | $3.9 \times 10^{-10}$ |

\*The carbonate and bicarbonate ions must occur with a positively charged ion such as  $\text{Na}^+$  that serves to balance the charge but does not have any part in the ionization reaction. For example, it is the bicarbonate ion that makes sodium bicarbonate ( $\text{NaHCO}_3$ ) basic. We look more closely at ionic bases in Section 15.8.

**► FIGURE 15.11** Lone Pairs in Weak Bases

Many weak bases have a nitrogen atom with a lone pair that acts as the proton acceptor.



### Finding the $\text{[OH}^-]$ and pH of Basic Solutions

Finding the  $\text{[OH}^-]$  and pH of a strong base solution is relatively straightforward, as shown in Example 15.11. As we did in calculating the  $\text{[H}_3\text{O}^+]$  in strong acid solutions, we can neglect the contribution of the autoionization of water to the  $\text{[OH}^-]$  and focus solely on the strong base itself.

#### **EXAMPLE 15.11** Finding the $\text{[OH}^-]$ and pH of a Strong Base Solution

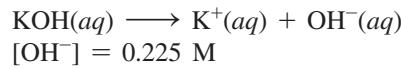
What is the  $\text{OH}^-$  concentration and pH in each solution?

- (a) 0.225 M KOH                          (b) 0.0015 M  $\text{Sr(OH)}_2$

#### SOLUTION

(a) Since KOH is a strong base, it completely dissociates into  $\text{K}^+$  and  $\text{OH}^-$  in solution. The concentration of  $\text{OH}^-$  will therefore be the same as the given concentration of KOH. Use this concentration and  $K_w$  to find  $\text{[H}_3\text{O}^+]$ .

Then substitute  $\text{[H}_3\text{O}^+]$  into the pH expression to find the pH.

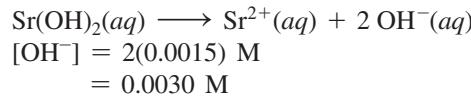


$$\begin{aligned} [\text{H}_3\text{O}^+][\text{OH}^-] &= K_w = 1.0 \times 10^{-14} \\ [\text{H}_3\text{O}^+](0.225) &= 1.0 \times 10^{-14} \\ [\text{H}_3\text{O}^+] &= 4.44 \times 10^{-14} \text{ M} \\ \text{pH} &= -\log[\text{H}_3\text{O}^+] \\ &= -\log(4.44 \times 10^{-14}) \\ &= 13.35 \end{aligned}$$

(b) Since  $\text{Sr(OH)}_2$  is a strong base, it completely dissociates into 1 mol of  $\text{Sr}^{2+}$  and 2 mol of  $\text{OH}^-$  in solution. The concentration of  $\text{OH}^-$  will therefore be twice the given concentration of  $\text{Sr(OH)}_2$ .

Use this concentration and  $K_w$  to find  $\text{[H}_3\text{O}^+]$ .

Substitute  $\text{[H}_3\text{O}^+]$  into the pH expression to find the pH.



$$\begin{aligned} [\text{H}_3\text{O}^+][\text{OH}^-] &= K_w = 1.0 \times 10^{-14} \\ [\text{H}_3\text{O}^+](0.0030) &= 1.0 \times 10^{-14} \\ [\text{H}_3\text{O}^+] &= 3.3 \times 10^{-12} \text{ M} \\ \text{pH} &= -\log[\text{H}_3\text{O}^+] \\ &= -\log(3.3 \times 10^{-12}) \\ &= 11.48 \end{aligned}$$

#### FOR PRACTICE 15.11

Find the  $\text{[OH}^-]$  and pH of a 0.010 M  $\text{Ba(OH)}_2$  solution.

Finding the  $\text{[OH}^-]$  and pH of a *weak base* solution is analogous to finding the  $\text{[H}_3\text{O}^+]$  and pH of a weak acid. Similarly, we can neglect the contribution of the autoionization of water to the  $\text{[OH}^-]$  and focus solely on the weak base itself. We find the contribution of the weak base by preparing an ICE table showing the relevant concentrations of all species and then use the base ionization constant expression to find the  $\text{[OH}^-]$ . Example 15.12 shows how to find the  $\text{[OH}^-]$  and pH of a weak base solution.

### EXAMPLE 15.12 Finding the $[OH^-]$ and pH of a Weak Base Solution

Find the  $[OH^-]$  and pH of a 0.100 M  $NH_3$  solution.

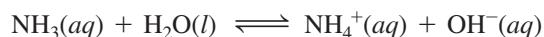
#### SOLUTION

- Write the balanced equation for the ionization of water by the base and use it as a guide to prepare an ICE table showing the given concentration of the weak base as its initial concentration. Leave room in the table for the changes in concentrations and for the equilibrium concentrations. (Note that you should list the  $OH^-$  concentration as approximately zero. Although a little  $OH^-$  is present from the autoionization of water, this amount is negligibly small compared to the amount of  $OH^-$  formed by the base.)



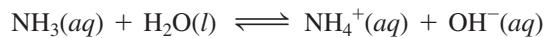
| $[NH_3]$ | $[NH_4^+]$ | $[OH^-]$ |
|----------|------------|----------|
| Initial  | 0.100      | 0.00     |
| Change   |            |          |
| Equil    |            |          |

- Represent the change in the concentration of  $OH^-$  with the variable  $x$ . Define the changes in the concentrations of the other reactants and products in terms of  $x$ .



| $[NH_3]$ | $[NH_4^+]$ | $[OH^-]$ |
|----------|------------|----------|
| Initial  | 0.100      | 0.00     |
| Change   | $-x$       | $+x$     |
| Equil    |            |          |

- Sum each column to determine the equilibrium concentrations in terms of the initial concentrations and the variable  $x$ .



| $[NH_3]$ | $[NH_4^+]$  | $[OH^-]$ |
|----------|-------------|----------|
| Initial  | 0.100       | 0.00     |
| Change   | $-x$        | $+x$     |
| Equil    | $0.100 - x$ | $x$      |

- Substitute the expressions for the equilibrium concentrations (from step 3) into the expression for the base ionization constant.

In many cases, you can make the approximation that  $x$  is small (as discussed in Chapter 14).

Substitute the value of the base ionization constant (from Table 15.8) into the  $K_b$  expression and solve for  $x$ .

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} \\ = \frac{x^2}{0.100 - x} \quad (x \text{ is small})$$

$$1.76 \times 10^{-5} = \frac{x^2}{0.100}$$

$$\sqrt{1.76 \times 10^{-5}} = \sqrt{\frac{x^2}{0.100}}$$

$$x = \sqrt{(0.100)(1.76 \times 10^{-5})} \\ = 1.33 \times 10^{-3}$$

$$\frac{1.33 \times 10^{-3}}{0.100} \times 100\% = 1.33\%$$

Therefore, the approximation is valid.

- Determine the  $OH^-$  concentration from the calculated value of  $x$ .

Use the expression for  $K_w$  to find  $[H_3O^+]$ .

Substitute  $[H_3O^+]$  into the pH equation to find pH.

$$[OH^-] = 1.33 \times 10^{-3} M$$

$$[H_3O^+][OH^-] = K_w = 1.00 \times 10^{-14}$$

$$[H_3O^+](1.33 \times 10^{-3}) = 1.00 \times 10^{-14}$$

$$[H_3O^+] = 7.52 \times 10^{-12} M$$

$$pH = -\log[H_3O^+] \\ = -\log(7.52 \times 10^{-12}) \\ = 11.124$$

#### FOR PRACTICE 15.12

Find the  $[OH^-]$  and pH of a 0.33 M methylamine solution.



## Chemistry and Medicine

### What's in My Antacid?

In the opening section of this chapter, we discussed heartburn and its treatment with antacids. Some common antacids and their active ingredients include the following:

|                  |   |
|------------------|---|
| Amphogel         | $\text{Al(OH)}_3$                       |
| Milk of magnesia | $\text{Mg(OH)}_2$                       |
| Maalox           | $\text{Mg(OH)}_2$ and $\text{Al(OH)}_3$ |
| Mylanta          | $\text{Mg(OH)}_2$ and $\text{Al(OH)}_3$ |
| Tums             | $\text{CaCO}_3$                         |

We categorize antacids into three main groups: calcium-based, magnesium-based, and aluminum-based. Calcium-based antacids may cause acid rebound—which means that, although they initially relieve heartburn, they can also cause the stomach to produce more acid, resulting in a quick return of the symptoms. Aluminum- and magnesium-based antacids do not cause acid rebound but have downsides of their own. Aluminum-based antacids tend to cause constipation, and magnesium-based ones tend to cause diarrhea. (In fact, milk of magnesia is sometimes used as a laxative.) A person who takes repeated doses of these antacids should alternate between the two or choose a product that contains both.

Notice the absence of group 1A metal hydroxides, such as KOH or NaOH, in the list of antacids. Why are those substances—which are completely soluble and act as strong bases—not used in antacids? Because a solution containing sufficient KOH or NaOH to neutralize stomach acid would also burn the mouth and throat. In contrast,  $\text{Mg(OH)}_2$  and  $\text{Al(OH)}_3$

are only slightly soluble. Therefore liquid antacids containing these are actually *suspensions* of  $\text{Mg(OH)}_2$  and  $\text{Al(OH)}_3$ —they are heterogeneous mixtures in which the solid is finely divided into the liquid. As a result, the concentration of  $\text{OH}^-$  in these suspensions is relatively small compared to what it would be with a group 1A metal hydroxide.

- Antacids contain a variety of bases that effectively neutralize excess stomach acid.



Initially, it might seem as though the relatively lower  $\text{OH}^-$  concentration would make the antacid much less effective. However, the solid  $\text{Mg(OH)}_2$  or  $\text{Al(OH)}_3$  continues to dissolve as the  $\text{OH}^-$  neutralizes stomach acid. For example, a suspension of magnesium hydroxide contains solid  $\text{Mg(OH)}_2$  in equilibrium with dissolved  $\text{Mg}^{2+}$  and  $\text{OH}^-$  ions:



As stomach acid is neutralized,  $\text{OH}^-$  is used up, and the equilibrium shifts to the right providing additional  $\text{OH}^-$  ions. In this way, a suspension of  $\text{Mg(OH)}_2$  provides a steady concentration of dissolved  $\text{OH}^-$  ions to neutralize stomach acid.

#### Question

Write chemical equations showing the reactions of each of the bases in the antacids discussed here with stomach acid ( $\text{HCl}$ ).

## 15.8 The Acid–Base Properties of Ions and Salts

We have already seen that some ions act as bases. For example, the bicarbonate ion acts as a base according to the following equation:



The bicarbonate ion, like any ion, does not exist by itself—in order to be charge neutral, it must pair with a counter ion (in this case a cation) to form an ionic compound, called a *salt*. For example, the sodium salt of bicarbonate is sodium bicarbonate. Like all soluble salts, sodium bicarbonate dissociates in solution to form a sodium cation and bicarbonate anion:



The sodium ion has neither acidic nor basic properties (it does not ionize water), as we will see shortly. The bicarbonate ion, by contrast, acts as a weak base, ionizing water as just shown to form a basic solution. Consequently, the pH of a sodium bicarbonate solution is above 7 (the solution is basic). In this section, we consider some of the acid–base properties of salts and the ions they contain. Some salts are pH-neutral when put into water, others are acidic, and still others are basic, depending on their constituent anions and cations. In general, anions tend to form either *basic* or neutral solutions, while cations tend to form either *acidic* or neutral solutions.

## Anions as Weak Bases

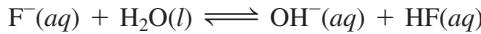
We can think of any anion as the conjugate base of an acid. Consider the following anions and their corresponding acids:

| This anion                         | is the conjugate base of | this acid                         |
|------------------------------------|--------------------------|-----------------------------------|
| $\text{Cl}^-$                      |                          | HCl                               |
| $\text{F}^-$                       |                          | HF                                |
| $\text{NO}_3^-$                    |                          | $\text{HNO}_3$                    |
| $\text{C}_2\text{H}_3\text{O}_2^-$ |                          | $\text{HC}_2\text{H}_3\text{O}_2$ |

In general, the anion  $\text{A}^-$  is the conjugate base of the acid  $\text{HA}$ . Since every anion can be regarded as the conjugate base of an acid, every anion itself can potentially act as a base. However, *not every anion does act as a base*—it depends on the strength of the corresponding acid. In general:

- An anion that is the conjugate base of a *weak acid* is itself a *weak base*.
- An anion that is the conjugate base of a *strong acid* is pH-*neutral* (forms solutions that are neither acidic nor basic).

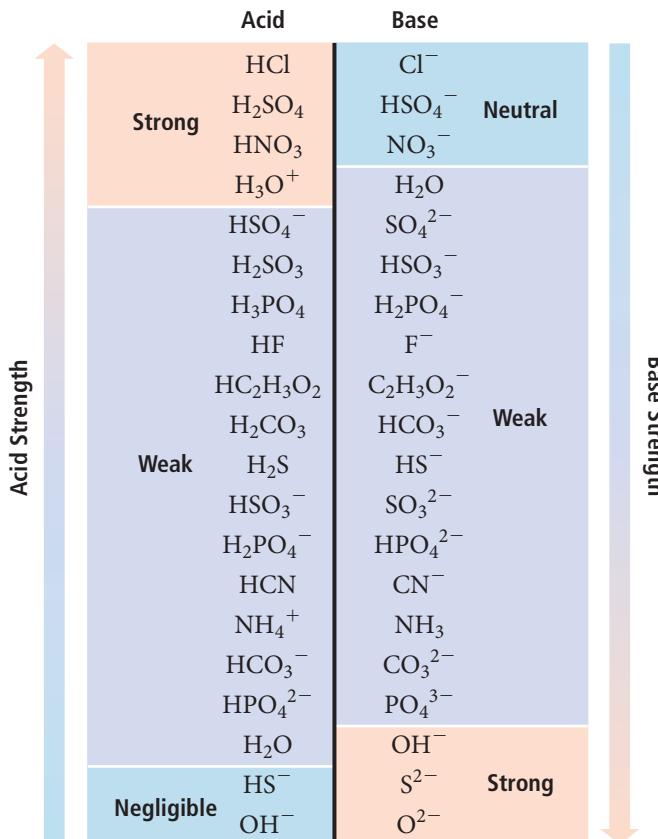
For example, the  $\text{Cl}^-$  anion is the conjugate base of HCl, a strong acid. Therefore the  $\text{Cl}^-$  anion is pH-neutral (neither acidic nor basic). The  $\text{F}^-$  anion, however, is the conjugate base of HF, a weak acid. Therefore the  $\text{F}^-$  ion is itself a weak base and ionizes water according to the reaction:



We can understand why the conjugate base of a weak acid is basic by asking ourselves why an acid is weak to begin with. Hydrofluoric acid is a weak acid because the following reaction lies to the left:

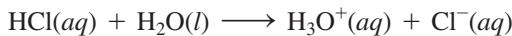


The equilibrium lies to the left because the  $\text{F}^-$  ion has a significant affinity for  $\text{H}^+$  ions. Consequently, when  $\text{F}^-$  is put into water, its affinity for  $\text{H}^+$  ions allows it to remove  $\text{H}^+$  ions from water molecules, thus acting as a weak base. In general, as shown in Figure 15.12 ▼,



◀ FIGURE 15.12 Strength of Conjugate Acid-Base Pairs The stronger an acid, the weaker its conjugate base.

the weaker the acid, the stronger the conjugate base (as we saw in Section 15.4). In contrast, the conjugate base of a strong acid, such as  $\text{Cl}^-$ , does not act as a base because this reaction lies far to the right:



The reaction lies far to the right because the  $\text{Cl}^-$  ion has a low affinity for  $\text{H}^+$  ions. Consequently, when  $\text{Cl}^-$  is put into water, it does not remove  $\text{H}^+$  ions from water molecules.

### EXAMPLE 15.13 Determining Whether an Anion Is Basic or pH-Neutral

Classify each anion as a weak base or pH-neutral:

- (a)  $\text{NO}_3^-$       (b)  $\text{NO}_2^-$       (c)  $\text{C}_2\text{H}_3\text{O}_2^-$

#### SOLUTION

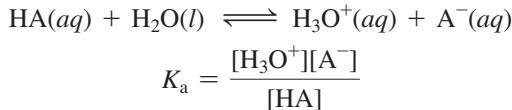
- (a) From Table 15.3, we can see that  $\text{NO}_3^-$  is the conjugate base of a *strong* acid ( $\text{HNO}_3$ ) and is therefore pH-neutral.
- (b) From Table 15.5 (or from its absence in Table 15.3), we know that  $\text{NO}_2^-$  is the conjugate base of a weak acid ( $\text{HNO}_2$ ) and is therefore a weak base.
- (c) From Table 15.5 (or from its absence in Table 15.3), we know that  $\text{C}_2\text{H}_3\text{O}_2^-$  is the conjugate base of a weak acid ( $\text{HC}_2\text{H}_3\text{O}_2$ ) and is therefore a weak base.

#### FOR PRACTICE 15.13

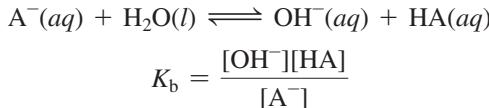
Classify each anion as a weak base or pH-neutral:

- (a)  $\text{CHO}_2^-$       (b)  $\text{ClO}_4^-$

We can determine the pH of a solution containing an anion that acts as a weak base in a manner similar to how we determine the pH of any weak base solution. However, we need to know  $K_b$  for the anion acting as a base, which we can readily determine from  $K_a$  of the corresponding acid. Recall from Section 15.4 the expression for  $K_a$  for a generic acid HA:



Similarly, the expression for  $K_b$  for the conjugate base ( $\text{A}^-$ ) is:



If we multiply the expressions for  $K_a$  and  $K_b$  we get  $K_w$ :

$$K_a \times K_b = \frac{[\text{H}_3\text{O}^+][\text{A}^-][\text{OH}^-][\text{HA}]}{[\text{HA}][\text{A}^-]} = [\text{H}_3\text{O}^+][\text{OH}^-] = K_w$$

Or simply,

$$K_a \times K_b = K_w$$

The product of  $K_a$  for an acid and  $K_b$  for its conjugate base is  $K_w$  ( $1.0 \times 10^{-14}$  at  $25^\circ\text{C}$ ). Consequently, we can find  $K_b$  for an anion acting as a base from the value of  $K_a$  for the corresponding acid. For example, for acetic acid ( $\text{HC}_2\text{H}_3\text{O}_2$ ),  $K_a = 1.8 \times 10^{-5}$ . We calculate  $K_b$  for the conjugate base ( $\text{C}_2\text{H}_3\text{O}_2^-$ ) by substituting into the equation:

$$K_a \times K_b = K_w$$

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Knowing  $K_b$ , we can find the pH of a solution containing an anion acting as a base, as demonstrated in Example 15.14.

**EXAMPLE 15.14** Determining the pH of a Solution Containing an Anion Acting as a Base


Find the pH of a 0.100 M  $\text{NaCHO}_2$  solution. The salt completely dissociates into  $\text{Na}^+(aq)$  and  $\text{CHO}_2^-(aq)$ , and the  $\text{Na}^+$  ion has no acid or base properties.

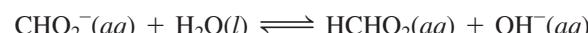
**SOLUTION**

1. Since the  $\text{Na}^+$  ion does not have any acidic or basic properties, you can ignore it. Write the balanced equation for the ionization of water by the basic anion and use it as a guide to prepare an ICE table showing the given concentration of the weak base as its initial concentration.



|         | $[\text{CHO}_2^-]$ | $[\text{HCHO}_2]$ | $[\text{OH}^-]$ |
|---------|--------------------|-------------------|-----------------|
| Initial | 0.100              | 0.00              | $\approx 0.00$  |
| Change  |                    |                   |                 |
| Equil   |                    |                   |                 |

2. Represent the change in the concentration of  $\text{OH}^-$  with the variable  $x$ . Define the changes in the concentrations of the other reactants and products in terms of  $x$ .



|         | $[\text{CHO}_2^-]$ | $[\text{HCHO}_2]$ | $[\text{OH}^-]$ |
|---------|--------------------|-------------------|-----------------|
| Initial | 0.100              | 0.00              | $\approx 0.00$  |
| Change  | $-x$               | $+x$              | $+x$            |
| Equil   |                    |                   |                 |

3. Sum each column to determine the equilibrium concentrations in terms of the initial concentrations and the variable  $x$ .



|         | $[\text{CHO}_2^-]$ | $[\text{HCHO}_2]$ | $[\text{OH}^-]$ |
|---------|--------------------|-------------------|-----------------|
| Initial | 0.100              | 0.00              | $\approx 0.00$  |
| Change  | $-x$               | $+x$              | $+x$            |
| Equil   | $0.100 - x$        | $x$               | $x$             |

4. Find  $K_b$  from  $K_a$  (for the conjugate acid).

Substitute the expressions for the equilibrium concentrations (from step 3) into the expression for  $K_b$ . In many cases, you can make the approximation that  $x$  is small.

Substitute the value of  $K_b$  into the  $K_b$  expression and solve for  $x$ .

Confirm that the  $x$  is small approximation is valid by calculating the ratio of  $x$  to the number it was subtracted from in the approximation. The ratio should be less than 0.05 (or 5%).

$$\begin{aligned} K_a \times K_b &= K_w \\ K_b &= \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-4}} = 5.6 \times 10^{-11} \\ K_b &= \frac{[\text{HCHO}_2][\text{OH}^-]}{[\text{CHO}_2^-]} \\ &= \frac{x^2}{0.100 - x} \\ 5.6 \times 10^{-11} &= \frac{x^2}{0.100} \\ x &= 2.4 \times 10^{-6} \\ \frac{2.4 \times 10^{-6}}{0.100} \times 100\% &= 0.0024\% \end{aligned}$$

Therefore, the approximation is valid.

5. Determine the  $\text{OH}^-$  concentration from the calculated value of  $x$ .

Use the expression for  $K_w$  to find  $[\text{H}_3\text{O}^+]$ .

Substitute  $[\text{H}_3\text{O}^+]$  into the pH equation to find pH.

$$\begin{aligned} [\text{OH}^-] &= 2.4 \times 10^{-6} \text{ M} \\ [\text{H}_3\text{O}^+][\text{OH}^-] &= K_w = 1.0 \times 10^{-14} \\ [\text{H}_3\text{O}^+](2.4 \times 10^{-6}) &= 1.0 \times 10^{-14} \\ [\text{H}_3\text{O}^+] &= 4.2 \times 10^{-9} \text{ M} \\ \text{pH} &= -\log[\text{H}_3\text{O}^+] \\ &= -\log(4.2 \times 10^{-9}) \\ &= 8.38 \end{aligned}$$

**FOR PRACTICE 15.14**

Find the pH of a 0.250 M  $\text{NaC}_2\text{H}_3\text{O}_2$  solution.

We can also express the relationship between  $K_a$  and  $K_b$  in terms of  $pK_a$  and  $pK_b$ . By taking the log of both sides of  $K_a \times K_b = K_w$ , we get:

$$\log(K_a \times K_b) = \log K_w$$

$$\log K_a + \log K_b = \log K_w$$

Since  $K_w = 10^{-14}$ , we can rearrange the equation to get:

$$\log K_a + \log K_b = \log 10^{-14} = -14$$

Rearranging further:

$$-\log K_a - \log K_b = 14$$

Since  $-\log K = pK$ , we get:

$$pK_a + pK_b = 14$$

## Cations as Weak Acids

In contrast to anions, which in some cases act as weak bases, cations can in some cases act as *weak acids*. We can generally divide cations into three categories: cations that are the counterions of strong bases; cations that are the conjugate acids of *weak bases*; and cations that are small, highly charged metals. We examine each individually.

**Cations That Are the Counterions of Strong Bases** Strong bases such as NaOH or Ca(OH)<sub>2</sub> generally contain hydroxide ions and a counterion. In solution, a strong base completely dissociates to form OH<sup>-</sup>(aq) and the solvated (in solution) counterion. Although these counterions interact with water molecules via ion-dipole forces, they do not ionize water and they do not contribute to the acidity or basicity of the solution. In general *cations that are the counterions of strong bases are themselves pH-neutral* (they form solutions that are neither acidic nor basic). For example, Na<sup>+</sup>, K<sup>+</sup>, and Ca<sup>2+</sup> are the counterions of the strong bases NaOH, KOH, and Ca(OH)<sub>2</sub> and are therefore themselves pH-neutral.

**Cations That Are the Conjugate Acids of Weak Bases** A cation can be formed from any nonionic weak base by adding a proton (H<sup>+</sup>) to its formula. The cation will be the conjugate acid of the base. Consider the following cations and their corresponding weak bases:

**This cation    is the conjugate acid of    this weak base**



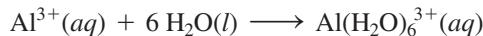
Any of these cations, with the general formula BH<sup>+</sup>, will act as a weak acid according to the equation:



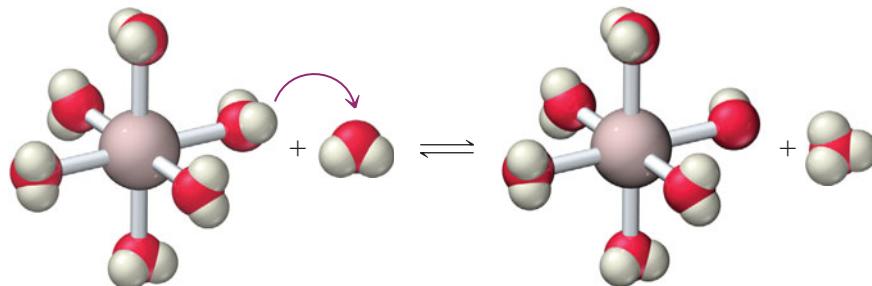
In general, *a cation that is the conjugate acid of a weak base is a weak acid*.

We can calculate the pH of a solution containing the conjugate acid of a weak base just like that of any other weakly acidic solution. However, the value of  $K_a$  for the acid must be derived from  $K_b$  using the previously derived relationship:  $K_a \times K_b = K_w$ .

**Cations That Are Small, Highly Charged Metals** *Small, highly charged metal cations such as Al<sup>3+</sup> and Fe<sup>3+</sup> form weakly acidic solutions.* For example, when Al<sup>3+</sup> is dissolved in water, it becomes hydrated according to the equation:



The hydrated form of the ion then acts as a Brønsted-Lowry acid:



In effect, the binding of a water molecule to the cation makes the water more acidic. See Section 15.10.

Neither the alkali metal cations nor the alkaline earth metal cations ionize water in this way, but the cations of many other metals do. The smaller and more highly charged the cation, the more acidic its behavior.

### EXAMPLE 15.15 Determining Whether a Cation Is Acidic or pH-Neutral

Classify each cation as a weak acid or pH-neutral.

- (a)  $\text{C}_5\text{H}_5\text{NH}^+$       (b)  $\text{Ca}^{2+}$       (c)  $\text{Cr}^{3+}$

#### SOLUTION

- (a) The  $\text{C}_5\text{H}_5\text{NH}^+$  cation is the conjugate acid of a weak base and is therefore a weak acid.
- (b) The  $\text{Ca}^{2+}$  cation is the counterion of a strong base and is therefore pH-neutral (neither acidic nor basic).
- (c) The  $\text{Cr}^{3+}$  cation is a small, highly charged metal cation and is therefore a weak acid.

#### FOR PRACTICE 15.15

Classify each cation as a weak acid or pH-neutral.

- (a)  $\text{Li}^+$       (b)  $\text{CH}_3\text{NH}_3^+$       (c)  $\text{Fe}^{3+}$

### Classifying Salt Solutions as Acidic, Basic, or Neutral

Since salts contain both a cation and an anion, they can form acidic, basic, or neutral solutions when dissolved in water. The pH of the solution depends on the specific cation and anion involved. We examine the four possibilities individually.

- 1. Salts in which neither the cation nor the anion acts as an acid or a base form pH-neutral solutions.** A salt in which the cation is the counterion of a strong base and in which the anion is the conjugate base of strong acid form *neutral* solutions. Some salts in this category include:

$\text{NaCl}$   
sodium chloride

$\text{Ca}(\text{NO}_3)_2$   
calcium nitrate

$\text{KBr}$   
potassium bromide

Cations are pH-neutral

Anions are conjugate bases of strong acids.

- 2. Salts in which the cation does not act as an acid and the anion acts as a base form basic solutions.** A salt in which the cation is the counterion of a strong base and in which the anion is the conjugate base of *weak* acid form *basic* solutions. Salts in this category include:

$\text{NaF}$   
sodium fluoride

$\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$   
calcium acetate

$\text{KNO}_2$   
potassium nitrite

Cations are pH-neutral

Anions are conjugate bases of weak acids.

- 3. Salts in which the cation acts as an acid and the anion does not act as a base form acidic solutions.** A salt in which the cation is either the conjugate acid of a weak base or a small, highly charged metal ion and in which the anion is the conjugate base of a strong acid form *acidic* solutions. Salts in this category include:



Cations are conjugate acids  
of *weak* bases or small,  
highly charged metal ions.

Anions are conjugate bases of *strong* acids.

- 4. Salts in which the cation acts as an acid and the anion acts as a base form solutions in which the pH depends on the relative strengths of the acid and the base.** A salt in which the cation is either the conjugate acid of a weak base or a small, highly charged metal ion and in which the anion is the conjugate base of a weak acid form a solution in which the pH depends on the relative strengths of the acid and base. Salts in this category include:



Cations are conjugate acids  
of *weak* bases or small,  
highly charged metal ions.

Anions are conjugate bases of *weak* acids.

We can determine the overall pH of a solution containing one of these salts by comparing the  $K_a$  of the acid to the  $K_b$  of the base—the ion with the higher value of  $K$  dominates and determines whether the solution will be acidic or basic, as shown in part (e) of Example 15.16. Table 15.9 summarizes all of these possibilities.

TABLE 15.9 pH of Salt Solutions

|        |                                 | ANION                         |                               |
|--------|---------------------------------|-------------------------------|-------------------------------|
|        |                                 | Conjugate base of strong acid | Conjugate base of weak acid   |
| CATION | Conjugate acid of weak base     | Acidic                        | Depends on relative strengths |
|        | Small, highly charged metal ion | Acidic                        | Depends on relative strengths |
|        | Counterion of strong base       | Neutral                       | Basic                         |

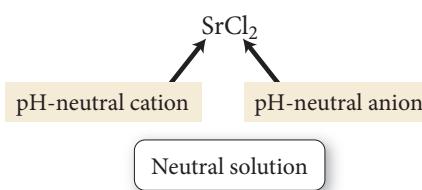
### EXAMPLE 15.16 Determining the Overall Acidity or Basicity of Salt Solutions

Determine if the solution formed by each salt is acidic, basic, or neutral.

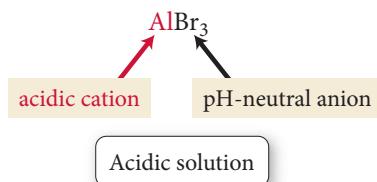
- (a)  $\text{SrCl}_2$       (b)  $\text{AlBr}_3$       (c)  $\text{CH}_3\text{NH}_3\text{NO}_3$   
 (d)  $\text{NaCHO}_2$       (e)  $\text{NH}_4\text{F}$

#### SOLUTION

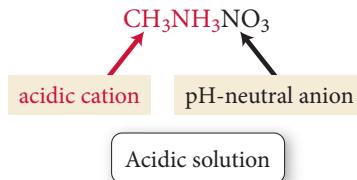
- (a) The  $\text{Sr}^{2+}$  cation is the counterion of a strong base ( $\text{Sr}(\text{OH})_2$ ) and is pH-neutral. The  $\text{Cl}^-$  anion is the conjugate base of a strong acid ( $\text{HCl}$ ) and is pH-neutral as well. The  $\text{SrCl}_2$  solution is therefore pH-neutral (neither acidic nor basic).



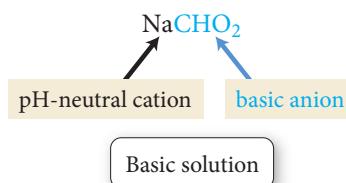
- (b) The  $\text{Al}^{3+}$  cation is a small, highly charged metal ion (that is not an alkali metal or an alkaline earth metal) and is a weak acid. The  $\text{Br}^-$  anion is the conjugate base of a strong acid ( $\text{HBr}$ ) and is pH-neutral. The  $\text{AlBr}_3$  solution is therefore acidic.



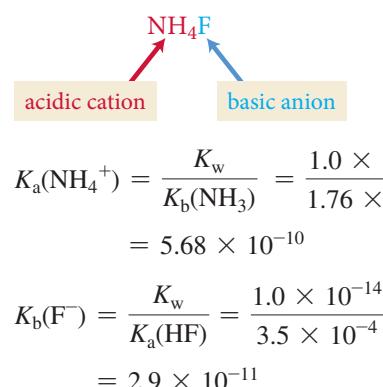
- (c) The  $\text{CH}_3\text{NH}_3^+$  ion is the conjugate acid of a weak base ( $\text{CH}_3\text{NH}_2$ ) and is acidic. The  $\text{NO}_3^-$  anion is the conjugate base of a strong acid ( $\text{HNO}_3$ ) and is pH-neutral. The  $\text{CH}_3\text{NH}_3\text{NO}_3$  solution is therefore acidic.



- (d) The  $\text{Na}^+$  cation is the counterion of a strong base and is pH-neutral. The  $\text{CHO}_2^-$  anion is the conjugate base of a weak acid and is basic. The  $\text{NaCHO}_2$  solution is therefore basic.



- (e) The  $\text{NH}_4^+$  ion is the conjugate acid of a weak base ( $\text{NH}_3$ ) and is acidic. The  $\text{F}^-$  ion is the conjugate base of a weak acid and is basic. To determine the overall acidity or basicity of the solution, compare the values of  $K_a$  for the acidic cation and  $K_b$  for the basic anion. Obtain each value of  $K$  from the conjugate by using  $K_a \times K_b = K_w$ .



Since  $K_a$  is greater than  $K_b$ , the solution is acidic.

$K_a > K_b$       Acidic solution

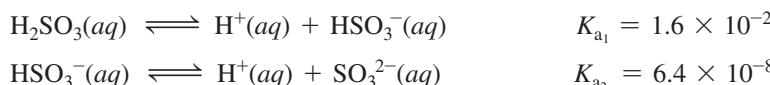
### FOR PRACTICE 15.16

Determine if the solution formed by each salt is acidic, basic, or neutral.

- (a)  $\text{NaHCO}_3$     (b)  $\text{CH}_3\text{CH}_2\text{NH}_3\text{Cl}$     (c)  $\text{KNO}_3$     (d)  $\text{Fe}(\text{NO}_3)_3$

## 15.9 Polyprotic Acids

In Section 15.4, we discussed that some acids, called polyprotic acids, contain two or more ionizable protons. Recall that sulfuric acid ( $\text{H}_2\text{SO}_4$ ) is a diprotic acid containing two ionizable protons and phosphoric acid ( $\text{H}_3\text{PO}_4$ ) is a triprotic acid containing three ionizable protons. Typically, a **polyprotic acid** ionizes in successive steps, each with its own  $K_a$ . For example, sulfuric acid ionizes in two steps:



$K_{a_1}$  is the acid ionization constant for the first step and  $K_{a_2}$  is the acid ionization constant for the second step. Notice that  $K_{a_2}$  is smaller than  $K_{a_1}$ . This is true for all polyprotic acids and makes sense because the first proton separates from a neutral molecule while the

second must separate from an anion. The negatively charged anion holds the positively charged proton more tightly, making the proton more difficult to remove and resulting in a smaller value of  $K_a$ . Table 15.10 lists some common polyprotic acids and their acid ionization constants. Notice that in all cases, the value of  $K_a$  for each step becomes successively smaller. The value of  $K_{a_1}$  for sulfuric acid is listed as strong because sulfuric acid is strong in the first step and weak in the second.

**TABLE 15.10 Common Polyprotic Acids and Ionization Constants at 25 °C**

| Name (Formula)                   | Structure | Space-filling model | $K_{a_1}$            | $K_{a_2}$             | $K_{a_3}$             |
|----------------------------------|-----------|---------------------|----------------------|-----------------------|-----------------------|
| Sulfuric Acid ( $H_2SO_4$ )      |           |                     | Strong               | $1.2 \times 10^{-2}$  |                       |
| Oxalic Acid ( $H_2C_2O_4$ )      |           |                     | $6.0 \times 10^{-2}$ | $6.1 \times 10^{-5}$  |                       |
| Sulfurous Acid ( $H_2SO_3$ )     |           |                     | $1.6 \times 10^{-2}$ | $6.4 \times 10^{-8}$  |                       |
| Phosphoric Acid ( $H_3PO_4$ )    |           |                     | $7.5 \times 10^{-3}$ | $6.2 \times 10^{-8}$  | $4.2 \times 10^{-13}$ |
| Citric Acid ( $H_3C_6H_5O_7$ )   |           |                     | $7.4 \times 10^{-4}$ | $1.7 \times 10^{-5}$  | $4.0 \times 10^{-7}$  |
| Ascorbic Acid ( $H_2C_6H_6O_6$ ) |           |                     | $8.0 \times 10^{-5}$ | $1.6 \times 10^{-12}$ |                       |
| Carbonic Acid ( $H_2CO_3$ )      |           |                     | $4.3 \times 10^{-7}$ | $5.6 \times 10^{-11}$ |                       |

### Finding the pH of Polyprotic Acid Solutions

Finding the pH of a polyprotic acid solution is less difficult than we might first imagine because, for most polyprotic acids,  $K_{a_1}$  is much larger than  $K_{a_2}$  (or  $K_{a_3}$  for triprotic acids). Therefore the amount of  $H_3O^+$  formed by the first ionization step is much larger than that formed by the second or third ionization step. In addition, the formation of  $H_3O^+$  in the first

step inhibits the formation of additional  $\text{H}_3\text{O}^+$  in the second step (because of Le Châtelier's principle). Consequently, we treat most polyprotic acid solutions as if the first step were the only one that contributes to the  $\text{H}_3\text{O}^+$  concentration, as shown in Example 15.17. A major exception is a dilute solution of sulfuric acid, which we examine in Example 15.18.

### EXAMPLE 15.17 Finding the pH of a Polyprotic Acid Solution

Find the pH of a 0.100 M ascorbic acid ( $\text{H}_2\text{C}_6\text{H}_6\text{O}_6$ ) solution.

#### SOLUTION

To find the pH, you must find the equilibrium concentration of  $\text{H}_3\text{O}^+$ . Treat the problem as a weak acid pH problem with a single ionizable proton. The second proton contributes a negligible amount to the concentration of  $\text{H}_3\text{O}^+$  and can be ignored. Follow the procedure from Example 15.6, shown in condensed form here. Use  $K_{\text{a}_1}$  for ascorbic acid from Table 15.10.



|         | $[\text{H}_2\text{C}_6\text{H}_6\text{O}_6]$ | $[\text{H}_3\text{O}^+]$ | $[\text{HC}_6\text{H}_6\text{O}_6^-]$ |
|---------|--|--------------------------|---------------------------------------|
| Initial | 0.100  | $\approx 0.00$           | 0.000                                 |
| Change  | $-x$   | $+x$                     | $+x$                                  |
| Equil   | $0.100 - x$                                  | $x$                      | $x$                                   |

$$K_{\text{a}_1} = \frac{[\text{H}_3\text{O}^+][\text{HC}_6\text{H}_6\text{O}_6^-]}{[\text{H}_2\text{C}_6\text{H}_6\text{O}_6]}$$

$$= \frac{x^2}{0.100 - x} \quad (\text{is small})$$

$$8.0 \times 10^{-5} = \frac{x^2}{0.100}$$

$$x = 2.8 \times 10^{-3}$$

$$\frac{2.8 \times 10^{-3}}{0.100} \times 100\% = 2.8\%$$

The approximation is valid. Therefore,

$$[\text{H}_3\text{O}^+] = 2.8 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log(2.8 \times 10^{-3}) = 2.55$$

Confirm that the  $x$  is small approximation is valid by calculating the ratio of  $x$  to the number it was subtracted from in the approximation. The ratio should be less than 0.05 (or 5%).

Calculate the pH from  $\text{H}_3\text{O}^+$  concentration.

#### FOR PRACTICE 15.17

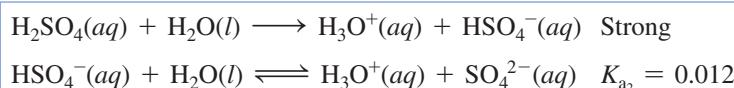
Find the pH of a 0.050 M  $\text{H}_2\text{CO}_3$  solution.

### EXAMPLE 15.18 Dilute $\text{H}_2\text{SO}_4$ Solutions

Find the pH of a 0.0100 M sulfuric acid ( $\text{H}_2\text{SO}_4$ ) solution.

#### SOLUTION

Sulfuric acid is strong in its first ionization step and weak in its second. Begin by writing the equations for the two steps. As the concentration of an  $\text{H}_2\text{SO}_4$  solution becomes smaller, the second ionization step becomes more significant because the percent ionization increases (as discussed in Section 15.6). Therefore, for a concentration of 0.0100 M, you can't neglect the  $\text{H}_3\text{O}^+$  contribution from the second step, as you can for other polyprotic acids. You must calculate the  $\text{H}_3\text{O}^+$  contributions from both steps.



The  $[\text{H}_3\text{O}^+]$  that results from the first ionization step is 0.0100 M (because the first step is strong). To determine the  $[\text{H}_3\text{O}^+]$  formed by the second step, prepare an ICE table for the second step in which the initial concentration of  $\text{H}_3\text{O}^+$  is 0.0100 M. The initial concentration of  $\text{HSO}_4^-$  must also be 0.0100 M (due to the stoichiometry of the ionization reaction).

Substitute the expressions for the equilibrium concentrations (from the table just shown) into the expression for  $K_{a_2}$ . In this case, you cannot make the  $x$  is small approximation because the equilibrium constant (0.012) is not small relative to the initial concentration (0.0100).

Substitute the value of  $K_{a_2}$  and multiply out the expression to arrive at the standard quadratic form.

|         | $[\text{HSO}_4^-]$ | $[\text{H}_3\text{O}^+]$ | $[\text{SO}_4^{2-}]$ |
|---------|--------------------|--------------------------|----------------------|
| Initial | 0.0100             | $\approx 0.0100$         | 0.000                |
| Change  | $-x$               | $+x$                     | $+x$                 |
| Equil   | $0.0100 - x$       | $0.0100 + x$             | $x$                  |

Solve the quadratic equation using the quadratic formula.

$$\begin{aligned} K_{a_2} &= \frac{[\text{H}_3\text{O}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} \\ &= \frac{(0.0100 + x)x}{0.0100 - x} \\ 0.012 &= \frac{0.0100x + x^2}{0.0100 - x} \\ 0.012(0.0100 - x) &= 0.0100x + x^2 \\ 0.00012 - 0.012x &= 0.0100x + x^2 \\ x^2 + 0.022x - 0.00012 &= 0 \end{aligned}$$

$$\begin{aligned} x &= \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \\ &= \frac{-(0.022) \pm \sqrt{(0.022)^2 - 4(1)(-0.00012)}}{2(1)} \\ &= \frac{-0.022 \pm 0.031}{2} \\ x &= -0.027 \text{ or } x = 0.0045 \end{aligned}$$

Since  $x$  represents a concentration, and since concentrations cannot be negative, we reject the negative root.  
 $x = 0.0045$

Determine the  $\text{H}_3\text{O}^+$  concentration from the calculated value of  $x$  and calculate the pH. Notice that the second step produces almost half as much  $\text{H}_3\text{O}^+$  as the first step—an amount that must not be neglected. This will always be the case with dilute  $\text{H}_2\text{SO}_4$  solutions.

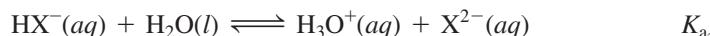
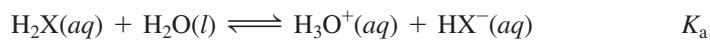
$$\begin{aligned} [\text{H}_3\text{O}^+] &= 0.0100 + x \\ &= 0.0100 + 0.0045 \\ &= 0.0145 \text{ M} \\ \text{pH} &= -\log[\text{H}_3\text{O}^+] \\ &= -\log(0.0145) \\ &= 1.84 \end{aligned}$$

### FOR PRACTICE 15.18

Find the pH and  $[\text{SO}_4^{2-}]$  of a 0.0075 M sulfuric acid solution.

## Finding the Concentration of the Anions for a Weak Diprotic Acid Solution

In some cases, we may want to know the concentrations of the anions formed by a polyprotic acid. Consider the following generic polyprotic acid  $\text{H}_2\text{X}$  and its ionization steps:



In Examples 15.17 and 15.18, we illustrated how to find the concentration of  $\text{H}_3\text{O}^+$  for such a solution, which is equal to the concentration of  $\text{HX}^-$ . What if instead we needed to find the concentration of  $\text{X}^{2-}$ ? To find the concentration of  $\text{X}^{2-}$ , we use the concentration of  $\text{HX}^-$  and  $\text{H}_3\text{O}^+$  (from the first ionization step) as the initial concentrations for the second ionization step. We then solve a second equilibrium problem using the second ionization equation and  $K_{a_2}$ , as shown in Example 15.19.

**EXAMPLE 15.19** Finding the Concentration of the Anions for a Weak Diprotic Acid Solution

Find the  $[C_6H_6O_6^{2-}]$  of the 0.100 M ascorbic acid ( $H_2C_6H_6O_6$ ) solution in Example 15.17.

**SOLUTION**

To find the  $[C_6H_6O_6^{2-}]$ , use the concentrations of  $[HC_6H_6O_6^-]$  and  $H_3O^+$  produced by the first ionization step (as calculated in Example 15.17) as the initial concentrations for the second step. Because of the 1:1 stoichiometry,  $[HC_6H_6O_6^-] = [H_3O^+]$ . Then solve an equilibrium problem for the second step similar to that of Example 15.6, shown in condensed form here. Use  $K_{a_2}$  for ascorbic acid from Table 15.10.



|         | $[HC_6H_6O_6^-]$         | $[H_3O^+]$               | $[C_6H_6O_6^{2-}]$ |
|---------|--------------------------|--------------------------|--------------------|
| Initial | $2.8 \times 10^{-3}$     | $2.8 \times 10^{-3}$     | 0.000              |
| Change  | $-x$                     | $+x$                     | $+x$               |
| Equil   | $2.8 \times 10^{-3} - x$ | $2.8 \times 10^{-3} + x$ | $x$                |

$$\begin{aligned} K_{a_2} &= \frac{[H_3O^+][C_6H_6O_6^{2-}]}{[HC_6H_6O_6^-]} \\ &= \frac{(2.8 \times 10^{-3} + x)x}{2.8 \times 10^{-3} - x} \quad (x \text{ is small}) \\ &= \frac{(2.8 \times 10^{-3})x}{2.8 \times 10^{-3}} \end{aligned}$$

$$x = K_{a_2} = 1.6 \times 10^{-12}$$

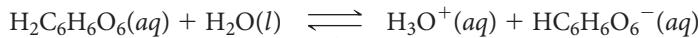
Since  $x$  is much smaller than  $2.8 \times 10^{-3}$ , the  $x$  is small approximation is valid. Therefore,

$$[C_6H_6O_6^{2-}] = 1.6 \times 10^{-12} \text{ M.}$$

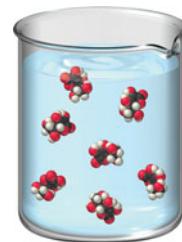
**FOR PRACTICE 15.19**

Find the  $[CO_3^{2-}]$  of the 0.050 M carbonic acid ( $H_2CO_3$ ) solution in For Practice 15.17.

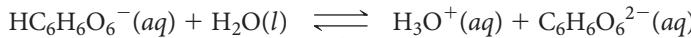
Notice from the results of Example 15.19 that the concentration of  $X^{2-}$  for a weak diprotic acid  $H_2X$  is equal to  $K_{a_2}$ . This general result applies to all diprotic acids in which the  $x$  is small approximation is valid. Notice also that the concentration of  $H_3O^+$  produced by the second ionization step of a diprotic acid is very small compared to the concentration produced by the first step, as shown in Figure 15.13 ▶.

**Dissociation of a Polyprotic Acid**


$$\boxed{[H_3O^+] = 2.8 \times 10^{-3} \text{ M}}$$



0.100 M  $H_2C_6H_6O_6$



$$\boxed{[H_3O^+] = 1.6 \times 10^{-12} \text{ M}}$$

$$\text{Total } [H_3O^+] = 2.8 \times 10^{-3} \text{ M} + 1.6 \times 10^{-12} \text{ M}$$

$$= 2.8 \times 10^{-3} \text{ M}$$

◀ **FIGURE 15.13** Dissociation of a Polyprotic Acid A 0.100 M  $H_2C_6H_6O_6$  solution contains an  $H_3O^+$  concentration of  $2.8 \times 10^{-3}$  M from the first step. The amount of  $H_3O^+$  contributed by the second step is only  $1.6 \times 10^{-12}$  M, which is insignificant compared to the amount produced by the first step.

## 15.10 Acid Strength and Molecular Structure

We have learned that a Brønsted–Lowry acid is a proton ( $\text{H}^+$ ) donor. However, we have not explored why some hydrogen-containing molecules act as acids while others do not, or why some acids are strong and others weak. For example, why is  $\text{H}_2\text{S}$  acidic while  $\text{CH}_4$  is not? Or why is HF a weak acid while HCl is a strong acid? We will divide our discussion about these issues into two categories: binary acids (those containing hydrogen and only one other element) and oxyacids (those containing hydrogen bonded to an oxygen atom that is bonded to another element).

### Binary Acids

Consider the bond between a hydrogen atom and some other generic element (which we will call Y):

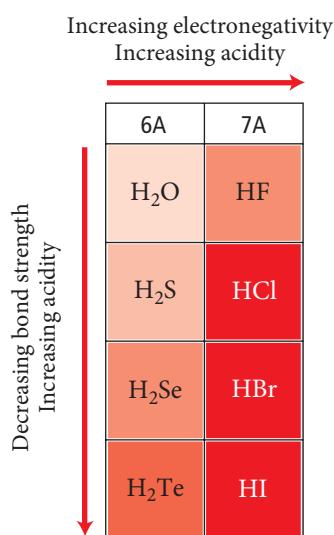
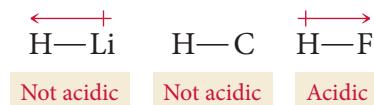


The factors affecting the ease with which this hydrogen is donated (and therefore be acidic) are the *polarity* of the bond and the *strength* of the bond.

**Bond Polarity** Using the notation introduced in Chapter 9, the H—Y bond must be polarized with the hydrogen atom as the positive pole in order for HY to be acidic:



This requirement makes physical sense because the hydrogen atom must be lost as a positively charged ion ( $\text{H}^+$ ). A partial positive charge on the hydrogen atom facilitates its loss. Consider the following three bonds and their corresponding dipole moments:



**▲ FIGURE 15.14** Acidity of the Group 6A and 7A Hydrides From left to right, the hydrides become more acidic because the H—Y bond becomes more polar. From top to bottom, these hydrides become more acidic because the H—Y bond becomes weaker.

LiH is ionic with *the negative charge on the hydrogen atom*; therefore, LiH is not acidic. The C—H bond is virtually nonpolar because the electronegativities of carbon and hydrogen are similar; therefore C—H is not acidic. In contrast, the H—F bond is polar with the positive charge on the hydrogen atom. As we know from this chapter, HF is an acid. This is because the partial positive charge on the hydrogen atom makes it easier for the hydrogen to be lost as an  $\text{H}^+$  ion.

**Bond Strength** The strength of the H—Y bond also affects the strength of the corresponding acid. As you might expect, the stronger the bond, the weaker the acid—the more tightly the hydrogen atom is held, the less likely it is to come off. We can see the effect of bond strength by comparing the bond strengths and acidities of the hydrogen halides:

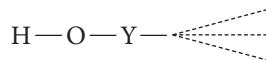
| Acid | Bond Energy (kJ/mol) | Type of Acid |
|------|----------------------|--------------|
| H—F  | 565                  | Weak         |
| H—Cl | 431                  | Strong       |
| H—Br | 364                  | Strong       |

HCl and HBr have weaker bonds and are both strong acids. HF, however, has a stronger bond and is therefore a weak acid, despite the greater bond polarity of HF.

**The Combined Effect of Bond Polarity and Bond Strength** We can see the combined effect of bond polarity and bond strength by examining the trends in acidity of the group 6A and 7A hydrides as shown in Figure 15.14 ▲. The hydrides become more acidic from left to right as the H—Y bond becomes more polar. The hydrides also become more acidic from top to bottom as the H—Y bond becomes weaker.

## Oxyacids

Oxyacids contain a hydrogen atom bonded to an oxygen atom. The oxygen atom is in turn bonded to another atom (which we will call Y):



Oxyacids are sometimes called oxoacids.

Y may or may not be bonded to yet other atoms. The factors affecting the ease with which the hydrogen in an oxyacid will be donated (and therefore be acidic) are the *electronegativity of the element Y* and the *number of oxygen atoms attached to the element Y*.

**The Electronegativity of Y** The more electronegative the element Y, the more it weakens and polarizes the H—O bond and the more acidic the oxyacid is. We can see this effect by comparing the electronegativity of Y and the acid ionization constants of the following oxyacids:

| Acid   | Electronegativity of Y | $K_a$                 |
|--------|------------------------|-----------------------|
| H—O—I  | 2.5                    | $2.3 \times 10^{-11}$ |
| H—O—Br | 2.8                    | $2.0 \times 10^{-9}$  |
| H—O—Cl | 3.0                    | $2.9 \times 10^{-8}$  |

Chlorine is the most electronegative of the three elements and the corresponding acid has the greatest  $K_a$ .

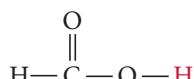
**The Number of Oxygen Atoms Bonded to Y** Oxyacids may contain additional oxygen atoms bonded to the element Y. Because these additional oxygen atoms are electronegative, they draw electron density away from Y, which in turn draws electron density away from the H—O bond, further weakening and polarizing it, and leading to increasing acidity. We can see this effect by comparing the following series of acid ionization constants:

| Acid              | Structure   | $K_a$                |
|-------------------|---|----------------------|
| HClO <sub>4</sub> | $\begin{array}{c} \text{O} \\    \\ \text{H}—\text{O}—\text{Cl}=\text{O} \\    \\ \text{O} \end{array}$ | Strong               |
| HClO <sub>3</sub> | $\begin{array}{c} \text{O} \\    \\ \text{H}—\text{O}—\text{Cl}=\text{O} \end{array}$                   | 1                    |
| HClO <sub>2</sub> | $\begin{array}{c} \text{H}—\text{O}—\text{Cl}=\text{O} \end{array}$                                     | $1.1 \times 10^{-2}$ |
| HClO              | $\begin{array}{c} \text{H}—\text{O}—\text{Cl} \end{array}$  | $2.9 \times 10^{-8}$ |

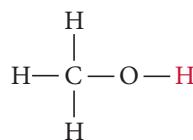
The greater the number of oxygen atoms bonded to Y, the stronger the acid. On this basis we would predict that H<sub>2</sub>SO<sub>4</sub> is a stronger acid than H<sub>2</sub>SO<sub>3</sub> and that HNO<sub>3</sub> is stronger than HNO<sub>2</sub>. As we have seen in this chapter, both H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> are strong acids, while H<sub>2</sub>SO<sub>3</sub> and HNO<sub>2</sub> are weak acids, as predicted.

### Conceptual Connection 15.7 Acid Strength and Molecular Structure

Which of the protons shown in red is more acidic?



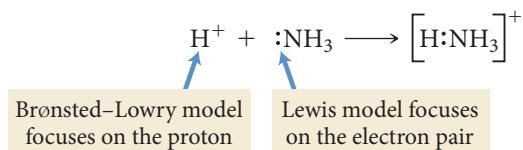
(a)



(b)

## 15.11 Lewis Acids and Bases

We began our definitions of acids and bases with the Arrhenius model. We then saw how the Brønsted–Lowry model, by introducing the concept of a proton donor and proton acceptor, expanded the range of substances that we consider acids and bases. We now introduce a third model, which further broadens the range of substances that we can consider acids. This third model is the *Lewis model*, named after G. N. Lewis, the American chemist who devised the electron-dot representation of chemical bonding (Section 9.1). While the Brønsted–Lowry model focuses on the transfer of a proton, the Lewis model focuses on the transfer of an electron pair. Consider the simple acid–base reaction between the  $\text{H}^+$  ion and  $\text{NH}_3$ , shown here with Lewis structures:



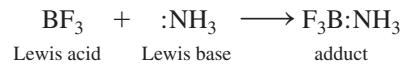
According to the Brønsted–Lowry model, the ammonia accepts a proton, thus acting as a base. According to the Lewis model, the ammonia acts as a base by *donating an electron pair*. The general definitions of acids and bases according to the Lewis model focus on the electron pair.

**Lewis acid:** electron pair acceptor

**Lewis base:** electron pair donor

According to the Lewis definition,  $\text{H}^+$  in the reaction just shown is acting as an acid because it is accepting an electron pair from  $\text{NH}_3$ .  $\text{NH}_3$  is acting as a Lewis base because it is donating an electron pair to  $\text{H}^+$ .

Although the Lewis model does not significantly expand the substances that can be considered a base—because all proton acceptors must have an electron pair to bind the proton—it does significantly expand the substances that can be considered an acid. According to the Lewis model, a substance need not even contain hydrogen to be an acid. For example, consider the gas-phase reaction between boron trifluoride and ammonia shown here:



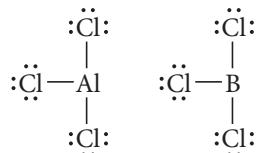
Boron trifluoride has an empty orbital that can accept the electron pair from ammonia and form the product (the product of a Lewis acid–base reaction is sometimes called an *adduct*). The reaction just shown demonstrates an important property of Lewis acids:

*A Lewis acid has an empty orbital (or can rearrange electrons to create an empty orbital) that can accept an electron pair.*

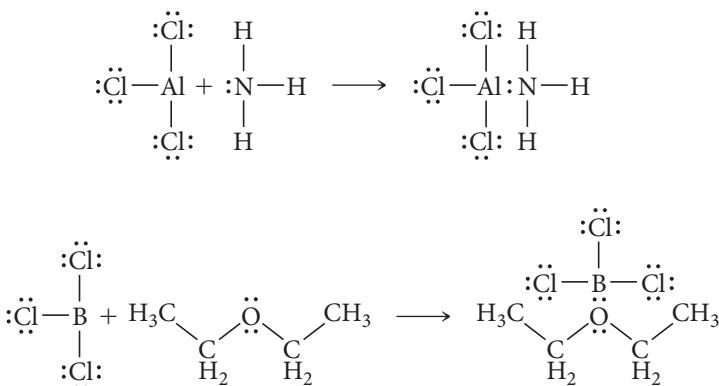
Consequently, the Lewis definition subsumes a whole new class of acids. Next we examine a few examples.

### Molecules That Act as Lewis Acids

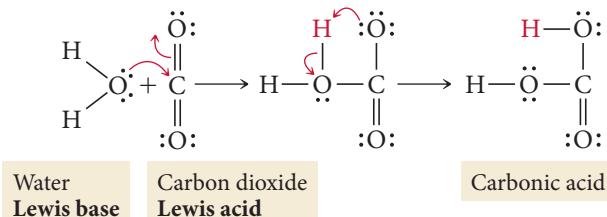
Since molecules with incomplete octets have empty orbitals, they can serve as Lewis acids. For example, both  $\text{AlCl}_3$  and  $\text{BCl}_3$  have incomplete octets:



These both act as Lewis acids, as shown in the following reactions:



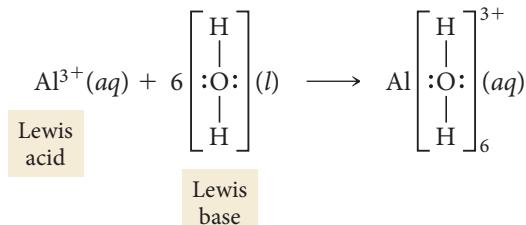
Some molecules that may not initially contain empty orbitals can rearrange their electrons to act as Lewis acids. Consider the reaction between carbon dioxide and water:



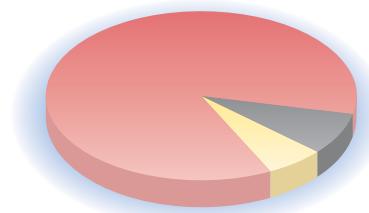
The electrons in the double bond on carbon move to the terminal oxygen atom, allowing carbon dioxide to act as a Lewis acid by accepting an electron pair from water. The molecule then undergoes a rearrangement in which the hydrogen atom shown in red bonds with the terminal oxygen atom instead of the internal one.

## Cations That Act as Lewis Acids

Some cations, since they are positively charged and have lost some electrons, have empty orbitals that allow them to also act as Lewis acids. Consider the hydration process of the  $\text{Al}^{3+}$  ion discussed in Section 15.8 shown here:



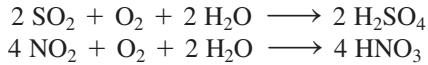
U.S. Energy Consumption by Source, 2010



The aluminum ion acts as a Lewis acid, accepting lone pairs from six water molecules to form the hydrated ion. Many other small, highly charged metal ions also act as Lewis acids in this way.

## 15.12 Acid Rain

About 83% of U.S. energy comes from the combustion of fossil fuels, including petroleum, natural gas, and coal (Figure 15.15 ▶). Some fossil fuels, especially coal, contain small amounts of sulfur impurities. During combustion, these impurities react with oxygen to form  $\text{SO}_2$ . In addition, during combustion of any fossil fuel, nitrogen from the air reacts with oxygen to form  $\text{NO}_2$ .  $\text{SO}_2$  and  $\text{NO}_2$  react with water and  $\text{O}_2$  in the atmosphere to form sulfuric acid and nitric acid:

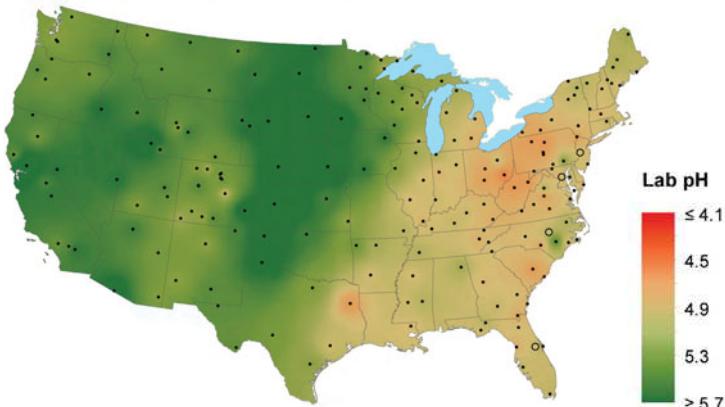


▲ FIGURE 15.15 Sources of U.S. Energy About 83% of U.S. energy comes from fossil fuel combustion. Source: U.S. EIA Annual Energy Review 2011

**► FIGURE 15.16 Acid Rain** Acid rain is a significant problem in the northeastern United States. The map shows the pH of rain that falls across the United States.

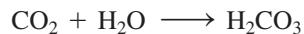
Source: National Atmospheric Deposition Program, National Trends Network

Hydrogen ion concentration as pH from measurements made at the Central Analytical Laboratory, 2010



These acids combine with rain to form *acid rain*. The problem is greatest in the northeastern portion of the United States, where the rain is significantly acidic because the sulfur and nitrogen oxides produced by coal combustion in the Midwest are carried toward the Northeast by natural air currents.

Even in relatively unpolluted areas, rain is naturally somewhat acidic because of atmospheric carbon dioxide. Carbon dioxide combines with rainwater to form carbonic acid:



However, carbonic acid is a relatively weak acid. Rain that is saturated with  $\text{CO}_2$  has a pH of about 5.6, which is only mildly acidic. When nitric acid and sulfuric acid mix with rain, the pH of the rain can fall below 4.3 (Figure 15.16 ▲). Remember that because of the logarithmic nature of the pH scale, rain with a pH of 4.3 has an  $[\text{H}_3\text{O}^+]$  that is 20 times greater than rain with a pH of 5.6. Rain that is this acidic has a harmful impact.

**▼ FIGURE 15.17 The Effects of Acid Rain** (a) Buildings, gravestones, and statues damaged by acid rain are a common sight in the northeastern United States and in many other industrialized nations. (b) Some species of trees are highly susceptible to the effects of acid rain.

### Effects of Acid Rain

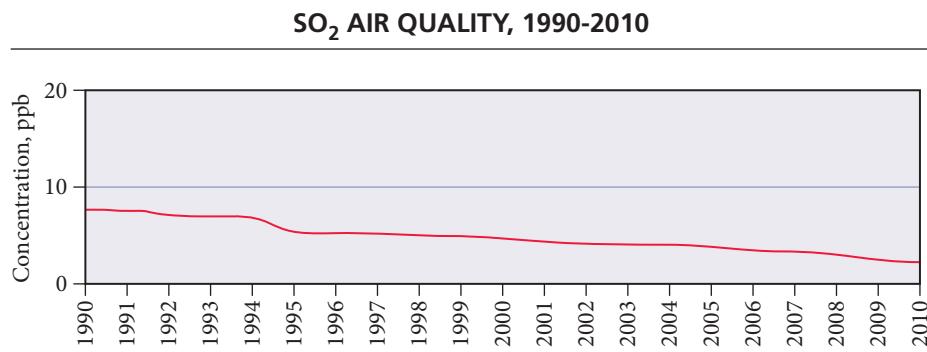
Acids dissolve metals and acid rain degrades metal structures. Bridges, railroads, and even automobiles can be damaged by acid rain. Since acids react with carbonates, acid rain also harms building materials that contain carbonates ( $\text{CO}_3^{2-}$ ), including marble, cement, and limestone. Statues, buildings, and pathways in the Northeast show significant signs of acid rain damage (Figure 15.17a ▼).



Acid rain also accumulates in lakes and rivers and affects aquatic life. Many lakes, especially those whose surrounding land contains significant amounts of limestone ( $\text{CaCO}_3$ ), have the ability to neutralize acidic rain. In the Midwest, for example, limestone-rich soils prevent most lakes from becoming acidified. In the northeastern United States, however, the lack of limestone makes lakes more susceptible, and over 2000 lakes and streams have increased acidity levels due to acid rain. Aquatic plants, frogs, salamanders, and some species of fish are sensitive to acid levels and cannot survive in the acidified water. Trees can also be affected by acid rain because the acid removes nutrients from the soil, making survival difficult (Figure 15.17b ▲).

## Acid Rain Legislation

In 1990, the U.S. Congress passed amendments to the Clean Air Act specifically targeted at reducing acid rain. These amendments force electrical utilities—which are the most significant source of  $\text{SO}_2$ —to lower their  $\text{SO}_2$  emissions gradually over time. The result has been a 75% decrease in  $\text{SO}_2$  pollutant levels in the United States since 1990 (Figure 15.18 ▼). The acidity of rain over the northeastern United States has begun to decrease, and lakes are beginning to recover. In the early 1990s, scientists categorized 30% of the lakes in the Northeast as being of *acute concern*, which means that a complete loss of fish population is expected. Today, the fraction of lakes in this category has been reduced to less than 18%. The acid rain program has been a dramatic success, and today's environmental legislation—such as legislation aimed at global warming—is using the acid rain legislation as a model for what can work.



◀ FIGURE 15.18 U.S. Sulfur Dioxide

Pollutant Levels As a result of amendments to the Clean Air Act passed in 1990,  $\text{SO}_2$  levels have been decreasing and will continue to decrease in the coming years.

Source: U.S. EPA Air Trends, 2011

## CHAPTER IN REVIEW

### Self Assessment Quiz

- Q1.** Identify the conjugate base in the reaction shown here:



- a)  $\text{HClO}_2$
- b)  $\text{H}_2\text{O}$
- c)  $\text{H}_3\text{O}^+$
- d)  $\text{ClO}_2^-$

- Q2.** Which pair is a Brønsted–Lowry conjugate acid–base pair?

- a)  $\text{NH}_3; \text{NH}_4^+$
- b)  $\text{H}_3\text{O}^+; \text{OH}^-$
- c)  $\text{HCl}; \text{HBr}$
- d)  $\text{ClO}_4^-; \text{ClO}_3^-$

- Q3.** Consider the given acid ionization constants. Identify the strongest conjugate base.

| Acid                 | $K_a$                 |
|----------------------|-----------------------|
| $\text{HNO}_2(aq)$   | $4.6 \times 10^{-4}$  |
| $\text{HCHO}_2(aq)$  | $1.8 \times 10^{-4}$  |
| $\text{HClO}(aq)$    | $2.9 \times 10^{-8}$  |
| $\text{HCN}(aq)$     | $4.9 \times 10^{-10}$ |
| $\text{NO}_2^-(aq)$  |                       |
| $\text{CHO}_2^-(aq)$ |                       |
| $\text{ClO}^-(aq)$   |                       |
| $\text{CN}^-(aq)$    |                       |

- Q4.** What is the  $\text{OH}^-$  concentration in an aqueous solution at 25 °C in which  $[\text{H}_3\text{O}^+] = 1.9 \times 10^{-9}$  M?
- $1.9 \times 10^{-9}$  M
  - $5.3 \times 10^{-6}$  M
  - $5.3 \times 10^6$  M
  - $1.9 \times 10^{-23}$  M
- Q5.** An  $\text{HNO}_3(aq)$  solution has a pH of 1.75. What is the molar concentration of the  $\text{HNO}_3(aq)$  solution?
- 1.75 M
  - $5.6 \times 10^{-13}$  M
  - 56 M
  - 0.018 M
- Q6.** Find the pH of a 0.350 M aqueous benzoic acid solution. For benzoic acid,  $K_a = 6.5 \times 10^{-5}$ .
- 4.64
  - 4.19
  - 2.32
  - 11.68
- Q7.** Find the pH of a 0.155 M  $\text{HClO}_2(aq)$  solution. For  $\text{HClO}_2$ ,  $K_a = 0.011$ .
- 0.92
  - 1.44
  - 1.39
  - 0.69
- Q8.** Calculate the percent ionization of 1.45 M aqueous acetic acid solution. For acetic acid,  $K_a = 1.8 \times 10^{-5}$ .
- 0.35%
  - 0.0018%
  - 0.29%
  - 0.0051%
- Q9.** Consider two aqueous solutions of nitrous acid ( $\text{HNO}_2$ ). Solution A has a concentration of  $[\text{HNO}_2] = 0.55$  M and solution B has a concentration of  $[\text{HNO}_2] = 1.25$  M. Which statement about the two solutions is true?
- Solution A has the higher percent ionization and the higher pH.
  - Solution B has the higher percent ionization and the higher pH.
  - Solution A has the higher percent ionization and solution B has the higher pH.
  - Solution B has the higher percent ionization and solution A has the higher pH.
- Q10.** Find the  $[\text{OH}^-]$  in a 0.200 M solution of ethylamine ( $\text{C}_2\text{H}_5\text{NH}_2$ ). For ethylamine,  $K_b = 5.6 \times 10^{-4}$ .
- 11.52 M
  - 2.48 M
  - 0.033 M
  - 0.011 M
- Q11.** Which ion will form a basic solution when dissolved in water?
- $\text{Br}^-$
  - $\text{NO}_3^-$
  - $\text{HSO}_4^-$
  - $\text{SO}_3^{2-}$
- Q12.** Which compound will form an acidic solution when dissolved in water?
- $\text{NH}_4\text{Cl}$
  - $\text{NaCl}$
  - $\text{KNO}_2$
  - $\text{Ca}(\text{NO}_3)_2$
- Q13.** Find the pH of 0.175 M  $\text{NaCN}$  solution. For  $\text{HCN}$ ,  $K_a = 4.9 \times 10^{-10}$ .
- 5.03
  - 11.28
  - 2.31
  - 8.97
- Q14.** What is the concentration of  $\text{X}^{2-}$  in a 0.150 M solution of the diprotic acid  $\text{H}_2\text{X}$ ? For  $\text{H}_2\text{X}$ ,  $K_{a_1} = 4.5 \times 10^{-6}$  and  $K_{a_2} = 1.2 \times 10^{-11}$ .
- $9.9 \times 10^{-8}$  M
  - $2.0 \times 10^{-9}$  M
  - $8.2 \times 10^{-4}$  M
  - $1.2 \times 10^{-11}$  M
- Q15.** Which acid has the largest  $K_a$ :  $\text{HClO}_2(aq)$ ,  $\text{HBrO}_2(aq)$ , or  $\text{HIO}_2(aq)$ ?
- $\text{HClO}_2(aq)$
  - $\text{HBrO}_2(aq)$
  - $\text{HIO}_2(aq)$
  - All three acids have the same  $K_a$ .

Answers: 1. (d) 2. (a) 3. (d) 4. (b) 5. (d) 6. (c) 7. (a) 8. (a) 9. (b) 10. (d) 11. (d) 12. (a) 13. (b) 14. (d) 15. (a)

## Key Terms

### Section 15.2

carboxylic acid (699)  
alkaloid (700)

### Section 15.3

Arrhenius definitions (of acids and bases) (700)  
hydronium ion (701)  
Brønsted–Lowry definitions (of acids and bases) (701)

amphoteric (701)  
conjugate acid–base pair (702)  
conjugate acid (702)  
conjugate base (702)

### Section 15.4

strong acid (703)  
weak acid (703)  
monoprotic acid (703)  
diprotic acid (703)

triprotic acid (704)  
acid ionization constant ( $K_a$ ) (705)

### Section 15.5

autoionization (706)  
ion product constant for water ( $K_w$ ) (706)  
neutral (706)  
acidic solution (706)

basic solution (707)  
pH (708)

**Section 15.6**  
percent ionization (716)

**Section 15.7**  
strong base (720)  
weak base (720)  
base ionization constant  
( $K_b$ ) (721)

**Section 15.9**  
polyprotic acid (731)

**Section 15.11**  
Lewis acid (738)  
Lewis base (738)

## Key Concepts

### Heartburn (15.1)

- ▶ Hydrochloric acid from the stomach sometimes comes in contact with the esophageal lining, resulting in irritation, called heartburn. Heartburn is treated with antacids, bases that neutralize stomach acid.

### The Nature of Acids and Bases (15.2)

- ▶ Acids generally taste sour, dissolve metals, turn blue litmus paper red, and neutralize bases. Common acids are hydrochloric, sulfuric, nitric, and carboxylic acids.
- ▶ Bases generally taste bitter, feel slippery, turn red litmus paper blue, and neutralize acids. Common bases are sodium hydroxide, sodium bicarbonate, and potassium hydroxide.

### Definitions of Acids and Bases (15.3)

- ▶ The Arrhenius definition of acids and bases states that in an aqueous solution, an acid produces hydrogen ions and a base produces hydroxide ions.
- ▶ The Brønsted–Lowry definition states that an acid is a proton (hydrogen ion) donor and a base is a proton acceptor. According to the Brønsted–Lowry definition, two substances related by the transfer of a proton are a conjugate acid–base pair.

### Acid Strength and the Acid Dissociation Constant, $K_a$ (15.4)

- ▶ In a solution, a strong acid completely ionizes but a weak acid only partially ionizes.
- ▶ Generally, the stronger the acid, the weaker the conjugate base, and vice versa.
- ▶ The extent of dissociation of a weak acid is quantified by the acid dissociation constant,  $K_a$ , which is the equilibrium constant for the ionization of the weak acid.

### Autoionization of Water and pH (15.5)

- ▶ In an acidic solution, the concentration of hydrogen ions is always greater than the concentration of hydroxide ions.  $[\text{H}_3\text{O}^+]$  multiplied by  $[\text{OH}^-]$  is always constant at a constant temperature.
- ▶ There are two types of logarithmic acid–base scales: pH and pOH. At 25 °C, the sum of the pH and pOH is always 14.

### Finding the $[\text{H}_3\text{O}^+]$ and pH of Strong and Weak Acid Solutions (15.6)

- ▶ In a strong acid solution, the hydrogen ion concentration equals the initial concentration of the acid.
- ▶ In a weak acid solution, the hydrogen ion concentration—which can be determined by solving an equilibrium problem—is lower than the initial acid concentration.
- ▶ The percent ionization of weak acids decreases as the acid (and hydrogen ion) concentration increases.

- ▶ In mixtures of two acids with large  $K_a$  differences, the concentration of hydrogen ions can usually be determined by considering only the stronger of the two acids.

### Base Solutions (15.7)

- ▶ A strong base dissociates completely; a weak base does not.
- ▶ Most weak bases produce hydroxide ions through the ionization of water. The base ionization constant,  $K_b$ , indicates the extent of ionization.

### Ions as Acids and Bases (15.8)

- ▶ A cation is a weak acid if it is the conjugate acid of a weak base; it is neutral if it is the conjugate acid of a strong base.
- ▶ An anion is a weak base if it is the conjugate base of a weak acid; it is neutral if it is the conjugate base of a strong acid.
- ▶ To calculate the pH of an acidic cation or basic anion, we determine  $K_a$  or  $K_b$  from the equation  $K_a \times K_b = K_w$ .

### Polyprotic Acids (15.9)

- ▶ Polyprotic acids contain two or more ionizable protons.
- ▶ Generally, polyprotic acids ionize in successive steps, with the value of  $K_a$  becoming smaller for each step.
- ▶ In many cases, we can determine the  $[\text{H}_3\text{O}^+]$  of a polyprotic acid solution by considering only the first ionization step; then, the concentration of the acid anion formed in the second ionization step is equivalent to the value of  $K_{a_2}$ .

### Acid Strength and Molecular Structure (15.10)

- ▶ For binary acids, acid strength decreases with increasing bond energy and increases with increasing bond polarity.
- ▶ For oxyacids, acid strength increases with the electronegativity of the atoms bonded to the oxygen atom and also increases with the number of oxygen atoms in the molecule.

### Lewis Acids and Bases (15.11)

- ▶ A third model of acids and bases, the Lewis model, defines a base as an electron pair donor and an acid as an electron pair acceptor; therefore, according to this definition, an acid does not have to contain hydrogen. According to this definition an acid can be a compound with an empty orbital—or one that will rearrange to make an empty orbital—or a cation.

### Acid Rain (15.12)

- ▶ The combustion of fossil fuels produces oxides of sulfur and nitrogen, which react with oxygen and water to form sulfuric and nitric acids. These acids then combine with rain to form acid rain.
- ▶ Acid rain corrodes man-made structures and damages aquatic environments and forests. Environmental legislation has helped stabilize the amount of acid rain being produced.

## Key Equations and Relationships

Note: In all of these equations  $[H^+]$  is interchangeable with  $[H_3O^+]$ .

Expression for the Acid Ionization Constant,  $K_a$  (15.4)

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

The Ion Product Constant for Water,  $K_w$  (15.5)

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ (at } 25^\circ\text{C)}$$

Expression for the pH Scale (15.5)

$$pH = -\log[H_3O^+]$$

Expression for the pOH Scale (15.5)

$$pOH = -\log[OH^-]$$

Relationship between pH and pOH (15.5)

$$pH + pOH = 14.00$$

Expression for the  $pK_a$  Scale (15.5)

$$pK_a = -\log K_a$$

Expression for Percent Ionization (15.6)

$$\begin{aligned} \text{Percent ionization} &= \frac{\text{concentration of ionized acid}}{\text{initial concentration of acid}} \times 100\% \\ &= \frac{[H_3O^+]_{\text{equil}}}{[HA]_{\text{init}}} \times 100\% \end{aligned}$$

Relationship between  $K_a$ ,  $K_b$ , and  $K_w$  (15.8)

$$K_a \times K_b = K_w$$

## Key Learning Outcomes

| Chapter Objectives   | Assessment  |
|--|---|
| Identifying Brønsted–Lowry Acids and Bases and Their Conjugates (15.3)   | Example 15.1 For Practice 15.1 Exercises 35, 36                         |
| $H_2SO_4(aq) + H_2O(l) \longrightarrow HSO_4^-(aq) + H_3O^+(aq)$   |   |
| $\begin{array}{ccccc} \text{Acid} & & \text{Base} & & \\ \boxed{H_2SO_4(aq)} & & \boxed{H_2O(l)} & & \\ & & \boxed{\downarrow} & & \\ & & \text{Conjugate} & & \text{Conjugate} \\ & & \text{base} & & \text{acid} \\ & & \boxed{\quad} & & \boxed{\quad} \end{array}$ |   |
| Using $K_w$ in Calculations (15.5)   | Example 15.2 For Practice 15.2 Exercises 47, 48                         |
| Calculating pH from $[H_3O^+]$ or $[OH^-]$ (15.5)  | Examples 15.3, 15.4 For Practice 15.3, 15.4 Exercises 49–52             |
| Finding the pH of a Weak Acid Solution (15.6)  | Examples 15.5, 15.6, 15.7 For Practice 15.5, 15.6, 15.7 Exercises 63–68 |
| Finding the Acid Ionization Constant from pH (15.6)  | Example 15.8 For Practice 15.8 Exercises 69, 70                         |
| Finding the Percent Ionization of a Weak Acid (15.6)   | Example 15.9 For Practice 15.9 Exercises 71–74                          |
| Mixtures of Weak Acids (15.6)  | Example 15.10 For Practice 15.10 Exercises 79, 80                       |
| Finding the $[OH^-]$ and pH of a Strong Base Solution (15.7)   | Example 15.11 For Practice 15.11 Exercises 81, 82                       |
| Finding the $[OH^-]$ and pH of a Weak Base Solution (15.7)   | Example 15.12 For Practice 15.12 Exercises 89, 90                       |
| <br>Ammonia      Methylamine      Pyridine   |   |
| Determining Whether an Anion Is Basic or Neutral (15.8)  | Example 15.13 For Practice 15.13 Exercises 95, 96                       |
| Determining the pH of a Solution Containing an Anion Acting as a Base (15.8)   | Example 15.14 For Practice 15.14 Exercises 97, 98                       |
| Determining Whether a Cation Is Acidic or Neutral (15.8)   | Example 15.15 For Practice 15.15 Exercises 99, 100                      |
| Determining the Overall Acidity or Basicity of Salt Solutions (15.8)   | Example 15.16 For Practice 15.16 Exercises 101, 102                     |

## Key Learning Outcomes, continued

Finding the pH of a Polyprotic Acid Solution (15.9)

Example 15.17 For Practice 15.17 Exercises 111, 112

Finding the  $[H_3O^+]$  in Dilute  $H_2SO_4$  Solutions (15.9)

Example 15.18 For Practice 15.18 Exercise 115

Finding the Concentration of the Anions for a Weak Diprotic Acid Solution (15.9)

Example 15.19 For Practice 15.19 Exercises 113, 114

## EXERCISES

### Review Questions

1. What causes heartburn? What are some possible ways to alleviate heartburn?
2. What are the general physical and chemical properties of acids? Of bases?
3. What is a carboxylic acid? Give an example.
4. What is the Arrhenius definition of an acid? Of a base?
5. What is a hydronium ion? Does  $H^+$  exist in solution by itself?
6. What is the Brønsted–Lowry definition of an acid? Of a base?
7. Why is there more than one definition of acid–base behavior? Which definition is the right one?
8. Describe amphoteric behavior and give an example.
9. What is a conjugate acid–base pair? Provide an example.
10. Explain the difference between a strong acid and a weak acid and list one example of each.
11. What are diprotic and tripotic acids? List an example of each.
12. Define the acid ionization constant and explain its significance.
13. Write an equation for the autoionization of water and an expression for the ion product constant for water ( $K_w$ ). What is the value of  $K_w$  at 25 °C?
14. What happens to the  $[OH^-]$  of a solution when the  $[H_3O^+]$  is increased? Decreased?
15. Define pH. What pH range is considered acidic? Basic? Neutral?
16. Define pOH. What pOH range is considered acidic? Basic? Neutral?
17. In most solutions containing a strong or weak acid, the autoionization of water can be neglected when calculating  $[H_3O^+]$ . Explain why this statement is valid.
18. When calculating  $[H_3O^+]$  for weak acid solutions, we can often use the *x is small* approximation. Explain the nature of this approximation and why it is valid.
19. What is the percent ionization of an acid? Explain what happens to the percent ionization of a weak acid as a function of the concentration of the weak acid solution.
20. In calculating  $[H_3O^+]$  for a mixture of a strong acid and weak acid, the weak acid can often be neglected. Explain why this statement is valid.
21. Write a generic equation showing how a weak base ionizes water.
22. How can you determine if an anion will act as a weak base? Write a generic equation showing the reaction by which an anion,  $A^-$ , acts as a weak base.
23. What is the relationship between the acid ionization constant for a weak acid ( $K_a$ ) and the base ionization constant for its conjugate base ( $K_b$ )?
24. What kinds of cations act as weak acids? List some examples.
25. When calculating the  $[H_3O^+]$  for a polyprotic acid, the second ionization step can often be neglected. Explain why this statement is valid.
26. For a weak diprotic acid  $H_2X$ , what is the relationship between  $[X^{2-}]$  and  $K_{a_2}$ ? Under what conditions does this relationship exist?
27. For a binary acid, H—Y, which factors affect the relative ease with which the acid ionizes?
28. Which factors affect the relative acidity of an oxyacid?
29. What is the Lewis definition of an acid? Of a base?
30. What is a general characteristic of a Lewis acid? Of a Lewis base?
31. What is acid rain? What causes it and where is the problem the greatest?
32. What are the main detrimental effects of acid rain? What is being done to address the problem of acid rain?

### Problems by Topic

#### The Nature and Definitions of Acids and Base

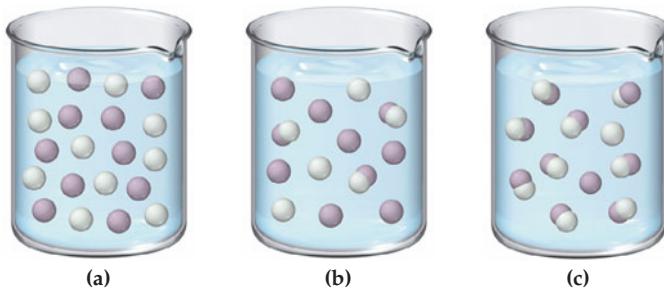
33. Identify each substance as an acid or a base and write a chemical equation showing how it is an acid or a base according to the Arrhenius definition.
- a.  $HNO_3(aq)$
  - b.  $NH_4^+(aq)$
  - c.  $KOH(aq)$
  - d.  $HC_2H_3O_2(aq)$

34. Identify each substance as an acid or a base and write a chemical equation showing how it is an acid or a base in aqueous solution according to the Arrhenius definition.
- a.  $NaOH(aq)$
  - b.  $H_2SO_4(aq)$
  - c.  $HBr(aq)$
  - d.  $Sr(OH)_2(aq)$

- 35.** In each reaction, identify the Brønsted–Lowry acid, the Brønsted–Lowry base, the conjugate acid, and the conjugate base.
- $\text{H}_2\text{CO}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{HCO}_3^-(aq)$
  - $\text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq)$
  - $\text{HNO}_3(aq) + \text{H}_2\text{O}(l) \longrightarrow \text{H}_3\text{O}^+(aq) + \text{NO}_3^-(aq)$
  - $\text{C}_5\text{H}_5\text{N}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{C}_5\text{H}_5\text{NH}^+(aq) + \text{OH}^-(aq)$
- 36.** In each reaction, identify the Brønsted–Lowry acid, the Brønsted–Lowry base, the conjugate acid, and the conjugate base.
- $\text{HI}(aq) + \text{H}_2\text{O}(l) \longrightarrow \text{H}_3\text{O}^+(aq) + \text{I}^-(aq)$
  - $\text{CH}_3\text{NH}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CH}_3\text{NH}_3^+(aq) + \text{OH}^-(aq)$
  - $\text{CO}_3^{2-}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCO}_3^-(aq) + \text{OH}^-(aq)$
  - $\text{HBr}(aq) + \text{H}_2\text{O}(l) \longrightarrow \text{H}_3\text{O}^+(aq) + \text{Br}^-(aq)$
- 37.** Write the formula for the conjugate base of each acid.
- $\text{HCl}$
  - $\text{H}_2\text{SO}_3$
  - $\text{HCHO}_2$
  - $\text{HF}$
- 38.** Write the formula for the conjugate acid of each base.
- $\text{NH}_3$
  - $\text{ClO}_4^-$
  - $\text{HSO}_4^-$
  - $\text{CO}_3^{2-}$
- 39.** Both  $\text{H}_2\text{O}$  and  $\text{H}_2\text{PO}_4^-$  are amphoteric. Write an equation to show how each substance can act as an acid and another equation to show how each can act as a base.
- 40.** Both  $\text{HCO}_3^-$  and  $\text{HS}^-$  are amphoteric. Write an equation to show how each substance can act as an acid and another equation to show how each can act as a base.

### Acid Strength and $K_a$

- 41.** Classify each acid as strong or weak. If the acid is weak, write an expression for the acid ionization constant ( $K_a$ ).
- $\text{HNO}_3$
  - $\text{HCl}$
  - $\text{HBr}$
  - $\text{H}_2\text{SO}_3$
- 42.** Classify each acid as strong or weak. If the acid is weak, write an expression for the acid ionization constant ( $K_a$ ).
- $\text{HF}$
  - $\text{HCHO}_2$
  - $\text{H}_2\text{SO}_4$
  - $\text{H}_2\text{CO}_3$
- 43.** The three diagrams represent three different solutions of the binary acid HA. Water molecules have been omitted for clarity and hydronium ions ( $\text{H}_3\text{O}^+$ ) are represented by hydrogen ions ( $\text{H}^+$ ). Rank the acids in order of decreasing acid strength.



- 44.** Rank the solutions in order of decreasing  $[\text{H}_3\text{O}^+]$ : 0.10 M HCl; 0.10 M HF; 0.10 M  $\text{HClO}$ ; 0.10 M  $\text{HC}_6\text{H}_5\text{O}$ .
- 45.** Pick the stronger base from each pair.
- $\text{F}^-$  or  $\text{Cl}^-$
  - $\text{NO}_2^-$  or  $\text{NO}_3^-$
  - $\text{F}^-$  or  $\text{ClO}^-$
- 46.** Pick the stronger base from each pair.
- $\text{ClO}_4^-$  or  $\text{ClO}_2^-$
  - $\text{Cl}^-$  or  $\text{H}_2\text{O}$
  - $\text{CN}^-$  or  $\text{ClO}^-$

### Autoionization of Water and pH

- 47.** Calculate  $[\text{OH}^-]$  in each aqueous solution at  $25^\circ\text{C}$ , and classify the solution as acidic or basic.
- $[\text{H}_3\text{O}^+] = 1.2 \times 10^{-8} \text{ M}$
  - $[\text{H}_3\text{O}^+] = 8.5 \times 10^{-5} \text{ M}$
  - $[\text{H}_3\text{O}^+] = 3.5 \times 10^{-2} \text{ M}$

- 48.** Calculate  $[\text{H}_3\text{O}^+]$  in each aqueous solution at  $25^\circ\text{C}$ , and classify each solution as acidic or basic.
- $[\text{OH}^-] = 1.1 \times 10^{-9} \text{ M}$
  - $[\text{OH}^-] = 2.9 \times 10^{-2} \text{ M}$
  - $[\text{OH}^-] = 6.9 \times 10^{-12} \text{ M}$
- 49.** Calculate the pH and pOH of each solution.
- $[\text{H}_3\text{O}^+] = 1.7 \times 10^{-8} \text{ M}$
  - $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-7} \text{ M}$
  - $[\text{H}_3\text{O}^+] = 2.2 \times 10^{-6} \text{ M}$
- 50.** Calculate  $[\text{H}_3\text{O}^+]$  and  $[\text{OH}^-]$  for each solution.
- pH = 8.55
  - pH = 11.23
  - pH = 2.87
- 51.** Complete the table. (All solutions are at  $25^\circ\text{C}$ .)

| $[\text{H}_3\text{O}^+]$ | $[\text{OH}^-]$       | pH    | Acidic or Basic |
|--------------------------|-----------------------|-------|-----------------|
| _____                    | _____                 | 3.15  | _____           |
| $3.7 \times 10^{-9}$     | _____                 | _____ | _____           |
| _____                    | _____                 | 11.1  | _____           |
| _____                    | $1.6 \times 10^{-11}$ | _____ | _____           |

- 52.** Complete the table. (All solutions are at  $25^\circ\text{C}$ .)

| $[\text{H}_3\text{O}^+]$ | $[\text{OH}^-]$      | pH    | Acidic or Basic |
|--------------------------|----------------------|-------|-----------------|
| $3.5 \times 10^{-3}$     | _____                | _____ | _____           |
| _____                    | $3.8 \times 10^{-7}$ | _____ | _____           |
| $1.8 \times 10^{-9}$     | _____                | _____ | _____           |
| _____                    | _____                | 7.15  | _____           |

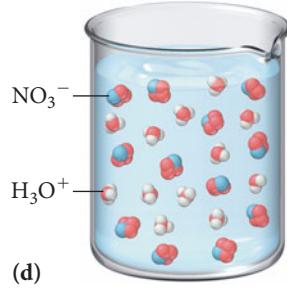
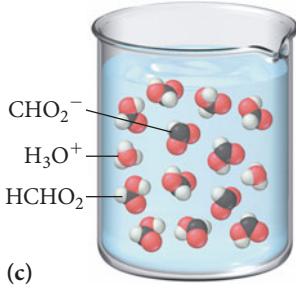
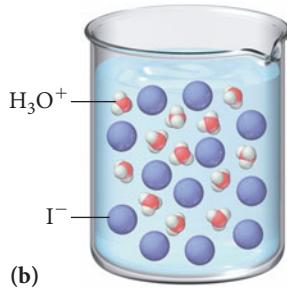
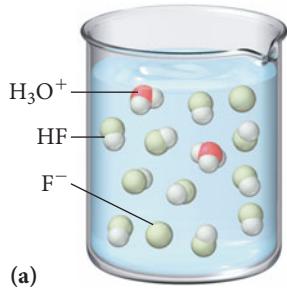
- 53.** Like all equilibrium constants, the value of  $K_w$  depends on temperature. At body temperature ( $37^\circ\text{C}$ ),  $K_w = 2.4 \times 10^{-14}$ . What are the  $[\text{H}_3\text{O}^+]$  and pH of pure water at body temperature?
- 54.** The value of  $K_w$  increases with increasing temperature. Is the autoionization of water endothermic or exothermic?
- 55.** Calculate the pH of each acid solution. Explain how the resulting pH values demonstrate that the pH of an acid solution should carry as many digits to the right of the decimal place as the number of significant figures in the concentration of the solution.
- $$\begin{aligned} [\text{H}_3\text{O}^+] &= 0.044 \text{ M} \\ [\text{H}_3\text{O}^+] &= 0.045 \text{ M} \\ [\text{H}_3\text{O}^+] &= 0.046 \text{ M} \end{aligned}$$
- 56.** Determine the concentration of  $\text{H}_3\text{O}^+$  to the correct number of significant figures in a solution with each pH. Describe how these calculations show the relationship between the number of digits to the right of the decimal place in pH and the number of significant figures in concentration.
- $$\begin{aligned} \text{pH} &= 2.50 \\ \text{pH} &= 2.51 \\ \text{pH} &= 2.52 \end{aligned}$$
- ### Acid Solutions
- 57.** For each strong acid solution, determine  $[\text{H}_3\text{O}^+]$ ,  $[\text{OH}^-]$ , and pH.
- 0.25 M HCl
  - 0.015 M  $\text{HNO}_3$
  - a solution that is 0.052 M in HBr and 0.020 M in  $\text{HNO}_3$
  - a solution that is 0.655%  $\text{HNO}_3$  by mass (assume a density of 1.01 g/mL for the solution)

- 58.** Determine the pH of each solution.
- 0.048 M HI
  - 0.0895 M  $\text{HClO}_4$
  - a solution that is 0.045 M in  $\text{HClO}_4$  and 0.048 M in HCl
  - a solution that is 1.09% HCl by mass (assume a density of 1.01 g/mL for the solution)
- 59.** What mass of HI should be present in 0.250 L of solution to obtain a solution with each pH value?
- pH = 1.25
  - pH = 1.75
  - pH = 2.85
- 60.** What mass of  $\text{HClO}_4$  should be present in 0.500 L of solution to obtain a solution with each pH value?
- pH = 2.50
  - pH = 1.50
  - pH = 0.50
- 61.** What is the pH of a solution in which 224 mL of  $\text{HCl}(g)$ , measured at 27.2 °C and 1.02 atm, is dissolved in 1.5 L of aqueous solution?
- 62.** What volume of a concentrated HCl solution, which is 36.0% HCl by mass and has a density of 1.179 g/mL, should be used to make 5.00 L of an HCl solution with a pH of 1.8?
- 63.** Determine the  $[\text{H}_3\text{O}^+]$  and pH of a 0.100 M solution of benzoic acid.
- 64.** Determine the  $[\text{H}_3\text{O}^+]$  and pH of a 0.200 M solution of formic acid.
- 65.** Determine the pH of an  $\text{HNO}_2$  solution of each concentration. In which cases can you *not* make the simplifying assumption that *x is small*?
- 0.500 M
  - 0.100 M
  - 0.0100 M
- 66.** Determine the pH of an HF solution of each concentration. In which cases can you *not* make the simplifying assumption that *x is small*?
- 0.250 M
  - 0.0500 M
  - 0.0250 M
- 67.** If 15.0 mL of glacial acetic acid (pure  $\text{HC}_2\text{H}_3\text{O}_2$ ) is diluted to 1.50 L with water, what is the pH of the resulting solution? The density of glacial acetic acid is 1.05 g/mL.
- 68.** Calculate the pH of a formic acid solution that contains 1.35% formic acid by mass. (Assume a density of 1.01 g/mL for the solution.)
- 69.** A 0.185 M solution of a weak acid (HA) has a pH of 2.95. Calculate the acid ionization constant ( $K_a$ ) for the acid.
- 70.** A 0.115 M solution of a weak acid (HA) has a pH of 3.29. Calculate the acid ionization constant ( $K_a$ ) for the acid.
- 71.** Determine the percent ionization of a 0.125 M HCN solution.
- 72.** Determine the percent ionization of a 0.225 M solution of benzoic acid.
- 73.** Calculate the percent ionization of an acetic acid solution having the given concentration.
- 1.00 M
  - 0.500 M
  - 0.100 M
  - 0.0500 M
- 74.** Calculate the percent ionization of a formic acid solution having the given concentration.
- 1.00 M
  - 0.500 M
  - 0.100 M
  - 0.0500 M
- 75.** A 0.148 M solution of a monoprotic acid has a percent ionization of 1.55%. Determine the acid ionization constant ( $K_a$ ) for the acid.
- 76.** A 0.085 M solution of a monoprotic acid has a percent ionization of 0.59%. Determine the acid ionization constant ( $K_a$ ) for the acid.
- 77.** Find the pH and percent ionization of each HF solution.
- 0.250 M HF
  - 0.100 M HF
  - 0.050 M HF
- 78.** Find the pH and percent ionization of a 0.100 M solution of a weak monoprotic acid having the given  $K_a$  values.
- $K_a = 1.0 \times 10^{-5}$
  - $K_a = 1.0 \times 10^{-3}$
  - $K_a = 1.0 \times 10^{-1}$
- 79.** Find the pH of each mixture of acids.
- 0.115 M in HBr and 0.125 M in  $\text{HCHO}_2$
  - 0.150 M in  $\text{HNO}_2$  and 0.085 M in  $\text{HNO}_3$
  - 0.185 M in  $\text{HCHO}_2$  and 0.225 M in  $\text{HC}_2\text{H}_3\text{O}_2$
  - 0.050 M in acetic acid and 0.050 M in hydrocyanic acid
- 80.** Find the pH of each mixture of acids.
- 0.075 M in  $\text{HNO}_3$  and 0.175 M in  $\text{HC}_7\text{H}_5\text{O}_2$
  - 0.020 M in HBr and 0.015 M in  $\text{HClO}_4$
  - 0.095 M in HF and 0.225 M in  $\text{HC}_6\text{H}_5\text{O}$
  - 0.100 M in formic acid and 0.050 M in hypochlorous acid
- ### Base Solutions
- 81.** For each strong base solution, determine  $[\text{OH}^-]$ ,  $[\text{H}_3\text{O}^+]$ , pH, and pOH.
- 0.15 M NaOH
  - $1.5 \times 10^{-3}$  M  $\text{Ca}(\text{OH})_2$
  - $4.8 \times 10^{-4}$  M  $\text{Sr}(\text{OH})_2$
  - $8.7 \times 10^{-5}$  M KOH
- 82.** For each strong base solution, determine  $[\text{OH}^-]$ ,  $[\text{H}_3\text{O}^+]$ , pH, and pOH.
- $8.77 \times 10^{-3}$  M LiOH
  - 0.0112 M  $\text{Ba}(\text{OH})_2$
  - $1.9 \times 10^{-4}$  M KOH
  - $5.0 \times 10^{-4}$  M  $\text{Ca}(\text{OH})_2$
- 83.** Determine the pH of a solution that is 3.85% KOH by mass. Assume that the solution has density of 1.01 g/mL.
- 84.** Determine the pH of a solution that is 1.55% NaOH by mass. Assume that the solution has density of 1.01 g/mL.
- 85.** What volume of 0.855 M KOH solution is required to make 3.55 L of a solution with pH of 12.4?
- 86.** What volume of a 15.0% by mass NaOH solution, which has a density of 1.116 g/mL, should be used to make 5.00 L of an NaOH solution with a pH of 10.8?
- 87.** Write equations showing how each weak base ionizes water to form  $\text{OH}^-$ . Also write the corresponding expression for  $K_b$ .
- $\text{NH}_3$
  - $\text{HCO}_3^-$
  - $\text{CH}_3\text{NH}_2$
- 88.** Write equations showing how each weak base ionizes water to form  $\text{OH}^-$ . Also write the corresponding expression for  $K_b$ .
- $\text{CO}_3^{2-}$
  - $\text{C}_6\text{H}_5\text{NH}_2$
  - $\text{C}_2\text{H}_5\text{NH}_2$
- 89.** Determine the  $[\text{OH}^-]$ , pH, and pOH of a 0.15 M ammonia solution.
- 90.** Determine the  $[\text{OH}^-]$ , pH, and pOH of a solution that is 0.125 M in  $\text{CO}_3^{2-}$ .
- 91.** Caffeine ( $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$ ) is a weak base with a  $pK_b$  of 10.4. Calculate the pH of a solution containing a caffeine concentration of 455 mg/L.
- 92.** Amphetamine ( $\text{C}_9\text{H}_{13}\text{N}$ ) is a weak base with a  $pK_b$  of 4.2. Calculate the pH of a solution containing an amphetamine concentration of 225 mg/L.
- 93.** Morphine is a weak base. A 0.150 M solution of morphine has a pH of 10.5. What is  $K_b$  for morphine?
- 94.** A 0.135 M solution of a weak base has a pH of 11.23. Determine  $K_b$  for the base.
- ### Acid-Base Properties of Ions and Salts
- 95.** Determine if each anion acts as a weak base in solution. For those anions that are basic, write an equation that shows how the anion acts as a base.
- $\text{Br}^-$
  - $\text{ClO}^-$
  - $\text{CN}^-$
  - $\text{Cl}^-$
- 96.** Determine whether each anion is basic or neutral. For those anions that are basic, write an equation that shows how the anion acts as a base.
- $\text{C}_7\text{H}_5\text{O}_2^-$
  - $\text{I}^-$
  - $\text{NO}_3^-$
  - $\text{F}^-$

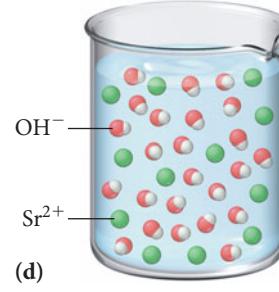
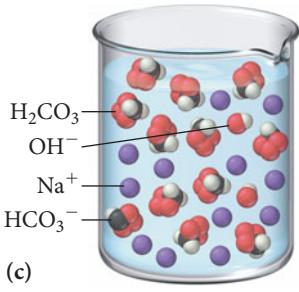
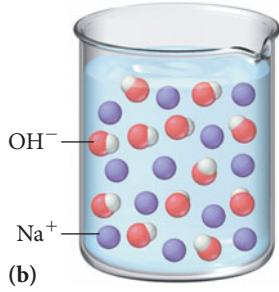
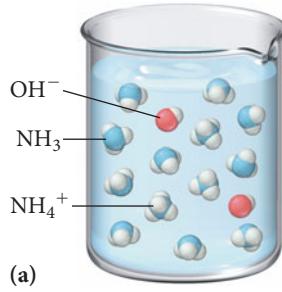
- 97.** Determine the  $[OH^-]$  and pH of a solution that is 0.140 M in  $F^-$ .
- 98.** Determine the  $[OH^-]$  and pH of a solution that is 0.250 M in  $HCO_3^-$ .
- 99.** Determine whether each cation is acidic or pH-neutral. For those cations that are acidic, write an equation that shows how the cation acts as an acid.
- $NH_4^+$
  - $Na^+$
  - $Co^{3+}$
  - $CH_2NH_3^+$
- 100.** Determine whether each cation is acidic or pH-neutral. For those cations that are acidic, write an equation that shows how the cation acts as an acid.
- $Sr^{2+}$
  - $Mn^{3+}$
  - $C_5H_5NH^+$
  - $Li^+$
- 101.** Determine if each salt will form a solution that is acidic, basic, or pH-neutral.
- $FeCl_3$
  - $NaF$
  - $CaBr_2$
  - $NH_4Br$
  - $C_6H_5NH_3NO_2$
- 102.** Determine if each salt will form a solution that is acidic, basic, or pH-neutral.
- $Al(NO_3)_3$
  - $C_2H_5NH_3NO_3$
  - $K_2CO_3$
  - $RbI$
  - $NH_4ClO$
- 103.** Arrange the solutions in order of increasing acidity.  
 $NaCl$ ,  $NH_4Cl$ ,  $NaHCO_3$ ,  $NH_4ClO_2$ ,  $NaOH$
- 104.** Arrange the solutions in order of increasing basicity.  
 $CH_3NH_3Br$ ,  $KOH$ ,  $KBr$ ,  $KCN$ ,  $C_5H_5NHNO_2$
- 105.** Determine the pH of each solution.
- 0.10 M  $NH_4Cl$
  - 0.10 M  $NaC_2H_3O_2$
  - 0.10 M  $NaCl$
- 106.** Determine the pH of each solution.
- 0.20 M  $KCHO_2$
  - 0.20 M  $CH_3NH_3I$
  - 0.20 M  $KI$
- 107.** Calculate the concentration of all species in a 0.15 M KF solution.
- 108.** Calculate the concentration of all species in a 0.225 M  $C_6H_5NH_3Cl$  solution.
- ### Polyprotic Acids
- 109.** Write chemical equations and corresponding equilibrium expressions for each of the three ionization steps of phosphoric acid.
- 110.** Write chemical equations and corresponding equilibrium expressions for each of the two ionization steps of carbonic acid.
- 111.** Calculate the  $[H_3O^+]$  and pH of each polyprotic acid solution.
- 0.350 M  $H_3PO_4$
  - 0.350 M  $H_2C_2O_4$
- 112.** Calculate the  $[H_3O^+]$  and pH of each polyprotic acid solution.
- 0.125 M  $H_2CO_3$
  - 0.125 M  $H_3C_6H_5O_7$
- 113.** Calculate the concentration of all species in a 0.500 M solution of  $H_2SO_3$ .
- 114.** Calculate the concentration of all species in a 0.155 M solution of  $H_2CO_3$ .
- 115.** Calculate the  $[H_3O^+]$  and pH of each  $H_2SO_4$  solution. At approximately what concentration does the  $x$  is small approximation break down?
- 0.50 M
  - 0.10 M
  - 0.050 M
- 116.** Consider a 0.10 M solution of a weak polyprotic acid ( $H_2A$ ) with the possible values of  $K_{a_1}$  and  $K_{a_2}$  given here.
- $K_{a_1} = 1.0 \times 10^{-4}$ ;  $K_{a_2} = 5.0 \times 10^{-5}$
  - $K_{a_1} = 1.0 \times 10^{-4}$ ;  $K_{a_2} = 1.0 \times 10^{-5}$
  - $K_{a_1} = 1.0 \times 10^{-4}$ ;  $K_{a_2} = 1.0 \times 10^{-6}$
- Calculate the contributions to  $[H_3O^+]$  from each ionization step. At what point can the contribution of the second step be neglected?
- ### Molecular Structure and Acid Strength
- 117.** Based on their molecular structure, pick the stronger acid from each pair of binary acids. Explain your choice.
- HF and HCl
  - $H_2O$  or HF
  - $H_2Se$  or  $H_2S$
- 118.** Based on molecular structure, arrange the binary compounds in order of increasing acid strength. Explain your choice.
- $H_2Te$ ,  $HI$ ,  $H_2S$ ,  $NaH$
- 119.** Based on their molecular structure, pick the stronger acid from each pair of oxyacids. Explain your choice.
- $H_2SO_4$  or  $H_2SO_3$
  - $HClO_2$  or  $HClO$
  - $HClO$  or  $HBrO$
  - $CCl_3COOH$  or  $CH_3COOH$
- 120.** Based on molecular structure, arrange the oxyacids in order of increasing acid strength. Explain your choice.
- $HClO_3$ ,  $HIO_3$ ,  $HBrO_3$
- 121.** Which is a stronger base,  $S^{2-}$  or  $Se^{2-}$ ? Explain.
- 122.** Which is a stronger base,  $PO_4^{3-}$  or  $AsO_4^{3-}$ ? Explain.
- ### Lewis Acids and Bases
- 123.** Classify each species as either a Lewis acid or a Lewis base.
- $Fe^{3+}$
  - $BH_3$
  - $NH_3$
  - $F^-$
- 124.** Classify each species as either a Lewis acid or a Lewis base.
- $BeCl_2$
  - $OH^-$
  - $B(OH)_3$
  - $CN^-$
- 125.** Identify the Lewis acid and Lewis base from among the reactants in each equation.
- $Fe^{3+}(aq) + 6 H_2O(l) \rightleftharpoons Fe(H_2O)_6^{3+}(aq)$
  - $Zn^{2+}(aq) + 4 NH_3(aq) \rightleftharpoons Zn(NH_3)_4^{2+}(aq)$
  - $(CH_3)_3N(g) + BF_3(g) \rightleftharpoons (CH_3)_3NBF_3(s)$
- 126.** Identify the Lewis acid and Lewis base from among the reactants in each equation.
- $Ag^+(aq) + 2 NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$
  - $AlBr_3 + NH_3 \rightleftharpoons H_3NAlBr_3$
  - $F^-(aq) + BF_3(aq) \rightleftharpoons BF_4^-(aq)$

## Cumulative Problems

- 127.** Based on these molecular views, determine whether each pictured acid is weak or strong.



- 128.** Based on these molecular views, determine whether each pictured base is weak or strong.

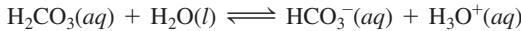
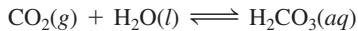


- 129.** The binding of oxygen by hemoglobin in the blood involves the equilibrium reaction:



In this equation, Hb is hemoglobin. The pH of normal human blood is highly controlled within a range of 7.35 to 7.45. Given the above equilibrium, why is this important? What would happen to the oxygen-carrying capacity of hemoglobin if blood became too acidic (a dangerous condition known as acidosis)?

- 130.** Carbon dioxide dissolves in water according to the equations:



Carbon dioxide levels in the atmosphere have increased about 20% over the last century. Given that Earth's oceans are exposed to atmospheric carbon dioxide, what effect might the increased CO<sub>2</sub> have on the pH of the world's oceans? What effect might this change have on the limestone structures (primarily CaCO<sub>3</sub>) of coral reefs and marine shells?

- 131.** People often take milk of magnesia to reduce the discomfort associated with acid stomach or heartburn. The recommended dose is 1 teaspoon, which contains  $4.00 \times 10^2$  mg of Mg(OH)<sub>2</sub>. What volume of an HCl solution with a pH of 1.3 can be neutralized by one dose of milk of magnesia? If the stomach contains  $2.00 \times 10^2$  mL of pH 1.3 solution, will all the acid be neutralized? If not, what fraction will be neutralized?

- 132.** Lakes that have been acidified by acid rain can be neutralized by liming, the addition of limestone (CaCO<sub>3</sub>). How much limestone (in kg) is required to completely neutralize a 4.3 billion liter lake with a pH of 5.5?

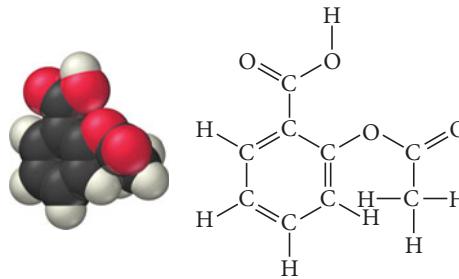


▲ Liming a lake.

- 133.** Acid rain over the Great Lakes has a pH of about 4.5. Calculate the [H<sub>3</sub>O<sup>+</sup>] of this rain and compare that value to the [H<sub>3</sub>O<sup>+</sup>] of rain over the West Coast that has a pH of 5.4. How many times more concentrated is the acid in rain over the Great Lakes?

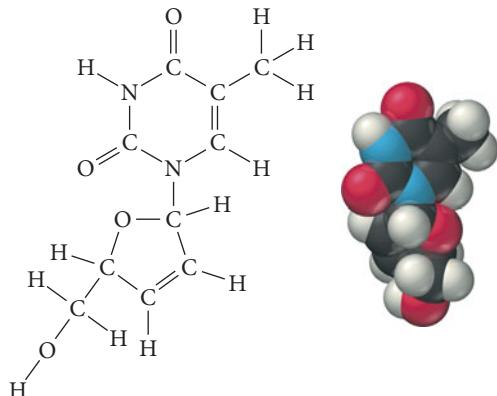
- 134.** White wines tend to be more acidic than red wines. Find the [H<sub>3</sub>O<sup>+</sup>] in a Sauvignon Blanc with a pH of 3.23 and a Cabernet Sauvignon with a pH of 3.64. How many times more acidic is the Sauvignon Blanc?

- 135.** Common aspirin is acetylsalicylic acid, which has the structure shown here and a *pK<sub>a</sub>* of 3.5.



Calculate the pH of a solution in which one normal adult dose of aspirin ( $6.5 \times 10^2$  mg) is dissolved in 8.0 ounces of water.

- 136.** The AIDS drug zalcitabine (also known as ddC) is a weak base with the structure shown here and a  $pK_b$  of 9.8.



What percentage of the base is protonated in an aqueous zalcitabine solution containing 565 mg/L?

- 137.** Determine the pH of each solution.

- a. 0.0100 M  $\text{HClO}_4$
- b. 0.115 M  $\text{HClO}_2$
- c. 0.045 M  $\text{Sr}(\text{OH})_2$
- d. 0.0852 M  $\text{KCN}$
- e. 0.155 M  $\text{NH}_4\text{Cl}$

- 138.** Determine the pH of each solution.

- a. 0.0650 M  $\text{HNO}_3$
- b. 0.150 M  $\text{HNO}_2$
- c. 0.0195 M  $\text{KOH}$
- d. 0.245 M  $\text{CH}_3\text{NH}_3\text{I}$
- e. 0.318 M  $\text{KC}_6\text{H}_5\text{O}$

- 139.** Determine the pH of each two-component solution.

- a. 0.0550 M in  $\text{HI}$  and 0.00850 M in  $\text{HF}$
- b. 0.112 M in  $\text{NaCl}$  and 0.0953 M in  $\text{KF}$
- c. 0.132 M in  $\text{NH}_4\text{Cl}$  and 0.150 M  $\text{HNO}_3$
- d. 0.0887 M in sodium benzoate and 0.225 M in potassium bromide
- e. 0.0450 M in  $\text{HCl}$  and 0.0225 M in  $\text{HNO}_3$

- 140.** Determine the pH of each two-component solution.

- a. 0.050 M  $\text{KOH}$  and 0.015 M  $\text{Ba}(\text{OH})_2$
- b. 0.265 M  $\text{NH}_4\text{NO}_3$  and 0.102 M  $\text{HCN}$
- c. 0.075 M  $\text{RbOH}$  and 0.100 M  $\text{NaHCO}_3$
- d. 0.088 M  $\text{HClO}_4$  and 0.022 M  $\text{KOH}$
- e. 0.115 M  $\text{NaClO}$  and 0.0500 M  $\text{KI}$

- 141.** Write net ionic equations for the reactions that take place when aqueous solutions of the following substances are mixed:

- a. sodium cyanide and nitric acid
- b. ammonium chloride and sodium hydroxide
- c. sodium cyanide and ammonium bromide
- d. potassium hydrogen sulfate and lithium acetate
- e. sodium hypochlorite and ammonia

- 142.** Morphine has the formula  $\text{C}_{17}\text{H}_{19}\text{NO}_3$ . It is a base and accepts one proton per molecule. It is isolated from opium. A 0.682 g sample of opium is found to require 8.92 mL of a 0.0116 M solution of sulfuric acid for neutralization. Assuming that morphine is the only acid or base present in opium, calculate the percent morphine in the sample of opium.

- 143.** The pH of a 1.00 M solution of urea, a weak organic base, is 7.050. Calculate the  $K_a$  of protonated urea.

- 144.** A solution is prepared by dissolving 0.10 mol of acetic acid and 0.10 mol of ammonium chloride in enough water to make 1.0 L of solution. Find the concentration of ammonia in the solution.

- 145.** Lactic acid is a weak acid found in milk. Its calcium salt is a source of calcium for growing animals. A saturated solution of this salt, which we can represent as  $\text{Ca}(\text{Lact})_2$  has a  $[\text{Ca}^{2+}] = 0.26 \text{ M}$  and a  $\text{pH} = 8.40$ . Assuming the salt is completely dissociated, calculate the  $K_a$  of lactic acid.

- 146.** A solution of 0.23 mol of the chloride salt of protonated quinine ( $\text{QH}^+$ ), a weak organic base, in 1.0 L of solution has  $\text{pH} = 4.58$ . Find the  $K_b$  of quinine ( $\text{Q}$ ).

## Challenge Problems

- 147.** A student mistakenly calculates the pH of a  $1.0 \times 10^{-7} \text{ M}$   $\text{HI}$  solution to be 7.0. Explain why the student is incorrect and calculate the correct pH.

- 148.** When 2.55 g of an unknown weak acid (HA) with a molar mass of 85.0 g/mol is dissolved in 250.0 g of water, the freezing point of the resulting solution is  $-0.257^\circ\text{C}$ . Calculate  $K_a$  for the unknown weak acid.

- 149.** Calculate the pH of a solution that is 0.00115 M in  $\text{HCl}$  and 0.0100 M in  $\text{HClO}_2$ .

- 150.** To what volume should you dilute 1 L of a solution of a weak acid HA to reduce the  $[\text{H}^+]$  to one-half of that in the original solution?

- 151.** HA, a weak acid, with  $K_a = 1.0 \times 10^{-8}$ , also forms the ion  $\text{HA}_2^-$ . The reaction is  $\text{HA}(aq) + \text{A}^-(aq) \rightleftharpoons \text{HA}_2^-(aq)$  and its  $K = 4.0$ . Calculate the  $[\text{H}^+]$ ,  $[\text{A}^-]$ , and  $[\text{HA}_2^-]$  in a 1.0 M solution of HA.

- 152.** Basicity in the gas phase can be defined as the proton affinity of the base, for example,  $\text{CH}_3\text{NH}_2(g) + \text{H}^+(g) \rightleftharpoons \text{CH}_3\text{NH}_3^+(g)$ . In the gas phase,  $(\text{CH}_3)_3\text{N}$  is more basic than  $\text{CH}_3\text{NH}_2$  while in solution the reverse is true. Explain this observation.

- 153.** Calculate the pH of a solution prepared from 0.200 mol of  $\text{NH}_4\text{CN}$  and enough water to make 1.00 L of solution.

- 154.** To 1.0 L of a 0.30 M solution of  $\text{HClO}_2$  is added 0.20 mol of NaF. Calculate the  $[\text{HClO}_2]$  at equilibrium.

- 155.** A mixture of  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  has a mass of 82.2 g. It is dissolved in 1.00 L of water and the pH is found to be 9.95. Find the mass of  $\text{NaHCO}_3$  in the mixture.

- 156.** A mixture of  $\text{NaCN}$  and  $\text{NaHSO}_4$  consists of a total of 0.60 mol. When the mixture is dissolved in 1.0 L of water and comes to equilibrium the pH is found to be 9.9. Find the amount of  $\text{NaCN}$  in the mixture.

## Conceptual Problems

**157.** Without doing any calculations, determine which solution in each pair is more acidic.

- a. 0.0100 M in HCl and 0.0100 M in KOH
- b. 0.0100 M in HF and 0.0100 M in KBr
- c. 0.0100 M in NH<sub>4</sub>Cl and 0.0100 M in CH<sub>3</sub>NH<sub>3</sub>Br
- d. 0.100 M in NaCN and 0.100 M in CaCl<sub>2</sub>

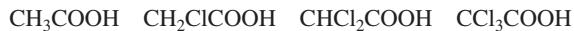
**158.** Without doing any calculations, determine which solution in each pair is more basic.

- a. 0.100 M in NaClO and 0.100 M in NaF
- b. 0.0100 M in KCl and 0.0100 M in KClO<sub>2</sub>

- c. 0.0100 M in HNO<sub>3</sub> and 0.0100 M in NaOH

- d. 0.0100 M in NH<sub>4</sub>Cl and 0.0100 M in HCN

**159.** Rank the acids in order of increasing acid strength.



## Answers to Conceptual Connections

### Conjugate Acid–Base Pairs

**15.1** (b) H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>SO<sub>3</sub> are both acids; this is not a conjugate acid–base pair.

### Relative Strengths of Weak Acids

**15.2** HF is stronger because it has a larger acid ionization constant.

### The *x* is small Approximation

**15.3** (c) The validity of the *x* is small approximation depends on both the value of the equilibrium constant and the initial concentration—the closer that these are to one another, the less likely the approximation will be valid.

### Strong and Weak Acids

**15.4** (a) A weak acid solution will usually be less than 5% dissociated. Since HCl is a strong acid, the 0.10 M solution is much more acidic than either a weak acid with the same concentration or even a weak acid that is twice as concentrated.

### Percent Ionization

**15.5** Solution (c) has the greatest percent ionization because percent ionization increases with decreasing weak acid concentration. Solution (b) has the lowest pH because the equilibrium H<sub>3</sub>O<sup>+</sup> concentration increases with increasing weak acid concentration.

### Judging Relative pH

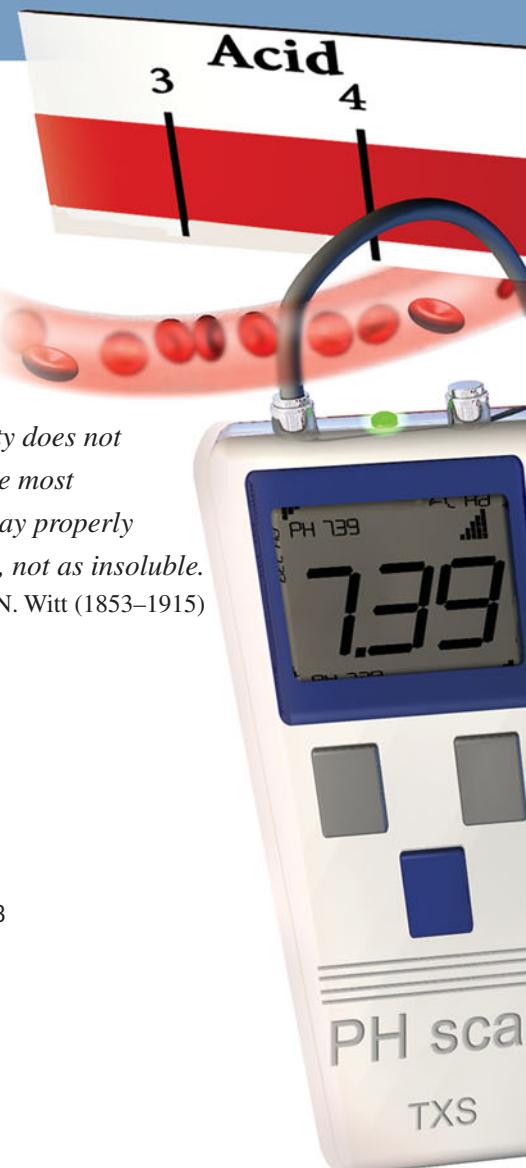
**15.6** (a) A weak acid solution will usually be less than 5% dissociated. Therefore, since HCl is the only strong acid, the 1.0 M solution is much more acidic than either a weak acid that is twice as concentrated or a combination of two weak acids with the same concentrations.

### Acid Strength and Molecular Structure

**15.7** (a) Since the carbon atom in (a) is bonded to another oxygen atom, which draws electron density away from the O—H bond (weakening and polarizing it), and the carbon atom in (b) is bonded only to other hydrogen atoms, the proton in structure (a) is more acidic.

# 16

## Aqueous Ionic Equilibrium



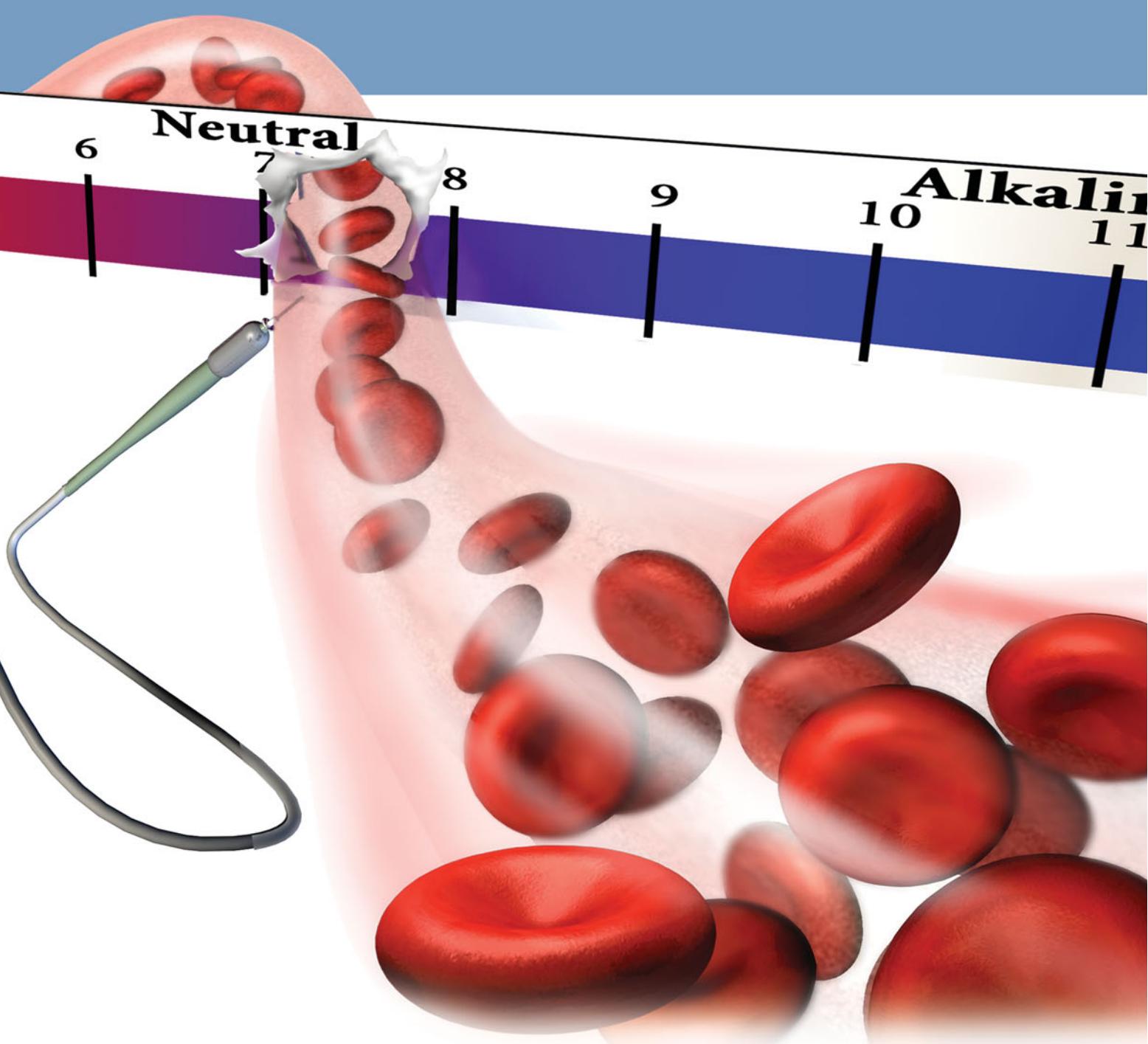
*In the strictly scientific sense of the word, insolubility does not exist, and even those substances characterized by the most obstinate resistance to the solvent action of water may properly be designated as extraordinarily difficult of solution, not as insoluble.*

—Otto N. Witt (1853–1915)

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Key Learning Outcomes 801

**W**E HAVE ALREADY seen the importance of aqueous solutions, first in Chapters 4, 12, and 14, and most recently in Chapter 15 on acids and bases. We now turn our attention to two additional topics involving aqueous solutions: buffers (solutions that resist pH change) and solubility equilibria (the extent to which slightly soluble ionic compounds dissolve in water). Buffers are tremendously important in biology because nearly all physiological processes must occur within a narrow pH range. Solubility equilibria are related to the solubility rules that we discussed in Chapter 4. In this chapter, we find a more complicated picture: solids that we considered insoluble under the simple “solubility rules” are actually better described as being only very slightly soluble, as the chapter-opening quotation from Otto Witt suggests. Solubility equilibria are important in predicting not only solubility, but also precipitation reactions that might occur when aqueous solutions are mixed.



Human blood is held at nearly constant pH by the action of buffers, a main topic of this chapter.

## 16.1 The Danger of Antifreeze

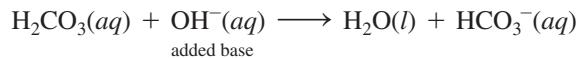
Every year, thousands of dogs and cats die from consuming a common household product: antifreeze that was improperly stored or that leaked out of a car radiator. Most types of antifreeze used in cars are aqueous solutions of ethylene glycol:

Some brands of antifreeze use propylene-glycol, which is less toxic than ethylene glycol.

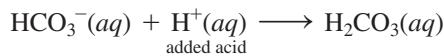


Ethylene glycol has a somewhat sweet taste that can attract curious dogs and cats—and sometimes even young children, who are also vulnerable to this toxic compound. The first stage of ethylene glycol poisoning is a state resembling drunkenness. Since the compound is an alcohol, it affects the brain much as an alcoholic beverage would. Once ethylene glycol starts to be metabolized, however, a second and more deadly stage commences.

In the liver, ethylene glycol is oxidized to glycolic acid ( $\text{HOCH}_2\text{COOH}$ ), which enters the bloodstream. The acidity of blood is critically important and tightly regulated because many proteins only function in a narrow pH range. In human blood, for example, pH is held between 7.36 and 7.42. This nearly constant blood pH is maintained by *buffers*. We discuss buffers more carefully later in this chapter, but for now know that a buffer is a chemical system that resists pH changes by neutralizing added acid or base. An important buffer in blood is a mixture of carbonic acid ( $\text{H}_2\text{CO}_3$ ) and the bicarbonate ion ( $\text{HCO}_3^-$ ). The carbonic acid neutralizes added base:



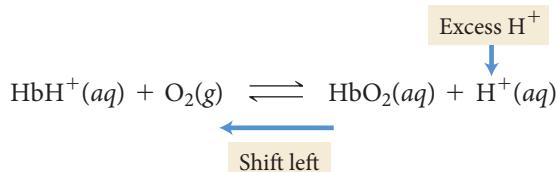
The bicarbonate ion neutralizes added acid:



In this way, the carbonic acid and bicarbonate ion buffering system keeps blood pH nearly constant.

When the glycolic acid generated by antifreeze consumption first enters the bloodstream, the acid's tendency to lower blood pH is countered by the buffering action of the bicarbonate ion. However, if the quantities of consumed antifreeze are large enough, the glycolic acid overwhelms the capacity of the buffer (we discuss buffer capacity in Section 16.3), causing blood pH to drop to dangerously low levels.

Low blood pH results in *acidosis*, a condition in which the acid affects the equilibrium between hemoglobin (Hb) and oxygen:



The excess acid causes the equilibrium to shift to the left, reducing the blood's ability to carry oxygen. At this point, the cat or dog may begin hyperventilating in an effort to overcome the acidic blood's lowered oxygen-carrying capacity. If no treatment is administered, the animal will eventually go into a coma and die.

One treatment for ethylene glycol poisoning is the administration of ethyl alcohol (the alcohol found in alcoholic beverages). The two molecules are similar enough that the liver enzyme that catalyzes the metabolism of ethylene glycol also acts on ethyl alcohol, but the enzyme has a higher affinity for ethyl alcohol than for ethylene glycol. Consequently, the enzyme preferentially metabolizes ethyl alcohol, allowing the unmetabolized ethylene glycol to escape through the urine. If administered early, this treatment can save the life of a dog or cat that has consumed ethylene glycol.

## 16.2 Buffers: Solutions That Resist pH Change

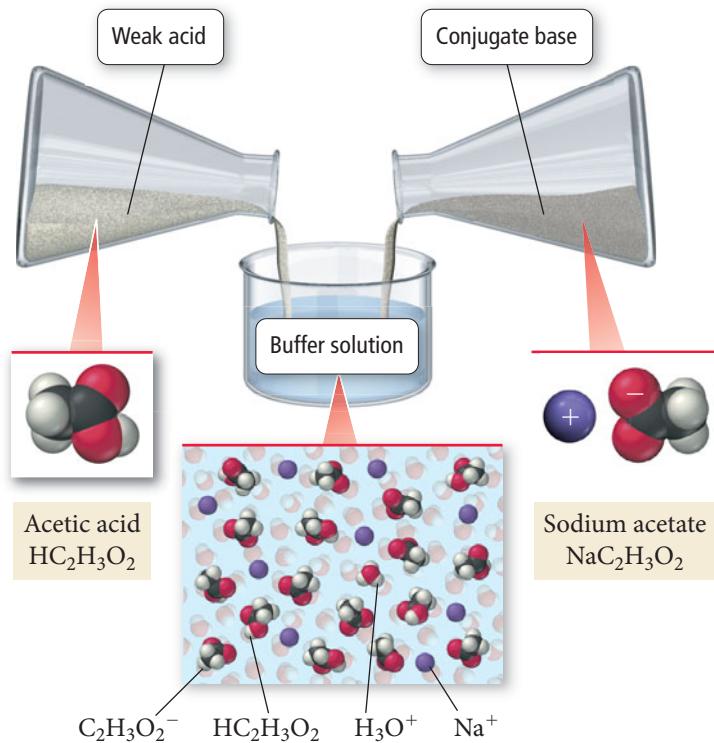
Most solutions significantly change pH when an acid or base is added to them. As we have just learned, however, a **buffer** resists pH change by neutralizing added acid or added base. A buffer contains either:

1. significant amounts of a weak acid and its conjugate base or
2. significant amounts of a weak base and its conjugate acid.

For example, the buffer in blood is composed of carbonic acid ( $\text{H}_2\text{CO}_3$ ) and its conjugate base, the bicarbonate ion ( $\text{HCO}_3^-$ ). When additional base is added to a buffer, the weak acid reacts with the base, neutralizing it. When additional acid is added to a buffer, the conjugate base reacts with the acid, neutralizing it. In this way, a buffer can maintain a nearly constant pH.

A weak acid by itself, even though it partially ionizes to form some of its conjugate base, does not contain sufficient base to be a buffer. Similarly, a weak base by itself, even though it partially ionizes water to form some of its conjugate acid, does not contain

### Formation of a Buffer



### ◀ FIGURE 16.1 A Buffer Solution

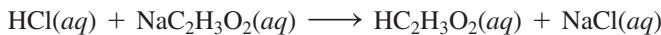
A buffer typically consists of a weak acid (which can neutralize added base) and its conjugate base (which can neutralize added acid).

sufficient acid to be a buffer. A *buffer must contain significant amounts of both a weak acid and its conjugate base (or vice versa)*. Consider the simple buffer made by dissolving acetic acid ( $\text{HC}_2\text{H}_3\text{O}_2$ ) and sodium acetate ( $\text{NaC}_2\text{H}_3\text{O}_2$ ) in water (Figure 16.1▲).

Suppose that we add a strong base, such as  $\text{NaOH}$ , to this solution. The acetic acid neutralizes the base:



As long as the amount of added  $\text{NaOH}$  is less than the amount of  $\text{HC}_2\text{H}_3\text{O}_2$  in solution, the buffer neutralizes the added  $\text{NaOH}$  and the resulting pH change is small. Suppose, on the other hand, that we add a strong acid, such as  $\text{HCl}$ , to the solution. In this case, the conjugate base,  $\text{NaC}_2\text{H}_3\text{O}_2$ , neutralizes the added  $\text{HCl}$ :



As long as the amount of added  $\text{HCl}$  is less than the amount of  $\text{NaC}_2\text{H}_3\text{O}_2$  in solution, the buffer neutralizes the added  $\text{HCl}$  and the resulting pH change is small.

#### **Summarizing Buffer Characteristics:**

- ▶ Buffers resist pH change.
- ▶ A buffer contains significant amounts of either 1) a weak acid and its conjugate base, or 2) a weak base and its conjugate acid.
- ▶ The weak acid neutralizes added base.
- ▶ The base neutralizes added acid.

### Conceptual Connection 16.1 Buffers

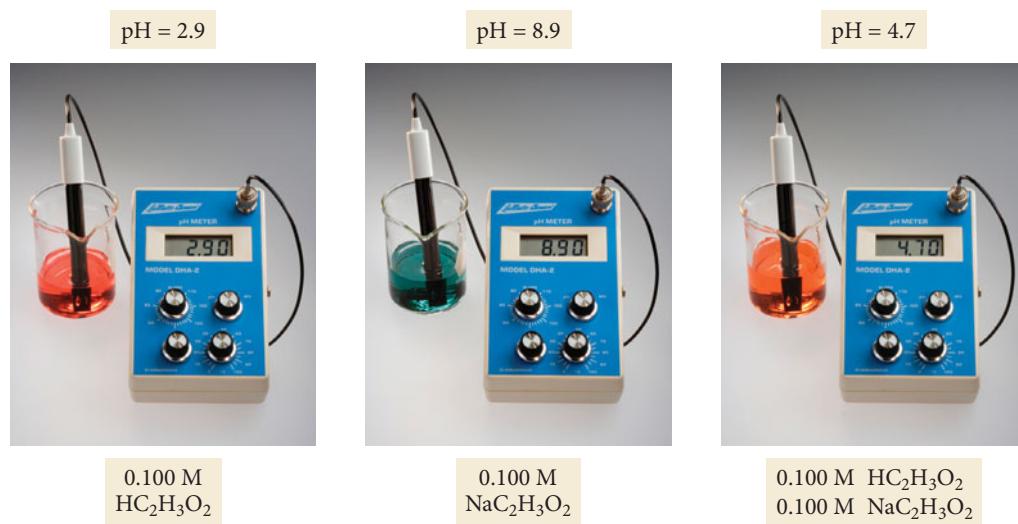
Which solution is a buffer?

- a solution that is 0.100 M in  $\text{HNO}_2$  and 0.100 M in  $\text{HCl}$
- a solution that is 0.100 M in  $\text{HNO}_3$  and 0.100 M in  $\text{NaNO}_3$
- a solution that is 0.100 M in  $\text{HNO}_2$  and 0.100 M in  $\text{NaCl}$
- a solution that is 0.100 M in  $\text{HNO}_2$  and 0.100 M in  $\text{NaNO}_2$

$\text{C}_2\text{H}_3\text{O}_2^-$  is the conjugate base of  $\text{HC}_2\text{H}_3\text{O}_2$ .

► **FIGURE 16.2** The Common Ion

**Effect** The pH of a 0.100 M acetic acid solution is 2.9. The pH of a 0.100 M sodium acetate solution is 8.9. The pH of a solution that is 0.100 M in acetic acid and 0.100 M in sodium acetate is 4.7.



## Calculating the pH of a Buffer Solution

In Chapter 15, we learned how to calculate the pH of a solution containing either a weak acid or its conjugate base, but not both. How do we calculate the pH of a buffer—a solution containing both? Consider a solution that initially contains HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> and NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>, each at a concentration of 0.100 M. The acetic acid ionizes according to the reaction:



Initial concentration: 0.100 M 0.100 M

However, the ionization of HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> in the solution is suppressed compared to its ionization in a solution that does not initially contain any C<sub>2</sub>H<sub>3</sub>O<sub>2</sub><sup>-</sup>, because the presence of C<sub>2</sub>H<sub>3</sub>O<sub>2</sub><sup>-</sup> shifts the equilibrium to the left (as we would expect from Le Châtelier's principle). In other words, the presence of the C<sub>2</sub>H<sub>3</sub>O<sub>2</sub><sup>-</sup>(aq) ion causes the acid to ionize even less than it normally would (Figure 16.2 ▲), resulting in a less acidic solution (higher pH). This effect is known as the **common ion effect**, so named because the solution contains two substances (HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> and NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>) that share a common ion (C<sub>2</sub>H<sub>3</sub>O<sub>2</sub><sup>-</sup>). To find the pH of a buffer solution containing common ions, we work an equilibrium problem in which the initial concentrations include both the acid and its conjugate base, as shown in Example 16.1.

### EXAMPLE 16.1 Calculating the pH of a Buffer Solution

Calculate the pH of a buffer solution that is 0.100 M in HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> and 0.100 M in NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>.

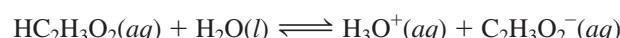
#### SOLUTION

- Write the balanced equation for the ionization of the acid and use it as a guide to prepare an ICE table showing the given concentrations of the acid and its conjugate base as the initial concentrations. Leave room in the table for the changes in concentrations and for the equilibrium concentrations.



|         | [HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ] | [H <sub>3</sub> O <sup>+</sup> ] | [C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup> ] |
|---------|--|----------------------------------|--|
| Initial | 0.100  | ≈ 0.00                           | 0.100  |
| Change  |  |                                  |  |
| Equil   |  |                                  |  |

- Represent the change in the concentration of H<sub>3</sub>O<sup>+</sup> with the variable *x*. Express the changes in the concentrations of the other reactants and products in terms of *x*.



|         | [HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ] | [H <sub>3</sub> O <sup>+</sup> ] | [C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup> ] |
|---------|--|----------------------------------|--|
| Initial | 0.100  | ≈ 0.00                           | 0.100  |
| Change  | - <i>x</i>                                       | + <i>x</i>                       | + <i>x</i>   |
| Equil   |  |                                  |  |

- 3.** Sum each column to determine the equilibrium concentrations in terms of the initial concentrations and the variable  $x$ .

| $\text{HC}_2\text{H}_3\text{O}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{C}_2\text{H}_3\text{O}_2^-(aq)$ |                                     |                          |                                      |
|--|-------------------------------------|--------------------------|--------------------------------------|
|  | $[\text{HC}_2\text{H}_3\text{O}_2]$ | $[\text{H}_3\text{O}^+]$ | $[\text{C}_2\text{H}_3\text{O}_2^-]$ |
| Initial  | 0.100                               | $\approx 0.00$           | 0.100                                |
| Change   | $-x$                                | $+x$                     | $+x$                                 |
| Equil  | $0.100 - x$                         | $x$                      | $0.100 + x$                          |

- 4.** Substitute the expressions for the equilibrium concentrations (from step 3) into the expression for the acid ionization constant.

In most cases, you can make the approximation that  $x$  is small. (See Sections 14.8 and 15.6 to review the  $x$  is small approximation.)

Substitute the value of the acid ionization constant (from Table 15.5) into the  $K_a$  expression and solve for  $x$ .

Confirm that  $x$  is small by calculating the ratio of  $x$  and the number it was subtracted from in the approximation. The ratio should be less than 0.05 (or 5%).

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}$$

$$= \frac{x(0.100 + x)}{0.100 - x} \quad (\text{ }x \text{ is small})$$

$$1.8 \times 10^{-5} = \frac{x(0.100)}{0.100}$$

$$x = 1.8 \times 10^{-5}$$

$$\frac{1.8 \times 10^{-5}}{0.100} \times 100\% = 0.018\%$$

Therefore the approximation is valid.

- 5.** Determine the  $\text{H}_3\text{O}^+$  concentration from the calculated value of  $x$  and substitute into the pH equation to find pH.

$$[\text{H}_3\text{O}^+] = x = 1.8 \times 10^{-5} \text{ M}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

$$= -\log(1.8 \times 10^{-5})$$

$$= 4.74$$

### FOR PRACTICE 16.1

Calculate the pH of a buffer solution that is 0.200 M in  $\text{HC}_2\text{H}_3\text{O}_2$  and 0.100 M in  $\text{NaC}_2\text{H}_3\text{O}_2$ .

### FOR MORE PRACTICE 16.1

Calculate the pH of the buffer that results from mixing 60.0 mL of 0.250 M  $\text{HCHO}_2$  and 15.0 mL of 0.500 M  $\text{NaCHO}_2$ .

## The Henderson-Hasselbalch Equation

We can derive an equation that relates the pH of a buffer solution to the initial concentration of the buffer components, thus simplifying the calculation of the pH of a buffer solution. Consider a buffer containing the generic weak acid HA and its conjugate base  $\text{A}^-$ . The acid ionizes as follows:



We derive an expression for the concentration of  $\text{H}_3\text{O}^+$  from the acid ionization equilibrium expression by solving the expression for  $[\text{H}_3\text{O}^+]$ :

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]} \quad [16.1]$$

If we make the same  $x$  is small approximation that we make for weak acid or weak base equilibrium problems, we can consider the equilibrium concentrations of HA and  $\text{A}^-$  to be essentially identical to the initial concentrations of HA and  $\text{A}^-$  (see step 4 of Example 16.1). Therefore, to determine  $[\text{H}_3\text{O}^+]$  for any buffer solution, we multiply  $K_a$  by the ratio of the

Recall that the variable  $x$  in a weak acid equilibrium problem represents the change in the initial acid concentration. The  $x$  is small approximation is valid because so little of the weak acid ionizes compared to its initial concentration.

concentrations of the acid and the conjugate base. To find the  $[H_3O^+]$  of the buffer in Example 16.1 (a solution that is 0.100 M in  $HC_2H_3O_2$  and 0.100 M in  $NaC_2H_3O_2$ ), we substitute the concentrations of  $HC_2H_3O_2$  and  $C_2H_3O_2^-$  into Equation 16.1:

$$\begin{aligned}[H_3O^+] &= K_a \frac{[HC_2H_3O_2]}{[C_2H_3O_2^-]} \\ &= K_a \frac{0.100}{0.100} \\ &= K_a\end{aligned}$$

In this buffer solution, as in any in which the acid and conjugate base concentrations are equal,  $[H_3O^+]$  is equal to  $K_a$ .

We can derive an equation for the pH of a buffer by taking the negative logarithm of both sides of Equation 16.1:

$$[H_3O^+] = K_a \frac{[HA]}{[A^-]}$$

$$-\log[H_3O^+] = -\log(K_a \frac{[HA]}{[A^-]})$$

$$-\log[H_3O^+] = -\log K_a - \log \frac{[HA]}{[A^-]} \quad [16.2]$$

We can rearrange Equation 16.2 to get:

$$-\log[H_3O^+] = -\log K_a + \log \frac{[A^-]}{[HA]}$$

Since  $pH = -\log[H_3O^+]$  and since  $pK_a = -\log K_a$ , we obtain the result:

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

Since  $A^-$  is a weak base and HA is a weak acid, we can generalize the equation:

$$pH = pK_a + \log \frac{[\text{base}]}{[\text{acid}]} \quad [16.3]$$

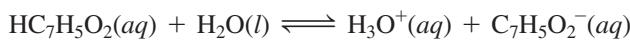
where the base is the conjugate base of the acid or the acid is the conjugate acid of the base. This equation, known as the **Henderson–Hasselbalch equation**, allows us to quickly calculate the pH of a buffer solution from the initial concentrations of the buffer components *as long as the x is small approximation is valid*. In Example 16.2, we show how to find the pH of a buffer in two ways: in the left column we solve a common ion effect equilibrium problem using a method similar to the one we used in Example 16.1; in the right column we use the Henderson–Hasselbalch equation.

### EXAMPLE 16.2 Calculating the pH of a Buffer Solution as an Equilibrium Problem and with the Henderson–Hasselbalch Equation

Calculate the pH of a buffer solution that is 0.050 M in benzoic acid ( $HC_7H_5O_2$ ) and 0.150 M in sodium benzoate ( $NaC_7H_5O_2$ ). For benzoic acid,  $K_a = 6.5 \times 10^{-5}$ .

#### SOLUTION

| Equilibrium Approach  | Henderson–Hasselbalch Approach  |
|---|---|
| Write the balanced equation for the ionization of the acid and use it as a guide to prepare an ICE table. | To find the pH of this solution, determine which component is the acid and which is the base and substitute their concentrations into the Henderson–Hasselbalch equation to calculate pH. |



|         | [HC <sub>7</sub> H <sub>5</sub> O <sub>2</sub> ] | [H <sub>3</sub> O <sup>+</sup> ] | [C <sub>7</sub> H <sub>5</sub> O <sub>2</sub> <sup>-</sup> ] |
|---------|--|----------------------------------|--|
| Initial | 0.050  | ≈ 0.00                           | 0.150  |
| Change  | -x   | +x                               | +x   |
| Equil   | 0.050 - x  | x                                | 0.150 + x  |

Substitute the expressions for the equilibrium concentrations into the expression for the acid ionization constant. Make the *x is small* approximation and solve for *x*.

$$\begin{aligned} K_a &= \frac{[\text{H}_3\text{O}^+][\text{C}_7\text{H}_5\text{O}_2^-]}{[\text{HC}_7\text{H}_5\text{O}_2]} \\ &= \frac{x(0.150 + x)}{0.050 - x} \quad (x \text{ is small}) \\ 6.5 \times 10^{-5} &= \frac{x(0.150)}{0.050} \\ x &= 2.2 \times 10^{-5} \end{aligned}$$

Since [H<sub>3</sub>O<sup>+</sup>] = *x*, we calculate pH as follows:

$$\begin{aligned} \text{pH} &= -\log[\text{H}_3\text{O}^+] \\ &= -\log(2.2 \times 10^{-5}) \\ &= 4.66 \end{aligned}$$

Confirm that the *x is small* approximation is valid by calculating the ratio of *x* to the number it was subtracted from in the approximation. The ratio should be less than 0.05 (or 5%). (See Sections 14.8 and 15.6 to review the *x is small* approximation.)

$$\frac{2.2 \times 10^{-5}}{0.050} \times 100\% = 0.044\%$$

The approximation is valid.

HC<sub>7</sub>H<sub>5</sub>O<sub>2</sub> is the acid and NaC<sub>7</sub>H<sub>5</sub>O<sub>2</sub> is the base. Therefore, we calculate the pH as follows:

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} \\ &= -\log(6.5 \times 10^{-5}) + \log \frac{0.150}{0.050} \\ &= 4.187 + 0.477 \\ &= 4.66 \end{aligned}$$

### FOR PRACTICE 16.2

Calculate the pH of a buffer solution that is 0.250 M in HCN and 0.170 M in KCN.

For HCN,  $K_a = 4.9 \times 10^{-10}$  ( $\text{p}K_a = 9.31$ ). Use both the equilibrium approach and the Henderson–Hasselbalch approach.

Confirm that the *x is small* approximation is valid by calculating the [H<sub>3</sub>O<sup>+</sup>] from the pH. Since [H<sub>3</sub>O<sup>+</sup>] is formed by ionization of the acid, the calculated [H<sub>3</sub>O<sup>+</sup>] has to be less than 0.05 (or 5%) of the initial concentration of the acid in order for the *x is small* approximation to be valid.

$$\begin{aligned} \text{pH} &= 4.66 = -\log [\text{H}_3\text{O}^+] \\ [\text{H}_3\text{O}^+] &= 10^{-4.66} = 2.2 \times 10^{-5} \text{ M} \\ \frac{2.2 \times 10^{-5}}{0.050} \times 100\% &= 0.044\% \end{aligned}$$

The approximation is valid.

You may be wondering how to decide whether to use the equilibrium approach or the Henderson–Hasselbalch equation when calculating the pH of buffer solutions. The answer depends on the specific problem. In cases where you can make the *x is small* approximation, the Henderson–Hasselbalch equation is adequate. However, as you can see from Example 16.2, checking the *x is small* approximation is not as convenient with the Henderson–Hasselbalch equation (because the approximation is implicit). Thus, the equilibrium approach, although lengthier, gives you a better sense of the important quantities in the problem and the nature of the approximation. When first working buffer problems, use the equilibrium approach until you get a good sense for when the *x is small* approximation is adequate. Then, you can switch to the more streamlined approach in cases where the approximation applies (and only in those cases). In general, remember that the *x is small* approximation applies to problems in which both of the following are true: (a) the initial concentrations of acids (and/or bases) are not too dilute; and (b) the equilibrium constant is fairly small. Although the exact values depend on the details of

the problem, for many buffer problems this means that the initial concentrations of acids and conjugate bases should be at least  $10^2$ – $10^3$  times greater than the equilibrium constant (depending on the required accuracy).

## Conceptual Connection 16.2 pH of Buffer Solutions

A buffer contains the weak acid HA and its conjugate base  $\text{A}^-$ . The weak acid has a  $pK_a$  of 4.82 and the buffer has a pH of 4.25. Which statement is true of the relative concentrations of the weak acid and conjugate base in the buffer?

- (a)  $[\text{HA}] > [\text{A}^-]$       (b)  $[\text{HA}] < [\text{A}^-]$       (c)  $[\text{HA}] = [\text{A}^-]$

Which buffer component would you add to change the pH of the buffer to 4.72?

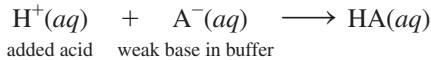
### Calculating pH Changes in a Buffer Solution

When we add acid or base to a buffer, the buffer resists a pH change. Nonetheless, the pH does change by a small amount. Calculating the pH change requires breaking up the problem into two parts:

- The stoichiometry calculation** in which we calculate how the addition changes the relative amounts of acid and conjugate base.
- The equilibrium calculation** in which we calculate the pH based on the new amounts of acid and conjugate base.

We demonstrate this calculation with a 1.0 L buffer solution that is 0.100 M in the generic acid HA and 0.100 M in its conjugate base  $\text{A}^-$ . Since the concentrations of the weak acid and the conjugate base are equal, the pH of the buffer is equal to  $pK_a$ . Let's calculate the pH of the solution after we add 0.025 mol of strong acid ( $\text{H}^+$ ) (assuming that the change in volume from adding the acid is negligible).

**The Stoichiometry Calculation** As the added acid is neutralized, it converts a stoichiometric amount of the base into its conjugate acid through the neutralization reaction (Figure 16.3a on p. 762):



Neutralizing 0.025 mol of the strong acid ( $\text{H}^+$ ) requires 0.025 mol of the weak base ( $\text{A}^-$ ). Consequently, the amount of  $\text{A}^-$  decreases by 0.025 mol and the amount of HA increases by 0.025 mol (because of the 1:1:1 stoichiometry of the neutralization reaction). We can track these changes in tabular form as follows:

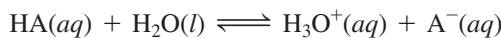
|                        | $\text{H}^+(\text{aq})$    | + | $\text{A}^-(\text{aq})$ | $\longrightarrow$ | $\text{HA}(\text{aq})$ |
|------------------------|----------------------------|---|-------------------------|-------------------|------------------------|
| <b>Before addition</b> | $\approx 0.00 \text{ mol}$ |   | $0.100 \text{ mol}$     |                   | $0.100 \text{ mol}$    |
| <b>Addition</b>        | $+ 0.025 \text{ mol}$      |   | $-$                     |                   | $-$                    |
| <b>After addition</b>  | $\approx 0.00 \text{ mol}$ |   | $0.075 \text{ mol}$     |                   | $0.125 \text{ mol}$    |

Notice that this table is not an ICE table. This table simply tracks the stoichiometric changes that occur during the neutralization of the added acid. We write  $\approx 0.00 \text{ mol}$  for the amount of  $\text{H}^+$  because the amount is so small compared to the amounts of  $\text{A}^-$  and HA. (Remember that weak acids ionize only to a small extent and that the presence of the common ion further suppresses the ionization.) The amount of  $\text{H}^+$ , of course, is not exactly zero, as we can see by completing the equilibrium part of the calculation.

**The Equilibrium Calculation** We have just seen that adding a small amount of acid to a buffer is equivalent to changing the initial concentrations of the acid and conjugate base present in the buffer (in this case, since the volume is 1.0 L,  $[\text{HA}]$  increased from 0.100 M to 0.125 M and  $[\text{A}^-]$  decreased from 0.100 M to 0.075 M). Knowing these new initial concentrations, we can calculate the new pH in the same way that we calculate the pH of any buffer: either by working a full equilibrium problem or by using the Henderson–Hasselbalch equation (see Examples 16.1 and 16.2). In this case, we work

It is best to work with amounts in moles instead of concentrations when tracking these changes, as explained later.

the full equilibrium problem. We begin by writing the balanced equation for the ionization of the acid and using it as a guide to prepare an ICE table. The initial concentrations for the ICE table are those that we calculated in the stoichiometry part of the calculation:



|         | [HA]      | [H <sub>3</sub> O <sup>+</sup> ] | [A <sup>-</sup> ] |                                |
|---------|-----------|----------------------------------|-------------------|--------------------------------|
| Initial | 0.125     | ≈ 0.00                           | 0.075             | From stoichiometry calculation |
| Change  | -x        | +x                               | +x                |                                |
| Equil   | 0.125 - x | x                                | 0.075 + x         |                                |

We then substitute the expressions for the equilibrium concentrations into the expression for the acid ionization constant. As long as  $K_a$  is sufficiently small relative to the initial concentrations, we can make the  $x$  is *small* approximation and solve for  $x$ , which is equal to [H<sub>3</sub>O<sup>+</sup>].

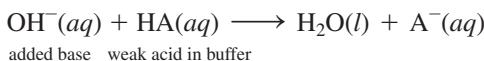
$$\begin{aligned} K_a &= \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \\ &= \frac{x(0.075 + x)}{0.125 - x} \quad (x \text{ is small}) \\ K_a &= \frac{x(0.075)}{0.125} \\ x &= [\text{H}_3\text{O}^+] = K_a \frac{0.125}{0.075} \end{aligned}$$

Once we calculate [H<sub>3</sub>O<sup>+</sup>], we can calculate the pH with the equation  $\text{pH} = -\log[\text{H}_3\text{O}^+]$ .

Notice that, since the expression for  $x$  contains a *ratio* of concentrations [HA]/[A<sup>-</sup>], the *amounts of acid and base in moles* may be substituted in place of concentration because, in a single buffer solution, the volume is the same for both the acid and the base. Therefore, the volumes cancel:

$$[\text{HA}]/[\text{A}^-] = \frac{\frac{n_{\text{HA}}}{V}}{\frac{n_{\text{A}^-}}{V}} = n_{\text{HA}}/n_{\text{A}^-}$$

The effect of adding a small amount of strong base to the buffer is exactly the opposite of adding acid. The added base converts a stoichiometric amount of the acid into its conjugate base through the neutralization reaction (Figure 16.3b ▶):



If we add 0.025 mol of OH<sup>-</sup>, the amount of A<sup>-</sup> goes *up* by 0.025 mol and the amount of HA goes *down* by 0.025 mol as shown in the following table:

|                        | $\text{OH}^-(aq)$ | + | $\text{HA}(aq)$ | → | $\text{H}_2\text{O}(l)$ | + | $\text{A}^-(aq)$ |  |
|------------------------|-------------------|---|-----------------|---|-------------------------|---|------------------|--|
| <b>Before addition</b> | ≈ 0.00 mol        |   | 0.100 mol       |   |                         |   | 0.100 mol        |  |
| <b>Addition</b>        | +0.025 mol        |   | —               |   |                         |   | —                |  |
| <b>After addition</b>  | ≈ 0.00 mol        |   | 0.075 mol       |   |                         |   | 0.125 mol        |  |

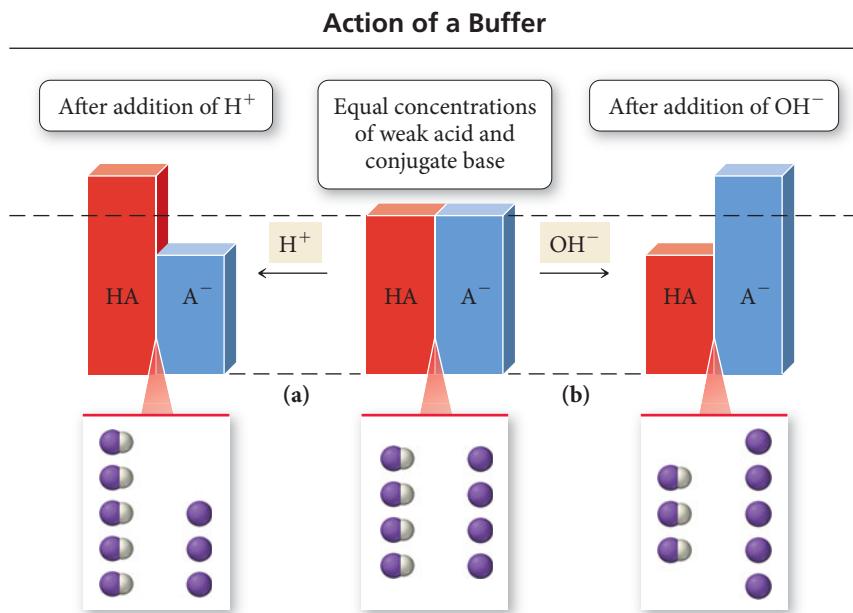
**When you calculate the pH of a buffer after adding small amounts of acid or base, remember the following:**

- ▶ Adding a small amount of strong acid to a buffer converts a stoichiometric amount of the base to the conjugate acid and decreases the pH of the buffer (adding acid decreases pH just as we would expect).
- ▶ Adding a small amount of strong base to a buffer converts a stoichiometric amount of the acid to the conjugate base and increases the pH of the buffer (adding base increases the pH just as we would expect).

The easiest way to remember these changes is relatively simple: adding acid creates more acid; adding base creates more base.

► **FIGURE 16.3 Buffering Action**

- (a) When an acid is added to a buffer, a stoichiometric amount of the weak base is converted to the conjugate acid.  
 (b) When a base is added to a buffer, a stoichiometric amount of the weak acid is converted to the conjugate base.



Example 16.3 and the For Practice Problems that follow it involve calculating pH changes in a buffer solution after small amounts of strong acid or strong base are added. As we have seen, these problems generally have two parts:

- Part I. Stoichiometry—use the stoichiometry of the neutralization equation to calculate the changes in the amounts (in moles) of the buffer components upon addition of the acid or base.
- Part II. Equilibrium—use the new amounts of buffer components to work an equilibrium problem to find pH. (For most buffers, this can also be done with the Henderson–Hasselbalch equation.)

**EXAMPLE 16.3 Calculating the pH Change in a Buffer Solution after the Addition of a Small Amount of Strong Acid or Base**

A 1.0 L buffer solution contains 0.100 mol  $\text{HC}_2\text{H}_3\text{O}_2$  and 0.100 mol  $\text{NaC}_2\text{H}_3\text{O}_2$ . The value of  $K_a$  for  $\text{HC}_2\text{H}_3\text{O}_2$  is  $1.8 \times 10^{-5}$ . Because the initial amounts of acid and conjugate base are equal, the pH of the buffer is equal to  $pK_a = -\log(1.8 \times 10^{-5}) = 4.74$ . Calculate the new pH after adding 0.010 mol of solid NaOH to the buffer. For comparison, calculate the pH after adding 0.010 mol of solid NaOH to 1.0 L of pure water. (Ignore any small changes in volume that might occur upon addition of the base.)

**SOLUTION**

Part I: Stoichiometry. The addition of the base converts a stoichiometric amount of acid to the conjugate base (adding base creates more base). Write an equation showing the neutralization reaction and then set up a table to track the changes.

| $\text{OH}^-(aq) + \text{HC}_2\text{H}_3\text{O}_2(aq) \longrightarrow \text{H}_2\text{O}(l) + \text{C}_2\text{H}_3\text{O}_2^-(aq)$ |            |           |           |
|--|------------|-----------|-----------|
| Before addition  | ≈ 0.00 mol | 0.100 mol | 0.100 mol |
| Addition   | 0.010 mol  | —         | —         |
| After addition   | ≈ 0.00 mol | 0.090 mol | 0.110 mol |

Part II: Equilibrium. Write the balanced equation for the ionization of the acid and use it as a guide to prepare an ICE table. Use the amounts of acid and conjugate base from part I as the initial amounts of acid and conjugate base in the ICE table.

| $\text{HC}_2\text{H}_3\text{O}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{C}_2\text{H}_3\text{O}_2^-(aq)$ |                                     |                          |                                      |
|--|-------------------------------------|--------------------------|--------------------------------------|
|  | $[\text{HC}_2\text{H}_3\text{O}_2]$ | $[\text{H}_3\text{O}^+]$ | $[\text{C}_2\text{H}_3\text{O}_2^-]$ |
| Initial  | 0.090                               | ≈ 0.00                   | 0.110                                |
| Change   | -x                                  | +x                       | +x                                   |
| Equil  | 0.090 - x                           | x                        | 0.110 + x                            |

Substitute the expressions for the equilibrium concentrations of acid and conjugate base into the expression for the acid ionization constant. Make the  $x$  is small approximation and solve for  $x$ . Calculate the pH from the value of  $x$ , which is equal to  $[\text{H}_3\text{O}^+]$ .

$$\begin{aligned} K_a &= \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{H}_3\text{O}_-]}{[\text{HC}_2\text{H}_3\text{O}_2]} \\ &= \frac{x(0.110 + x)}{0.090 - x} \quad (\text{ }x \text{ is small}) \end{aligned}$$

$$1.8 \times 10^{-5} = \frac{x(0.110)}{0.090}$$

$$x = [\text{H}_3\text{O}^+] = 1.47 \times 10^{-5} \text{ M}$$

$$\begin{aligned} \text{pH} &= -\log[\text{H}_3\text{O}^+] \\ &= -\log(1.47 \times 10^{-5}) \\ &= 4.83 \end{aligned}$$

$$\frac{1.47 \times 10^{-5}}{0.090} \times 100\% = 0.016\%$$

The approximation is valid.

Confirm that the  $x$  is small approximation is valid by calculating the ratio of  $x$  to the smallest number it was subtracted from in the approximation. The ratio should be less than 0.05 (or 5%).

**Part II: Equilibrium Alternative (using the Henderson–Hasselbalch equation).** As long as the  $x$  is small approximation is valid, you can substitute the quantities of acid and conjugate base after the addition (from part I) into the Henderson–Hasselbalch equation and calculate the new pH.

The pH of 1.0 L of water after adding 0.010 mol of NaOH is calculated from the  $[\text{OH}^-]$ . For a strong base,  $[\text{OH}^-]$  is simply the number of moles of  $\text{OH}^-$  divided by the number of liters of solution.

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} \\ &= -\log(1.8 \times 10^{-5}) + \log \frac{0.110}{0.090} \\ &= 4.74 + 0.087 \\ &= 4.83 \end{aligned}$$

$$[\text{OH}^-] = \frac{0.010 \text{ mol}}{1.0 \text{ L}} = 0.010 \text{ M}$$

$$\begin{aligned} \text{pOH} &= -\log[\text{OH}^-] = -\log(0.010) \\ &= 2.00 \end{aligned}$$

$$\text{pOH} + \text{pH} = 14.00$$

$$\begin{aligned} \text{pH} &= 14.00 - \text{pOH} \\ &= 14.00 - 2.00 \\ &= 12.00 \end{aligned}$$

**CHECK** Notice that the buffer solution changed from pH = 4.74 to pH = 4.83 upon addition of the base (a small fraction of a single pH unit). In contrast, the pure water changed from pH = 7.00 to pH = 12.00, five whole pH units (a factor of  $10^5$ ). Notice also that even the buffer solution got slightly more basic upon addition of a base, as we would expect. To check your answer, always make sure the pH goes in the direction you expect: adding base should make the solution more basic (higher pH); adding acid should make the solution more acidic (lower pH).

### FOR PRACTICE 16.3

Calculate the pH of the solution in Example 16.3 upon addition of 0.015 mol of NaOH to the original buffer.

### FOR MORE PRACTICE 16.3

Calculate the pH of the solution in Example 16.3 upon addition of 10.0 mL of 1.00 M HCl to the original buffer in Example 16.3.

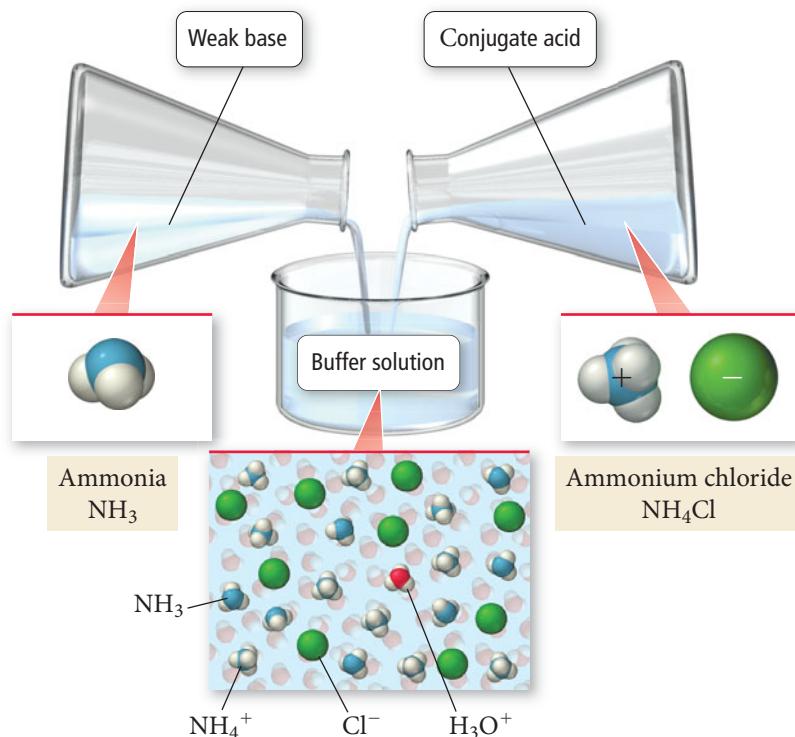
**Conceptual Connection 16.3**
**Adding Acid or Base to a Buffer**

A buffer contains equal amounts of a weak acid and its conjugate base and has a pH of 5.25. Which would be a reasonable value of buffer pH after the addition of a small amount of acid?

- (a) 4.15
- (b) 5.15
- (c) 5.35
- (d) 6.35

**Buffers Containing a Base and Its Conjugate Acid**

So far, we have seen examples of buffers composed of an acid and its conjugate base (where the conjugate base is an ion). A buffer can also be composed of a base and its conjugate acid (where the conjugate acid is an ion). For example, a solution containing significant amounts of both  $\text{NH}_3$  and  $\text{NH}_4\text{Cl}$  will act as a buffer (Figure 16.4 ▼). The  $\text{NH}_3$  is a weak base that neutralizes small amounts of added acid, and the  $\text{NH}_4^+$  ion is the conjugate acid that neutralizes small amounts of added base. We calculate the pH of a solution like this in the same way that we calculated the pH of a buffer containing a weak acid and its conjugate base. When using the Henderson–Hasselbalch equation, however, we must first calculate  $pK_a$  for the conjugate acid of the weak base. Recall from Section 15.8 that for a conjugate acid–base pair,  $K_a \times K_b = K_w$  and  $pK_a + pK_b = 14$ . Consequently, we can find  $pK_a$  of the conjugate acid by subtracting  $pK_b$  of the weak base from 14. Example 16.4 illustrates the procedure for calculating the pH of a buffer composed of a weak base and its conjugate acid.

**Formation of a Buffer**


**▲ FIGURE 16.4** Buffer Containing a Base A buffer can also consist of a weak base and its conjugate acid.

**EXAMPLE 16.4** Using the Henderson–Hasselbalch Equation to Calculate the pH of a Buffer Solution Composed of a Weak Base and Its Conjugate Acid

Use the Henderson–Hasselbalch equation to calculate the pH of a buffer solution that is 0.50 M in NH<sub>3</sub> and 0.20 M in NH<sub>4</sub>Cl. For ammonia, pK<sub>b</sub> = 4.75.

**SOLUTION**

Since K<sub>b</sub> for NH<sub>3</sub> ( $1.8 \times 10^{-5}$ ) is much smaller than the initial concentrations in this problem, you can use the Henderson–Hasselbalch equation to calculate the pH of the buffer. First calculate pK<sub>a</sub> from pK<sub>b</sub>.

$$\begin{aligned} pK_a + pK_b &= 14 \\ pK_a &= 14 - pK_b \\ &= 14 - 4.75 \\ &= 9.25 \end{aligned}$$

Then substitute the given quantities into the Henderson–Hasselbalch equation and calculate pH.

$$\begin{aligned} \text{pH} &= pK_a + \log \frac{[\text{base}]}{[\text{acid}]} \\ &= 9.25 + \log \frac{0.50}{0.20} \\ &= 9.25 + 0.40 \\ &= 9.65 \end{aligned}$$

**FOR PRACTICE 16.4**

Calculate the pH of 1.0 L of the solution in Example 16.4 upon addition of 0.010 mol of solid NaOH to the original buffer solution.

**FOR MORE PRACTICE 16.4**

Calculate the pH of 1.0 L of the solution in Example 16.4 upon addition of 30.0 mL of 1.0 M HCl to the original buffer solution.

## 16.3 Buffer Effectiveness: Buffer Range and Buffer Capacity

An effective buffer neutralizes small to moderate amounts of added acid or base. Recall from the opening section of this chapter, however, that a buffer can be destroyed by the addition of too much acid or too much base. What factors influence the effectiveness of a buffer? In this section, we examine two such factors: *the relative amounts of the acid and conjugate base and the absolute concentrations of the acid and conjugate base*. We then define the *capacity of a buffer* (how much added acid or base it can effectively neutralize) and the *range of a buffer* (the pH range over which a particular acid and its conjugate base can be effective).

### Relative Amounts of Acid and Base

A buffer is most effective (most resistant to pH changes) when the concentrations of acid and conjugate base are equal. Let's explore this idea by considering the behavior of a generic buffer composed of HA and A<sup>-</sup> for which pK<sub>a</sub> = 5.00 and calculating the percent change in pH upon addition of 0.010 mol of NaOH for two different 1.0-liter solutions of this buffer system. Both solutions have 0.20 mol of *total* acid and conjugate base. However, solution I has equal amounts of acid and conjugate base (0.10 mol of each), while solution II has much more acid than conjugate base (0.18 mol HA and 0.020 mol A<sup>-</sup>). We can calculate the initial pH values of each solution using the Henderson–Hasselbalch equation. Solution I has an initial pH of 5.00 and solution II has an initial pH of 4.05.

**Solution I: 0.10 mol HA and 0.10 mol A<sup>-</sup>; initial pH = 5.00**

| $\text{OH}^-(aq) + \text{HA}(aq) \longrightarrow \text{H}_2\text{O}(l) + \text{A}^-(aq)$ |            |           |
|--|------------|-----------|
| <b>Before addition</b>   | ≈ 0.00 mol | 0.100 mol |
| <b>Addition</b>  | 0.010 mol  | —         |
| <b>After addition</b>  | ≈ 0.00 mol | 0.090 mol |
|  |            | 0.110 mol |

$$\begin{aligned}\text{pH} &= \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} \\ &= 5.00 + \log \frac{0.110}{0.090} \\ &= 5.09 \\ \% \text{ change} &= \frac{5.09 - 5.00}{5.00} \times 100\% \\ &= 1.8\%\end{aligned}$$

**Solution II: 0.18 mol HA and 0.020 mol A<sup>-</sup>; initial pH = 4.05**

| $\text{OH}^-(aq) + \text{HA}(aq) \longrightarrow \text{H}_2\text{O}(l) + \text{A}^-(aq)$ |            |           |
|--|------------|-----------|
| <b>Before addition</b>   | ≈ 0.00 mol | 0.18 mol  |
| <b>Addition</b>  | 0.010 mol  | —         |
| <b>After addition</b>  | ≈ 0.00 mol | 0.17 mol  |
|  |            | 0.030 mol |

$$\begin{aligned}\text{pH} &= \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} \\ &= 5.00 + \log \frac{0.030}{0.17} \\ &= 4.25 \\ \% \text{ change} &= \frac{4.25 - 4.05}{4.05} \times 100\% \\ &= 5.0\%\end{aligned}$$

As you can see, the buffer with equal amounts of acid and conjugate base is more resistant to pH change and is therefore the more effective buffer. A buffer becomes less effective as the difference in the relative amounts of acid and conjugate base increases. As a guideline, we can say that an effective buffer must have a [base]/[acid] ratio in the range of 0.10 to 10. *In order for a buffer to be reasonably effective, the relative concentrations of acid and conjugate base should not differ by more than a factor of 10.*

**Absolute Concentrations of the Acid and Conjugate Base**

A buffer is most effective (most resistant to pH changes) when the concentrations of acid and conjugate base are high. Let's explore this idea by again considering a generic buffer composed of HA and A<sup>-</sup> and a pK<sub>a</sub> of 5.00 and calculating the percent change in pH upon addition of 0.010 mol of NaOH for two 1.0-liter solutions of this buffer system. In this case, both the acid and the base in solution I are ten times more concentrated than the acid and base in solution II. Both solutions have equal relative amounts of acid and conjugate base and therefore have the same initial pH of 5.00.

**Solution I: 0.50 mol HA and 0.50 mol A<sup>-</sup>; initial pH = 5.00      Solution II: 0.050 mol HA and 0.050 mol A<sup>-</sup>; initial pH = 5.00**

| $\text{OH}^-(aq) + \text{HA}(aq) \longrightarrow \text{H}_2\text{O}(l) + \text{A}^-(aq)$ |            |          |
|--|------------|----------|
| <b>Before addition</b>   | ≈ 0.00 mol | 0.50 mol |
| <b>Addition</b>  | 0.010 mol  | —        |
| <b>After addition</b>  | ≈ 0.00 mol | 0.49 mol |
|  |            | 0.51 mol |

$$\begin{aligned}\text{pH} &= \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} \\ &= 5.00 + \log \frac{0.51}{0.49} \\ &= 5.02 \\ \% \text{ change} &= \frac{5.02 - 5.00}{5.00} \times 100\% \\ &= 0.4\%\end{aligned}$$

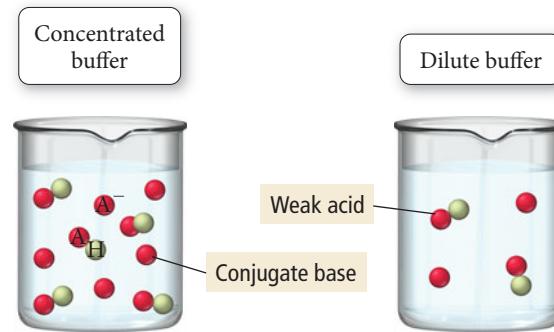
| $\text{OH}^-(aq) + \text{HA}(aq) \longrightarrow \text{H}_2\text{O}(l) + \text{A}^-(aq)$ |            |           |
|--|------------|-----------|
| <b>Before addition</b>   | ≈ 0.00 mol | 0.050 mol |
| <b>Addition</b>  | 0.010 mol  | —         |
| <b>After Addition</b>  | ≈ 0.00 mol | 0.040 mol |
|  |            | 0.060 mol |

$$\begin{aligned}\text{pH} &= \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} \\ &= 5.00 + \log \frac{0.060}{0.040} \\ &= 5.18 \\ \% \text{ change} &= \frac{5.18 - 5.00}{5.00} \times 100\% \\ &= 3.6\%\end{aligned}$$

As you can see, the buffer with greater amounts of acid and conjugate base is more resistant to pH changes and therefore the more effective buffer. The more dilute the buffer components, the less effective the buffer.

## Buffer Range

In light of the guideline that the relative concentrations of acid and conjugate base should not differ by more than a factor of 10 in order for a buffer to be reasonably effective, we can calculate the pH range over which a particular acid and its conjugate base make an effective buffer. Since the pH of a buffer is given by the Henderson–Hasselbalch equation, we can calculate the outermost points of the effective range as follows:



*Lowest pH* for effective buffer occurs when the base is one-tenth as concentrated as the acid.

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} \\ &= \text{p}K_a + \log 0.10 \\ &= \text{p}K_a - 1 \end{aligned}$$

*Highest pH* for effective buffer occurs when the base is ten times as concentrated as the acid.

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} \\ &= \text{p}K_a + \log 10 \\ &= \text{p}K_a + 1 \end{aligned}$$

▲ A concentrated buffer contains more of the weak acid and its conjugate base than a weak buffer does. It can therefore neutralize more added acid or added base.

The effective range for a buffering system is one pH unit on either side of  $\text{p}K_a$ . For example, we can use a weak acid with a  $\text{p}K_a$  of 5.0 (and its conjugate base) to prepare a buffer in the range of 4.0–6.0. We can adjust the relative amounts of acid and conjugate base to achieve any pH within this range. As we noted earlier, however, the buffer would be most effective at pH 5.0 because the buffer components would be exactly equal at that pH. Example 16.5 demonstrates how to pick an acid/conjugate base system for a buffer and how to calculate the relative amounts of acid and conjugate base required for a desired pH.

### EXAMPLE 16.5 Preparing a Buffer

Which acid would you choose to combine with its sodium salt to make a solution buffered at pH 4.25? For the best choice, calculate the ratio of the conjugate base to the acid required to attain the desired pH.

chlorous acid ( $\text{HClO}_2$ )     $\text{p}K_a = 1.95$     formic acid ( $\text{HCHO}_2$ )     $\text{p}K_a = 3.74$   
nitrous acid ( $\text{HNO}_2$ )     $\text{p}K_a = 3.34$     hypochlorous acid ( $\text{HClO}$ )     $\text{p}K_a = 7.54$

#### SOLUTION

The best choice is formic acid because its  $\text{p}K_a$  lies closest to the desired pH. You can calculate the ratio of conjugate base ( $\text{CHO}_2^-$ ) to acid ( $\text{HCHO}_2$ ) required by using the Henderson–Hasselbalch equation as follows:

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} \\ 4.25 &= 3.74 + \log \frac{[\text{base}]}{[\text{acid}]} \\ \log \frac{[\text{base}]}{[\text{acid}]} &= 4.25 - 3.74 \\ &= 0.51 \\ \frac{[\text{base}]}{[\text{acid}]} &= 10^{0.51} \\ &= 3.24 \end{aligned}$$

#### FOR PRACTICE 16.5

Which acid in Example 16.5 would you choose to create a buffer with  $\text{pH} = 7.35$ ? If you have 500.0 mL of a 0.10 M solution of the acid, what mass of the corresponding sodium salt of the conjugate base do you need to make the buffer?



## Chemistry and Medicine

### Buffer Effectiveness in Human Blood

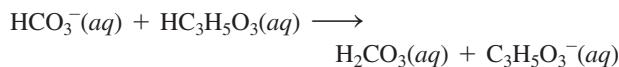
As we discussed in the opening section of this chapter, blood contains several buffering systems, the most important of which consists of carbonic acid and the carbonate ion. The concentrations of these buffer components in normal blood plasma are  $[HCO_3^-] = 0.024\text{ M}$  and  $[H_2CO_3] = 0.0012\text{ M}$ . The  $pK_a$  for carbonic acid at body temperature is 6.1. If we substitute these quantities into the Henderson–Hasselbalch equation, we can calculate the normal pH of blood:

$$\begin{aligned} \text{pH} &= pK_a + \log \frac{[\text{base}]}{[\text{acid}]} \\ &= 6.1 + \log \frac{[HCO_3^-]}{[H_2CO_3]} \\ &= 6.1 + \log \frac{0.024\text{ M}}{0.0012\text{ M}} \\ &= 7.4 \end{aligned}$$

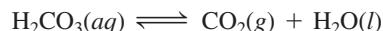
Normal blood has a pH of 7.4. Notice that the concentration of the bicarbonate ion is 20 times higher than the concentration of carbonic acid and the pH of the buffer is more than one pH unit away from  $pK_a$ . Why?

The higher bicarbonate ion concentration in blood makes the buffer capacity of blood greater for acid than for base, which is necessary because the products of metabolism that enter blood are mostly acidic. For example, when we exercise, our bodies produce lactic acid ( $HC_3H_5O_3$ ). The lactic acid enters the bloodstream and must be neutralized.

The bicarbonate ion neutralizes the lactic acid according to the equation:



An enzyme called carbonic anhydrase then catalyzes the conversion of carbonic acid into carbon dioxide and water:



We eliminate the carbon dioxide from our blood when we breathe. When large amounts of lactic acid are produced, we must breathe faster to keep up with the need to eliminate carbon dioxide. This is why we pant when we exert ourselves.

#### Question

A 70 kg person has a total blood volume of about 5.0 L. Given the carbonic acid and bicarbonate concentrations stated, what volume (in mL) of 6.0 M HCl can be neutralized by blood without the blood pH dropping below 7.0 (which would result in death)?

► Normal blood has a pH of 7.4.



### Buffer Capacity

**Buffer capacity** is the amount of acid or base that you can add to a buffer without causing a large change in pH. Given what we just learned about the absolute concentrations of acid and conjugate base in an effective buffer, we can conclude that the *buffer capacity increases with increasing absolute concentrations of the buffer components*. The more concentrated the weak acid and conjugate base that compose the buffer, the higher the buffer capacity. In addition, *overall buffer capacity increases as the relative concentrations of the buffer components become more similar to each other*. As the ratio of the buffer components gets closer to 1, the *overall capacity of the buffer (the ability to neutralize added acid and added base)* becomes greater. In some cases, however, a buffer that must neutralize primarily added acid (or primarily added base) may be overweighted in one of the buffer components, as shown in the *Chemistry and Medicine* box in this section.

#### Conceptual Connection 16.4 Buffer Capacity

A 1.0 L buffer solution is 0.10 M in HF and 0.050 M in NaF. Which action destroys the buffer?

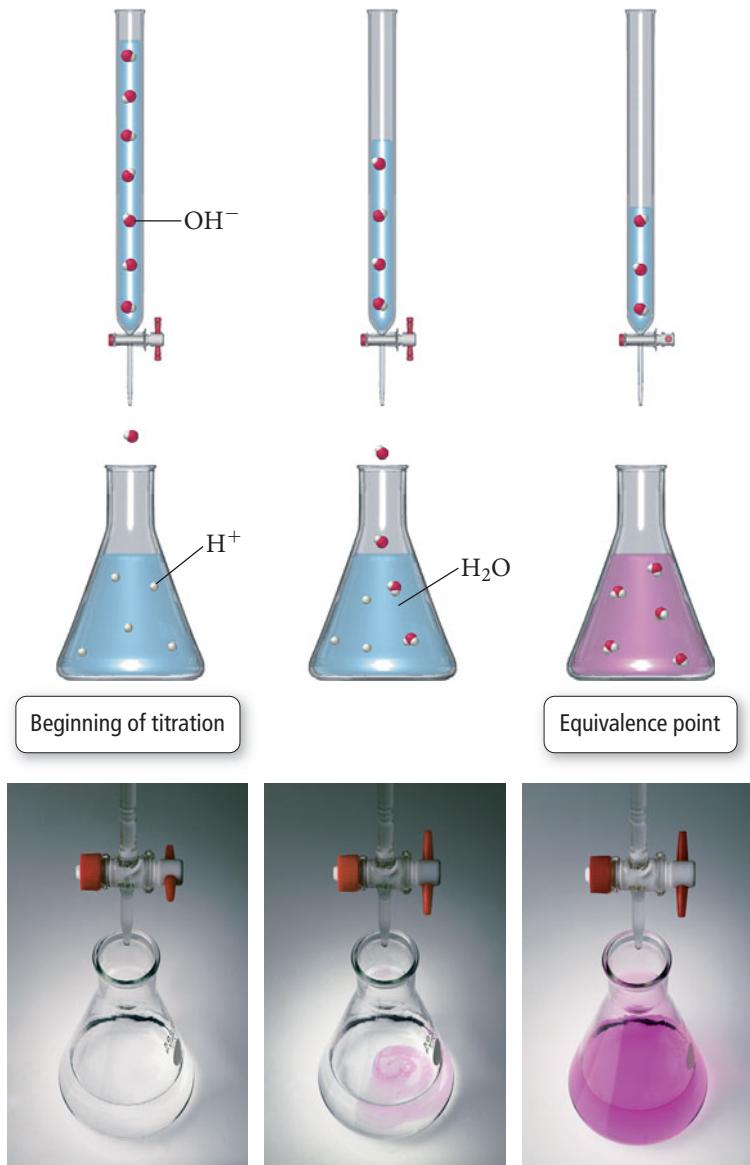
- (a) adding 0.050 mol of HCl
- (b) adding 0.050 mol of NaOH
- (c) adding 0.050 mol of NaF
- (d) none of the above

## 16.4 Titrations and pH Curves

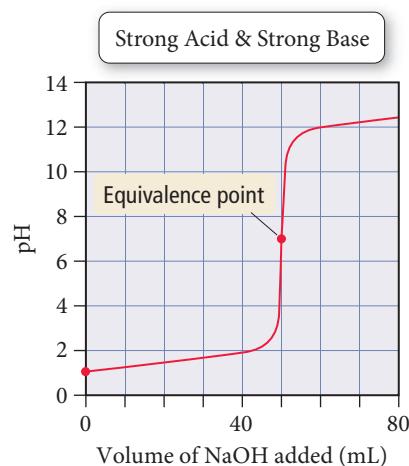
We first examined acid–base titrations in Section 4.8. In an **acid–base titration**, a basic (or acidic) solution of unknown concentration reacts with an acidic (or basic) solution of known concentration. The known solution is slowly added to the unknown one while the pH is monitored with either a pH meter or an **indicator** (a substance whose color depends on the pH). As the acid and base combine, they neutralize each other. At the **equivalence point**—the point in the titration when the number of moles of base is stoichiometrically equal to the number of moles of acid—the titration is complete. When the equivalence point is reached, neither reactant is in excess and the number of moles of the reactants are related by the reaction stoichiometry (Figure 16.5 ▶).

In this section, we examine acid–base titrations more closely, concentrating on the pH changes that occur during the titration. A plot of the pH of the solution during a titration is known as a *titration curve* or *pH curve*. Figure 16.6 ▶ is a pH curve for the titration of HCl with NaOH. Before any base is added to the solution, the pH is low (as expected for a solution of HCl). As the NaOH is added, the solution becomes less acidic because the NaOH begins to neutralize the HCl. The point of inflection in the middle of the curve is the equivalence point. Notice that the pH changes very quickly near the

The equivalence point is so named because the number of moles of acid and base are stoichiometrically equivalent at this point.



▲ FIGURE 16.5 Acid–Base Titration As  $\text{OH}^-$  is added in a titration, it neutralizes the  $\text{H}^+$ , forming water. At the equivalence point, the titration is complete.



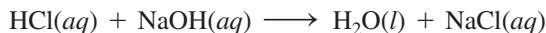
▲ FIGURE 16.6 Titration Curve: Strong Acid + Strong Base This curve represents the titration of 50.0 mL of 0.100 M HCl with 0.100 M NaOH.

equivalence point (small amounts of added base cause large changes in pH). Beyond the equivalence point, the solution is basic because the HCl has been completely neutralized and excess base is being added to the solution. The exact shape of the pH curve depends on several factors, including the strength of the acid or base being titrated. Let's consider several combinations individually.

## The Titration of a Strong Acid with a Strong Base

Consider the titration of 25.0 mL of 0.100 M HCl with 0.100 M NaOH. We begin by calculating the volume of base required to reach the equivalence point, and then the pH at several points during the titration.

**Volume of NaOH Required to Reach the Equivalence Point** During the titration, the added sodium hydroxide neutralizes the hydrochloric acid:



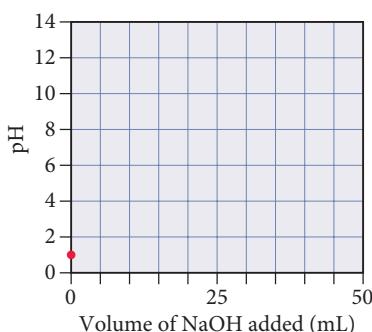
The equivalence point is reached when the number of moles of base added equals the number of moles of acid initially in solution. We calculate the amount of acid initially in solution from its volume and its concentration:

$$\text{Initial mol HCl} = 0.0250 \text{ L} \times \frac{0.100 \text{ mol}}{1 \text{ L}} = 0.00250 \text{ mol HCl}$$

The amount of NaOH that must be added is 0.00250 mol NaOH. We calculate the volume of NaOH required from its concentration:

$$\text{Volume NaOH solution} = 0.00250 \text{ mol} \times \frac{1 \text{ L}}{0.100 \text{ mol}} = 0.0250 \text{ L}$$

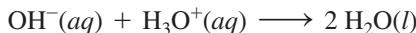
The equivalence point is reached when 25.0 mL of NaOH has been added. In this case, the concentrations of both solutions are identical, so the volume of NaOH solution required to reach the equivalence point is equal to the volume of the HCl solution that is being titrated.



**Initial pH (before Adding Any Base)** The initial pH of the solution is simply the pH of a 0.100 M HCl solution. Since HCl is a strong acid, the concentration of  $\text{H}_3\text{O}^+$  is also 0.100 M and the pH is 1.00:

$$\begin{aligned}\text{pH} &= -\log[\text{H}_3\text{O}^+] \\ &= -\log(0.100) \\ &= 1.00\end{aligned}$$

**pH after Adding 5.00 mL NaOH** As NaOH is added to the solution, it neutralizes  $\text{H}_3\text{O}^+$ :



We calculate the amount of  $\text{H}_3\text{O}^+$  at any given point (before the equivalence point) by using the reaction stoichiometry—1 mol of NaOH neutralizes 1 mol of  $\text{H}_3\text{O}^+$ . The initial number of moles of  $\text{H}_3\text{O}^+$  (as just calculated) is 0.00250 mol. We calculate the number of moles of NaOH added at 5.00 mL by multiplying the added volume (in L) by the concentration of the NaOH solution:

$$\text{mol NaOH added} = 0.00500 \text{ L} \times \frac{0.100 \text{ mol}}{1 \text{ L}} = 0.000500 \text{ mol NaOH}$$

The addition of  $\text{OH}^-$  causes the amount of  $\text{H}^+$  to decrease as shown in the following table:

|                        | $\text{OH}^-(aq)$          | $+ \text{H}_3\text{O}^+(aq) \longrightarrow 2 \text{H}_2\text{O}(l)$ |
|------------------------|----------------------------|--|
| <b>Before addition</b> | $\approx 0.00 \text{ mol}$ | 0.00250 mol  |
| <b>Addition</b>        | 0.000500 mol               | —  |
| <b>After addition</b>  | $\approx 0.00 \text{ mol}$ | 0.00200 mol  |

We calculate the  $\text{H}_3\text{O}^+$  concentration by dividing the number of moles of  $\text{H}_3\text{O}^+$  remaining by the *total volume* (initial volume plus added volume):

$$[\text{H}_3\text{O}^+] = \frac{0.00200 \text{ mol H}_3\text{O}^+}{0.0250 \text{ L} + 0.00500 \text{ L}} = 0.0667 \text{ M}$$

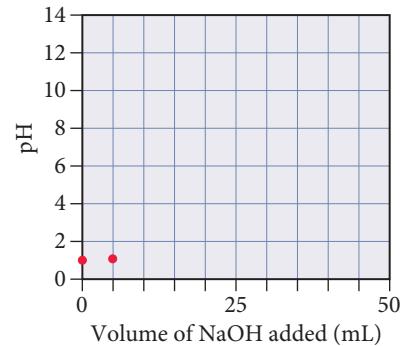
Initial volume                          Added volume

The pH is therefore 1.18:

$$\begin{aligned}\text{pH} &= -\log 0.0667 \\ &= 1.18\end{aligned}$$

**pH's after Adding 10.0, 15.0, and 20.0 mL NaOH** As more NaOH is added, it further neutralizes the  $\text{H}_3\text{O}^+$  in the solution. We calculate the pH at each of these points in the same way that we calculated the pH at the 5.00 mL point. The results are tabulated as follows:

| Volume (mL) | pH   |
|-------------|------|
| 10.0        | 1.37 |
| 15.0        | 1.60 |
| 20.0        | 1.95 |



**pH after Adding 25.0 mL NaOH (Equivalence Point)** The pH at the equivalence point of a strong acid–strong base titration will always be 7.00 (at 25 °C). At the equivalence point, the strong base has completely neutralized the strong acid. The only source of hydronium ions then is the ionization of water. The  $[\text{H}_3\text{O}^+]$  at 25 °C from the ionization of water is  $1.00 \times 10^{-7} \text{ M}$  and the pH is 7.00.

**pH after Adding 30.00 mL NaOH** As NaOH is added beyond the equivalence point, it becomes the excess reagent. We calculate the amount of  $\text{OH}^-$  at any given point (past the equivalence point) by subtracting the initial amount of  $\text{H}_3\text{O}^+$  from the amount of  $\text{OH}^-$  added. The number of moles of  $\text{OH}^-$  added at 30.00 mL is:

$$\text{mol OH}^- \text{ added} = 0.0300 \text{ L} \times \frac{0.100 \text{ mol}}{1 \text{ L}} = 0.00300 \text{ mol OH}^-$$

The number of moles of  $\text{OH}^-$  remaining after neutralization is shown in the following table:

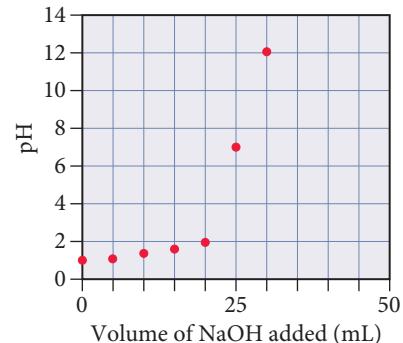
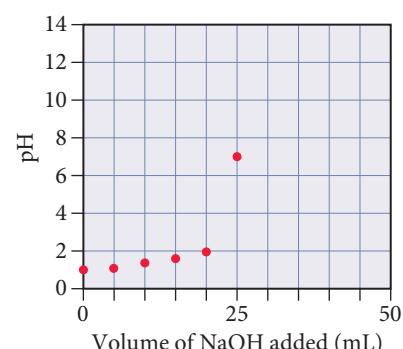
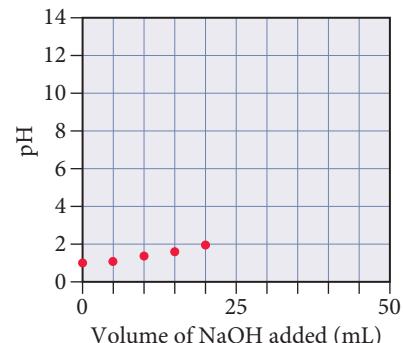
| $\text{OH}^-(aq) + \text{H}_3\text{O}^+(aq) \longrightarrow 2 \text{H}_2\text{O}(l)$ |                            |                            |
|--|----------------------------|----------------------------|
| <b>Before addition</b>   | $\approx 0.00 \text{ mol}$ | $0.00250 \text{ mol}$      |
| <b>Addition</b>  | $0.00300 \text{ mol}$      | —                          |
| <b>After addition</b>  | $0.00050 \text{ mol}$      | $\approx 0.00 \text{ mol}$ |

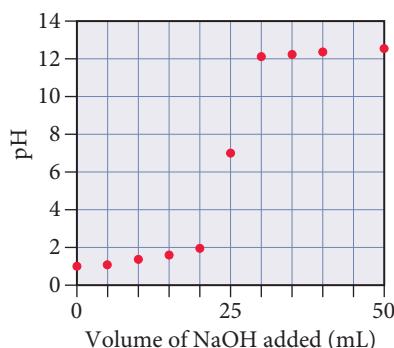
We calculate the  $\text{OH}^-$  concentration by dividing the number of moles of  $\text{OH}^-$  remaining by the *total volume* (initial volume plus added volume):

$$[\text{OH}^-] = \frac{0.000500 \text{ mol OH}^-}{0.0250 \text{ L} + 0.0300 \text{ L}} = 0.00909 \text{ M}$$

We can then calculate the  $[\text{H}_3\text{O}^+]$  and pH:

$$\begin{aligned}[\text{H}_3\text{O}^+][\text{OH}^-] &= 10^{-14} \\ [\text{H}_3\text{O}^+] &= \frac{10^{-14}}{[\text{OH}^-]} = \frac{10^{-14}}{0.00909} \\ &= 1.10 \times 10^{-12} \text{ M} \\ \text{pH} &= -\log(1.10 \times 10^{-12}) \\ &= 11.96\end{aligned}$$

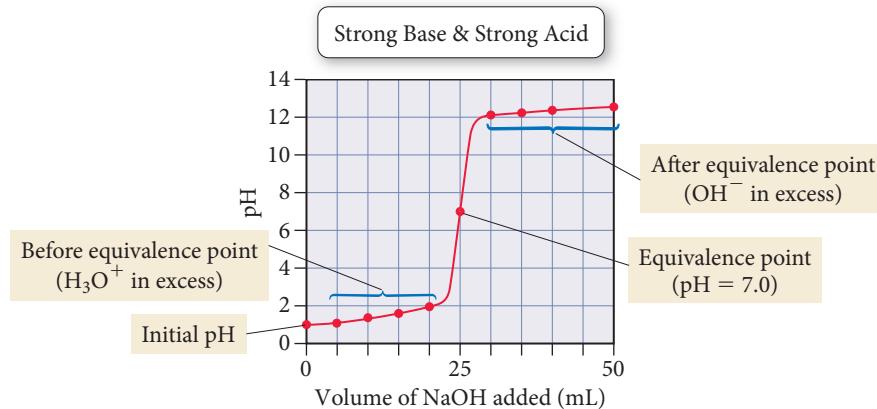




**pH's after Adding 35.0, 40.0, and 50.0 mL NaOH** As more NaOH is added, it further increases the basicity of the solution. We calculate the pH at each of these points in the same way that we calculated the pH at the 30.00 mL point. The results are tabulated as follows:

| Volume (mL) | pH    |
|-------------|-------|
| 35.0        | 12.22 |
| 40.0        | 12.36 |
| 50.0        | 12.52 |

**The Overall pH Curve** The overall pH curve for the titration of a strong acid with a strong base has the characteristic S-shape we just plotted. The overall curve is as follows:

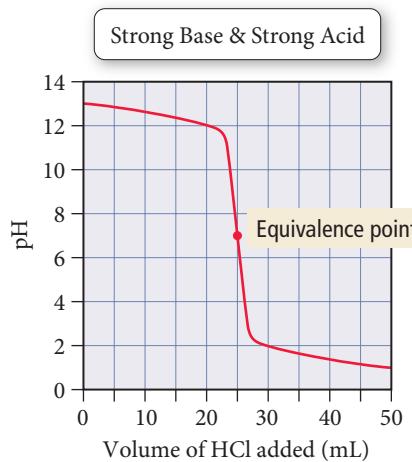


### Summarizing the Titration of a Strong Acid with a Strong Base:

- ▶ The initial pH is simply the pH of the strong acid solution to be titrated.
- ▶ Before the equivalence point,  $\text{H}_3\text{O}^+$  is in excess. Calculate the  $[\text{H}_3\text{O}^+]$  by subtracting the number of moles of added  $\text{OH}^-$  from the initial number of moles of  $\text{H}_3\text{O}^+$  and dividing by the *total* volume.
- ▶ At the equivalence point, neither reactant is in excess and the  $\text{pH} = 7.00$ .
- ▶ Beyond the equivalence point,  $\text{OH}^-$  is in excess. Calculate the  $[\text{OH}^-]$  by subtracting the initial number of moles of  $\text{H}_3\text{O}^+$  from the number of moles of added  $\text{OH}^-$  and dividing by the *total* volume.

The pH curve for the titration of a strong base with a strong acid is shown in Figure 16.7 ▶. Calculating the points along this curve is very similar to calculating the points along the pH curve for the titration of a strong acid with a strong base. The main difference is that the curve starts basic and then becomes acidic after the equivalence point (instead of vice versa).

**► FIGURE 16.7** Titration Curve: Strong Base + Strong Acid This curve represents the titration of 25.0 mL of 0.100 M NaOH with 0.100 M HCl.



### EXAMPLE 16.6 Strong Acid–Strong Base Titration pH Curve

A 50.0 mL sample of 0.200 M sodium hydroxide is titrated with 0.200 M nitric acid.

Calculate pH:

- (a) after adding 30.00 mL of HNO<sub>3</sub>      (b) at the equivalence point

#### SOLUTION

(a) Begin by calculating the initial amount of NaOH (in moles) from the volume and molarity of the NaOH solution. Because NaOH is a strong base, it dissociates completely, so the amount of OH<sup>-</sup> is equal to the amount of NaOH.

Calculate the amount of HNO<sub>3</sub> (in moles) added at 30.0 mL from the molarity of the HNO<sub>3</sub> solution.

As HNO<sub>3</sub> is added to the solution, it neutralizes some of the OH<sup>-</sup>. Calculate the number of moles of OH<sup>-</sup> remaining by setting up a table based on the neutralization reaction that shows the amount of OH<sup>-</sup> before the addition, the amount of H<sub>3</sub>O<sup>+</sup> added, and the amounts left after the addition.

Calculate the OH<sup>-</sup> concentration by dividing the amount of OH<sup>-</sup> remaining by the *total volume* (initial volume plus added volume).

Calculate the pOH from [OH<sup>-</sup>].

Calculate the pH from the pOH using the equation pH + pOH = 14.

(b) At the equivalence point, the strong base has completely neutralized the strong acid. The [H<sub>3</sub>O<sup>+</sup>] at 25 °C from the ionization of water is  $1.00 \times 10^{-7}$  M and the pH is therefore 7.00.

$$\text{moles NaOH} = 0.0500 \text{ L} \times \frac{0.200 \text{ mol}}{1 \text{ L}}$$

$$= 0.0100 \text{ mol}$$

$$\text{moles OH}^- = 0.0100 \text{ mol}$$

$$\text{mol HNO}_3 \text{ added} = 0.0300 \text{ L} \times \frac{0.200 \text{ mol}}{1 \text{ L}}$$

$$= 0.00600 \text{ mol HNO}_3$$

|                        | <b>OH<sup>-</sup>(aq)</b> | <b>+ H<sub>3</sub>O<sup>+</sup>(aq)</b> | <b>→ 2 H<sub>2</sub>O(l)</b> |
|------------------------|---------------------------|---|------------------------------|
| <b>Before addition</b> | 0.0100 mol                | ≈ 0.00 mol                              |                              |
| <b>Addition</b>        | —                         | 0.00600 mol                             |                              |
| <b>After addition</b>  | 0.0040 mol                | 0.00 mol                                |                              |

$$[\text{OH}^-] = \frac{0.0040 \text{ mol}}{0.0500 \text{ L} + 0.0300 \text{ L}}$$

$$= 0.0500 \text{ M}$$

$$\text{pOH} = -\log(0.0500)$$

$$= 1.30$$

$$\begin{aligned}\text{pH} &= 14 - \text{pOH} \\ &= 14 - 1.30 \\ &= 12.70\end{aligned}$$

$$\text{pH} = 7.00$$

#### FOR PRACTICE 16.6

Calculate the pH in the titration in Example 16.6 after the addition of 60.0 mL of 0.200 M HNO<sub>3</sub>.



#### Conceptual Connection 16.5 Titration Equivalence Point

The amount of acid in the flask at right is to be titrated by a strong base. Which mark on the burette next to the flask indicates the amount of base required to reach the equivalence point?

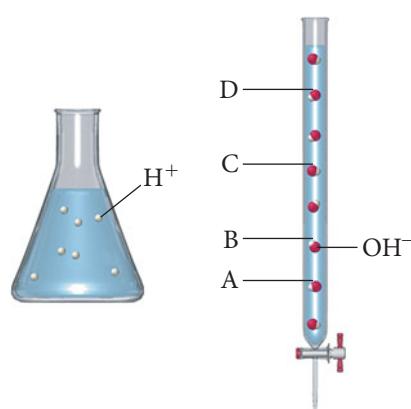
- (a) A      (b) B      (c) C      (d) D

#### The Titration of a Weak Acid with a Strong Base

Consider the titration of 25.0 mL of 0.100 M HCHO<sub>2</sub> with 0.100 M NaOH.



The concentrations and the volumes here are identical to those in our previous titration, in which we calculated the pH curve for the titration of a *strong* acid with a strong base. The only difference is that HCHO<sub>2</sub> is a *weak* acid rather than a strong one. We begin by calculating the volume required to reach the equivalence point of the titration.



**Volume of NaOH Required to Reach the Equivalence Point** From the stoichiometry of the equation, we can see that the equivalence point occurs when the amount (in moles) of added base equals the amount (in moles) of acid initially in solution.

$$\text{Initial mol HCHO}_2 = 0.0250 \text{ L} \times \frac{0.100 \text{ mol}}{1 \text{ L}} = 0.00250 \text{ mol HCHO}_2$$

The amount of NaOH that must be added is 0.00250 mol NaOH. The volume of NaOH required is therefore:

$$\text{Volume NaOH solution} = 0.00250 \text{ mol} \times \frac{1 \text{ L}}{0.100 \text{ mol}} = 0.0250 \text{ L NaOH solution}$$

The equivalence point occurs when 25.0 mL of base has been added. Notice that the volume of NaOH required to reach the equivalence point for this weak acid is identical to that required for a strong acid. *The volume at the equivalence point in an acid–base titration does not depend on whether the acid being titrated is a strong acid or a weak acid; it depends only on the amount (in moles) of acid present in solution before the titration begins and on the concentration of the added base.*

**Initial pH (before Adding Any Base)** The initial pH of the solution is the pH of a 0.100 M HCHO<sub>2</sub> solution. Since HCHO<sub>2</sub> is a weak acid, we calculate the concentration of H<sub>3</sub>O<sup>+</sup> and the pH by doing an equilibrium problem for the ionization of HCHO<sub>2</sub>. The procedure for solving weak acid ionization problems is given in Examples 15.5 and 15.6. We show a highly condensed calculation here ( $K_a$  for HCHO<sub>2</sub> is  $1.8 \times 10^{-4}$ ).



|         | [HCHO <sub>2</sub> ] | [H <sub>3</sub> O <sup>+</sup> ] | [CHO <sub>2</sub> <sup>-</sup> ] |
|---------|----------------------|----------------------------------|----------------------------------|
| Initial | 0.100                | ≈ 0.00                           | 0.00                             |
| Change  | -x                   | +x                               | +x                               |
| Equil   | 0.100 - x            | x                                | x                                |

$$\begin{aligned} K_a &= \frac{[\text{H}_3\text{O}^+][\text{CHO}_2^-]}{[\text{HCHO}_2]} \\ &= \frac{x^2}{0.100 - x} \quad (\text{x is small}) \\ 1.8 \times 10^{-4} &= \frac{x^2}{0.100} \\ x &= 4.24 \times 10^{-3} \end{aligned}$$

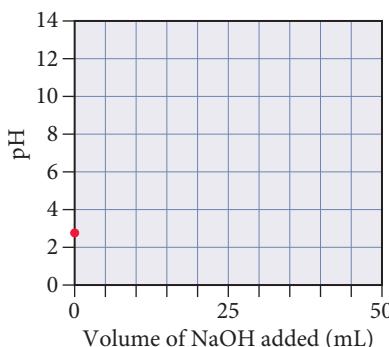
Therefore, [H<sub>3</sub>O<sup>+</sup>] = 4.24 × 10<sup>-3</sup> M.

$$\begin{aligned} \text{pH} &= -\log(4.24 \times 10^{-3}) \\ &= 2.37 \end{aligned}$$

Notice that the pH is initially at a higher value (less acidic) than it is for a strong acid of the same concentration, as we would expect because the acid is weak.

**pH after Adding 5.00 mL NaOH** When titrating a *weak acid* with a strong base, the added NaOH converts a stoichiometric amount of the acid into its conjugate base. As we calculated previously, 5.00 mL of the 0.100 M NaOH solution contains 0.000500 mol OH<sup>-</sup>. When the 0.000500 mol OH<sup>-</sup> is added to the weak acid solution, the OH<sup>-</sup> reacts stoichiometrically with HCHO<sub>2</sub> causing the amount of HCHO<sub>2</sub> to decrease by 0.000500 mol and the amount of CHO<sub>2</sub><sup>-</sup> to increase by 0.000500 mol. This is very similar to what happens when you add strong base to a buffer, and it is summarized in the following table:

|                 | OH <sup>-</sup> (aq) | + HCHO <sub>2</sub> (aq) | → H <sub>2</sub> O(l) | + CHO <sub>2</sub> <sup>-</sup> (aq) |
|-----------------|----------------------|--------------------------|-----------------------|--------------------------------------|
| Before addition | ≈ 0.00 mol           | 0.00250 mol              | —                     | 0.00 mol                             |
| Addition        | 0.000500 mol         | —                        | —                     | —                                    |
| After addition  | ≈ 0.00 mol           | 0.00200 mol              | —                     | 0.000500 mol                         |



Notice that, after the addition, the solution contains significant amounts of both an acid ( $\text{HCHO}_2$ ) and its conjugate base ( $\text{CHO}_2^-$ )—*the solution is now a buffer*. To calculate the pH of a buffer (when the  $x$  is small approximation applies as it does here), we can use the Henderson–Hasselbalch equation and  $pK_a$  for  $\text{HCHO}_2$  (which is 3.74):

$$\begin{aligned}\text{pH} &= \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} \\ &= 3.74 + \log \frac{0.000500}{0.00200} \\ &= 3.74 - 0.60 \\ &= 3.14\end{aligned}$$

**pH's after Adding 10.0, 12.5, 15.0, and 20.0 mL NaOH** As more NaOH is added, it converts more  $\text{HCHO}_2$  into  $\text{CHO}_2^-$ . We calculate the relative amounts of  $\text{HCHO}_2$  and  $\text{CHO}_2^-$  at each of these volumes using the reaction stoichiometry and then calculate the pH of the resulting buffer using the Henderson–Hasselbalch equation (as we did for the pH at 5.00 mL). The amounts of  $\text{HCHO}_2$  and  $\text{CHO}_2^-$  (after addition of the  $\text{OH}^-$ ) at each volume and the corresponding pH's are tabulated as follows:

| Volume (mL) | mol $\text{HCHO}_2$ | mol $\text{CHO}_2^-$ | pH   |
|-------------|---------------------|----------------------|------|
| 10.0        | 0.00150             | 0.00100              | 3.56 |
| 12.5        | 0.00125             | 0.00125              | 3.74 |
| 15.0        | 0.00100             | 0.00150              | 3.92 |
| 20.0        | 0.00050             | 0.00200              | 4.34 |

As the titration proceeds, more of the  $\text{HCHO}_2$  is converted to the conjugate base ( $\text{CHO}_2^-$ ). Notice that an added NaOH volume of 12.5 mL corresponds to one-half of the equivalence point. At this volume, one-half of the initial amount of  $\text{HCHO}_2$  has been converted to  $\text{CHO}_2^-$ , resulting in *equal amounts of weak acid and conjugate base*. For any buffer in which the amounts of weak acid and conjugate base are equal, the  $\text{pH} = \text{p}K_a$ :

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

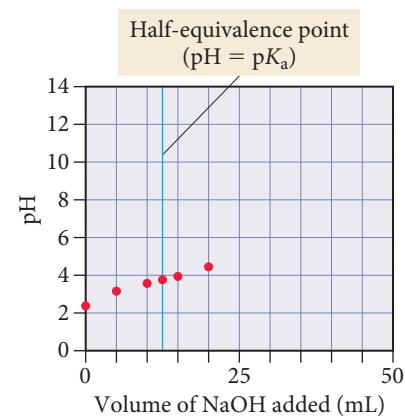
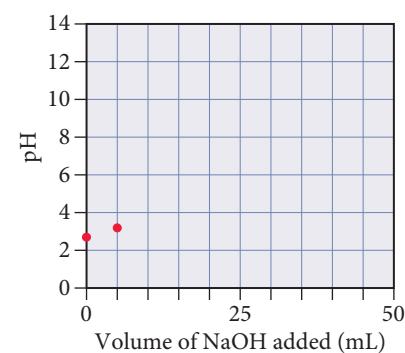
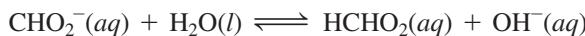
If  $[\text{base}] = [\text{acid}]$ , then  $[\text{base}]/[\text{acid}] = 1$ .

$$\begin{aligned}\text{pH} &= \text{p}K_a + \log 1 \\ &= \text{p}K_a + 0 \\ &= \text{p}K_a\end{aligned}$$

**pH after Adding 25.0 mL NaOH (Equivalence Point)** At the equivalence point, 0.000250 mol of  $\text{OH}^-$  have been added and therefore all of the  $\text{HCHO}_2$  has been converted into its conjugate base ( $\text{CHO}_2^-$ ) as summarized in the following table:

| $\text{OH}^-(aq) + \text{HCHO}_2(aq) \longrightarrow \text{H}_2\text{O}(l) + \text{CHO}_2^-(aq)$ |             |             |   |             |
|--|-------------|-------------|---|-------------|
| <b>Before addition</b>   | ≈ 0.00 mol  | 0.00250 mol | — | 0.00 mol    |
| <b>Addition</b>  | 0.00250 mol | —           | — | —           |
| <b>After addition</b>  | ≈ 0.00 mol  | 0.00 mol    | — | 0.00250 mol |

The solution is no longer a buffer (it no longer contains significant amounts of both a weak acid and its conjugate base). Instead, the solution contains an ion ( $\text{CHO}_2^-$ ) acting as a weak base. You learned how to calculate the pH of solutions such as this in Section 15.8 (see Example 15.14) by solving an equilibrium problem involving the ionization of water by the weak base ( $\text{CHO}_2^-$ ):



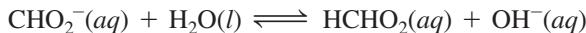
Since  $\text{pH} = \text{p}K_a$  halfway to the equivalence point, titrations can be used to measure the  $\text{p}K_a$  of an acid.

We calculate the initial concentration of  $\text{CHO}_2^-$  for the equilibrium problem by dividing the number of moles of  $\text{CHO}_2^-$  (0.00250 mol) by the *total* volume at the equivalence point (initial volume plus added volume):

$$\text{Moles } \text{CHO}_2^- \text{ at equivalence point} \\ \downarrow \\ [\text{CHO}_2^-] = \frac{0.00250 \text{ mol}}{0.0250 \text{ L} + 0.0250 \text{ L}} = 0.0500 \text{ M}$$

Initial volume                          Added volume  
at equivalence point

We then proceed to solve the equilibrium problem as shown in condensed form as follows:



|         | $[\text{CHO}_2^-]$ | $[\text{HCHO}_2]$ | $[\text{OH}^-]$ |
|---------|--------------------|-------------------|-----------------|
| Initial | 0.0500             | 0.00              | $\approx 0.00$  |
| Change  | $-x$               | $+x$              | $+x$            |
| Equil   | $0.0500 - x$       | $x$               | $x$             |

Before substituting into the expression for  $K_b$ , we find the value of  $K_b$  from  $K_a$  for formic acid ( $K_a = 1.8 \times 10^{-4}$ ) and  $K_w$ :

$$K_a \times K_b = K_w$$

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-4}} = 5.6 \times 10^{-11}$$

Then we substitute the equilibrium concentrations from the previous table into the expression for  $K_b$ :

$$K_b = \frac{[\text{HCHO}_2][\text{OH}^-]}{[\text{CHO}_2^-]}$$

$$= \frac{x^2}{0.0500 - x} \quad (x \text{ is small})$$

$$5.6 \times 10^{-11} = \frac{x^2}{0.0500}$$

$$x = 1.7 \times 10^{-6}$$

Remember that  $x$  represents the concentration of the hydroxide ion. We calculate  $[\text{H}_3\text{O}^+]$  and pH:

$$[\text{OH}^-] = 1.7 \times 10^{-6} \text{ M}$$

$$[\text{H}_3\text{O}^+][\text{OH}^-] = K_w = 1.0 \times 10^{-14}$$

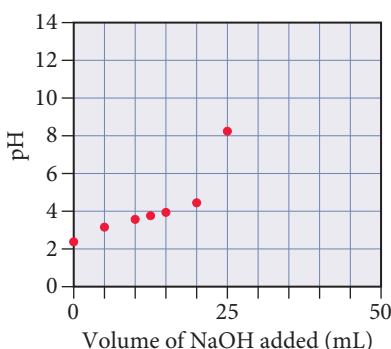
$$[\text{H}_3\text{O}^+](1.7 \times 10^{-6}) = 1.0 \times 10^{-14}$$

$$[\text{H}_3\text{O}^+] = 5.9 \times 10^{-9} \text{ M}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

$$= -\log(5.9 \times 10^{-9})$$

$$= 8.23$$



Notice that the pH at the equivalence point is *not* neutral but basic. *The titration of a weak acid by a strong base always has a basic equivalence point* because, at the equivalence point, all of the acid has been converted into its conjugate base, resulting in a weakly basic solution.

**pH after Adding 30.00 mL NaOH** At this point in the titration, 0.00300 mol of  $\text{OH}^-$  have been added. NaOH has thus become the excess reagent as shown in the following table:

|                        | $\text{OH}^-(aq)$          | $\text{HCHO}_2(aq)$        | $\text{H}_2\text{O}(l)$ | $\text{CHO}_2^-(aq)$ |
|------------------------|----------------------------|----------------------------|-------------------------|----------------------|
| <b>Before addition</b> | $\approx 0.00 \text{ mol}$ | 0.00250 mol                | —                       | 0.00 mol             |
| <b>Addition</b>        | 0.00300 mol                | —                          | —                       | —                    |
| <b>After addition</b>  | 0.00050 mol                | $\approx 0.00 \text{ mol}$ | —                       | 0.00250 mol          |

The solution is now a mixture of a strong base ( $\text{NaOH}$ ) and a weak base ( $\text{CHO}_2^-$ ). The strong base completely overwhelms the weak base and we can calculate the pH by considering the strong base alone (as we did for the titration of a strong acid and a strong base). We calculate the  $\text{OH}^-$  concentration by dividing the amount of  $\text{OH}^-$  remaining by the *total volume* (initial volume plus added volume):

$$[\text{OH}^-] = \frac{0.00050 \text{ mol OH}^-}{0.0250 \text{ L} + 0.0300 \text{ L}} = 0.0091 \text{ M}$$

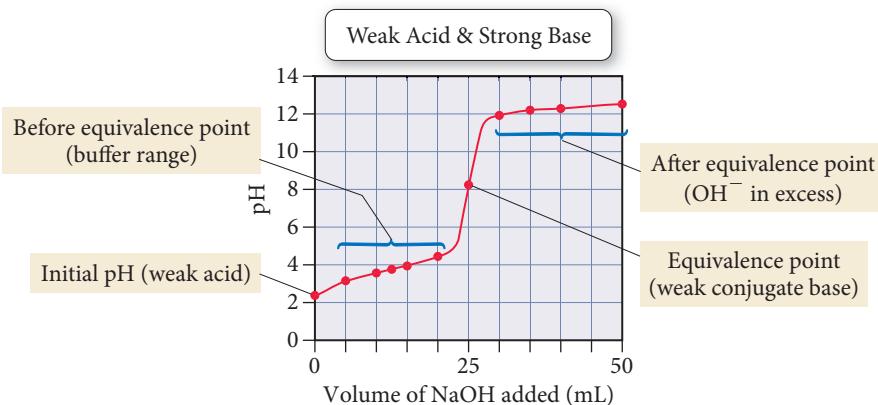
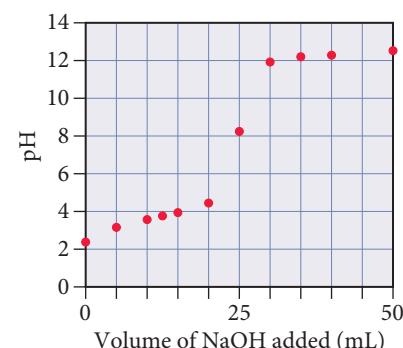
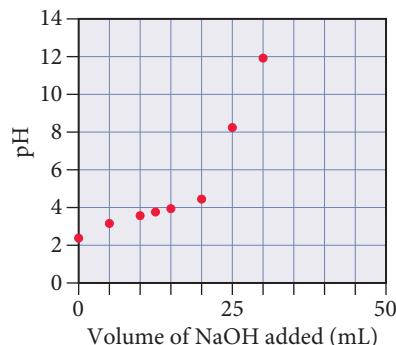
We can then calculate the  $[\text{H}_3\text{O}^+]$  and pH:

$$\begin{aligned} [\text{H}_3\text{O}^+][\text{OH}^-] &= 10^{-14} \\ [\text{H}_3\text{O}^+] &= \frac{10^{-14}}{[\text{OH}^-]} = \frac{10^{-14}}{0.0091} = 1.10 \times 10^{-12} \text{ M} \\ \text{pH} &= -\log(1.10 \times 10^{-12}) \\ &= 11.96 \end{aligned}$$

**pH's after Adding 35.0, 40.0, and 50.0 mL NaOH** As more NaOH is added, the basicity of the solution increases further. We calculate the pH at each of these volumes in the same way we calculated the pH at 30.00 mL of added NaOH. The results are tabulated as follows:

| Volume (mL) | pH    |
|-------------|-------|
| 35.0        | 12.22 |
| 40.0        | 12.36 |
| 50.0        | 12.52 |

**The Overall pH Curve** The overall pH curve for the titration of a weak acid with a strong base has a characteristic S-shape similar to that for the titration of a strong acid with a strong base. The main difference is that the equivalence point pH is basic (not neutral). Notice that calculating the pH in different regions throughout the titration involves working different kinds of acid–base problems, all of which we have encountered before.



### Summarizing Titration of a Weak Acid with a Strong Base:

- ▶ The initial pH is that of the weak acid solution to be titrated. Calculate the pH by working an equilibrium problem (similar to Examples 15.5 and 15.6) using the concentration of the weak acid as the initial concentration.
- ▶ Between the initial pH and the equivalence point, the solution becomes a buffer. Use the reaction stoichiometry to calculate the amounts of each buffer component and then use the Henderson–Hasselbalch equation to calculate the pH (as in Example 16.3).
- ▶ Halfway to the equivalence point, the buffer components are exactly equal and  $\text{pH} = \text{p}K_a$ .
- ▶ At the equivalence point, the acid has all been converted into its conjugate base. Calculate the pH by working an equilibrium problem for the ionization of water by the ion acting as a weak base (similar to Example 15.14). (Calculate the concentration of the ion acting as a weak base by dividing the number of moles of the ion by the total volume at the equivalence point.)
- ▶ Beyond the equivalence point,  $\text{OH}^-$  is in excess. Ignore the weak base and calculate the  $[\text{OH}^-]$  by subtracting the initial number of moles of the weak acid from the number of moles of added  $\text{OH}^-$  and dividing by the *total* volume.

### EXAMPLE 16.7 Weak Acid–Strong Base Titration pH Curve

A 40.0 mL sample of 0.100 M  $\text{HNO}_2$  is titrated with 0.200 M KOH. Calculate:

- the volume required to reach the equivalence point
- the pH after adding 5.00 mL of KOH
- the pH at one-half the equivalence point

#### SOLUTION

- (a) The equivalence point occurs when the amount (in moles) of added base equals the amount (in moles) of acid initially in the solution. Begin by calculating the amount (in moles) of acid initially in the solution. The amount (in moles) of KOH that must be added is equal to the amount of the weak acid.

Calculate the volume of KOH required from the number of moles of KOH and the molarity.

- (b) Use the concentration of the KOH solution to calculate the amount (in moles) of  $\text{OH}^-$  in 5.00 mL of the solution.

Prepare a table showing the amounts of  $\text{HNO}_2$  and  $\text{NO}_2^-$  before and after the addition of 5.00 mL KOH. The addition of the KOH stoichiometrically reduces the concentration of  $\text{HNO}_2$  and increases the concentration of  $\text{NO}_2^-$ .

Since the solution now contains significant amounts of a weak acid and its conjugate base, use the Henderson–Hasselbalch equation and  $\text{p}K_a$  for  $\text{HNO}_2$  (which is 3.34) to calculate the pH of the solution.

$$\begin{aligned}\text{mol HNO}_2 &= 0.0400 \text{ L} \times \frac{0.100 \text{ mol}}{\text{L}} \\ &= 4.00 \times 10^{-3} \text{ mol}\end{aligned}$$

$$\text{mol KOH required} = 4.00 \times 10^{-3} \text{ mol}$$

$$\begin{aligned}\text{volume KOH solution} &= 4.00 \times 10^{-3} \text{ mol} \times \frac{1 \text{ L}}{0.200 \text{ mol}} \\ &= 0.0200 \text{ L KOH solution} \\ &= 20.0 \text{ mL KOH solution}\end{aligned}$$

$$\begin{aligned}\text{mol OH}^- &= 5.00 \times 10^{-3} \text{ L} \times \frac{0.200 \text{ mol}}{1 \text{ L}} \\ &= 1.00 \times 10^{-3} \text{ mol OH}^-\end{aligned}$$

|                        | $\text{OH}^-(\text{aq})$          | $+$ | $\text{HNO}_2(\text{aq}) \longrightarrow \text{H}_2\text{O}(\text{l}) + \text{NO}_2^-(\text{aq})$ | $+$ | $\text{NO}_2^-(\text{aq})$        |
|------------------------|-----------------------------------|-----|---|-----|-----------------------------------|
| <b>Before addition</b> | $\approx 0.00 \text{ mol}$        |     | $4.00 \times 10^{-3} \text{ mol}$   |     | $0.00 \text{ mol}$                |
| <b>Addition</b>        | $1.00 \times 10^{-3} \text{ mol}$ |     | $-$   | $-$ | $-$                               |
| <b>After addition</b>  | $\approx 0.00 \text{ mol}$        |     | $3.00 \times 10^{-3} \text{ mol}$   |     | $1.00 \times 10^{-3} \text{ mol}$ |

$$\begin{aligned}\text{pH} &= \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} \\ &= 3.34 + \log \frac{1.00 \times 10^{-3}}{3.00 \times 10^{-3}} \\ &= 3.34 - 0.48 = 2.86\end{aligned}$$



- (c) At one-half the equivalence point, the amount of added base is exactly one-half the initial amount of acid. The base converts exactly half of the  $\text{HNO}_2$  into  $\text{NO}_2^-$ , resulting in equal amounts of the weak acid and its conjugate base. The pH is therefore equal to  $pK_a$ .

|                 | $\text{OH}^-(aq)$                 | + | $\text{HNO}_2(aq)$                | $\longrightarrow$ | $\text{H}_2\text{O}(l)$ | $+\text{NO}_2^-(aq)$              |                    |
|-----------------|-----------------------------------|---|-----------------------------------|-------------------|-------------------------|-----------------------------------|--------------------|
| Before addition | $\approx 0.00 \text{ mol}$        |   | $4.00 \times 10^{-3} \text{ mol}$ |                   | —                       | —                                 | $0.00 \text{ mol}$ |
| Addition        | $2.00 \times 10^{-3} \text{ mol}$ |   | —                                 | —                 | —                       | —                                 | —                  |
| After addition  | $\approx 0.00 \text{ mol}$        |   | $2.00 \times 10^{-3} \text{ mol}$ |                   | —                       | $2.00 \times 10^{-3} \text{ mol}$ |                    |

$$\begin{aligned}\text{pH} &= pK_a + \log \frac{[\text{base}]}{[\text{acid}]} \\ &= 3.34 + \log \frac{2.00 \times 10^{-3}}{2.00 \times 10^{-3}} \\ &= 3.34 + 0 = 3.34\end{aligned}$$

### FOR PRACTICE 16.7

Determine the pH at the equivalence point for the titration of  $\text{HNO}_2$  and KOH in Example 16.7.

## The Titration of a Weak Base with a Strong Acid

The pH curve for the titration of a weak base with a strong acid is shown in Figure 16.8 ▶. Calculating the points along this curve is very similar to calculating the points along the pH curve for the titration of a weak acid with a strong base (which we just did). The main differences are that the curve starts basic and has an acidic equivalence point. We calculate the pH in the buffer region using  $\text{pH} = pK_a + \log \frac{[\text{base}]}{[\text{acid}]}$  where the  $pK_a$  corresponds to the conjugate acid of the base being titrated.

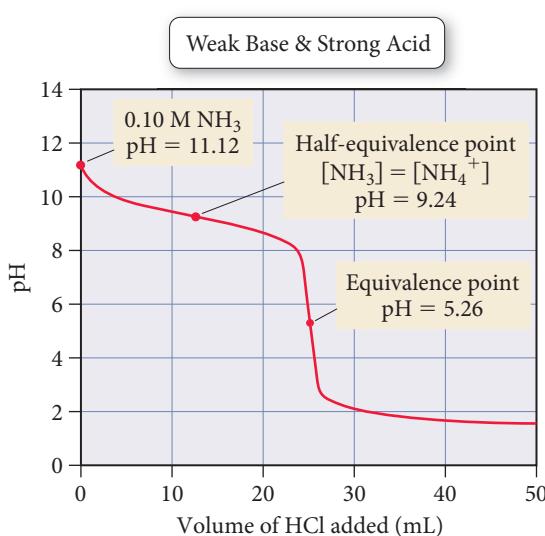
### Conceptual Connection 16.6 The Half-Equivalence Point

What is the pH at the half-equivalence point in the titration of a weak base with a strong acid? The  $pK_b$  of the weak base is 8.75.

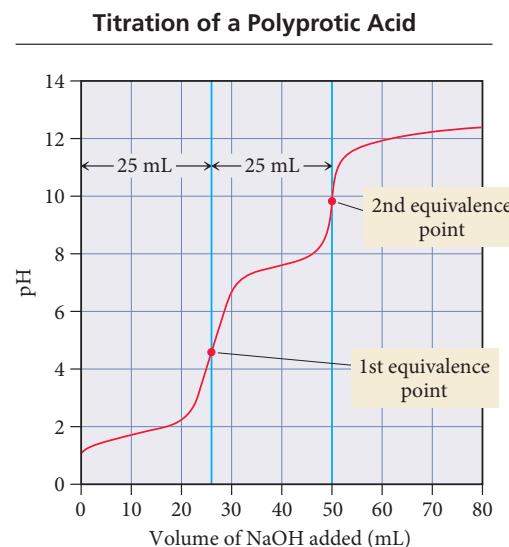
- (a) 8.75      (b) 7.0      (c) 5.25      (d) 4.37

## The Titration of a Polyprotic Acid

When a diprotic acid is titrated with a strong base, if  $K_{a_1}$  and  $K_{a_2}$  are sufficiently different, the pH curve will have two equivalence points. For example, Figure 16.9 ▶ shows the

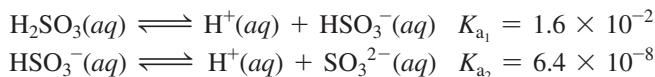


▲ FIGURE 16.8 Titration Curve: Weak Base with Strong Acid  
This curve represents the titration of 0.100 M  $\text{NH}_3$  with 0.100 M HCl.



▲ FIGURE 16.9 Titration Curve: Diprotic Acid with Strong Base  
This curve represents the titration of 25.0 mL of 0.100 M  $\text{H}_2\text{SO}_3$  with 0.100 M NaOH.

pH curve for the titration of sulfurous acid ( $\text{H}_2\text{SO}_3$ ) with sodium hydroxide. Recall from Section 15.9 that sulfurous acid ionizes in two steps as follows:



The first equivalence point in the titration curve represents the titration of the first proton while the second equivalence point represents the titration of the second proton. Notice that the volume required to reach the first equivalence point is identical to the volume required to reach the second one because the number of moles of  $\text{H}_2\text{SO}_3$  in the first step determines the number of moles of  $\text{HSO}_3^-$  in the second step.

### Conceptual Connection 16.7 Acid-Base Titrations

Consider these three titrations:

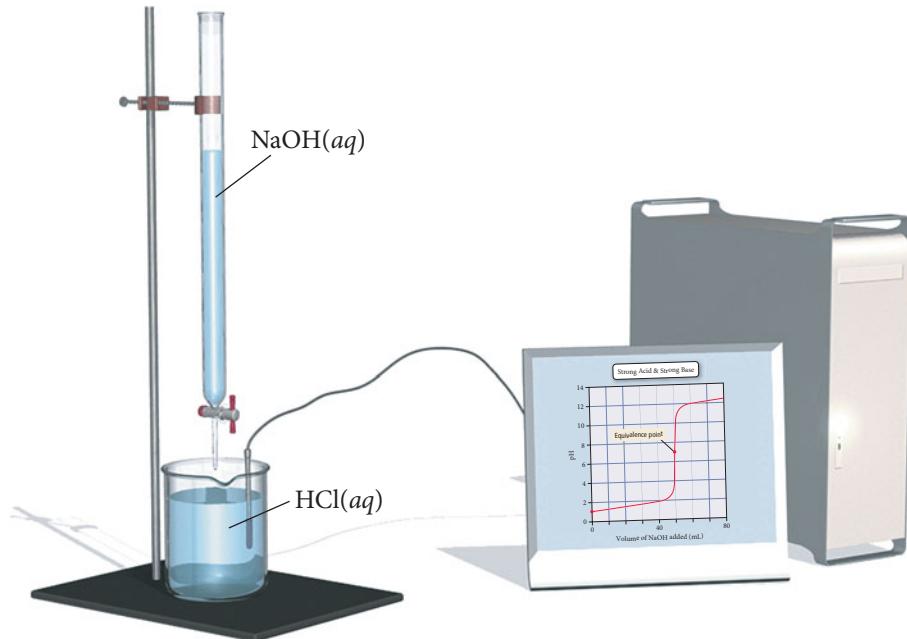
- (i) the titration of 25.0 mL of a 0.100 M monoprotic weak acid with 0.100 M NaOH
- (ii) the titration of 25.0 mL of a 0.100 M diprotic weak acid with 0.100 M NaOH
- (iii) the titration of 25.0 mL of a 0.100 M strong acid with 0.100 M NaOH

Which statement is most likely to be true?

- (a) All three titrations have the same initial pH.
- (b) All three titrations have the same pH at their first equivalence point.
- (c) All three titrations require the same volume of NaOH to reach their first equivalence point.

### Indicators: pH-Dependent Colors

We can monitor the pH of a titration with either a pH meter or an indicator. The direct monitoring of pH with a meter yields data like the pH curves we have examined previously, allowing determination of the equivalence point from the pH curve itself, as shown in Figure 16.10 ▶. With an indicator, we rely on the point where the indicator changes color—called the **endpoint**—to determine the equivalence point, as shown in



**▲ FIGURE 16.10 Monitoring the pH during a Titration** A pH meter monitors pH during titration. The inflection point in the resulting pH curve signifies the equivalence point.

### Using an Indicator

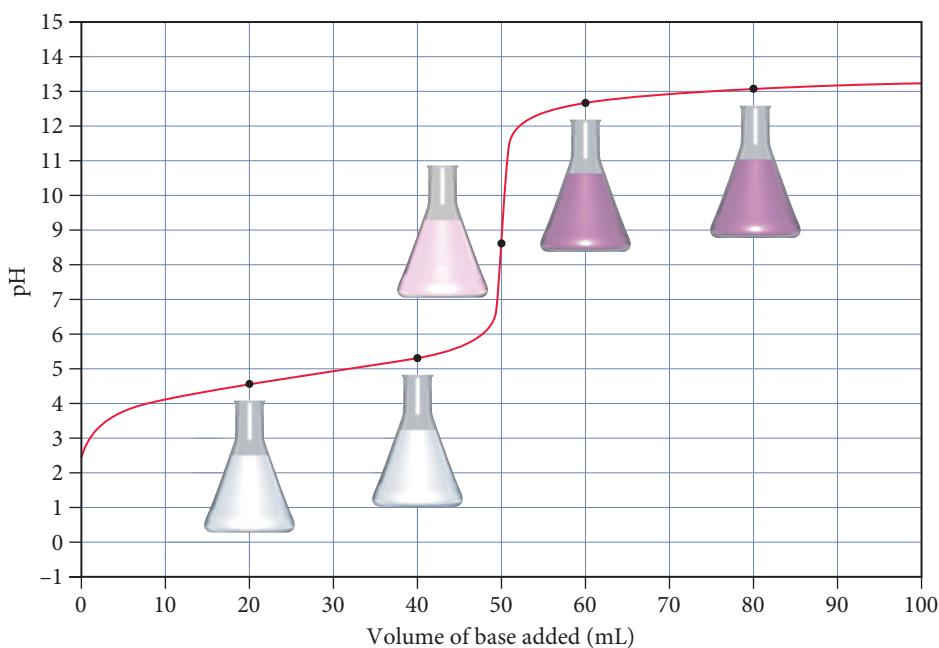
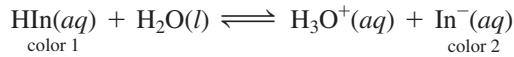


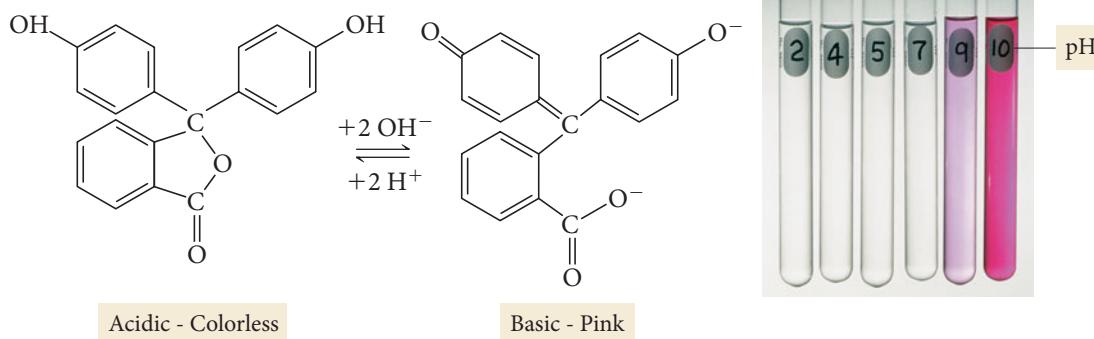
Figure 16.11 ▲. With the correct indicator, the endpoint of the titration (indicated by the color change) occurs at the equivalence point (when the amount of acid equals the amount of base).

An indicator is itself a weak organic acid that is a different color than its conjugate base. For example, phenolphthalein (whose structure is shown in Figure 16.12 ▼) is a common indicator whose acid form is colorless and conjugate base form is pink. If we let HIn represent the acid form of a generic indicator and In<sup>-</sup> the conjugate base form, we have the following equilibrium:



Because its color is intense, only a small amount of indicator is required—an amount that will not affect the pH of the solution or the equivalence point of the neutralization reaction. When the [H<sub>3</sub>O<sup>+</sup>] changes during the titration, the equilibrium shifts in response. At low pH, the [H<sub>3</sub>O<sup>+</sup>] is high and the equilibrium lies far to the left, resulting in a solution of color 1. As the titration proceeds, the [H<sub>3</sub>O<sup>+</sup>] decreases, shifting the equilibrium to the

### Phenolphthalein, a Common Indicator



▲ FIGURE 16.12 Phenolphthalein Phenolphthalein, a weakly acidic compound, is colorless. Its conjugate base is pink.

### ◀ FIGURE 16.11 Monitoring the Color Change during a Titration

Titration of 0.100 M HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> with 0.100 M NaOH. The endpoint of a titration is signaled by a color change in an appropriate indicator (in this case, phenolphthalein).

right. Since the pH change is large near the equivalence point of the titration, there is a large change in  $[H_3O^+]$  near the equivalence point. Provided that the correct indicator is chosen, there will also be a correspondingly significant change in color. For the titration of a strong acid with a strong base, one drop of the base near the endpoint is usually enough to change the indicator from color 1 to color 2.

The color of a solution containing an indicator depends on the relative concentrations of  $HIn$  and  $In^-$ . As a useful guideline, we can assume the following:

If  $\frac{[In^-]}{[HIn]} = 1$ , the indicator solution will be intermediate in color.

If  $\frac{[In^-]}{[HIn]} > 10$ , the indicator solution will be the color of  $In^-$ .

If  $\frac{[In^-]}{[HIn]} < 0.1$ , the indicator solution will be the color of  $HIn$ .

From the Henderson–Hasselbalch equation, we can derive an expression for the ratio of  $[In^-]/[HIn]$ :

$$pH = pK_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

$$= pK_a + \log \frac{[In^-]}{[HIn]}$$

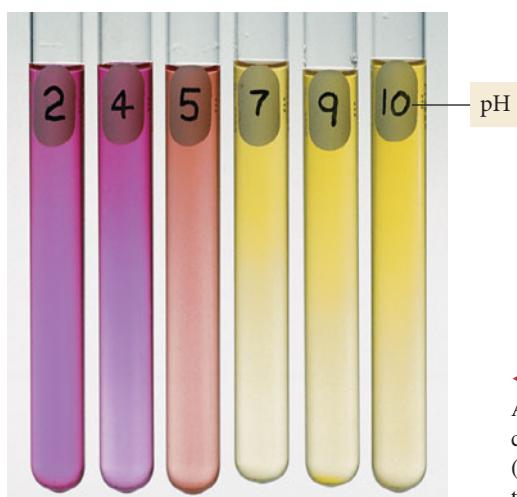
$$\log \frac{[In^-]}{[HIn]} = pH - pK_a$$

$$\frac{[In^-]}{[HIn]} = 10^{(pH - pK_a)}$$

Consider the following three pH values relative to  $pK_a$  and the corresponding colors of the indicator solution:

| pH (relative to $pK_a$ ) | $[In^-]/[HIn]$ ratio                    | Color of Indicator Solution |
|--------------------------|---|-----------------------------|
| $pH = pK_a$              | $\frac{[In^-]}{[HIn]} = 10^0 = 1$       | Intermediate color          |
| $pH = pK_a + 1$          | $\frac{[In^-]}{[HIn]} = 10^1 = 10$      | Color of $In^-$             |
| $pH = pK_a - 1$          | $\frac{[In^-]}{[HIn]} = 10^{-1} = 0.10$ | Color of $HIn$              |

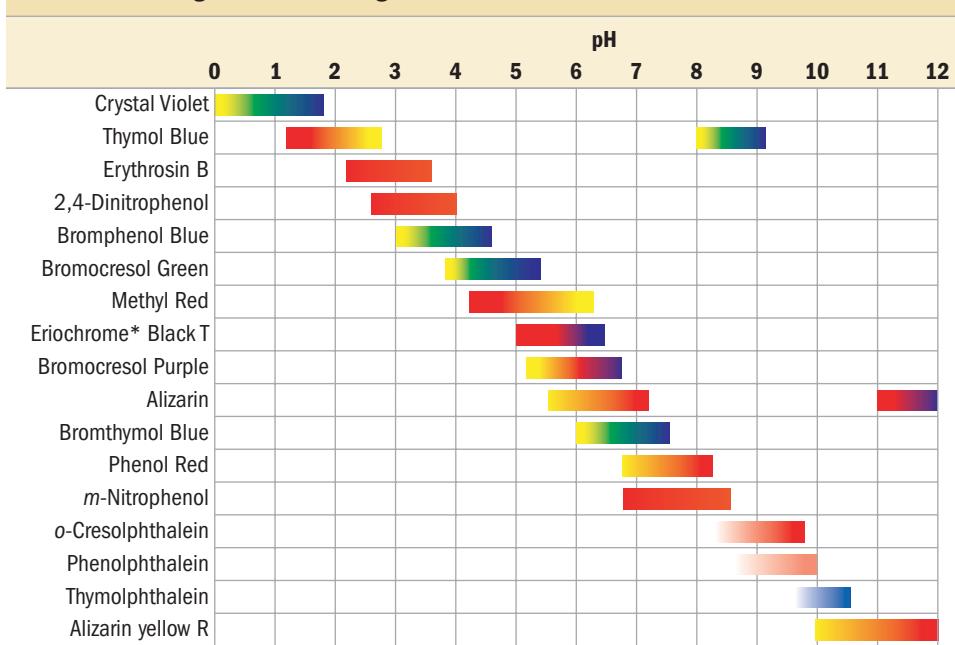
### Indicator Color Change: Methyl Red



When the pH of the solution equals the  $pK_a$  of the indicator, the solution will have an intermediate color. When the pH is 1 unit (or more) above  $pK_a$ , the indicator will be the color of  $In^-$ , and when the pH is 1 unit (or more) below  $pK_a$ , the indicator will be the color of  $HIn$ . As you can see, the indicator changes color within a range of two pH units centered at  $pK_a$  (Figure 16.13). Table 16.1 shows various indicators and their colors as a function of pH.

◀ FIGURE 16.13 Indicator Color Change

An indicator (in this case, methyl red) generally changes color within a range of two pH units. (The pH for each solution is marked on its test tube.)

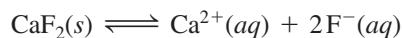
**TABLE 16.1** Ranges of Color Changes for Several Acid-Base Indicators

\*Trademark of CIBA GEIGY CORP.

## 16.5 Solubility Equilibria and the Solubility Product Constant

Recall from Chapter 4 that a compound is considered *soluble* if it dissolves in water and *insoluble* if it does not. Recall also that, with the *solubility rules* in Table 4.1, we were able to classify ionic compounds simply as soluble or insoluble. Now we have the tools to examine *degrees* of solubility.

We can better understand the solubility of an ionic compound by applying the concept of equilibrium to the process of dissolution. For example, we can represent the dissolution of calcium fluoride in water as an equilibrium:



The equilibrium constant for a chemical equation representing the dissolution of an ionic compound is the **solubility product constant** ( $K_{sp}$ ). For  $\text{CaF}_2$ , the expression of the solubility product constant is:

$$K_{sp} = [\text{Ca}^{2+}][\text{F}^-]^2$$

Notice that, as we discussed in Section 14.5, solids are omitted from the equilibrium expression because the concentration of a solid is constant (it is determined by its density and does not change when more solid is added).

The value of  $K_{sp}$  is a measure of the solubility of a compound. Table 16.2 lists the values of  $K_{sp}$  for a number of ionic compounds. A more complete list can be found in Appendix IIC.

### **$K_{sp}$ and Molar Solubility**

Recall from Section 12.2 that the *solubility* of a compound is the quantity of the compound that dissolves in a certain amount of liquid. The **molar solubility** is the solubility in units of moles per liter (mol/L). We can calculate the molar solubility of a compound directly from  $K_{sp}$ . Consider silver chloride:



**TABLE 16.2 Selected Solubility Product Constants ( $K_{\text{sp}}$ ) at 25 °C**

| Compound            | Formula                  | $K_{\text{sp}}$        | Compound            | Formula                   | $K_{\text{sp}}$        |
|---------------------|--------------------------|------------------------|---------------------|---------------------------|------------------------|
| Barium fluoride     | $\text{BaF}_2$           | $2.45 \times 10^{-5}$  | Lead(II) chloride   | $\text{PbCl}_2$           | $1.17 \times 10^{-5}$  |
| Barium sulfate      | $\text{BaSO}_4$          | $1.07 \times 10^{-10}$ | Lead(II) bromide    | $\text{PbBr}_2$           | $4.67 \times 10^{-6}$  |
| Calcium carbonate   | $\text{CaCO}_3$          | $4.96 \times 10^{-9}$  | Lead(II) sulfate    | $\text{PbSO}_4$           | $1.82 \times 10^{-8}$  |
| Calcium fluoride    | $\text{CaF}_2$           | $1.46 \times 10^{-10}$ | Lead(II) sulfide*   | $\text{PbS}$              | $9.04 \times 10^{-29}$ |
| Calcium hydroxide   | $\text{Ca}(\text{OH})_2$ | $4.68 \times 10^{-6}$  | Magnesium carbonate | $\text{MgCO}_3$           | $6.82 \times 10^{-6}$  |
| Calcium sulfate     | $\text{CaSO}_4$          | $7.10 \times 10^{-5}$  | Magnesium hydroxide | $\text{Mg}(\text{OH})_2$  | $2.06 \times 10^{-13}$ |
| Copper(II) sulfide* | $\text{CuS}$             | $1.27 \times 10^{-36}$ | Silver chloride     | $\text{AgCl}$             | $1.77 \times 10^{-10}$ |
| Iron(II) carbonate  | $\text{FeCO}_3$          | $3.07 \times 10^{-11}$ | Silver chromate     | $\text{Ag}_2\text{CrO}_4$ | $1.12 \times 10^{-12}$ |
| Iron(II) hydroxide  | $\text{Fe}(\text{OH})_2$ | $4.87 \times 10^{-17}$ | Silver bromide      | $\text{AgBr}$             | $5.35 \times 10^{-13}$ |
| Iron(II) sulfide*   | $\text{FeS}$             | $3.72 \times 10^{-19}$ | Silver iodide       | $\text{AgI}$              | $8.51 \times 10^{-17}$ |

\*Sulfide equilibrium is of the type:  $\text{MS}(s) + \text{H}_2\text{O}(l) \rightleftharpoons \text{M}^{2+}(aq) + \text{HS}^-(aq) + \text{OH}^-(aq)$

Notice that  $K_{\text{sp}}$  is *not* the molar solubility, but the solubility product constant. The solubility product constant has only one value at a given temperature. The solubility, however, can have different values in different kinds of solutions. For example, due to the common ion effect, the solubility of  $\text{AgCl}$  in pure water is different from its solubility in an  $\text{NaCl}$  solution, even though the solubility product constant is the same for both solutions. Notice also that the solubility of  $\text{AgCl}$  is directly related (by the reaction stoichiometry) to the amount of  $\text{Ag}^+$  or  $\text{Cl}^-$  present in solution when equilibrium is reached. Consequently, finding molar solubility from  $K_{\text{sp}}$  involves solving an equilibrium problem. For  $\text{AgCl}$ , we set up an ICE table for the dissolution of  $\text{AgCl}$  into its ions in pure water:



|         | $[\text{Ag}^+]$ | $[\text{Cl}^-]$ |
|---------|-----------------|-----------------|
| Initial | 0.00            | 0.00            |
| Change  | $+S$            | $+S$            |
| Equil   | $S$             | $S$             |

Alternatively, the variable  $x$  can be used in place of  $S$ , as it was for other equilibrium calculations.

We let  $S$  represent the concentration of  $\text{AgCl}$  that dissolves (which is the molar solubility) and then represent the concentrations of the ions formed in terms of  $S$ . In this case, for every 1 mol of  $\text{AgCl}$  that dissolves, 1 mol of  $\text{Ag}^+$  and 1 mol of  $\text{Cl}^-$  are produced. Therefore, the concentrations of  $\text{Ag}^+$  or  $\text{Cl}^-$  present in solution are equal to  $S$ . Substituting the equilibrium concentrations of  $\text{Ag}^+$  and  $\text{Cl}^-$  into the expression for the solubility product constant, we get:

$$\begin{aligned} K_{\text{sp}} &= [\text{Ag}^+][\text{Cl}^-] \\ &= S \times S \\ &= S^2 \end{aligned}$$

Therefore,

$$\begin{aligned} S &= \sqrt{K_{\text{sp}}} \\ &= \sqrt{1.77 \times 10^{-10}} \\ &= 1.33 \times 10^{-5} \text{ M} \end{aligned}$$

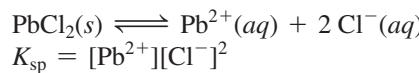
The molar solubility of  $\text{AgCl}$  is  $1.33 \times 10^{-5}$  mol per liter.

### EXAMPLE 16.8 Calculating Molar Solubility from $K_{\text{sp}}$

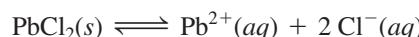
Calculate the molar solubility of  $\text{PbCl}_2$  in pure water.

#### SOLUTION

Begin by writing the reaction by which solid  $\text{PbCl}_2$  dissolves into its constituent aqueous ions and write the corresponding expression for  $K_{\text{sp}}$ .



Refer to the stoichiometry of the reaction and prepare an ICE table, showing the equilibrium concentrations of  $\text{Pb}^{2+}$  and  $\text{Cl}^-$  relative to  $S$ , the amount of  $\text{PbCl}_2$  that dissolves.



|         | $[\text{Pb}^{2+}]$ | $[\text{Cl}^-]$ |
|---------|--------------------|-----------------|
| Initial | 0.00               | 0.00            |
| Change  | $+S$               | $+2S$           |
| Equil   | $S$                | $2S$            |

Substitute the equilibrium expressions for  $[\text{Pb}^{2+}]$  and  $[\text{Cl}^-]$  from the previous step into the expression for  $K_{\text{sp}}$ .

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{Cl}^-]^2$$

$$= S(2S)^2 = 4S^3$$

Solve for  $S$  and substitute the numerical value of  $K_{\text{sp}}$  (from Table 16.2) to calculate  $S$ .

$$S = \sqrt[3]{\frac{K_{\text{sp}}}{4}}$$

$$S = \sqrt[3]{\frac{1.17 \times 10^{-5}}{4}} = 1.43 \times 10^{-2} \text{ M}$$

#### FOR PRACTICE 16.8

Calculate the molar solubility of  $\text{Fe(OH)}_2$  in pure water.



## Chemistry in Your Day

### Hard Water

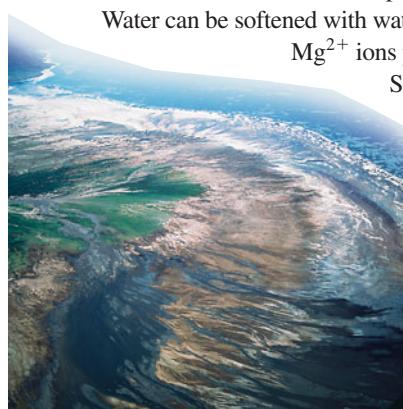
In many parts of the United States, significant concentrations of  $\text{CaCO}_3$  and  $\text{MgCO}_3$  dissolve into rainwater runoff as it flows through soils rich in these compounds.

Water containing dissolved calcium and magnesium ions is known as hard water.

Hard water is not a health hazard because both calcium and magnesium are part of a healthy diet. However, their presence in water can be a nuisance. Because of their relatively low solubility, the water becomes saturated with  $\text{CaCO}_3$  and  $\text{MgCO}_3$  as it evaporates. If evaporation continues, some dissolved ions precipitate out as salts. These precipitates show up as scaly deposits on faucets, sinks, or cookware. Washing cars or dishes with hard water leaves spots of  $\text{CaCO}_3$  and  $\text{MgCO}_3$ .

Water can be softened with water softeners. These devices replace the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions present in hard water with ions such as  $\text{K}^+$  or  $\text{Na}^+$ .

Since potassium and sodium salts are soluble, they do not form scaly deposits in the way that  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions do. However, when sodium is used to soften drinking water, the resulting water is high in sodium content, a disadvantage to those who must control their sodium intake due to high blood pressure.



### Question

Use the  $K_{\text{sp}}$  values from Table 16.2 to calculate the molar solubility of  $\text{CaCO}_3$  and  $\text{MgCO}_3$ . What mass of  $\text{CaCO}_3$  (in grams) is in 5 L of water that is saturated with  $\text{CaCO}_3$ ?



▲ The water in reservoirs where the soil is rich in limestone (calcium carbonate) contains  $\text{Ca}^{2+}$  ions. This so-called “hard water” contains dissolved  $\text{CaCO}_3$  and  $\text{MgCO}_3$ . When hard water evaporates, it can leave deposits of these salts on the shores of lakes and reservoirs (left) and on plumbing fixtures (such as the pipe shown here).

### EXAMPLE 16.9 Calculating $K_{\text{sp}}$ from Molar Solubility

The molar solubility of  $\text{Ag}_2\text{SO}_4$  in pure water is  $1.2 \times 10^{-5} \text{ M}$ . Calculate  $K_{\text{sp}}$ .

#### SOLUTION

Begin by writing the reaction by which solid  $\text{Ag}_2\text{SO}_4$  dissolves into its constituent aqueous ions, then write the corresponding expression for  $K_{\text{sp}}$ .



$$K_{\text{sp}} = [\text{Ag}^+]^2[\text{SO}_4^{2-}]$$

Use an ICE table to define  $[\text{Ag}^+]$  and  $[\text{SO}_4^{2-}]$  in terms of  $S$ , the amount of  $\text{Ag}_2\text{SO}_4$  that dissolves.



|         | $[\text{Ag}^+]$ | $[\text{SO}_4^{2-}]$ |
|---------|-----------------|----------------------|
| Initial | 0.00            | 0.00                 |
| Change  | $+2S$           | $+S$                 |
| Equil   | $2S$            | $S$                  |

Substitute the expressions for  $[\text{Ag}^+]$  and  $[\text{SO}_4^{2-}]$  from the previous step into the expression for  $K_{\text{sp}}$ . Substitute the given value of the molar solubility for  $S$  and calculate  $K_{\text{sp}}$ .

$$\begin{aligned} K_{\text{sp}} &= [\text{Ag}^+]^2[\text{SO}_4^{2-}] \\ &= (2S)^2 S \\ &= 4S^3 \\ &= 4(1.2 \times 10^{-5})^3 \\ &= 6.9 \times 10^{-15} \end{aligned}$$

#### FOR PRACTICE 16.9

The molar solubility of  $\text{AgBr}$  in pure water is  $7.3 \times 10^{-7} \text{ M}$ . Calculate  $K_{\text{sp}}$ .

### $K_{\text{sp}}$ and Relative Solubility

As we have just seen, molar solubility and  $K_{\text{sp}}$  are related, and each can be calculated from the other; however, you cannot generally use the  $K_{\text{sp}}$  values of two different compounds to directly compare their relative solubilities. For example, consider the following compounds, their  $K_{\text{sp}}$  values, and their molar solubilities:

| Compound          | $K_{\text{sp}}$        | Solubility                      |
|-------------------|------------------------|---------------------------------|
| $\text{Mg(OH)}_2$ | $2.06 \times 10^{-13}$ | $3.72 \times 10^{-5} \text{ M}$ |
| $\text{FeCO}_3$   | $3.07 \times 10^{-11}$ | $5.54 \times 10^{-6} \text{ M}$ |

Magnesium hydroxide has a smaller  $K_{\text{sp}}$  than iron(II) carbonate, but a higher molar solubility. Why? The relationship between  $K_{\text{sp}}$  and molar solubility depends on the stoichiometry of the dissociation reaction. Consequently, any direct comparison of  $K_{\text{sp}}$  values for different compounds can only be made if the compounds have the same dissociation stoichiometry. Consider the following compounds with the same dissociation stoichiometry, their  $K_{\text{sp}}$  values, and their molar solubilities:

| Compound          | $K_{\text{sp}}$        | Solubility                      |
|-------------------|------------------------|---------------------------------|
| $\text{Mg(OH)}_2$ | $2.06 \times 10^{-13}$ | $3.72 \times 10^{-5} \text{ M}$ |
| $\text{CaF}_2$    | $1.46 \times 10^{-10}$ | $3.32 \times 10^{-4} \text{ M}$ |

In this case, magnesium hydroxide and calcium fluoride have the same dissociation stoichiometry (1 mol of each compound produces 3 mol of dissolved ions); therefore, the  $K_{\text{sp}}$  values can be directly compared as a measure of relative solubility.

### The Effect of a Common Ion on Solubility

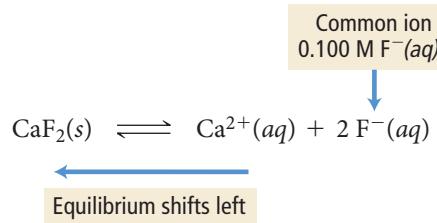
How is the solubility of an ionic compound affected when the compound is dissolved in a solution that already contains one of its ions? For example, what is the solubility of  $\text{CaF}_2$  in a solution that is  $0.100 \text{ M}$  in  $\text{NaF}$ ? We can determine the change in

solubility by considering the common ion effect, which we first encountered in Section 16.2. We represent the dissociation of  $\text{CaF}_2$  in a 0.100 M NaF solution as shown at right.

In accordance with Le Châtelier's principle, the presence of the  $\text{F}^-$  ion in solution causes the equilibrium to shift to the left (compared to its position in pure water), which means that less  $\text{CaF}_2$  dissolves—that is, its solubility is decreased.

**In general, the solubility of an ionic compound is lower in a solution containing a common ion than in pure water.**

We can calculate the exact value of the solubility by working an equilibrium problem in which the concentration of the common ion is accounted for in the initial conditions, as shown in Example 16.10.

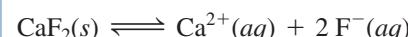


### EXAMPLE 16.10 Calculating Molar Solubility in the Presence of a Common Ion

What is the molar solubility of  $\text{CaF}_2$  in a solution containing 0.100 M NaF?

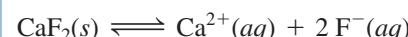
#### SOLUTION

Begin by writing the reaction by which solid  $\text{CaF}_2$  dissolves into its constituent aqueous ions. Write the corresponding expression for  $K_{\text{sp}}$ .



$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{F}^-]^2$$

Use the stoichiometry of the reaction to prepare an ICE table showing the initial concentration of the common ion. Fill in the equilibrium concentrations of  $\text{Ca}^{2+}$  and  $\text{F}^-$  relative to  $S$ , the amount of  $\text{CaF}_2$  that dissolves.



|         | $[\text{Ca}^{2+}]$ | $[\text{F}^-]$ |
|---------|--------------------|----------------|
| Initial | 0.00               | 0.100          |
| Change  | $+S$               | $+2S$          |
| Equil   | $S$                | $0.100 + 2S$   |

Substitute the equilibrium expressions for  $[\text{Ca}^{2+}]$  and  $[\text{F}^-]$  from the previous step into the expression for  $K_{\text{sp}}$ . Since  $K_{\text{sp}}$  is small, you can make the approximation that  $2S$  is much less than 0.100 and will therefore be insignificant when added to 0.100 (this is similar to the *x is small* approximation in equilibrium problems).

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{F}^-]^2$$

$$= S(0.100 + 2S)^2 \quad (\text{S is small})$$

$$= S(0.100)^2$$

Solve for  $S$  and substitute the numerical value of  $K_{\text{sp}}$  (from Table 16.2) to calculate  $S$ .

$$K_{\text{sp}} = S(0.100)^2$$

Note that the calculated value of  $S$  is indeed small compared to 0.100; our approximation is valid.

$$S = \frac{K_{\text{sp}}}{0.0100} = \frac{1.46 \times 10^{-10}}{0.0100} = 1.46 \times 10^{-8} \text{ M}$$

For comparison, the molar solubility of  $\text{CaF}_2$  in pure water is  $3.32 \times 10^{-4}$  M, which means  $\text{CaF}_2$  is over 20,000 times more soluble in water than in the NaF solution. (Confirm this for yourself by calculating its solubility in pure water from the value of  $K_{\text{sp}}$ ).

#### FOR PRACTICE 16.10

Calculate the molar solubility of  $\text{CaF}_2$  in a solution containing 0.250 M  $\text{Ca}(\text{NO}_3)_2$ .



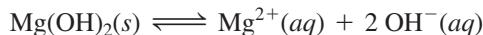
#### Conceptual Connection 16.8 Common Ion Effect

In which solution is  $\text{BaSO}_4$  most soluble?

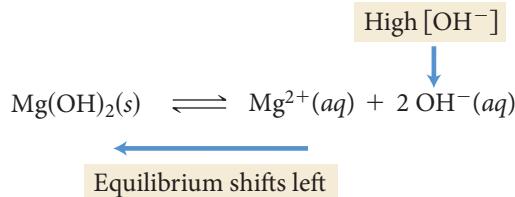
- (a) in a solution that is 0.10 M in  $\text{BaNO}_3$
- (b) in a solution that is 0.10 M in  $\text{Na}_2\text{SO}_4$
- (c) in a solution that is 0.10 M in  $\text{NaNO}_3$

## The Effect of pH on Solubility

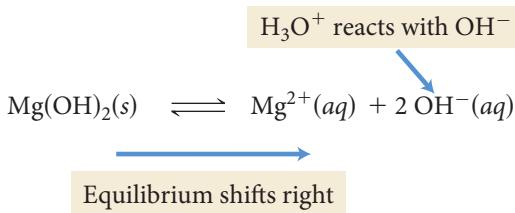
The pH of a solution can affect the solubility of a compound in that solution. For example, consider the dissociation of  $\text{Mg}(\text{OH})_2$ , the active ingredient in milk of magnesia:



The solubility of this compound is highly dependent on the pH of the solution into which it dissolves. If the pH is high, then the concentration of  $\text{OH}^-$  in the solution is high. In accordance with the common ion effect, this shifts the equilibrium to the left, lowering the solubility:



If the pH is low, then the concentration of  $\text{H}_3\text{O}^+(aq)$  in the solution is high. As the  $\text{Mg}(\text{OH})_2$  dissolves, these  $\text{H}_3\text{O}^+$  ions neutralize the newly dissolved  $\text{OH}^-$  ions, driving the reaction to the right:



Consequently, the solubility of  $\text{Mg}(\text{OH})_2$  in an acidic solution is higher than in a pH-neutral or basic solution.

**In general, the solubility of an ionic compound with a strongly basic or weakly basic anion increases with increasing acidity (decreasing pH).**

Common basic anions include  $\text{OH}^-$ ,  $\text{S}^{2-}$ , and  $\text{CO}_3^{2-}$ . Therefore, hydroxides, sulfides, and carbonates are more soluble in acidic water than in pure water. Since rainwater is naturally acidic due to dissolved carbon dioxide, it can dissolve rocks high in limestone ( $\text{CaCO}_3$ ) as it flows through the ground, sometimes resulting in huge underground caverns such as those at Carlsbad Caverns National Park in New Mexico. Dripping water saturated in  $\text{CaCO}_3$  within the cave creates the dramatic mineral formations known as stalagmites and stalactites.



▲ Stalactites (which hang from the ceiling) and stalagmites (which grow up from the ground) form as calcium carbonate precipitates out of the water evaporating in underground caves.

### EXAMPLE 16.11 The Effect of pH on Solubility

Determine whether each compound is more soluble in an acidic solution than in a neutral solution.

- (a)  $\text{BaF}_2$       (b)  $\text{AgI}$       (c)  $\text{Ca}(\text{OH})_2$

#### SOLUTION

- (a) The solubility of  $\text{BaF}_2$  is greater in acidic solution because the  $\text{F}^-$  ion is a weak base. ( $\text{F}^-$  is the conjugate base of the weak acid HF and is therefore a weak base.)
- (b) The solubility of  $\text{AgI}$  is not greater in acidic solution because the  $\text{I}^-$  is *not* a base. ( $\text{I}^-$  is the conjugate base of the *strong* acid HI and is therefore pH-neutral.)
- (c) The solubility of  $\text{Ca}(\text{OH})_2$  is greater in acidic solution because the  $\text{OH}^-$  ion is a strong base.

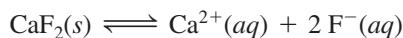
#### FOR PRACTICE 16.11

Which compound,  $\text{FeCO}_3$  or  $\text{PbBr}_2$ , is more soluble in acid than in base? Why?

## 16.6 Precipitation

In Chapter 4, we learned that a precipitation reaction can occur upon the mixing of two solutions containing ionic compounds when one of the possible cross products—the combination of a cation from one solution and the anion from the other—is insoluble. In this chapter, however, we have seen that the terms *soluble* and *insoluble* are extremes in a continuous range of solubility—many compounds are slightly soluble and even those that we categorized as insoluble in Chapter 4 actually have some limited degree of solubility (they have very small solubility product constants).

We can better understand precipitation reactions by revisiting a concept from Chapter 14—the reaction quotient ( $Q$ ). The reaction quotient for the reaction by which an ionic compound dissolves is the product of the concentrations of the ionic components raised to their stoichiometric coefficients. For example, consider the reaction by which  $\text{CaF}_2$  dissolves:



The reaction quotient for this reaction is:

$$Q = [\text{Ca}^{2+}][\text{F}^-]^2$$

The difference between  $Q$  and  $K_{\text{sp}}$  is that  $K_{\text{sp}}$  is the value of this product *at equilibrium only*, whereas  $Q$  is the value of the product under any conditions. We can therefore use the value of  $Q$  to compare a solution containing any concentrations of the component ions to a solution that is at equilibrium.

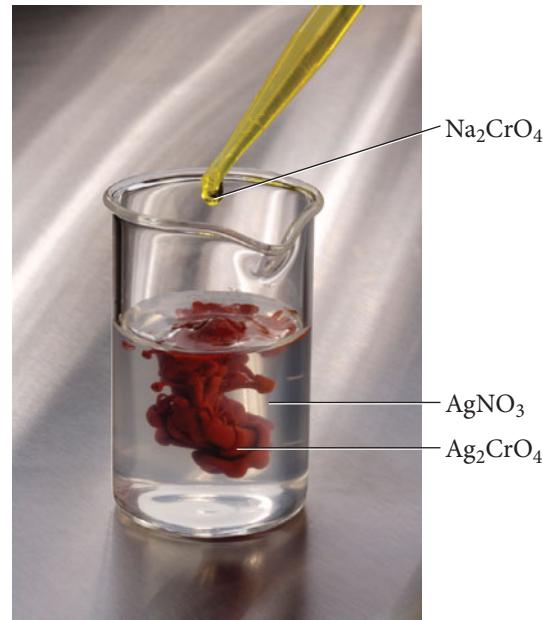
Consider a solution of calcium fluoride in which  $Q$  is less than  $K_{\text{sp}}$ . Recall from Chapter 14 that if  $Q$  is less than  $K_{\text{sp}}$ , the reaction will proceed to the right (toward products). Consequently, if the solution contains any solid  $\text{CaF}_2$ , the  $\text{CaF}_2$  will continue to dissolve. If all of the solid has already dissolved, the solution will simply remain as it is, containing less than the equilibrium amount of the dissolved ions. Such a solution is an *unsaturated solution*. If more solid is added to an unsaturated solution, it will dissolve, as long as  $Q$  remains less than  $K_{\text{sp}}$ .

Now consider a solution in which  $Q$  is exactly equal to  $K_{\text{sp}}$ . In this case, the reaction is at equilibrium and will not make progress in either direction. Such a solution most likely contains at least a small amount of the solid in equilibrium with its component ions. However, the amount of solid may be too small to be visible. Such a solution is a *saturated solution*.

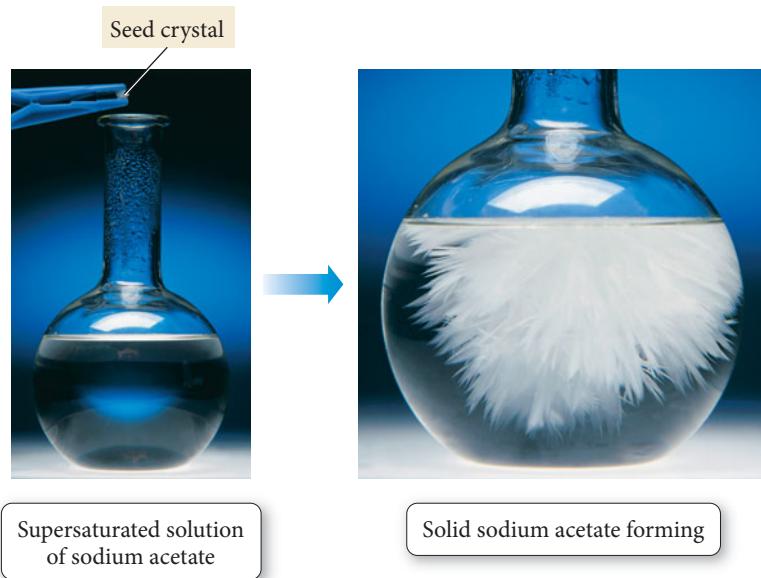
Finally, consider a solution in which  $Q$  is greater than  $K_{\text{sp}}$ . In this case, the reaction will proceed to the left (toward the reactants) and solid calcium fluoride will form from the dissolved calcium and fluoride ions. In other words, the solid normally precipitates out of a solution in which  $Q$  is greater than  $K_{\text{sp}}$ . Under certain circumstances, however,  $Q$  can remain greater than  $K_{\text{sp}}$  for an unlimited period of time. Such a solution, called a *supersaturated solution*, is unstable and will form a precipitate when sufficiently disturbed. Figure 16.14▶ shows a supersaturated solution of sodium acetate. When a small seed crystal of solid sodium acetate is dropped into the solution, it triggers the precipitation reaction.

### Summarizing the Relationship of $Q$ and $K_{\text{sp}}$ in Solutions Containing an Ionic Compound:

- If  $Q < K_{\text{sp}}$ , the solution is unsaturated and more of the solid ionic compound can dissolve in the solution.
- If  $Q = K_{\text{sp}}$ , the solution is saturated. The solution is holding the equilibrium amount of the dissolved ions and additional solid does not dissolve in the solution.
- If  $Q > K_{\text{sp}}$ , the solution is supersaturated. Under most circumstances, the excess solid precipitates out of a supersaturated solution.



**▼ FIGURE 16.14** Precipitation from a Supersaturated Solution The excess solute in a supersaturated solution of sodium acetate precipitates out if a small sodium acetate crystal is added.



We can use  $Q$  to predict whether a precipitation reaction will occur upon the mixing of two solutions containing dissolved ionic compounds. For example, consider mixing a silver nitrate solution with a potassium iodide solution to form a mixture that is 0.010 M in  $\text{AgNO}_3$  and 0.015 M in  $\text{KI}$ . Will a precipitate form in the newly mixed solution? From Chapter 4 we know that one of the cross products,  $\text{KNO}_3$ , is soluble and will therefore not precipitate. The other cross product,  $\text{AgI}$ , *may* precipitate if the concentrations of  $\text{Ag}^+$  and  $\text{I}^-$  are high enough in the newly mixed solution: we can compare  $Q$  to  $K_{\text{sp}}$  to determine if a precipitate will form. For  $\text{AgI}$ ,  $K_{\text{sp}} = 8.51 \times 10^{-17}$ . For the newly mixed solution,  $[\text{Ag}^+] = 0.010\text{M}$  and  $[\text{I}^-] = 0.015\text{M}$ . We calculate  $Q$  as follows:

$$Q = [\text{Ag}^+][\text{I}^-] = (0.010)(0.015) = 1.5 \times 10^{-4}$$

The value of  $Q$  is much greater than  $K_{\text{sp}}$ ; therefore,  $\text{AgI}$  should precipitate out of the newly mixed solution.

### EXAMPLE 16.12 Predicting Precipitation Reactions by Comparing $Q$ and $K_{\text{sp}}$

A solution containing lead(II) nitrate is mixed with one containing sodium bromide to form a solution that is 0.0150 M in  $\text{Pb}(\text{NO}_3)_2$  and 0.00350 M in  $\text{NaBr}$ . Does a precipitate form in the newly mixed solution?

#### SOLUTION

|  |   |
|--|---|
| First, determine the possible cross products and their $K_{\text{sp}}$ values (Table 16.2). Any cross products that are soluble will <i>not</i> precipitate (see Table 4.1). | Possible cross products:<br>$\text{NaNO}_3$ soluble<br>$\text{PbBr}_2 \quad K_{\text{sp}} = 4.67 \times 10^{-6}$                            |
| Calculate $Q$ and compare it to $K_{\text{sp}}$ . A precipitate will only form if $Q > K_{\text{sp}}$ .  | $Q = [\text{Pb}^{2+}][\text{Br}^-]^2$ $= (0.0150)(0.00350)^2$ $= 1.84 \times 10^{-7}$ $Q < K_{\text{sp}}$ ; therefore no precipitate forms. |

#### FOR PRACTICE 16.12

If the original solutions in Example 16.12 are concentrated through evaporation and mixed again to form a solution that is 0.0600 M in  $\text{Pb}(\text{NO}_3)_2$  and 0.0158 M in  $\text{NaBr}$ , will a precipitate form in this newly mixed solution?

### Selective Precipitation

A solution may contain several different dissolved metal cations that can often be separated by **selective precipitation**, a process involving the addition of a reagent that forms a precipitate with one of the dissolved cations but not the others. For example, seawater contains dissolved magnesium and calcium cations with the concentrations  $[\text{Mg}^{2+}] = 0.059\text{ M}$  and  $[\text{Ca}^{2+}] = 0.011\text{ M}$ . We can separate these ions by adding a reagent that will precipitate one of the ions but not the other. From Table 16.2, we find that  $\text{Mg}(\text{OH})_2$  has a  $K_{\text{sp}}$  of  $2.06 \times 10^{-13}$  and that  $\text{Ca}(\text{OH})_2$  has a  $K_{\text{sp}}$  of  $4.68 \times 10^{-6}$ , indicating that the hydroxide ion forms a precipitate with magnesium at a much lower concentration than it does with calcium. Consequently, a soluble hydroxide—such as KOH or NaOH—is a good choice for the precipitating reagent. When we add an appropriate amount of KOH or NaOH to seawater, the hydroxide ion causes the precipitation of  $\text{Mg}(\text{OH})_2$  (the compound with the lowest  $K_{\text{sp}}$ ) but not  $\text{Ca}(\text{OH})_2$ . Calculations for this selective precipitation are shown in Examples 16.13 and 16.14. In these calculations, you compare  $Q$  to  $K_{\text{sp}}$  to determine the concentration that triggers precipitation.

The difference in  $K_{\text{sp}}$  values required for selective precipitation is a factor of at least  $10^3$ .

### EXAMPLE 16.13 Finding the Minimum Required Reagent Concentration for Selective Precipitation

The magnesium and calcium ions present in seawater ( $[Mg^{2+}] = 0.059\text{ M}$  and  $[Ca^{2+}] = 0.011\text{ M}$ ) can be separated by selective precipitation with KOH. What minimum  $[OH^-]$  triggers the precipitation of the  $Mg^{2+}$  ion?

#### SOLUTION

The precipitation commences when the value of  $Q$  for the precipitating compound just equals the value of  $K_{sp}$ . Set the expression for  $Q$  for magnesium hydroxide equal to the value of  $K_{sp}$ , and solve for  $[OH^-]$ . This is the concentration above which  $Mg(OH)_2$  precipitates.

$$Q = [Mg^{2+}][OH^-]^2 \\ = (0.059)[OH^-]^2$$

When  $Q = K_{sp}$ ,

$$(0.059)[OH^-]^2 = K_{sp} = 2.06 \times 10^{-13}$$

$$[OH^-]^2 = \frac{2.06 \times 10^{-13}}{0.059}$$

$$[OH^-] = 1.9 \times 10^{-6}\text{ M}$$

#### FOR PRACTICE 16.13

If the concentration of  $Mg^{2+}$  in the previous solution was  $0.025\text{ M}$ , what minimum  $[OH^-]$  triggers precipitation of the  $Mg^{2+}$  ion?

### EXAMPLE 16.14 Finding the Concentrations of Ions Left in Solution after Selective Precipitation

You add potassium hydroxide to the solution in Example 16.13. When the  $[OH^-]$  reaches  $1.9 \times 10^{-6}\text{ M}$  (as you just calculated), magnesium hydroxide begins to precipitate out of solution. As you continue to add KOH, the magnesium hydroxide continues to precipitate. However, at some point, the  $[OH^-]$  becomes high enough to begin to precipitate the calcium ions as well. What is the concentration of  $Mg^{2+}$  when  $Ca^{2+}$  begins to precipitate?

#### SOLUTION

First, find the  $OH^-$  concentration at which  $Ca^{2+}$  begins to precipitate by writing the expression for  $Q$  for calcium hydroxide and substituting the concentration of  $Ca^{2+}$  from Example 16.13.

$$Q = [Ca^{2+}][OH^-]^2 \\ = (0.011)[OH^-]^2$$

Set the expression for  $Q$  equal to the value of  $K_{sp}$  for calcium hydroxide and solve for  $[OH^-]$ . This is the concentration above which  $Ca(OH)_2$  precipitates.

$$\begin{aligned} \text{When } Q &= K_{sp}, \\ (0.011)[OH^-]^2 &= K_{sp} = 4.68 \times 10^{-6} \\ [OH^-]^2 &= \frac{4.68 \times 10^{-6}}{0.011} \\ [OH^-] &= 2.06 \times 10^{-2}\text{ M} \end{aligned}$$

Find the concentration of  $Mg^{2+}$  when  $OH^-$  reaches the concentration you just calculated by writing the expression for  $Q$  for magnesium hydroxide and substituting the concentration of  $OH^-$  that you just calculated. Then set the expression for  $Q$  equal to the value of  $K_{sp}$  for magnesium hydroxide and solve for  $[Mg^{2+}]$ . This is the concentration of  $Mg^{2+}$  that remains when  $Ca(OH)_2$  begins to precipitate.

$$\begin{aligned} Q &= [Mg^{2+}][OH^-]^2 \\ &= [Mg^{2+}](2.06 \times 10^{-2})^2 \end{aligned}$$

When  $Q = K_{sp}$ ,

$$\begin{aligned} [Mg^{2+}](2.06 \times 10^{-2})^2 &= K_{sp} = 2.06 \times 10^{-13} \\ [Mg^{2+}] &= \frac{2.06 \times 10^{-13}}{(2.06 \times 10^{-2})^2} \\ [Mg^{2+}] &= 4.9 \times 10^{-10}\text{ M} \end{aligned}$$

As you can see from the results, the selective precipitation worked very well. The concentration of  $Mg^{2+}$  dropped from 0.059 M to  $4.9 \times 10^{-10}$  M before any calcium began to precipitate, which means that we separated 99.99% of the magnesium out of the solution.

#### FOR PRACTICE 16.14

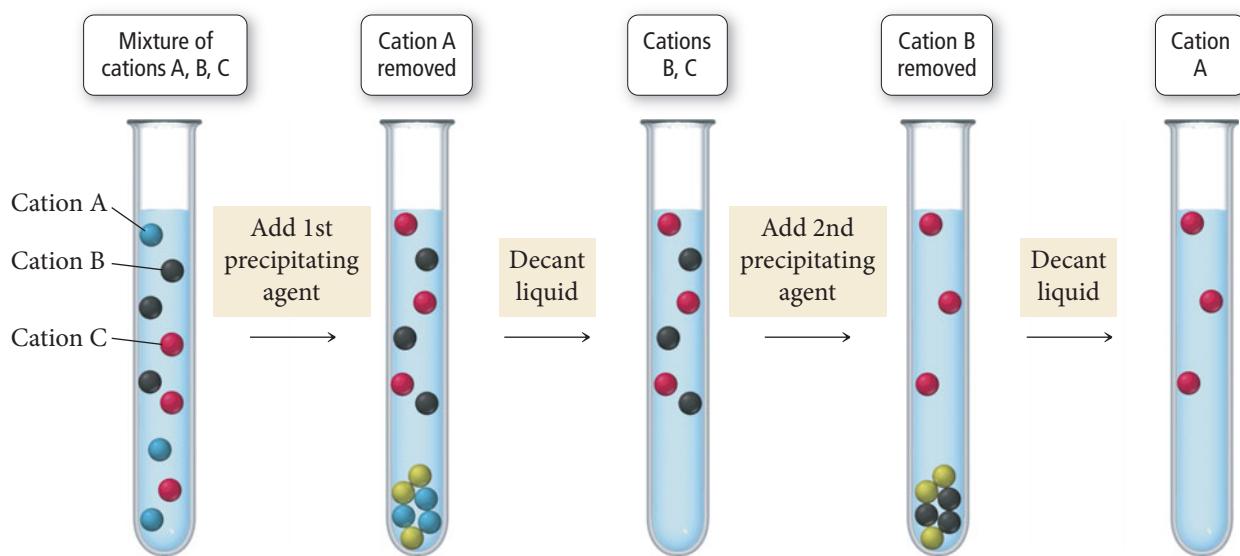
A solution is 0.085 M in  $Pb^{2+}$  and 0.025 M in  $Ag^+$ . (a) If selective precipitation is to be achieved using NaCl, what minimum concentration of NaCl do you need to begin to precipitate the ion that precipitates first? (b) What is the concentration of each ion left in solution at the point where the second ion begins to precipitate?

## 16.7 Qualitative Chemical Analysis

Selective precipitation as discussed in Section 16.6 can be used in a systematic way to determine which metal ions are present in an unknown solution. This method is known as **qualitative analysis**. The word *qualitative* means *involving quality or kind*. Qualitative analysis involves finding the *kind* of ions present in the solution. This stands in contrast to **quantitative analysis**, which is concerned with quantity, or the amounts of substances in a solution or mixture.

In the past, qualitative analysis by selective precipitation was used extensively to determine the metals present in a sample. This process—dubbed *wet chemistry* because it involves the mixing of many aqueous solutions in the lab—has been replaced by more precise and less time-intensive instrumental techniques. Nonetheless, both for the sake of history and also because of the importance of the principles involved, we now examine a traditional qualitative analysis scheme. You may use such a scheme in your general chemistry laboratory as an exercise in qualitative analysis.

The basic idea behind qualitative analysis is straightforward. A sample containing a mixture of metal cations is subjected to the addition of several precipitating agents. At each step, some of the metal cations—those that form insoluble compounds with the precipitating agent—precipitate from the mixture and are separated out as solids. The remaining aqueous mixture is then subjected to the next precipitating agent, and so on (Figure 16.15 ▶).



▲ **FIGURE 16.15** Qualitative Analysis In qualitative analysis, specific ions are precipitated successively by the addition of appropriate reagents.

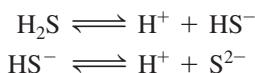
Figure 16.16 ▼ is a diagram of a general qualitative analysis scheme. The scheme involves separating a mixture of the common ions into five groups by sequentially adding five different precipitating agents. After each precipitating agent is added, the mixture is put into a centrifuge to separate the solid from the liquid. The liquid is decanted for the next step, and the solid is set aside for subsequent analysis. We examine each group separately.

## Group 1: Insoluble Chlorides

In the first step, the aqueous mixture containing the metal cations is treated with 6 M HCl. Since most chlorides are soluble, the chloride ions *do not form* a precipitate with the majority of the cations in the mixture. However,  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$ , and  $\text{Hg}_2^{2+}$  *do form* insoluble chlorides. So, if any of those metal cations are present, they precipitate out. The absence of a precipitate constitutes a negative test for  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$ , and  $\text{Hg}_2^{2+}$ . If a precipitate forms, one or more of these ions is present. After the solid is separated from the liquid, the solution is ready for the next step.

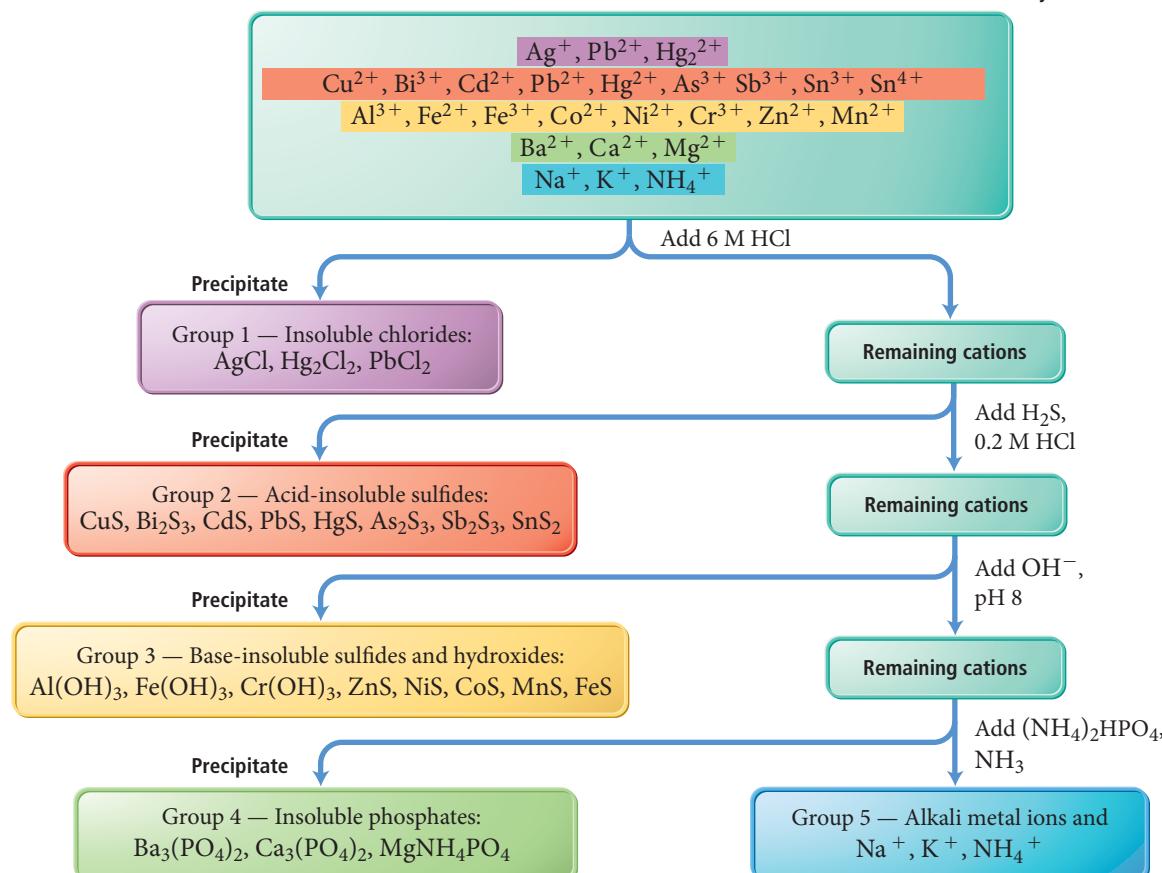
## Group 2: Acid-Insoluble Sulfides

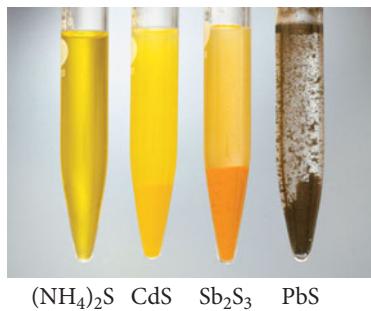
In the second step, the acidic aqueous mixture containing the remaining metal cations is treated with  $\text{H}_2\text{S}$ , a weak diprotic acid that dissociates in two steps:



The concentration of  $\text{S}^{2-}$  ions in an  $\text{H}_2\text{S}$  solution is pH-dependent. At low pH (high  $\text{H}^+$  concentration) the equilibria shift left, minimizing the amount of available  $\text{S}^{2-}$ . At high pH (low  $\text{H}^+$  concentration) the equilibria shift right, maximizing the amount of available  $\text{S}^{2-}$ .

▼ FIGURE 16.16 A General Qualitative Analysis Scheme





At this stage, the solution is acidic (from the addition of HCl in the previous step), and the concentration of S<sup>2-</sup> in solution is relatively low. Only the most insoluble metal sulfides (those with the smallest K<sub>sp</sub> values) precipitate under these conditions. These include Hg<sup>2+</sup>, Cd<sup>2+</sup>, Bi<sup>3+</sup>, Cu<sup>2+</sup>, Sn<sup>4+</sup>, As<sup>3+</sup>, Pb<sup>2+</sup>, and Sb<sup>3+</sup>. If any of these metal cations are present, they precipitate out as sulfides. After the solid is separated from the liquid, the solution is ready for the next step.

### Group 3: Base-Insoluble Sulfides and Hydroxides

In the third step, additional base and H<sub>2</sub>S are added to the acidic aqueous mixture containing the remaining metal cations. The added base reacts with acid, shifting the H<sub>2</sub>S ionization equilibria to the right and creating a higher S<sup>2-</sup> concentration. This causes the precipitation of those sulfides that were too soluble to precipitate out in the previous step but not soluble enough to prevent precipitation with the higher sulfide ion concentration. The ions that precipitate as sulfides at this point (if they are present) are Fe<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup>, and Ni<sup>2+</sup>. In addition, the additional base causes Cr<sup>3+</sup>, Fe<sup>3+</sup>, and Al<sup>3+</sup> to precipitate as hydroxides. After the solid is separated from the liquid, the solution is ready for the next step.

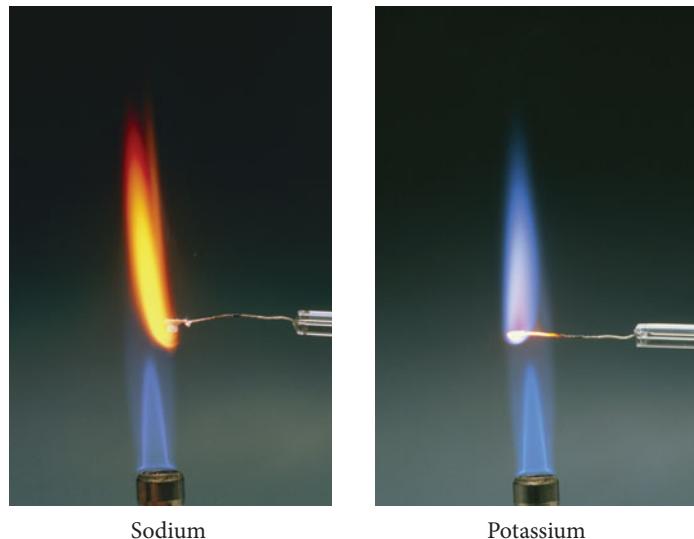
### Group 4: Insoluble Phosphates

At this stage, all of the cations have precipitated except those belonging to the alkali metal family (group 1A in the periodic table) and the alkaline earth metal family (group 2A in the periodic table). The alkaline earth metal cations can be precipitated by adding (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> to the solution, causing Mg<sup>2+</sup>, Ca<sup>2+</sup>, and Ba<sup>2+</sup> to precipitate as metal phosphates, which are separated from the liquid.

### Group 5: Alkali Metals and NH<sub>4</sub><sup>+</sup>

The only dissolved ions that the liquid decanted from the previous step can now contain are Na<sup>+</sup>, K<sup>+</sup>, and NH<sub>4</sub><sup>+</sup>. These cations do not form insoluble compounds with any anions and cannot be precipitated from the solution. Their presence can be determined, however, by other means. Sodium and potassium ions, for example, are usually identified through flame tests. The sodium ion produces a yellow-orange flame and the potassium ion produces a violet flame, as shown in Figure 16.17 ▶.

By applying this procedure, nearly two dozen metal cations can be separated from a solution initially containing all of them. Each of the groups can be further analyzed to determine which specific ions are present. The specific procedures for these steps are found in many general chemistry laboratory manuals.



► **FIGURE 16.17** Flame Tests The sodium ion produces a yellow-orange flame. The potassium ion produces a violet flame.

## 16.8 Complex Ion Equilibria

We have discussed several different types of equilibria so far, including acid–base equilibria and solubility equilibria. We now turn to equilibria of another type, which primarily involve transition metal ions in solution. Transition metal ions tend to be good electron acceptors (good Lewis acids). In aqueous solutions, water molecules can act as electron donors (Lewis bases) to hydrate transition metal ions. For example, silver ions are hydrated by water in solution to form  $\text{Ag}(\text{H}_2\text{O})_2^+(aq)$ . Chemists often write  $\text{Ag}^+(aq)$  as a shorthand notation for the hydrated silver ion, but the bare ion does not really exist by itself in solution.

Species such as  $\text{Ag}(\text{H}_2\text{O})_2^{2+}$  are known as *complex ions*. A **complex ion** contains a central metal ion bound to one or more *ligands*. A **ligand** is a neutral molecule or ion that acts as a Lewis base with the central metal ion. In  $\text{Ag}(\text{H}_2\text{O})_2^+$ , water is the ligand. If a stronger Lewis base is put into a solution containing  $\text{Ag}(\text{H}_2\text{O})_2^+$ , the stronger Lewis base displaces the water in the complex ion. For example, ammonia reacts with  $\text{Ag}(\text{H}_2\text{O})_2^+$  according to the following reaction:



For simplicity, we often leave water out of the equation:



The equilibrium constant associated with the reaction for the formation of a complex ion, such as the one just shown, is called the **formation constant** ( $K_f$ ). The expression for  $K_f$  is determined by the law of mass action, like any equilibrium constant. For  $\text{Ag}(\text{NH}_3)_2^+$ , the expression for  $K_f$  is:

$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2}$$

Notice that the value of  $K_f$  for  $\text{Ag}(\text{NH}_3)_2^+$  is large, indicating that the formation of the complex ion is highly favored. Table 16.3 lists the formation constants for a number of common complex ions. You can see that, in general, values of  $K_f$  are very large, indicating that the formation of complex ions is highly favored in each case. Example 16.15 illustrates how to use  $K_f$  in calculations.

We cover complex ions in more detail in Chapter 24. Here, we focus on the equilibria associated with their formation.

**TABLE 16.3 Formation Constants of Selected Complex Ions in Water at 25 °C**

| Complex Ion                              | $K_f$                | Complex Ion                     | $K_f$                |
|--|----------------------|---------------------------------|----------------------|
| $\text{Ag}(\text{CN})_2^-$               | $1 \times 10^{21}$   | $\text{Cu}(\text{NH}_3)_4^{2+}$ | $1.7 \times 10^{13}$ |
| $\text{Ag}(\text{NH}_3)_2^+$             | $1.7 \times 10^7$    | $\text{Fe}(\text{CN})_6^{4-}$   | $1.5 \times 10^{35}$ |
| $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ | $2.8 \times 10^{13}$ | $\text{Fe}(\text{CN})_6^{3-}$   | $2 \times 10^{43}$   |
| $\text{AlF}_6^{3-}$                      | $7 \times 10^{19}$   | $\text{Hg}(\text{CN})_4^{2-}$   | $1.8 \times 10^{41}$ |
| $\text{Al(OH)}_4^-$                      | $3 \times 10^{33}$   | $\text{HgCl}_4^{2-}$            | $1.1 \times 10^{16}$ |
| $\text{CdBr}_4^{2-}$                     | $5.5 \times 10^3$    | $\text{HgI}_4^{2-}$             | $2 \times 10^{30}$   |
| $\text{CdI}_4^{2-}$                      | $2 \times 10^6$      | $\text{Ni}(\text{NH}_3)_6^{2+}$ | $2.0 \times 10^8$    |
| $\text{Cd}(\text{CN})_4^{2-}$            | $3 \times 10^{18}$   | $\text{Pb}(\text{OH})_3^-$      | $8 \times 10^{13}$   |
| $\text{Co}(\text{NH}_3)_6^{3+}$          | $2.3 \times 10^{33}$ | $\text{Sn}(\text{OH})_3^-$      | $3 \times 10^{25}$   |
| $\text{Co}(\text{OH})_4^{2-}$            | $5 \times 10^9$      | $\text{Zn}(\text{CN})_4^{2-}$   | $2.1 \times 10^{19}$ |
| $\text{Co}(\text{SCN})_4^{2-}$           | $1 \times 10^3$      | $\text{Zn}(\text{NH}_3)_4^{2+}$ | $2.8 \times 10^9$    |
| $\text{Cr}(\text{OH})_4^-$               | $8.0 \times 10^{29}$ | $\text{Zn}(\text{OH})_4^{2-}$   | $2 \times 10^{15}$   |
| $\text{Cu}(\text{CN})_4^{2-}$            | $1.0 \times 10^{25}$ |                                 |                      |

### EXAMPLE 16.15 Complex Ion Equilibria

You mix a 200.0 mL sample of a solution that is  $1.5 \times 10^{-3}$  M in  $\text{Cu}(\text{NO}_3)_2$  with a 250.0 mL sample of a solution that is 0.20 M in  $\text{NH}_3$ . After the solution reaches equilibrium, what concentration of  $\text{Cu}^{2+}(aq)$  remains?

#### SOLUTION

Write the balanced equation for the complex ion equilibrium that occurs and look up the value of  $K_f$  in Table 16.3. Since this is an equilibrium problem, you have to create an ICE table, which requires the initial concentrations of  $\text{Cu}^{2+}$  and  $\text{NH}_3$ . Calculate those concentrations from the given values.

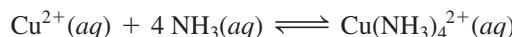
Construct an ICE table for the reaction and write down the initial concentrations of each species.

Since the equilibrium constant is large and the concentration of ammonia is much larger than the concentration of  $\text{Cu}^{2+}$ , you can assume that the reaction will be driven to the right so that most of the  $\text{Cu}^{2+}$  is consumed. Unlike previous ICE tables, where you let  $x$  represent the change in concentration in going to equilibrium, here you let  $x$  represent the small amount of  $\text{Cu}^{2+}$  that remains when equilibrium is reached.

Substitute the expressions for the equilibrium concentrations into the expression for  $K_f$  and solve for  $x$ .

Confirm that  $x$  is indeed small compared to the initial concentration of the metal cation.

The remaining  $\text{Cu}^{2+}$  is very small because the formation constant is very large.



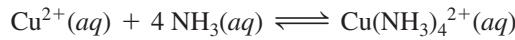
$$K_f = 1.7 \times 10^{13}$$

$$0.200 \text{ L} \times \frac{1.5 \times 10^{-3} \text{ mol}}{\text{L}}$$

$$[\text{Cu}^{2+}]_{\text{initial}} = \frac{0.200 \text{ L} + 0.250 \text{ L}}{0.200 \text{ L} + 0.250 \text{ L}} = 6.7 \times 10^{-4} \text{ M}$$

$$0.250 \text{ L} \times \frac{0.20 \text{ mol}}{1 \text{ L}}$$

$$[\text{NH}_3]_{\text{initial}} = \frac{0.200 \text{ L} + 0.250 \text{ L}}{0.200 \text{ L} + 0.250 \text{ L}} = 0.11 \text{ M}$$

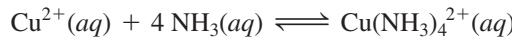


| $[\text{Cu}^{2+}]$ | $[\text{NH}_3]$ | $[\text{Cu}(\text{NH}_3)_4^{2+}]$ |
|--------------------|-----------------|-----------------------------------|
|--------------------|-----------------|-----------------------------------|

|         |                      |      |     |
|---------|----------------------|------|-----|
| Initial | $6.7 \times 10^{-4}$ | 0.11 | 0.0 |
|---------|----------------------|------|-----|

|        |  |  |  |
|--------|--|--|--|
| Change |  |  |  |
|--------|--|--|--|

|       |  |  |  |
|-------|--|--|--|
| Equil |  |  |  |
|-------|--|--|--|



| $[\text{Cu}^{2+}]$ | $[\text{NH}_3]$                 | $[\text{Cu}(\text{NH}_3)_4^{2+}]$ |
|--------------------|---------------------------------|-----------------------------------|
| Initial            | $6.7 \times 10^{-4}$            | 0.11                              |
| Change             | $\approx (-6.7 \times 10^{-4})$ | $\approx 4(-6.7 \times 10^{-4})$  |
| Equil              | $x$                             | $0.11$                            |

$$K_f = \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4}$$

$$= \frac{6.7 \times 10^{-4}}{x(0.11)^4}$$

$$x = \frac{6.7 \times 10^{-4}}{K_f(0.11)^4}$$

$$= \frac{6.7 \times 10^{-4}}{1.7 \times 10^{13}(0.11)^4}$$

$$= 2.7 \times 10^{-13}$$

Since  $x = 2.7 \times 10^{-13} \ll 6.7 \times 10^{-4}$ , the approximation is valid. The remaining  $[\text{Cu}^{2+}] = 2.7 \times 10^{-13} \text{ M}$ .

#### FOR PRACTICE 16.15

You mix a 125.0 mL sample of a solution that is 0.0117 M in  $\text{NiCl}_2$  with a 175.0 mL sample of a solution that is 0.250 M in  $\text{NH}_3$ . After the solution reaches equilibrium, what concentration of  $\text{Ni}^{2+}(aq)$  remains?

## The Effect of Complex Ion Equilibria on Solubility

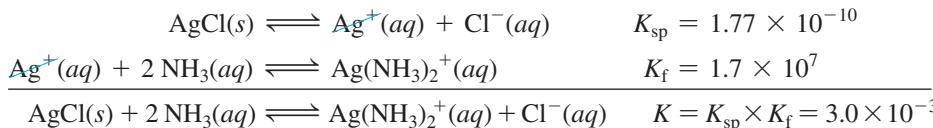
Recall from Section 16.5 that the solubility of an ionic compound with a basic anion increases with increasing acidity because the acid reacts with the anion and drives the reaction to the right. Similarly, *the solubility of an ionic compound containing a metal cation that forms complex ions increases in the presence of Lewis bases that complex with the cation*. The most common Lewis bases that increase the solubility of metal cations are  $\text{NH}_3$ ,  $\text{CN}^-$ , and  $\text{OH}^-$ . For example, silver chloride is only slightly soluble in pure water:



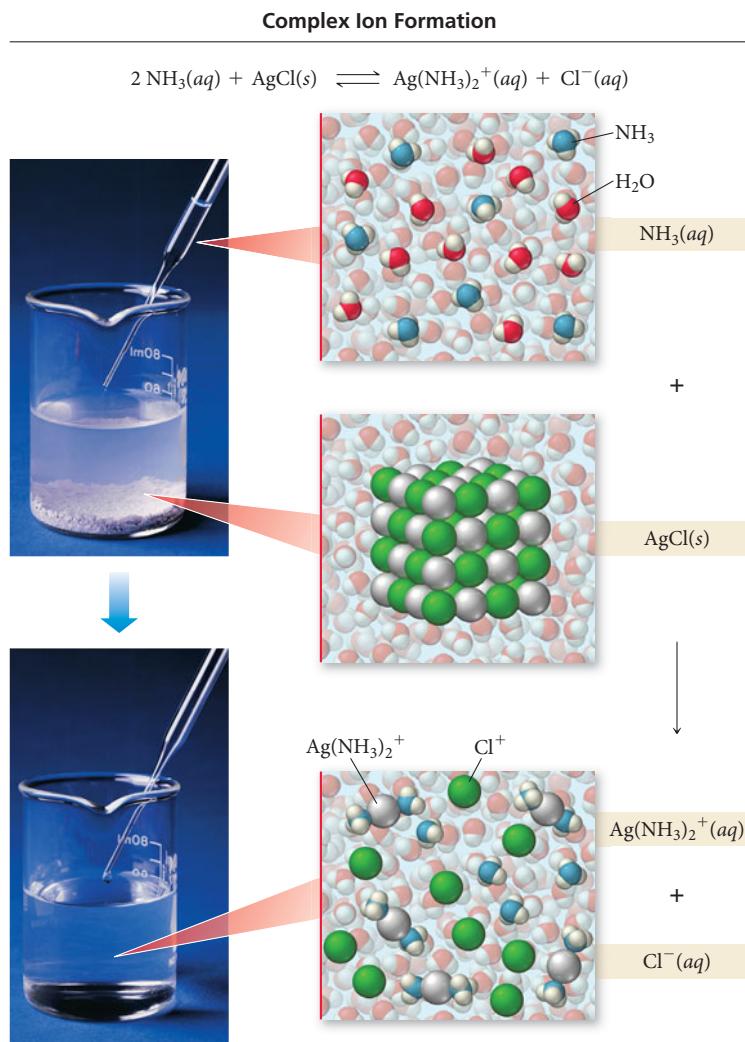
However, adding ammonia increases its solubility dramatically because, as we saw previously in this section, the ammonia forms a complex ion with the silver cations:



The large value of  $K_f$  significantly lowers the concentration of  $\text{Ag}^+(aq)$  in solution and therefore drives the dissolution of  $\text{AgCl}(s)$ . The two previous reactions can be added together:



As we learned in Section 14.3, the equilibrium constant for a reaction that is the sum of two other reactions is the product of the equilibrium constants for the two other reactions. Adding ammonia changes the equilibrium constant for the dissolution of  $\text{AgCl}(s)$  by a factor of  $3.0 \times 10^{-3}/1.77 \times 10^{-10} = 1.7 \times 10^7$  (17 million), which makes the otherwise relatively insoluble  $\text{AgCl}(s)$  quite soluble, as shown in Figure 16.18 ▼.



**◀ FIGURE 16.18** Complex Ion Formation Normally insoluble  $\text{AgCl}$  is made soluble by the addition of  $\text{NH}_3$ , which forms a complex ion with  $\text{Ag}^+$  and dissolves the  $\text{AgCl}$ .



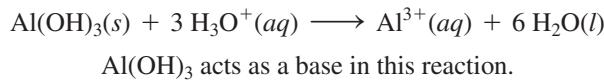
## Conceptual Connection 16.9 Solubility and Complex Ion Equilibria

Which compound, when added to water, is most likely to increase the solubility of CuS?

- (a) NaCl      (b) KNO<sub>3</sub>      (c) NaCN      (d) MgBr<sub>2</sub>

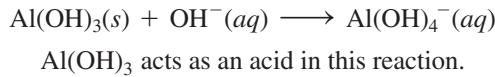
### The Solubility of Amphoteric Metal Hydroxides

Many metal hydroxides are insoluble or only very slightly soluble in pH-neutral water. For example, Al(OH)<sub>3</sub> has  $K_{sp} = 2 \times 10^{-32}$ , which means that if you put Al(OH)<sub>3</sub> in water, the vast majority of it will settle to the bottom as an undissolved solid. All metal hydroxides, however, have a basic anion (OH<sup>-</sup>) and therefore become more soluble in acidic solutions (see the previous subsection and Section 16.5). The metal hydroxides become more soluble because they can act as a base and react with H<sub>3</sub>O<sup>+</sup>(aq). For example, Al(OH)<sub>3</sub> dissolves in acid according to the reaction:



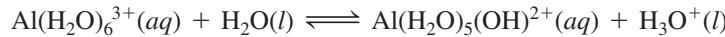
Recall from Section 15.3 that a substance that can act as either an acid or a base is said to be amphoteric.

Interestingly, some metal hydroxides can also act as acids—they are *amphoteric*. The ability of an amphoteric metal hydroxide to act as an acid increases its solubility in basic solution. For example, Al(OH)<sub>3</sub>(s) dissolves in basic solution according to the reaction:

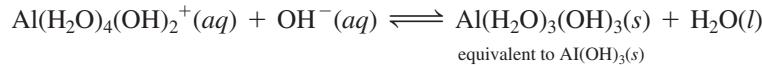


Al(OH)<sub>3</sub> is soluble at high pH and soluble at low pH but *insoluble* in a pH-neutral solution.

We can observe the whole range of the pH-dependent solubility behavior of Al<sup>3+</sup> by considering a hydrated aluminum ion in solution, beginning at an acidic pH. We know from Section 15.8 that Al<sup>3+</sup> in solution is inherently acidic because it complexes with water to form Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup>(aq). The complex ion then acts as an acid by losing a proton from one of the complexed water molecules according to the reaction:



Addition of base to the solution drives the reaction to the right and continues to remove protons from complexed water molecules:



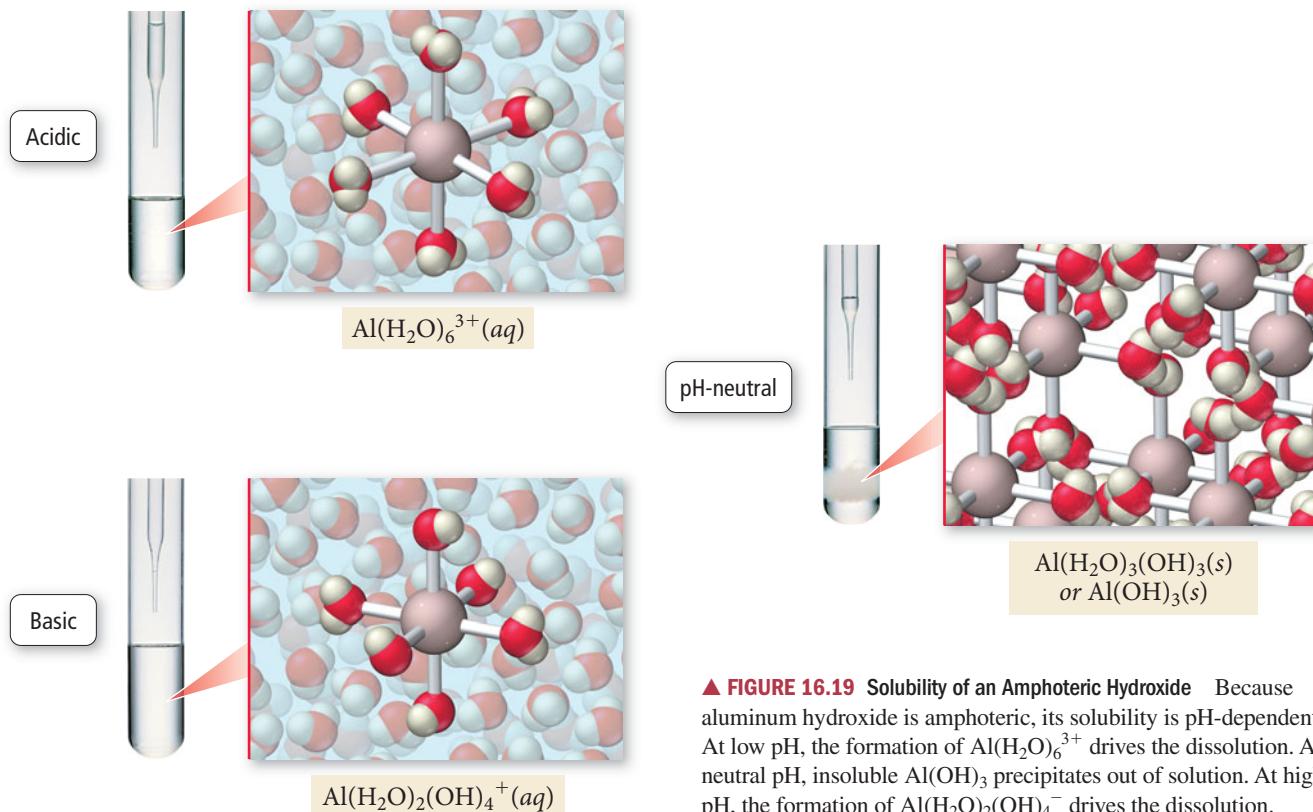
The result of removing three protons from Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> is the solid white precipitate Al(H<sub>2</sub>O)<sub>3</sub>(OH)<sub>3</sub>(s), which is more commonly written as Al(OH)<sub>3</sub>(s). The solution is now pH-neutral and the hydroxide is insoluble. Addition of more OH<sup>-</sup> makes the solution basic and dissolves the solid precipitate:



As the solution goes from acidic to neutral to basic, the solubility of Al<sup>3+</sup> changes accordingly, as illustrated in Figure 16.19 ►.

The extent to which a metal hydroxide dissolves in both acid and base depends on the degree to which it is amphoteric. Cations that form amphoteric hydroxides include Al<sup>3+</sup>, Cr<sup>3+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup>, and Sn<sup>2+</sup>. Other metal hydroxides, such as those of Ca<sup>2+</sup>, Fe<sup>2+</sup>, and Fe<sup>3+</sup>, are not amphoteric—they become soluble in acidic solutions, but not in basic ones.

### pH-Dependent Solubility of an Amphoteric Hydroxide



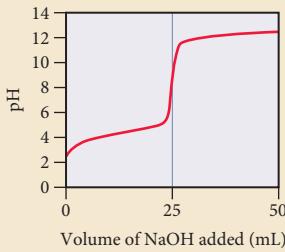
▲ **FIGURE 16.19** Solubility of an Amphoteric Hydroxide Because aluminum hydroxide is amphoteric, its solubility is pH-dependent. At low pH, the formation of  $\text{Al}(\text{H}_2\text{O})_6^{3+}$  drives the dissolution. At neutral pH, insoluble  $\text{Al}(\text{OH})_3$  precipitates out of solution. At high pH, the formation of  $\text{Al}(\text{H}_2\text{O})_2(\text{OH})_4^+$  drives the dissolution.

## CHAPTER IN REVIEW

### Self Assessment Quiz

- Q1.** A buffer is 0.100 M in  $\text{NH}_4\text{Cl}$  and 0.100 M in  $\text{NH}_3$ . When a small amount of hydrobromic acid is added to this buffer, which buffer component neutralizes the added acid?
- $\text{NH}_4^+$
  - $\text{Cl}^-$
  - $\text{NH}_3$
  - None of the above (hydrobromic acid will not be neutralized by this buffer).
- Q2.** What is the pH of a buffer that is 0.120 M in formic acid ( $\text{HCHO}_2$ ) and 0.080 M in potassium formate ( $\text{KCHO}_2$ )? For formic acid,  $K_a = 1.8 \times 10^{-4}$ .
- 2.33
  - 3.57
  - 3.74
  - 3.91
- Q3.** A buffer with a pH of 9.85 contains  $\text{CH}_3\text{NH}_2$  and  $\text{CH}_3\text{NH}_3\text{Cl}$  in water. What can you conclude about the relative concentrations of  $\text{CH}_3\text{NH}_2$  and  $\text{CH}_3\text{NH}_3\text{Cl}$  in this buffer? For  $\text{CH}_3\text{NH}_2$ ,  $pK_b = 3.36$ .
- $\text{CH}_3\text{NH}_2 > \text{CH}_3\text{NH}_3\text{Cl}$
  - $\text{CH}_3\text{NH}_2 < \text{CH}_3\text{NH}_3\text{Cl}$
  - $\text{CH}_3\text{NH}_2 = \text{CH}_3\text{NH}_3\text{Cl}$
  - Nothing can be concluded about the relative concentrations of  $\text{CH}_3\text{NH}_2$  and  $\text{CH}_3\text{NH}_3\text{Cl}$ .
- Q4.** A 500.0 mL buffer solution is 0.10 M in benzoic acid and 0.10 M in sodium benzoate and has an initial pH of 4.19. What is the pH of the buffer upon addition of 0.010 mol of  $\text{NaOH}$ ?
- 1.70
  - 4.01
  - 4.29
  - 4.37
- Q5.** Consider a buffer composed of the weak acid HA and its conjugate base  $\text{A}^-$ . Which pair of concentrations results in the most effective buffer?
- 0.10 M HA; 0.10 M  $\text{A}^-$
  - 0.50 M HA; 0.50 M  $\text{A}^-$
  - 0.90 M HA; 0.10 M  $\text{A}^-$
  - 0.10 M HA; 0.90 M  $\text{A}^-$
- Q6.** Which combination is the best choice to prepare a buffer with a pH of 9.0?
- $\text{NH}_3$ ;  $\text{NH}_4\text{Cl}$  ( $pK_b$  for  $\text{NH}_3$  is 4.75)
  - $\text{C}_5\text{H}_5\text{N}$ ;  $\text{C}_5\text{H}_5\text{NHCl}$  ( $pK_b$  for  $\text{C}_5\text{H}_5\text{N}$  is 8.76)
  - $\text{HNO}_2$ ;  $\text{NaNO}_2$  ( $pK_a$  for  $\text{HNO}_2$  is 3.33)
  - $\text{HCHO}_2$ ;  $\text{NaCHO}_2$  ( $pK_a$  for  $\text{HCHO}_2$  is 3.74)

- Q7.** A 25.0 mL sample of an unknown HBr solution is titrated with 0.100 M NaOH. The equivalence point is reached upon the addition of 18.88 mL of the base. What is the concentration of the HBr solution?
- 0.0755 M
  - 0.0376 M
  - 0.100 M
  - 0.00188 M
- Q8.** A 10.0 mL sample of 0.200 M hydrocyanic acid (HCN) is titrated with 0.0998 M NaOH. What is the pH at the equivalence point? For hydrocyanic acid,  $pK_a = 9.31$ .
- 7.00
  - 8.76
  - 9.31
  - 11.07
- Q9.** A 20.0 mL sample of 0.150 M ethylamine is titrated with 0.0981 M HCl. What is the pH after the addition of 5.0 mL of HCl? For ethylamine,  $pK_b = 3.25$ .
- 10.75
  - 11.04
  - 2.96
  - 11.46
- Q10.** Three 15.0 mL acid samples—0.10 M HA, 0.10 M HB, and 0.10 M  $H_2C$ —are all titrated with 0.100 M NaOH. If HA is a weak acid, HB is a strong acid, and  $H_2C$  is a diprotic acid, which statement is true of all three titrations?
- All three titrations have the same pH at the first equivalence point.
  - All three titrations have the same initial pH.
  - All three titrations have the same final pH.
  - All three titrations require the same volume of NaOH to reach the first equivalence point.
- Q11.** A weak unknown monoprotic acid is titrated with a strong base. The titration curve is shown below. Find  $K_a$  for the unknown acid.



- $2.5 \times 10^{-3}$
- $3.2 \times 10^{-5}$
- $3.2 \times 10^{-7}$
- $2.5 \times 10^{-9}$

Answers: 1. (c) 2. (b) 3. (b) 4. (d) 5. (b) 6. (a) 7. (a) 8. (d) 9. (d) 10. (d) 11. (b) 12. (b) 13. (b) 14. (d) 15. (d)

- Q12.** Calculate the molar solubility of lead(II) bromide ( $PbBr_2$ ).

For lead(II) bromide,  $K_{sp} = 4.67 \times 10^{-6}$ .

- 0.00153 M
- 0.0105 M
- 0.0167 M
- 0.0211 M

- Q13.** Calculate the molar solubility of magnesium fluoride ( $MgF_2$ ) in a solution that is 0.250 M in NaF. For magnesium fluoride,

$K_{sp} = 5.16 \times 10^{-11}$ .

- $2.35 \times 10^{-4}$  M
- $2.06 \times 10^{-10}$  M
- $2.87 \times 10^{-5}$  M
- $8.26 \times 10^{-10}$  M

- Q14.** A solution is 0.025 M in  $Pb^{2+}$ . What minimum concentration of  $Cl^-$  is required to begin to precipitate  $PbCl_2$ ? For  $PbCl_2$ ,

$K_{sp} = 1.17 \times 10^{-5}$ .

- $1.17 \times 10^{-5}$  M
- 0.0108 M
- 0.0216 M
- $5.41 \times 10^{-4}$  M

- Q15.** Which compound is more soluble in an acidic solution than in a neutral solution?

- $PbBr_2$
- $CuCl$
- $AgI$
- $BaF_2$

## Key Terms

### Section 16.2

buffer (754)  
common ion effect (756)  
Henderson–Hasselbalch equation (758)

### Section 16.3

buffer capacity (768)

### Section 16.4

acid–base titration (769)  
indicator (769)  
equivalence point (769)  
endpoint (780)

### Section 16.5

solubility product constant ( $K_{sp}$ ) (783)  
molar solubility (783)

### Section 16.6

selective precipitation (790)

### Section 16.7

qualitative analysis (792)  
quantitative analysis (792)

### Section 16.8

complex ion (795)  
ligand (795)  
formation constant ( $K_f$ ) (795)

## Key Concepts

### The Dangers of Antifreeze (16.1)

- ▶ Although buffers closely regulate the pH of mammalian blood, the capacity of these buffers to neutralize can be overwhelmed.
- ▶ Ethylene glycol, the main component of antifreeze, is metabolized by the liver into glycolic acid. The resulting acidity can exceed the buffering capacity of blood and cause acidosis, a serious condition that results in oxygen deprivation.

### Buffers: Solutions That Resist pH Change (16.2)

- ▶ Buffers contain significant amounts of both a weak acid and its conjugate base (or a weak base and its conjugate acid), enabling the buffer to neutralize added acid or added base.
- ▶ Adding a small amount of acid to a buffer converts a stoichiometric amount of base to the conjugate acid. Adding a small amount of base to a buffer converts a stoichiometric amount of the acid to the conjugate base.
- ▶ We can determine the pH of a buffer solution by solving an equilibrium problem, focusing on the common ion effect, or by using the Henderson–Hasselbalch equation.

### Buffer Range and Buffer Capacity (16.3)

- ▶ A buffer works best when the amounts of acid and conjugate base it contains are large and approximately equal.
- ▶ If the relative amounts of acid and base in a buffer differ by more than a factor of 10, the ability of the buffer to neutralize added acid and added base diminishes. The maximum pH range at which a buffer is effective is one pH unit on either side of the acid's  $pK_a$ .

### Titrations and pH Curves (16.4)

- ▶ A titration curve is a graph of the change in pH versus added volume of acid or base during a titration.
- ▶ This chapter examines three types of titration curves, representing three types of acid–base reactions: a strong acid with a strong base, a weak acid with a strong base (or vice versa), and a polyprotic acid with a base.
- ▶ The equivalence point of a titration can be made visible by an indicator, a compound that changes color over a specific pH range.

### Solubility Equilibria and the Solubility Product Constant (16.5)

- ▶ The solubility product constant ( $K_{sp}$ ) is an equilibrium constant for the dissolution of an ionic compound in water.
- ▶ We can determine the molar solubility of an ionic compound from  $K_{sp}$  and vice versa. Although the value of  $K_{sp}$  is constant at a given temperature, the solubility of an ionic substance can depend on other factors such as the presence of common ions and the pH of the solution.

### Precipitation (16.6)

- ▶ We can compare the magnitude of  $K_{sp}$  to the reaction quotient,  $Q$ , in order to determine the relative saturation of a solution.
- ▶ Substances with cations that have sufficiently different values of  $K_{sp}$  can be separated by selective precipitation, in which an added reagent forms a precipitate with one of the dissolved cations but not others.

### Qualitative Chemical Analysis (16.7)

- ▶ Qualitative analysis operates on the principle that a mixture of cations can be separated and analyzed based on the differences in the solubilities of their salts.
- ▶ In a classic qualitative analysis scheme, an unknown mixture of cations is sequentially treated with different reagents, each of which precipitates a known subgroup of cations.

### Complex Ion Equilibria (16.8)

- ▶ A complex ion contains a central metal ion coordinated to two or more ligands.
- ▶ The equilibrium constant for the formation of a complex ion is called a formation constant and is usually quite large.
- ▶ The solubility of an ionic compound containing a metal cation that forms complex ions increases in the presence of Lewis bases that complex with the cation because the formation of the complex ion drives the dissolution reaction to the right.
- ▶ All metal hydroxides become more soluble in the presence of acids, but amphoteric metal hydroxides also become more soluble in the presence of bases.

## Key Equations and Relationships

### The Henderson–Hasselbalch Equation (16.2)

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

### Effective Buffer Range (16.3)

$$\text{pH range} = \text{p}K_a \pm 1$$

### The Relation between $Q$ and $K_{sp}$ (16.3)

If  $Q < K_{sp}$ , the solution is unsaturated. More of the solid ionic compound can dissolve in the solution.

If  $Q = K_{sp}$ , the solution is saturated. The solution is holding the equilibrium amount of the dissolved ions, and additional solid will not dissolve in the solution.

If  $Q > K_{sp}$ , the solution is supersaturated. Under most circumstances, the solid will precipitate out of a supersaturated solution.

## Key Learning Outcomes

| Chapter Objectives   | Assessment   |
|--|--|
| Calculating the pH of a Buffer Solution (16.2)   | Example 16.1 For Practice 16.1 For More Practice 16.1 Exercises 29, 30, 33, 34 |
| Using the Henderson–Hasselbalch Equation to Calculate the pH of a Buffer Solution (16.2) | Example 16.2 For Practice 16.2 Exercises 37–42                                 |

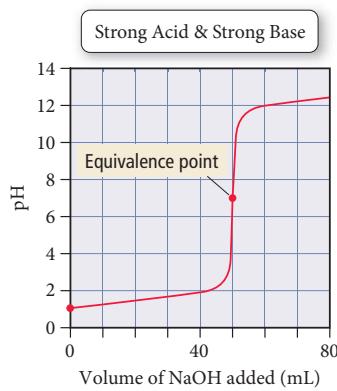
## Key Learning Outcomes, continued

Calculating the pH Change in a Buffer Solution after the Addition of a Small Amount of Strong Acid or Base (16.2)

Using the Henderson-Hasselbalch Equation to Calculate the pH of a Buffer Solution Composed of a Weak Base and Its Conjugate Acid (16.2)

Determining Buffer Range (16.3)

Strong Acid–Strong Base Titration pH Curve (16.4)



Weak Acid–Strong Base Titration pH Curve (16.4)

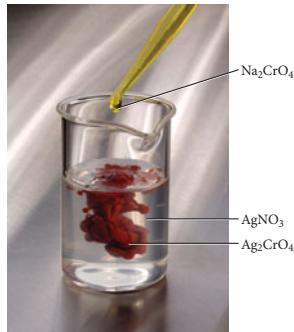
Calculating Molar Solubility from  $K_{sp}$  (16.5)

Calculating  $K_{sp}$  from Molar Solubility (16.5)

Calculating Molar Solubility in the Presence of a Common Ion (16.5)

Determining the Effect of pH on Solubility (16.5)

Predicting Precipitation Reactions by Comparing  $Q$  and  $K_{sp}$  (16.6)



Finding the Minimum Required Reagent Concentration for Selective Precipitation (16.6)

Finding the Concentrations of Ions Left in Solution after Selective Precipitation (16.6)

Working with Complex Ion Equilibria (16.8)

Example 16.3 For Practice 16.3 For More Practice 16.3 Exercises 47–50

Example 16.4 For Practice 16.4 For More Practice 16.4 Exercises 37–40

Example 16.5 For Practice 16.5 Exercises 57–58

Example 16.6 For Practice 16.6 Exercises 67–70

Example 16.7 For Practice 16.7 Exercises 65–66, 71–72, 75, 77–80

Example 16.8 For Practice 16.8 Exercises 87–88

Example 16.9 For Practice 16.9 Exercises 89–90, 92, 94

Example 16.10 For Practice 16.10 Exercises 95–96

Example 16.11 For Practice 16.11 Exercises 97–100

Example 16.12 For Practice 16.12 Exercises 101–104

Example 16.13 For Practice 16.13 Exercises 105–106

Example 16.14 For Practice 16.14 Exercises 107–108

Example 16.15 For Practice 16.15 Exercises 109–112

## EXERCISES

### Review Questions

1. What is the pH range of human blood? How is human blood maintained in this pH range?
2. What is a buffer? How does a buffer work? How does it neutralize added acid? Added base?
3. What is the common ion effect?
4. What is the Henderson–Hasselbalch equation and why is it useful?
5. What is the pH of a buffer solution when the concentrations of both buffer components (the weak acid and its conjugate base) are equal? What happens to the pH when the buffer contains more of the weak acid than the conjugate base? More of the conjugate base than the weak acid?
6. Suppose that a buffer contains equal amounts of a weak acid and its conjugate base. What happens to the relative amounts of the weak acid and conjugate base when a small amount of strong acid is added to the buffer? What happens when a small amount of strong base is added?
7. How do you use the Henderson–Hasselbalch equation to calculate the pH of a buffer containing a base and its conjugate acid? Specifically, how do you determine the correct value for  $pK_a$ ?
8. What factors influence the effectiveness of a buffer? What are the characteristics of an effective buffer?
9. What is the effective pH range of a buffer (relative to the  $pK_a$  of the weak acid component)?
10. Describe acid–base titration. What is the equivalence point?
11. The pH at the equivalence point of the titration of a strong acid with a strong base is 7.0. However, the pH at the equivalence point of the titration of a *weak* acid with a strong base is above 7.0. Explain.
12. The volume required to reach the equivalence point of an acid–base titration depends on the volume and concentration of the acid or base to be titrated and on the concentration of the acid or base used to do the titration. It does not, however, depend on the whether or not the acid or base being titrated is strong or weak. Explain.
13. In the titration of a strong acid with a strong base, how would you calculate these quantities?
  - a. initial pH
  - b. pH before the equivalence point
  - c. pH at the equivalence point
  - d. pH beyond the equivalence point
14. In the titration of a weak acid with a strong base, how would you calculate these quantities?
  - a. initial pH
  - b. pH before the equivalence point
  - c. pH at one-half the equivalence point
  - d. pH at the equivalence point
  - e. pH beyond the equivalence point
15. The titration of a polyprotic acid with sufficiently different  $pK_a$ 's displays two equivalence points. Why?
16. In the titration of a polyprotic acid, the volume required to reach the first equivalence point is identical to the volume required to reach the second one. Why?
17. What is the difference between the endpoint and the equivalence point in a titration?
18. What is an indicator? How can an indicator signal the equivalence point of a titration?
19. What is the solubility product constant? Write a general expression for the solubility constant of a compound with the general formula  $A_mX_n$ .
20. What is molar solubility? How can you obtain the molar solubility of a compound from  $K_{sp}$ ?
21. How does a common ion affect the solubility of a compound? More specifically, how is the solubility of a compound with the general formula  $AX$  different in a solution containing one of the common ions ( $A^+$  or  $X^-$ ) than it is in pure water? Explain.
22. How is the solubility of an ionic compound with a basic anion affected by pH? Explain.
23. For a given solution containing an ionic compound, what is the relationship between  $Q$ ,  $K_{sp}$ , and the relative saturation of the solution?
24. What is selective precipitation? Under which conditions does selective precipitation occur?
25. What is qualitative analysis? How does *qualitative* analysis differ from *quantitative* analysis?
26. What are the main groups in the general qualitative analysis scheme described in this chapter? Describe the steps and reagents necessary to identify each group.

### Problems by Topic

#### The Common Ion Effect and Buffers

27. In which of these solutions will  $HNO_2$  ionize less than it does in pure water?
  - a. 0.10 M NaCl
  - b. 0.10 M  $KNO_3$
  - c. 0.10 M NaOH
  - d. 0.10 M  $NaNO_2$

28. A formic acid solution has a pH of 3.25. Which of these substances will raise the pH of the solution upon addition? Explain your answer.
  - a. HCl
  - b. NaBr
  - c.  $NaCHO_2$
  - d. KCl

- 29.** Solve an equilibrium problem (using an ICE table) to calculate the pH of each solution.
- a solution that is 0.20 M in  $\text{HCHO}_2$  and 0.15 M in  $\text{NaCHO}_2$
  - a solution that is 0.16 M in  $\text{NH}_3$  and 0.22 M in  $\text{NH}_4\text{Cl}$
- 30.** Solve an equilibrium problem (using an ICE table) to calculate the pH of each solution.
- a solution that is 0.195 M in  $\text{HC}_2\text{H}_3\text{O}_2$  and 0.125 M in  $\text{KC}_2\text{H}_3\text{O}_2$
  - a solution that is 0.255 M in  $\text{CH}_3\text{NH}_2$  and 0.135 M in  $\text{CH}_3\text{NH}_3\text{Br}$
- 31.** Calculate the percent ionization of a 0.15 M benzoic acid solution in pure water and in a solution containing 0.10 M sodium benzoate. Why does the percent ionization differ significantly in the two solutions?
- 32.** Calculate the percent ionization of a 0.13 M formic acid solution in pure water and also in a solution containing 0.11 M potassium formate. Explain the difference in percent ionization in the two solutions.
- 33.** Solve an equilibrium problem (using an ICE table) to calculate the pH of each solution.
- 0.15 M HF
  - 0.15 M  $\text{NaF}$
  - a mixture that is 0.15 M in HF and 0.15 M in  $\text{NaF}$
- 34.** Solve an equilibrium problem (using an ICE table) to calculate the pH of each solution.
- 0.18 M  $\text{CH}_3\text{NH}_2$
  - 0.18 M  $\text{CH}_3\text{NH}_3\text{Cl}$
  - a mixture that is 0.18 M in  $\text{CH}_3\text{NH}_2$  and 0.18 M in  $\text{CH}_3\text{NH}_3\text{Cl}$
- 35.** A buffer contains significant amounts of acetic acid and sodium acetate. Write equations showing how this buffer neutralizes added acid and added base.
- 36.** A buffer contains significant amounts of ammonia and ammonium chloride. Write equations showing how this buffer neutralizes added acid and added base.
- 37.** Use the Henderson–Hasselbalch equation to calculate the pH of each solution in Problem 29.
- 38.** Use the Henderson–Hasselbalch equation to calculate the pH of each solution in Problem 30.
- 39.** Use the Henderson–Hasselbalch equation to calculate the pH of each solution.
- a solution that is 0.135 M in  $\text{HClO}$  and 0.155 M in  $\text{KClO}$
  - a solution that contains 1.05%  $\text{C}_2\text{H}_5\text{NH}_2$  by mass and 1.10%  $\text{C}_2\text{H}_5\text{NH}_3\text{Br}$  by mass
  - a solution that contains 10.0 g of  $\text{HC}_2\text{H}_3\text{O}_2$  and 10.0 g of  $\text{NaC}_2\text{H}_3\text{O}_2$  in 150.0 mL of solution
- 40.** Use the Henderson–Hasselbalch equation to calculate the pH of each solution.
- a solution that is 0.145 M in propanoic acid and 0.115 M in potassium propanoate
  - a solution that contains 0.785%  $\text{C}_5\text{H}_5\text{N}$  by mass and 0.985%  $\text{C}_5\text{H}_5\text{NHCl}$  by mass
  - a solution that contains 15.0 g of HF and 25.0 g of NaF in 125 mL of solution
- 41.** Calculate the pH of the solution that results from each mixture.
- 50.0 mL of 0.15 M  $\text{HCHO}_2$  with 75.0 mL of 0.13 M  $\text{NaCHO}_2$
  - 125.0 mL of 0.10 M  $\text{NH}_3$  with 250.0 mL of 0.10 M  $\text{NH}_4\text{Cl}$
- 42.** Calculate the pH of the solution that results from each mixture.
- 150.0 mL of 0.25 M HF with 225.0 mL of 0.30 M NaF
  - 175.0 mL of 0.10 M  $\text{C}_2\text{H}_5\text{NH}_2$  with 275.0 mL of 0.20 M  $\text{C}_2\text{H}_5\text{NH}_3\text{Cl}$
- 43.** Calculate the ratio of NaF to HF required to create a buffer with  $\text{pH} = 4.00$ .
- 44.** Calculate the ratio of  $\text{CH}_3\text{NH}_2$  to  $\text{CH}_3\text{NH}_3\text{Cl}$  concentration required to create a buffer with  $\text{pH} = 10.24$ .
- 45.** What mass of sodium benzoate should you add to 150.0 mL of a 0.15 M benzoic acid solution to obtain a buffer with a pH of 4.25? (Assume no volume change.)
- 46.** What mass of ammonium chloride should you add to 2.55 L of a 0.155 M  $\text{NH}_3$  to obtain a buffer with a pH of 9.55? (Assume no volume change.)
- 47.** A 250.0 mL buffer solution is 0.250 M in acetic acid and 0.250 M in sodium acetate.
- What is the initial pH of this solution?
  - What is the pH after addition of 0.0050 mol of HCl?
  - What is the pH after addition of 0.0050 mol of NaOH?
- 48.** A 100.0 mL buffer solution is 0.175 M in  $\text{HClO}$  and 0.150 M in  $\text{NaClO}$ .
- What is the initial pH of this solution?
  - What is the pH after addition of 150.0 mg of HBr?
  - What is the pH after addition of 85.0 mg of NaOH?
- 49.** For each solution, calculate the initial and final pH after adding 0.010 mol of HCl.
- 500.0 mL of pure water
  - 500.0 mL of a buffer solution that is 0.125 M in  $\text{HC}_2\text{H}_3\text{O}_2$  and 0.115 M in  $\text{NaC}_2\text{H}_3\text{O}_2$
  - 500.0 mL of a buffer solution that is 0.155 M in  $\text{C}_2\text{H}_5\text{NH}_2$  and 0.145 M in  $\text{C}_2\text{H}_5\text{NH}_3\text{Cl}$
- 50.** For each solution, calculate the initial and final pH after adding 0.010 mol of NaOH.
- 250.0 mL of pure water
  - 250.0 mL of a buffer solution that is 0.195 M in  $\text{HCHO}_2$  and 0.275 M in  $\text{KCHO}_2$
  - 250.0 mL of a buffer solution that is 0.255 M in  $\text{CH}_3\text{CH}_2\text{NH}_2$  and 0.235 M in  $\text{CH}_3\text{CH}_2\text{NH}_3\text{Cl}$
- 51.** A 350.0 mL buffer solution is 0.150 M in HF and 0.150 M in NaF. What mass of NaOH can this buffer neutralize before the pH rises above 4.00? If the same volume of the buffer were 0.350 M in HF and 0.350 M in NaF, what mass of NaOH could be handled before the pH rises above 4.00?
- 52.** A 100.0 mL buffer solution is 0.100 M in  $\text{NH}_3$  and 0.125 M in  $\text{NH}_4\text{Br}$ . What mass of HCl can this buffer neutralize before the pH falls below 9.00? If the same volume of the buffer were 0.250 M in  $\text{NH}_3$  and 0.400 M in  $\text{NH}_4\text{Br}$ , what mass of HCl could be handled before the pH fell below 9.00?
- 53.** Determine whether or not the mixing of each pair of solutions results in a buffer.
- 100.0 mL of 0.10 M  $\text{NH}_3$ ; 100.0 mL of 0.15 M  $\text{NH}_4\text{Cl}$
  - 50.0 mL of 0.10 M HCl; 35.0 mL of 0.150 M NaOH
  - 50.0 mL of 0.15 M HF; 20.0 mL of 0.15 M NaOH
  - 175.0 mL of 0.10 M  $\text{NH}_3$ ; 150.0 mL of 0.12 M NaOH
  - 125.0 mL of 0.15 M  $\text{NH}_3$ ; 150.0 mL of 0.20 M NaOH
- 54.** Determine whether or not the mixing of each pair of solutions results in a buffer.
- 75.0 mL of 0.10 M HF; 55.0 mL of 0.15 M NaF
  - 150.0 mL of 0.10 M HF; 135.0 mL of 0.175 M HCl
  - 165.0 mL of 0.10 M HF; 135.0 mL of 0.050 M KOH
  - 125.0 mL of 0.15 M  $\text{CH}_3\text{NH}_2$ ; 120.0 mL of 0.25 M  $\text{CH}_3\text{NH}_3\text{Cl}$
  - 105.0 mL of 0.15 M  $\text{CH}_3\text{NH}_2$ ; 95.0 mL of 0.10 M HCl

55. Blood is buffered by carbonic acid and the bicarbonate ion. Normal blood plasma is 0.024 M in  $\text{HCO}_3^-$  and 0.0012 M  $\text{H}_2\text{CO}_3$  ( $pK_{\text{a}_1}$  for  $\text{H}_2\text{CO}_3$  at body temperature is 6.1).
- What is the pH of blood plasma?
  - If the volume of blood in a normal adult is 5.0 L, what mass of HCl can be neutralized by the buffering system in blood before the pH falls below 7.0 (which would result in death)?
  - Given the volume from part (b), what mass of NaOH can be neutralized before the pH rises above 7.8?

56. The fluids within cells are buffered by  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$ .
- Calculate the ratio of  $\text{HPO}_4^{2-}$  to  $\text{H}_2\text{PO}_4^-$  required to maintain a pH of 7.1 within a cell.
  - Could a buffer system employing  $\text{H}_3\text{PO}_4$  as the weak acid and  $\text{H}_2\text{PO}_4^-$  as the weak base be used as a buffer system within cells? Explain.

57. Which buffer system is the best choice to create a buffer with pH = 7.20? For the best system, calculate the ratio of the masses of the buffer components required to make the buffer.



58. Which buffer system is the best choice to create a buffer with pH = 9.00? For the best system, calculate the ratio of the masses of the buffer components required to make the buffer.

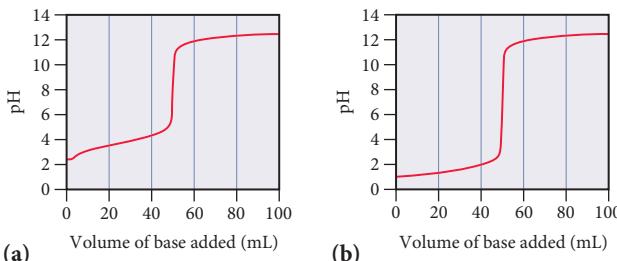


59. A 500.0 mL buffer solution is 0.100 M in  $\text{HNO}_2$  and 0.150 M in  $\text{KNO}_2$ . Determine if each addition would exceed the capacity of the buffer to neutralize it.

- 250 mg NaOH
  - 350 mg KOH
  - 1.25 g HBr
  - 1.35 g HI
60. A 1.0 L buffer solution is 0.125 M in  $\text{HNO}_2$  and 0.145 M in  $\text{NaNO}_2$ . Determine the concentrations of  $\text{HNO}_2$  and  $\text{NaNO}_2$  after the addition of each substance:
- 1.5 g HCl
  - 1.5 g NaOH
  - 1.5 g HI

### Titration, pH Curves, and Indicators

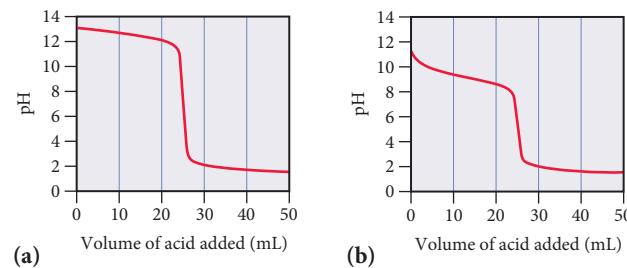
61. The graphs labeled (a) and (b) show the titration curves for two equal-volume samples of monoprotic acids, one weak and one strong. Both titrations were carried out with the same concentration of strong base.



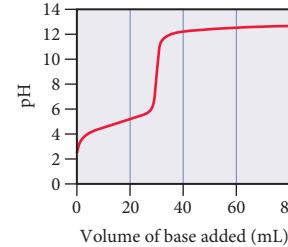
- What is the approximate pH at the equivalence point of each curve?
- Which graph corresponds to the titration of the strong acid and which one to the titration of the weak acid?

62. Two 25.0 mL samples, one 0.100 M HCl and the other 0.100 M HF, are titrated with 0.200 M KOH.
- What is the volume of added base at the equivalence point for each titration?
  - Is the pH at the equivalence point for each titration acidic, basic, or neutral?
  - Which titration curve has the lower initial pH?
  - Sketch each titration curve.
63. Two 20.0 mL samples, one 0.200 M KOH and the other 0.200 M  $\text{CH}_3\text{NH}_2$  are titrated with 0.100 M HI.
- What is the volume of added acid at the equivalence point for each titration?
  - Is the pH at the equivalence point for each titration acidic, basic, or neutral?
  - Which titration curve has the lower initial pH?
  - Sketch each titration curve.

64. The graphs labeled (a) and (b) show the titration curves for two equal-volume samples of bases, one weak and one strong. Both titrations were carried out with the same concentration of strong acid.

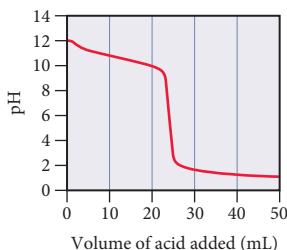


- What is the approximate pH at the equivalence point of each curve?
  - Which graph corresponds to the titration of the strong base and which one to the weak base?
65. Consider the curve shown here for the titration of a weak monoprotic acid with a strong base and answer each question.



- What is the pH and what is the volume of added base at the equivalence point?
- At what volume of added base is the pH calculated by working an equilibrium problem based on the initial concentration and  $K_a$  of the weak acid?
- At what volume of added base does  $\text{pH} = \text{p}K_a$ ?
- At what volume of added base is the pH calculated by working an equilibrium problem based on the concentration and  $K_b$  of the conjugate base?
- Beyond what volume of added base is the pH calculated by focusing on the amount of excess strong base added?

66. Consider the curve shown here for the titration of a weak base with a strong acid and answer each question.



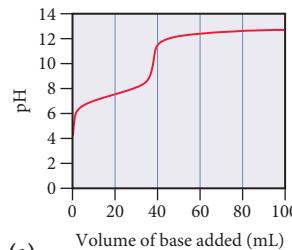
- What is the pH and what is the volume of added acid at the equivalence point?
  - At what volume of added acid is the pH calculated by working an equilibrium problem based on the initial concentration and  $K_b$  of the weak base?
  - At what volume of added acid does  $\text{pH} = 14 - \text{p}K_b$ ?
  - At what volume of added acid is the pH calculated by working an equilibrium problem based on the concentration and  $K_a$  of the conjugate acid?
  - Beyond what volume of added acid is the pH calculated by focusing on the amount of excess strong acid added?
67. Consider the titration of a 35.0 mL sample of 0.175 M HBr with 0.200 M KOH. Determine each quantity.
- the initial pH
  - the volume of added base required to reach the equivalence point
  - the pH at 10.0 mL of added base
  - the pH at the equivalence point
  - the pH after adding 5.0 mL of base beyond the equivalence point
68. A 20.0 mL sample of 0.125 M  $\text{HNO}_3$  is titrated with 0.150 M NaOH. Calculate the pH for at least five different points throughout the titration curve and sketch the curve. Indicate the volume at the equivalence point on your graph.
69. Consider the titration of a 25.0 mL sample of 0.115 M RbOH with 0.100 M HCl. Determine each quantity.
- the initial pH
  - the volume of added acid required to reach the equivalence point
  - the pH at 5.0 mL of added acid
  - the pH at the equivalence point
  - the pH after adding 5.0 mL of acid beyond the equivalence point
70. A 15.0 mL sample of 0.100 M  $\text{Ba}(\text{OH})_2$  is titrated with 0.125 M HCl. Calculate the pH for at least five different points throughout the titration curve and sketch the curve. Indicate the volume at the equivalence point on your graph.
71. Consider the titration of a 20.0 mL sample of 0.105 M  $\text{HC}_2\text{H}_3\text{O}_2$  with 0.125 M NaOH. Determine each quantity.
- the initial pH
  - the volume of added base required to reach the equivalence point
  - the pH at 5.0 mL of added base
  - the pH at one-half of the equivalence point
  - the pH at the equivalence point
  - the pH after adding 5.0 mL of base beyond the equivalence point

72. A 30.0 mL sample of 0.165 M propanoic acid is titrated with 0.300 M KOH. Calculate the pH at each volume of added base: 0 mL, 5 mL, 10 mL, equivalence point, one-half equivalence point, 20 mL, 25 mL. Sketch the titration curve.

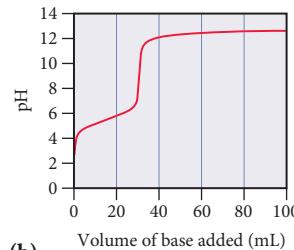
73. Consider the titration of a 25.0 mL sample of 0.175 M  $\text{CH}_3\text{NH}_2$  with 0.150 M HBr. Determine each quantity.
- the initial pH
  - the volume of added acid required to reach the equivalence point
  - the pH at 5.0 mL of added acid
  - the pH at one-half of the equivalence point
  - the pH at the equivalence point
  - the pH after adding 5.0 mL of acid beyond the equivalence point

74. A 25.0 mL sample of 0.125 M pyridine is titrated with 0.100 M HCl. Calculate the pH at each volume of added acid: 0 mL, 10 mL, 20 mL, equivalence point, one-half equivalence point, 40 mL, 50 mL. Sketch the titration curve.

75. Consider the titration curves (labeled a and b) for two weak acids, both titrated with 0.100 M NaOH.



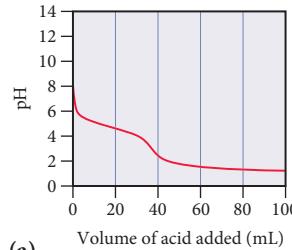
(a)



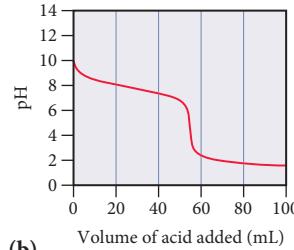
(b)

- Which acid solution is more concentrated?
- Which acid has the larger  $K_a$ ?

76. Consider the titration curves (labeled a and b) for two weak bases, both titrated with 0.100 M HCl.



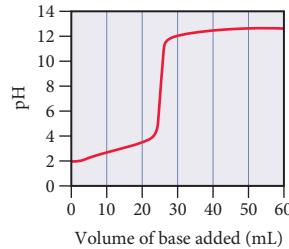
(a)



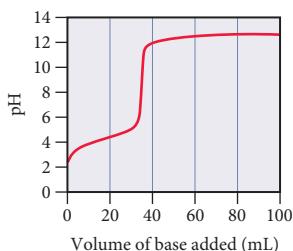
(b)

- Which base solution is more concentrated?
- Which base has the larger  $K_b$ ?

77. A 0.229 g sample of an unknown monoprotic acid is titrated with 0.112 M NaOH. The resulting titration curve is shown here. Determine the molar mass and  $\text{p}K_a$  of the acid.



78. A 0.446 g sample of an unknown monoprotic acid is titrated with 0.105 M KOH. The resulting titration curve is shown here. Determine the molar mass and  $pK_a$  of the acid.



79. A 20.0 mL sample of 0.115 M sulfurous acid ( $H_2SO_3$ ) solution is titrated with 0.1014 M KOH. At what added volume of base solution does each equivalence point occur?
80. A 20.0 mL sample of a 0.125 M diprotic acid ( $H_2A$ ) solution is titrated with 0.1019 M KOH. The acid ionization constants for the acid are  $K_{a_1} = 5.2 \times 10^{-5}$  and  $K_{a_2} = 3.4 \times 10^{-10}$ . At what added volume of base does each equivalence point occur?
81. Methyl red has a  $pK_a$  of 5.0 and is red in its acid form and yellow in its basic form. If several drops of this indicator are placed in a 25.0 mL sample of 0.100 M HCl, what color will the solution appear? If 0.100 M NaOH is slowly added to the HCl sample, in what pH range will the indicator change color?
82. Phenolphthalein has a  $pK_a$  of 9.7. It is colorless in its acid form and pink in its basic form. For each of the pH's, calculate  $[In^-]/[HIn]$  and predict the color of a phenolphthalein solution.
- pH = 2.0
  - pH = 5.0
  - pH = 8.0
  - pH = 11.0
83. Referring to Table 16.1, pick an indicator for use in the titration of each acid with a strong base.
- HF
  - HCl
  - HCN
84. Referring to Table 16.1, pick an indicator for use in the titration of each base with a strong acid.
- $CH_3NH_2$
  - NaOH
  - $C_6H_5NH_2$

## Solubility Equilibria

85. Write balanced equations and expressions for  $K_{sp}$  for the dissolution of each ionic compound.
- $BaSO_4$
  - $PbBr_2$
  - $Ag_2CrO_4$
86. Write balanced equations and expressions for  $K_{sp}$  for the dissolution of each ionic compound.
- $CaCO_3$
  - $PbCl_2$
  - $AgI$
87. Refer to the  $K_{sp}$  values in Table 16.2 to calculate the molar solubility of each compound in pure water.
- $AgBr$
  - $Mg(OH)_2$
  - $CaF_2$
88. Refer to the  $K_{sp}$  values in Table 16.2 to calculate the molar solubility of each compound in pure water.
- $MX$  ( $K_{sp} = 1.27 \times 10^{-36}$ )
  - $Ag_2CrO_4$
  - $Ca(OH)_2$
89. Use the given molar solubilities in pure water to calculate  $K_{sp}$  for each compound.
- $MX$ ; molar solubility =  $3.27 \times 10^{-11}$  M
  - $PbF_2$ ; molar solubility =  $5.63 \times 10^{-3}$  M
  - $MgF_2$ ; molar solubility =  $2.65 \times 10^{-4}$  M
90. Use the given molar solubilities in pure water to calculate  $K_{sp}$  for each compound.
- $BaCrO_4$ ; molar solubility =  $1.08 \times 10^{-5}$  M
  - $Ag_2SO_3$ ; molar solubility =  $1.55 \times 10^{-5}$  M
  - $Pd(SCN)_2$ ; molar solubility =  $2.22 \times 10^{-8}$  M
91. Two compounds with general formulas  $AX$  and  $AX_2$  have  $K_{sp} = 1.5 \times 10^{-5}$ . Which of the two compounds has the higher molar solubility?
92. Consider the compounds with the generic formulas listed and their corresponding molar solubilities in pure water. Which compound has the smallest value of  $K_{sp}$ ?
- $AX$ ; molar solubility =  $1.35 \times 10^{-4}$  M
  - $AX_2$ ; molar solubility =  $2.25 \times 10^{-4}$  M
  - $A_2X$ ; molar solubility =  $1.75 \times 10^{-4}$  M
93. Refer to the  $K_{sp}$  value from Table 16.2 to calculate the solubility of iron(II) hydroxide in pure water in grams per 100.0 mL of solution.
94. The solubility of copper(I) chloride is 3.91 mg per 100.0 mL of solution. Calculate  $K_{sp}$  for  $CuCl$ .
95. Calculate the molar solubility of barium fluoride in each liquid or solution.
- pure water
  - 0.10 M  $Ba(NO_3)_2$
  - 0.15 M  $NaF$
96. Calculate the molar solubility of  $MX$  ( $K_{sp} = 1.27 \times 10^{-36}$ ) in each liquid or solution.
- pure water
  - 0.25 M  $MCl_2$
  - 0.20 M  $Na_2X$
97. Calculate the molar solubility of calcium hydroxide in a solution buffered at each pH.
- pH = 4
  - pH = 7
  - pH = 9
98. Calculate the solubility (in grams per  $1.00 \times 10^2$  mL of solution) of magnesium hydroxide in a solution buffered at pH = 10. How does this compare to the solubility of  $Mg(OH)_2$  in pure water?
99. Determine if each compound is more soluble in acidic solution than in pure water. Explain.
- $BaCO_3$
  - $CuS$
  - $AgCl$
  - $PbI_2$

- 100.** Determine if each compound is more soluble in acidic solution than in pure water. Explain.

- $\text{Hg}_2\text{Br}_2$
- $\text{Mg}(\text{OH})_2$
- $\text{CaCO}_3$
- $\text{AgI}$

### Precipitation and Qualitative Analysis

- 101.** A solution containing sodium fluoride is mixed with one containing calcium nitrate to form a solution that is 0.015 M in  $\text{NaF}$  and 0.010 M in  $\text{Ca}(\text{NO}_3)_2$ . Does a precipitate form in the mixed solution? If so, identify the precipitate.

- 102.** A solution containing potassium bromide is mixed with one containing lead acetate to form a solution that is 0.013 M in  $\text{KBr}$  and 0.0035 M in  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ . Does a precipitate form in the mixed solution? If so, identify the precipitate.

- 103.** Predict whether a precipitate will form if you mix 75.0 mL of a  $\text{NaOH}$  solution with  $\text{pOH} = 2.58$  with 125.0 mL of a 0.018 M  $\text{MgCl}_2$  solution. Identify the precipitate, if any.

- 104.** Predict whether a precipitate will form if you mix 175.0 mL of a 0.0055 M  $\text{KCl}$  solution with 145.0 mL of a 0.0015 M  $\text{AgNO}_3$  solution. Identify the precipitate, if any.

- 105.** Potassium hydroxide is used to precipitate each of the cations from their respective solution. Determine the minimum concentration of  $\text{KOH}$  required for precipitation to begin in each case.

- 0.015 M  $\text{CaCl}_2$
- 0.0025 M  $\text{Fe}(\text{NO}_3)_2$
- 0.0018 M  $\text{MgBr}_2$

- 106.** Determine the minimum concentration of the precipitating agent on the right to cause precipitation of the cation from the solution on the left.

- 0.035 M  $\text{BaNO}_3$ ;  $\text{NaF}$
- 0.085 M  $\text{CaI}_2$ ;  $\text{K}_2\text{SO}_4$
- 0.0018 M  $\text{AgNO}_3$ ;  $\text{RbCl}$

### Cumulative Problems

- 113.** A 150.0 mL solution contains 2.05 g of sodium benzoate and 2.47 g of benzoic acid. Calculate the pH of the solution.

- 114.** A solution is made by combining 10.0 mL of 17.5 M acetic acid with 5.54 g of sodium acetate and diluting to a total volume of 1.50 L. Calculate the pH of the solution.

- 115.** A buffer is created by combining 150.0 mL of 0.25 M  $\text{HCHO}_2$  with 75.0 mL of 0.20 M  $\text{NaOH}$ . Determine the pH of the buffer.

- 116.** A buffer is created by combining 3.55 g of  $\text{NH}_3$  with 4.78 g of  $\text{HCl}$  and diluting to a total volume of 750.0 mL. Determine the pH of the buffer.

- 117.** A 1.0 L buffer solution initially contains 0.25 mol of  $\text{NH}_3$  and 0.25 mol of  $\text{NH}_4\text{Cl}$ . In order to adjust the buffer pH to 8.75, should you add  $\text{NaOH}$  or  $\text{HCl}$  to the buffer mixture? What mass of the correct reagent should you add?

- 118.** A 250.0 mL buffer solution initially contains 0.025 mol of  $\text{HCHO}_2$  and 0.025 mol of  $\text{NaCHO}_2$ . In order to adjust the buffer pH to 4.10, should you add  $\text{NaOH}$  or  $\text{HCl}$  to the buffer mixture? What mass of the correct reagent should you add?

- 107.** A solution is 0.010 M in  $\text{Ba}^{2+}$  and 0.020 M in  $\text{Ca}^{2+}$ .

- If sodium sulfate is used to selectively precipitate one of the cations while leaving the other cation in solution, which cation will precipitate first? What minimum concentration of  $\text{Na}_2\text{SO}_4$  will trigger the precipitation of the cation that precipitates first?

- What is the remaining concentration of the cation that precipitates first, when the other cation begins to precipitate?

- 108.** A solution is 0.022 M in  $\text{Fe}^{2+}$  and 0.014 M in  $\text{Mg}^{2+}$ .

- If potassium carbonate is used to selectively precipitate one of the cations while leaving the other cation in solution, which cation will precipitate first? What minimum concentration of  $\text{K}_2\text{CO}_3$  will trigger the precipitation of the cation that precipitates first?

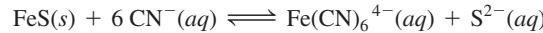
- What is the remaining concentration of the cation that precipitates first, when the other cation begins to precipitate?

### Complex Ion Equilibria

- 109.** A solution is made  $1.1 \times 10^{-3}$  M in  $\text{Zn}(\text{NO}_3)_2$  and 0.150 M in  $\text{NH}_3$ . After the solution reaches equilibrium, what concentration of  $\text{Zn}^{2+}(aq)$  remains?

- 110.** A 120.0 mL sample of a solution that is  $2.8 \times 10^{-3}$  M in  $\text{AgNO}_3$  is mixed with a 225.0 mL sample of a solution that is 0.10 M in  $\text{NaCN}$ . After the solution reaches equilibrium, what concentration of  $\text{Ag}^+(aq)$  remains?

- 111.** Use the appropriate values of  $K_{\text{sp}}$  and  $K_f$  to find the equilibrium constant for the reaction.



- 112.** Use the appropriate values of  $K_{\text{sp}}$  and  $K_f$  to find the equilibrium constant for the reaction.



- 119.** In analytical chemistry, bases used for titrations must often be standardized; that is, their concentration must be precisely determined. Standardization of sodium hydroxide solutions can be accomplished by titrating potassium hydrogen phthalate ( $\text{KHC}_8\text{H}_4\text{O}_4$ ) also known as KHP, with the  $\text{NaOH}$  solution to be standardized.

- Write an equation for the reaction between  $\text{NaOH}$  and KHP.
- The titration of 0.5527 g of KHP required 25.87 mL of an  $\text{NaOH}$  solution to reach the equivalence point. What is the concentration of the  $\text{NaOH}$  solution?

- 120.** A 0.5224 g sample of an unknown monoprotic acid was titrated with 0.0998 M  $\text{NaOH}$ . The equivalence point of the titration occurs at 23.82 mL. Determine the molar mass of the unknown acid.

- 121.** A 0.25 mol sample of a weak acid with an unknown  $\text{p}K_a$  was combined with 10.0 mL of 3.00 M  $\text{KOH}$ , and the resulting solution was diluted to 1.500 L. The measured pH of the solution was 3.85. What is the  $\text{p}K_a$  of the weak acid?

- 122.** A 5.55 g sample of a weak acid with  $K_a = 1.3 \times 10^{-4}$  was combined with 5.00 mL of 6.00 M NaOH, and the resulting solution was diluted to 750 mL. The measured pH of the solution was 4.25. What is the molar mass of the weak acid?
- 123.** A 0.552 g sample of ascorbic acid (vitamin C) was dissolved in water to a total volume of 20.0 mL and titrated with 0.1103 M KOH. The equivalence point occurred at 28.42 mL. The pH of the solution at 10.0 mL of added base was 3.72. From this data, determine the molar mass and  $K_a$  for vitamin C.
- 124.** Sketch the titration curve from Problem 123 by calculating the pH at the beginning of the titration, at one-half of the equivalence point, at the equivalence point, and at 5.0 mL beyond the equivalence point. Pick a suitable indicator for this titration from Table 16.1.
- 125.** One of the main components of hard water is  $\text{CaCO}_3$ . When hard water evaporates, some of the  $\text{CaCO}_3$  is left behind as a white mineral deposit. If a hard water solution is saturated with calcium carbonate, what volume of the solution has to evaporate to deposit  $1.00 \times 10^2$  mg of  $\text{CaCO}_3$ ?
- 126.** Gout—a condition that results in joint swelling and pain—is caused by the formation of sodium urate ( $\text{NaC}_5\text{H}_3\text{N}_4$ ) crystals within tendons, cartilage, and ligaments. Sodium urate precipitates out of blood plasma when uric acid levels become abnormally high. This sometimes happens as a result of eating too many rich foods and consuming too much alcohol, which is why gout is sometimes referred to as the “disease of kings.” If the sodium concentration in blood plasma is 0.140 M, and  $K_{\text{sp}}$  for sodium urate is  $5.76 \times 10^{-8}$ , what minimum concentration of urate would result in precipitation?
- 127.** Pseudogout, a condition with symptoms similar to those of gout (see Problem 126), is caused by the formation of calcium diphosphate ( $\text{Ca}_2\text{P}_2\text{O}_7$ ) crystals within tendons, cartilage, and ligaments. Calcium diphosphate will precipitate out of blood plasma when diphosphate levels become abnormally high. If the calcium concentration in blood plasma is 9.2 mg/dL, and  $K_{\text{sp}}$  for calcium diphosphate is  $8.64 \times 10^{-13}$ , what minimum concentration of diphosphate results in precipitation?
- 128.** Calculate the solubility of silver chloride in a solution that is 0.100 M in  $\text{NH}_3$ .
- 129.** Calculate the solubility of  $\text{CuX}$  in a solution that is 0.150 M in  $\text{NaCN}$ .  $K_{\text{sp}}$  for  $\text{CuX}$  is  $1.27 \times 10^{-36}$ .
- 130.** Aniline, abbreviated  $\phi\text{NH}_2$ , where  $\phi$  is  $\text{C}_6\text{H}_5$ , is an important organic base used in the manufacture of dyes. It has  $K_b = 4.3 \times 10^{-10}$ . In a certain manufacturing process it is necessary to keep the concentration of  $\phi\text{NH}_3^+$  (aniline’s conjugate acid, the anilinium ion) below  $1.0 \times 10^{-9}$  M in a solution that is 0.10 M in aniline. Find the concentration of NaOH required for this process.
- 131.** The  $K_b$  of hydroxylamine,  $\text{NH}_2\text{OH}$ , is  $1.10 \times 10^{-8}$ . A buffer solution is prepared by mixing 100.0 mL of a 0.36 M hydroxyl amine solution with 50.0 mL of a 0.26 M HCl solution. Determine the pH of the resulting solution.
- 132.** A 0.867 g sample of an unknown acid requires 32.2 mL of a 0.182 M barium hydroxide solution for neutralization. Assuming the acid is diprotic, calculate the molar mass of the acid.
- 133.** A 25.0 mL volume of a sodium hydroxide solution requires 19.6 mL of a 0.189 M hydrochloric acid for neutralization. A 10.0 mL volume of a phosphoric acid solution requires 34.9 mL of the sodium hydroxide solution for complete neutralization. Calculate the concentration of the phosphoric acid solution.
- 134.** Find the mass of sodium formate that must be dissolved in  $250.0 \text{ cm}^3$  of a 1.4 M solution of formic acid to prepare a buffer solution with  $\text{pH} = 3.36$ .
- 135.** What relative masses of dimethyl amine and dimethyl ammonium chloride do you need to prepare a buffer solution of  $\text{pH} = 10.43$ ?
- 136.** You are asked to prepare 2.0 L of a HCN/NaCN buffer that has a pH of 9.8 and an osmotic pressure of 1.35 atm at 298 K. What masses of HCN and NaCN should you use to prepare the buffer? (Assume complete dissociation of NaCN.)
- 137.** What should the molar concentrations of benzoic acid and sodium benzoate be in a solution that is buffered at a pH of 4.55 and has a freezing point of  $-2.0^\circ\text{C}$ ? (Assume complete dissociation of sodium benzoate and a density of 1.01 g/mL for the solution.)

## Challenge Problems

- 138.** Derive an equation similar to the Henderson–Hasselbalch equation for a buffer composed of a weak base and its conjugate acid. Instead of relating pH to  $pK_a$  and the relative concentrations of an acid and its conjugate base (as the Henderson–Hasselbalch equation does), the equation should relate  $\text{pOH}$  to  $pK_b$  and the relative concentrations of a base and its conjugate acid.
- 139.** Since soap and detergent action is hindered by hard water, laundry formulations usually include water softeners—called builders—designed to remove hard water ions (especially  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) from the water. A common builder used in North America is sodium carbonate. Suppose that the hard water used to do laundry contains 75 ppm  $\text{CaCO}_3$  and 55 ppm  $\text{MgCO}_3$  (by mass). What mass of  $\text{Na}_2\text{CO}_3$  is required to remove 90.0% of these ions from 10.0 L of laundry water?
- 140.** A 0.558 g sample of a diprotic acid with a molar mass of 255.8 g/mol is dissolved in water to a total volume of 25.0 mL. The solution is then titrated with a saturated calcium hydroxide solution.
- Assuming that the  $pK_a$  values for each ionization step are sufficiently different to see two equivalence points, determine the volume of added base for the first and second equivalence points.
  - The pH after adding 25.0 mL of the base is 3.82. Find the value of  $K_{a_1}$ .
  - The pH after adding 20.0 mL past the first equivalence point is 8.25. Find the value of  $K_{a_2}$ .
- 141.** When excess solid  $\text{Mg(OH)}_2$  is shaken with 1.00 L of 1.0 M  $\text{NH}_4\text{Cl}$  solution, the resulting saturated solution has  $\text{pH} = 9.00$ . Calculate the  $K_{\text{sp}}$  of  $\text{Mg(OH)}_2$ .

- 142.** What amount of solid NaOH must be added to 1.0 L of a 0.10 M  $\text{H}_2\text{CO}_3$  solution to produce a solution with  $[\text{H}^+] = 3.2 \times 10^{-11}$  M? There is no significant volume change as the result of the addition of the solid.
- 143.** Calculate the solubility of  $\text{Au}(\text{OH})_3$  in (a) water and (b) 1.0 M nitric acid solution. ( $K_{\text{sp}} = 5.5 \times 10^{-46}$ ).
- 144.** Calculate the concentration of  $\text{I}^-$  in a solution obtained by shaking 0.10 M KI with an excess of  $\text{AgCl}(s)$ .
- 145.** What volume of 0.100 M sodium carbonate solution is required to precipitate 99% of the Mg from 1.00 L of 0.100 M magnesium nitrate solution?

- 146.** Find the solubility of CuI in 0.40 M HCN solution. The  $K_{\text{sp}}$  of CuI is  $1.1 \times 10^{-12}$  and the  $K_f$  for the  $\text{Cu}(\text{CN})_2^-$  complex ion is  $1 \times 10^{24}$ .
- 147.** Find the pH of a solution prepared from 1.0 L of a 0.10 M solution of  $\text{Ba}(\text{OH})_2$  and excess  $\text{Zn}(\text{OH})_2(s)$ . The  $K_{\text{sp}}$  of  $\text{Zn}(\text{OH})_2$  is  $3 \times 10^{-15}$  and the  $K_f$  of  $\text{Zn}(\text{OH})_4^{2-}$  is  $2 \times 10^{15}$ .
- 148.** What amount of HCl gas must be added to 1.00 L of a buffer solution that contains [acetic acid] = 2.0 M and [acetate] = 1.0 M in order to produce a solution with  $\text{pH} = 4.00$ ?

## Conceptual Problems

- 149.** Without doing any calculations, determine if  $\text{pH} = \text{p}K_a$ ,  $\text{pH} > \text{p}K_a$ , or  $\text{pH} < \text{p}K_a$ . Assume that HA is a weak monoprotic acid.
- 0.10 mol HA and 0.050 mol of  $\text{A}^-$  in 1.0 L of solution
  - 0.10 mol HA and 0.150 mol of  $\text{A}^-$  in 1.0 L of solution
  - 0.10 mol HA and 0.050 mol of  $\text{OH}^-$  in 1.0 L of solution
  - 0.10 mol HA and 0.075 mol of  $\text{OH}^-$  in 1.0 L of solution

- 150.** A buffer contains 0.10 mol of a weak acid and 0.20 mol of its conjugate base in 1.0 L of solution. Determine whether or not each addition exceeds the capacity of the buffer.
- adding 0.020 mol of NaOH
  - adding 0.020 mol of HCl
  - adding 0.10 mol of NaOH
  - adding 0.010 mol of HCl

- 151.** Consider three solutions:

- 0.10 M solution of a weak monoprotic acid
- 0.10 M solution of strong monoprotic acid
- 0.10 M solution of a weak diprotic acid

Each solution is titrated with 0.15 M NaOH. Which quantity is the same for all three solutions?

- the volume required to reach the final equivalence point
- the volume required to reach the first equivalence point
- the pH at the first equivalence point
- the pH at one-half the first equivalence point

- 152.** Two monoprotic acid solutions (A and B) are titrated with identical NaOH solutions. The volume to reach the equivalence point for solution A is twice the volume required to reach the equivalence point for solution B, and the pH at the equivalence point of solution A is higher than the pH at the equivalence point for solution B. Which statement is true?
- The acid in solution A is more concentrated than in solution B and is also a stronger acid than that in solution B.
  - The acid in solution A is less concentrated than in solution B and is also a weaker acid than that in solution B.
  - The acid in solution A is more concentrated than in solution B and is also a weaker acid than that in solution B.
  - The acid in solution A is less concentrated than in solution B and is also a stronger acid than that in solution B.
- 153.** Describe the solubility of  $\text{CaF}_2$  in each solution compared to its solubility in water.
- in a 0.10 M NaCl solution
  - in a 0.10 M NaF solution
  - in a 0.10 M HCl solution

## Answers to Conceptual Connections

### Buffers

- 16.1** (d) Only this solution contains significant amounts of a weak acid and its conjugate base. (Remember that  $\text{HNO}_3$  is a strong acid, but  $\text{HNO}_2$  is a weak acid.)

### pH of Buffer Solutions

- 16.2** (a) Since the pH of the buffer is less than the  $\text{p}K_a$  of the acid, the buffer must contain more acid than base ( $[\text{HA}] > [\text{A}^-]$ ). In order to raise the pH of the buffer from 4.25 to 4.72, you must add more of the weak base (adding a base will make the buffer solution more basic).

### Adding Acid or Base to a Buffer

- 16.3** (b) Since acid is added to the buffer, the pH will become slightly lower (slightly more acidic). Answer (a) reflects too large a change in pH for a buffer, and answers (c) and (d) have the pH changing in the wrong direction.

### Buffer Capacity

- 16.4** (a) Adding 0.050 mol of HCl destroys the buffer because it will react with all of the NaF, leaving no conjugate base in the buffer mixture.

### Titration Equivalence Point

**16.5** (d) Because the flask contains 7 H<sup>+</sup> ions, the equivalence point is reached when 7 OH<sup>-</sup> ions have been added.

### The Half-Equivalence Point

**16.6** (c) The pH at the half-equivalence point is the pK<sub>a</sub> of the conjugate acid, which is equal to 14.00 – 8.75 = 5.25.

### Acid-Base Titrations

**16.7** (c) Since the volumes and concentrations of all three acids are the same, the volume of NaOH required to reach the first equivalence point (and the only equivalence point for titrations i and iii) is the same for all three titrations.

### Common Ion Effect

**16.8** (c) The sodium nitrate solution is the only one that has no common ion with barium sulfate. The other two solutions have common ions with barium sulfate; therefore, the solubility of barium sulfate is lower in these solutions.

### Solubility and Complex Ion Equilibria

**16.9** (c) Only NaCN contains an anion (CN<sup>-</sup>) that forms a complex ion with Cu<sup>2+</sup> [from Table 16.3 we can see that K<sub>f</sub> = 1.0 × 10<sup>25</sup> for Cu(CN)<sub>4</sub><sup>2-</sup>]. Therefore, the presence of CN<sup>-</sup> will drive the dissolution reaction of CuS.

# 17

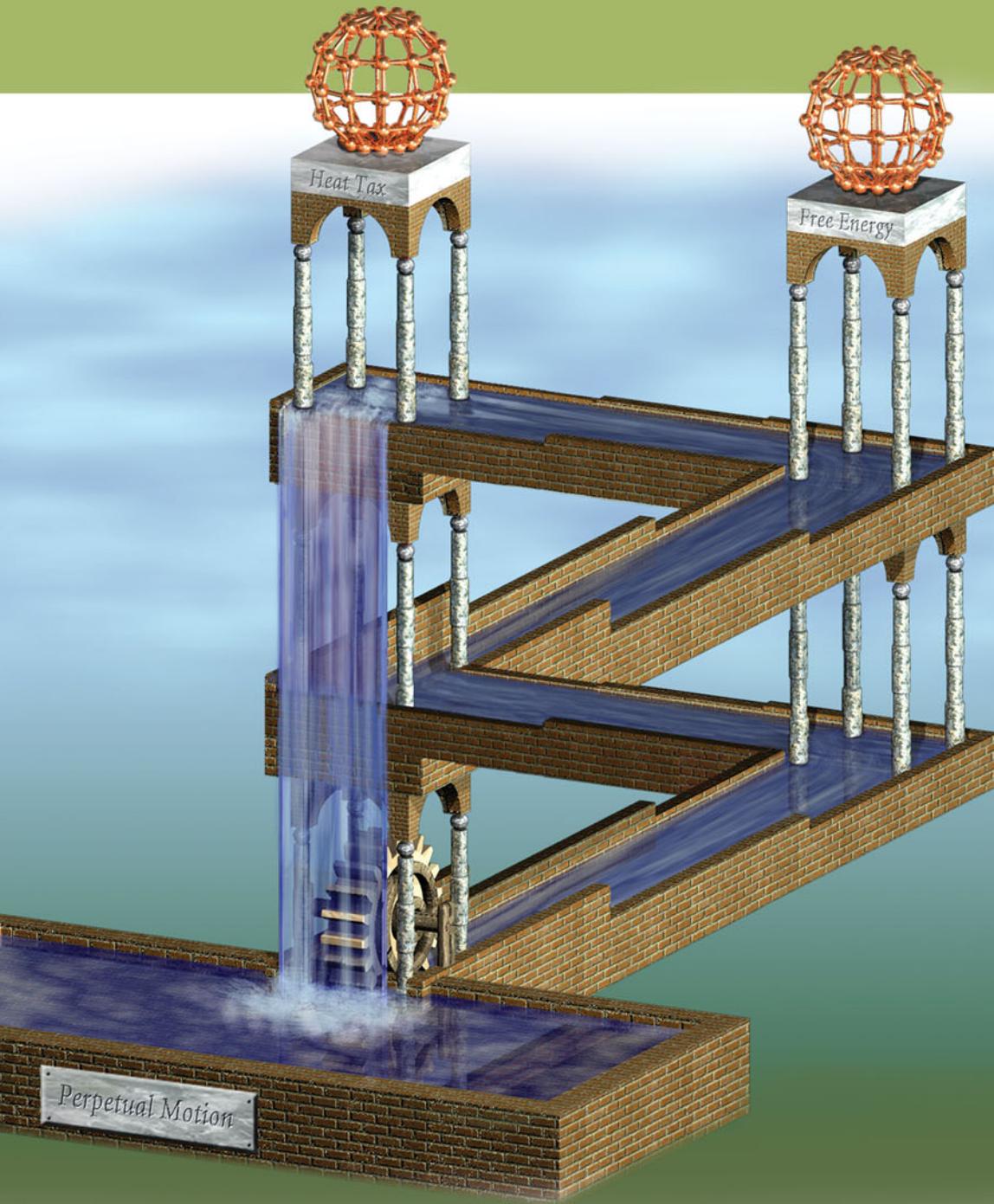
# Free Energy and Thermodynamics

*Die Energie der Welt ist konstant. Die Entropie der Welt strebt einem Maximum zu. (The energy of the world is constant. The entropy of the world tends towards a maximum.)*

—Rudolf Clausius (1822–1888)

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**T**HROUGHOUT THIS BOOK, we have examined and learned about chemical and physical changes. We have studied how fast chemical changes occur (kinetics) and how to predict how far they will go (through the use of equilibrium constants). We have learned that acids neutralize bases and that gases expand to fill their containers. We now turn to the following question: why do these changes occur in the first place? What ultimately drives physical and chemical changes in matter? The answer may surprise you. The driving force behind chemical and physical change in the universe is a quantity called *entropy*, which is related to the dispersion (or spreading out) of energy. Nature tends toward that state in which energy is spread out to the greatest extent possible. Although it does not seem obvious at first glance, the freezing of water below 0 °C, the dissolving of a solid into a solution, the neutralization of an acid by a base, and even the development of a person from an embryo all increase the entropy in the universe (they all result in greater energy dispersion). In our universe, entropy always increases.



*In this clever illusion, it seems that the water can perpetually flow through the canal. However, perpetual motion is forbidden under the laws of thermodynamics.*

## 17.1 Nature's Heat Tax: You Can't Win and You Can't Break Even

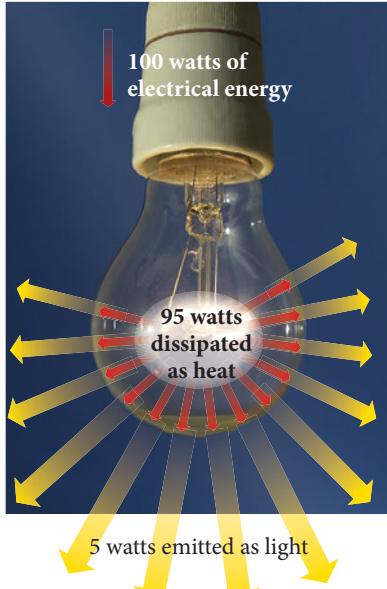
Energy transactions are like gambling—you walk into the casino with your pockets full of cash and (if you keep gambling long enough) you walk out empty-handed. In the long run, you lose money in gambling because the casino takes a cut on each transaction. So it is with energy. Nature takes a cut—sometimes called nature's heat tax—on every energy transaction so that, in the end, energy is dissipated.

Recall from Chapter 6 that, according to the first law of thermodynamics, energy is conserved in chemical processes. When we burn gasoline to run a car, for example, the amount of energy produced by the chemical reaction does not vanish, nor does any



▲ A rechargeable battery always requires more energy to charge than the energy available for work during discharging because some energy is always lost to the surroundings during the charging/discharging cycle.

See the box entitled *Redheffer's Perpetual Motion Machine* in Section 6.3.



▲ FIGURE 17.1 Energy Loss In most energy transactions, some energy is lost to the surroundings, so each transaction is only fractionally efficient.

new energy appear that was not present as potential energy (within the gasoline) before the combustion. Some of the energy from the combustion reaction goes toward driving the car forward (about 20%), and the rest is dissipated into the surroundings as heat (feel your engine after a drive if you doubt this). The total energy given off by the combustion reaction exactly equals the sum of the amount of energy that goes to propel the car and the amount dissipated as heat—energy is conserved. In other words, when it comes to energy, you can't win; you cannot create energy that was not there to begin with.

The picture becomes more interesting, however, when we consider the second law of thermodynamics. The second law—which we examine in more detail throughout this chapter—implies that not only can we not win in an energy transaction, we cannot even break even. For example, consider a rechargeable battery. Suppose that when we use the fully charged battery for some application, the energy from the battery does 100 kJ of work. Recharging the battery to its original state will *necessarily* (according to the second law of thermodynamics) require *more than* 100 kJ of energy. Energy is not destroyed during the cycle of discharging and recharging the battery, but some energy must be lost to the surroundings in order for the process to occur at all. Nature imposes a *heat tax*, an unavoidable cut of every energy transaction. The implications of the second law for energy use are significant. First of all, according to the second law, we cannot create a perpetual motion machine (a machine that perpetually moves *without any energy input*). If the machine is to be in motion, it must pay the heat tax with each cycle of its motion—over time, it will therefore run down and stop moving.

Secondly, in most energy transactions, not only is the “heat tax” lost to the surroundings, but additional energy is also lost as heat because real-world processes do not achieve the theoretically possible maximum efficiency (Figure 17.1 ▷). Consequently, the most efficient use of energy generally occurs with the smallest number of transactions. For example, heating your home with natural gas is generally cheaper and more efficient than heating it with electricity (Figure 17.2 ▷). When you heat your home with natural gas, there is only one energy transaction—you burn the gas and the heat from the reaction warms the house. When you heat your home with electricity, several transactions occur. Most electricity is generated from the combustion of fossil fuels; the heat from the burning fuel boils water to create steam. The steam then turns a turbine on a generator to create electricity. The electricity travels from the power plant to your home, and some of the energy is lost as heat during the trip. Finally, the electricity runs the heater that generates heat. With each transaction, energy is lost to the surroundings, resulting in a less efficient use of energy than if you had burned natural gas directly.

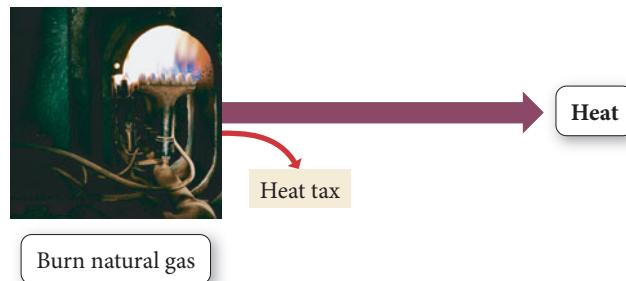
### Conceptual Connection 17.1 Nature's Heat Tax and Diet

Advocates of a vegetarian diet argue that the amount of cropland required for one person to maintain a meat-based diet is about 6–10 times greater than the amount required for the same person to maintain a vegetarian diet. Apply the concept of nature's heat tax to explain this assertion.

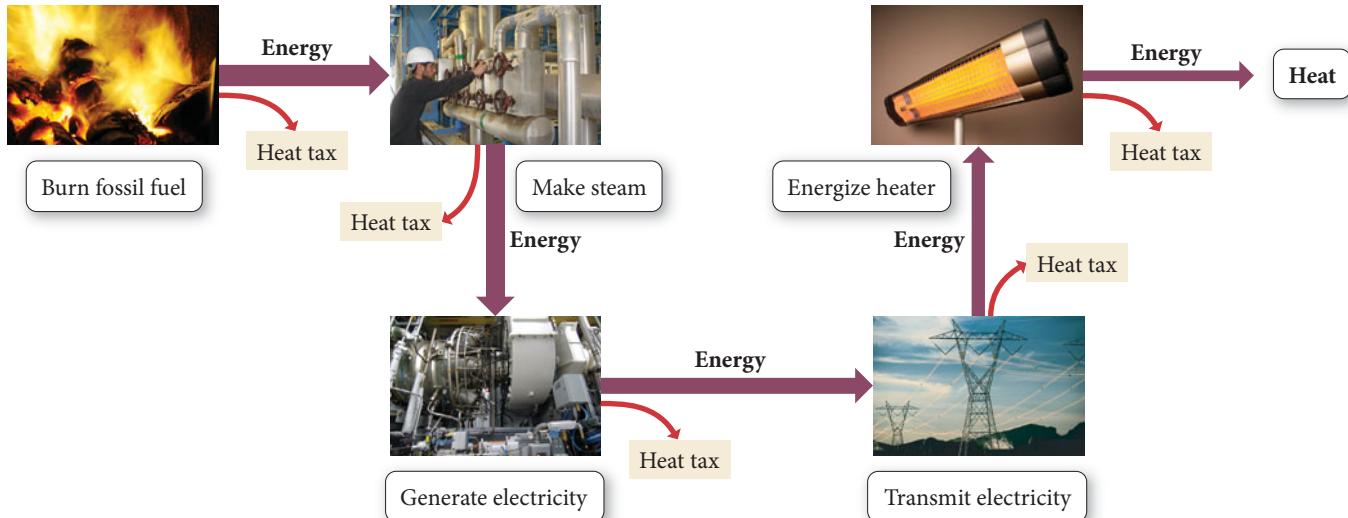
## 17.2 Spontaneous and Nonspontaneous Processes

A fundamental goal of thermodynamics is to predict *spontaneity*. For example, will rust spontaneously form when iron comes into contact with oxygen? Will water spontaneously decompose into hydrogen and oxygen? A **spontaneous process** is one that occurs *without ongoing outside intervention* (such as the performance of work by some external force). For example, when you drop a book in a gravitational field, it spontaneously drops to the floor. When you place a ball on a slope, it spontaneously rolls down the slope. For simple mechanical systems, such as the

### Heating with Natural Gas



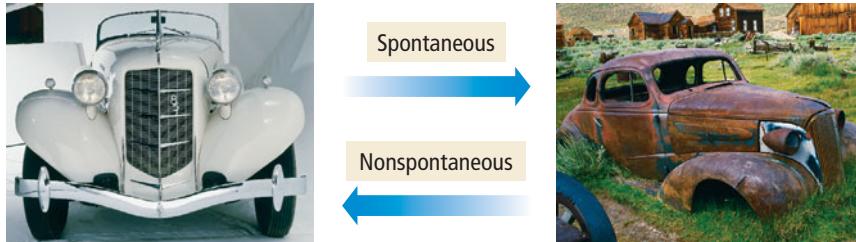
### Heating with Electricity



**▲ FIGURE 17.2 Heating with Gas versus Heating with Electricity** When natural gas heats a home, only a single energy transaction is involved, so the heat tax is minimized. When electricity is used to heat a home, a number of energy transactions are required, each of which involves some loss. The result is a much lower efficiency.

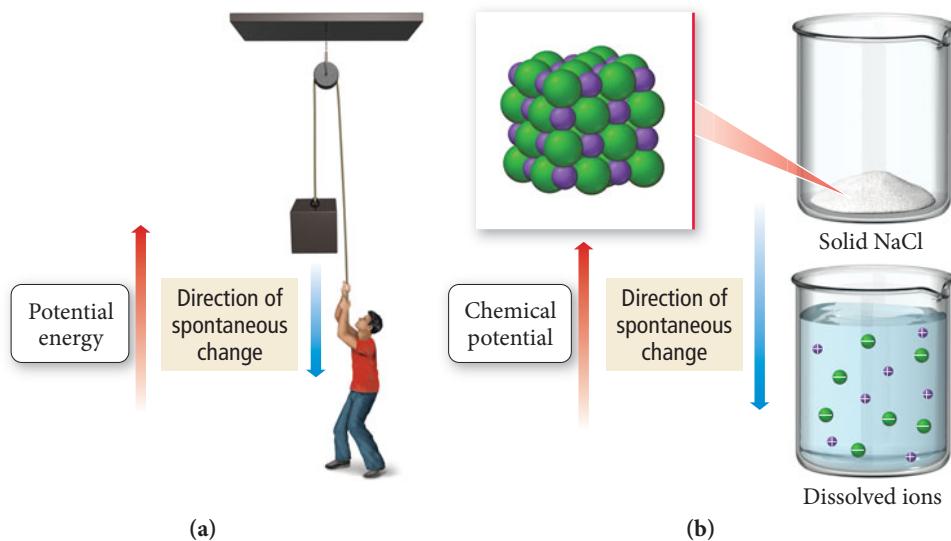
dropping of a book or the rolling of a ball, predicting spontaneity is fairly intuitive. A mechanical system tends toward lowest potential energy, which is usually easy to see (at least in *simple* mechanical systems). However, the prediction of spontaneity for chemical systems is not so intuitively obvious. To make these predictions, we need to develop a criterion for the spontaneity of chemical systems. In other words, we need to develop a *chemical potential* that predicts the direction of a chemical system, much as mechanical potential energy predicts the direction of a mechanical system (Figure 17.3 ▶).

We must not confuse the *spontaneity* of a chemical reaction with the *speed* of a chemical reaction. In thermodynamics, we study the *spontaneity* of a reaction—the direction in which and extent to which a chemical reaction proceeds. In kinetics, we



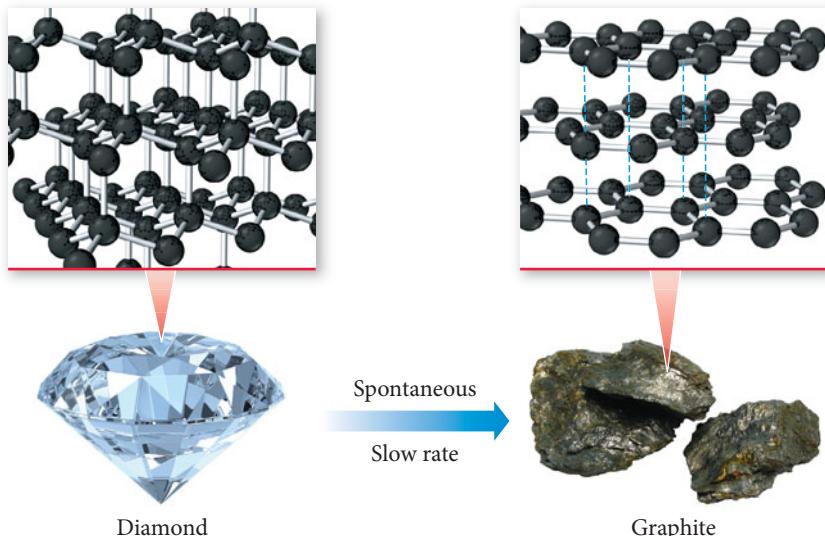
◀ Iron spontaneously rusts when it comes in contact with oxygen.

## The Concept of Chemical Potential



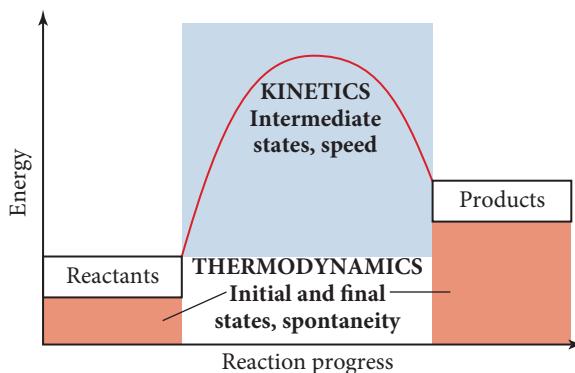
**▲ FIGURE 17.3** Mechanical Potential Energy and Chemical Potential (a) Mechanical potential energy predicts the direction in which a mechanical system will spontaneously move. (b) We seek a chemical potential that predicts the direction in which a chemical system will spontaneously move.

study the *speed* of the reaction—how fast a reaction takes place (Figure 17.4 ►). A reaction may be thermodynamically spontaneous but kinetically slow at a given temperature. For example, the conversion of diamond to graphite is thermodynamically spontaneous. But your diamonds will not become worthless anytime soon, because the process is extremely slow kinetically. Although the rate of a spontaneous process can be increased by the use of a catalyst, a nonspontaneous process cannot be made spontaneous by the use of a catalyst. Catalysts affect only the rate of a reaction, not the spontaneity.



- Even though graphite is thermodynamically more stable than diamond, the conversion of diamond to graphite is kinetically so slow that it does not occur at any measurable rate.

One last word about nonspontaneity—a nonspontaneous process is not *impossible*. For example, the extraction of iron metal from iron ore is a nonspontaneous process; it does not happen if the iron ore is left to itself, but that does not mean it is impossible. As we will see later in this chapter, a nonspontaneous process can be made spontaneous by coupling it to another process that is spontaneous or by supplying energy from an external source. Iron can be separated from its ore if external energy is supplied, usually by means of another reaction (that is itself highly spontaneous).



**◀ FIGURE 17.4 Thermodynamics and Kinetics** Thermodynamics deals with the relative chemical potentials of the reactants and products. It enables us to predict whether a reaction will be spontaneous and to calculate how much work it can do. Kinetics deals with the chemical potential of intermediate states and enables us to determine why a reaction is slow or fast.

## 17.3 Entropy and the Second Law of Thermodynamics

The first candidate in our search for a chemical potential might be enthalpy, which we defined in Chapter 6. Perhaps, just as a mechanical system proceeds in the direction of lowest potential energy, so a chemical system might proceed in the direction of lowest enthalpy. If this were the case, all exothermic reactions would be spontaneous and all endothermic reactions would not. However, although *most* spontaneous processes are exothermic, some spontaneous processes are *endothermic*. For example, above 0 °C, ice spontaneously melts (an endothermic process). So enthalpy must not be the sole criterion for spontaneity.

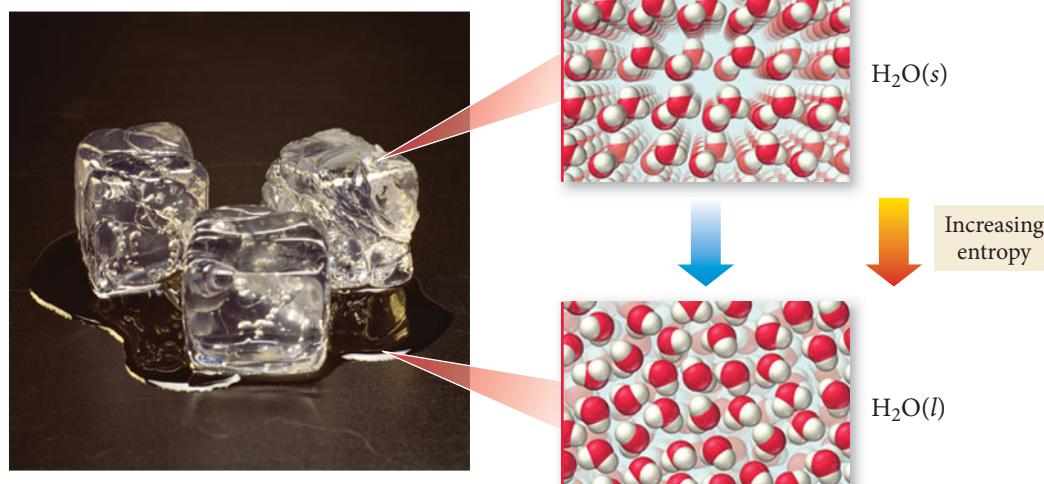
See Section 6.6 for the definition of enthalpy.

We can learn more about the driving force behind chemical reactions by considering several processes (like ice melting) that involve an increase in enthalpy. The processes listed here are energetically uphill (they are endothermic), yet they occur spontaneously. What drives them?

- the melting of ice above 0 °C
- the evaporation of liquid water to gaseous water
- the dissolution of sodium chloride in water

Each of these processes is endothermic *and* spontaneous. Do they have anything in common? Notice that, in each process, disorder or randomness increases. In the melting of ice, the arrangement of the water molecules changes from a highly ordered one (in ice) to a somewhat disorderly one (in liquid water).

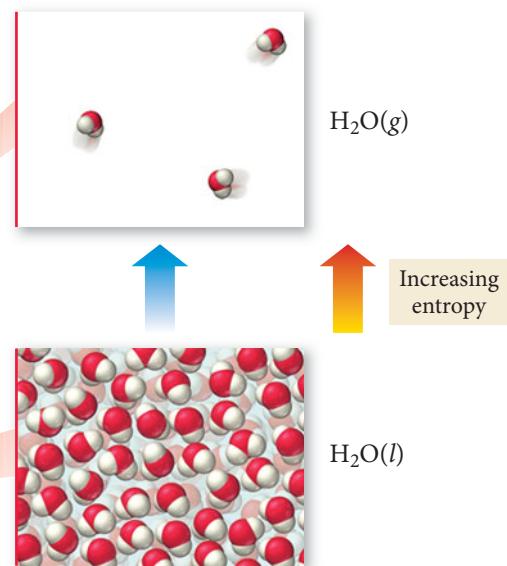
The use of the word *disorder* here is analogous to our macroscopic notions of disorder. The definition of molecular disorder, which is covered shortly, is very specific.



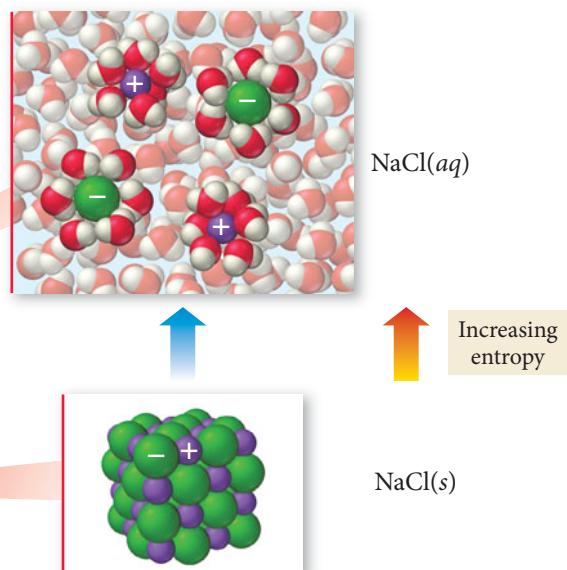
◀ When ice melts, the arrangement of water molecules changes from orderly to more disorderly.

During the evaporation of a liquid to a gas, the arrangement changes from a *somewhat* disorderly one (atoms or molecules in the liquid) to a *highly* disorderly one (atoms or molecules in the gas).

► When water evaporates, the arrangement of water molecules becomes still more disorderly.



In the dissolution of a salt into water, the arrangement again changes from an orderly one (in which the ions in the salt occupy regular positions in the crystal lattice) to a more disorderly one (in which the ions are randomly dispersed throughout the liquid water).



► When salt dissolves in water, the arrangement of the molecules and ions becomes more disorderly.

In all three of these processes, a quantity called *entropy*—related to disorder or randomness at the molecular level—increases.

## Entropy

We have now hit upon the criterion for spontaneity in chemical systems: entropy. Informally, we can think of entropy as disorder or randomness. But the concept of disorder or randomness on the macroscopic scale—such as the messiness of a drawer—is only *analogous* to the concept of disorder or randomness on the molecular scale. Formally, **entropy**, abbreviated by the symbol  $S$ , has the following definition:

**Entropy ( $S$ ) is a thermodynamic function that increases with the number of energetically equivalent ways to arrange the components of a system to achieve a particular state.**

This definition was expressed mathematically by Ludwig Boltzmann in the 1870s as:

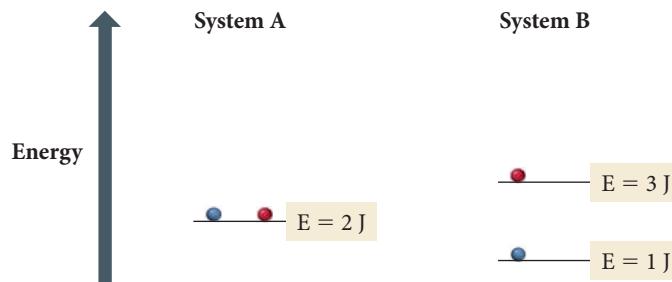
$$S = k \ln W$$

where  $k$  is the Boltzmann constant (the gas constant divided by Avogadro's number,  $R/N_A = 1.38 \times 10^{-23} \text{ J/K}$ ) and  $W$  is the number of energetically equivalent ways to arrange the components of the system. Since  $W$  is unitless (it is simply a number), the units of entropy are joules per kelvin ( $\text{J/K}$ ). We talk about the significance of the units shortly. As you can see from the equation, as  $W$  increases, entropy increases.

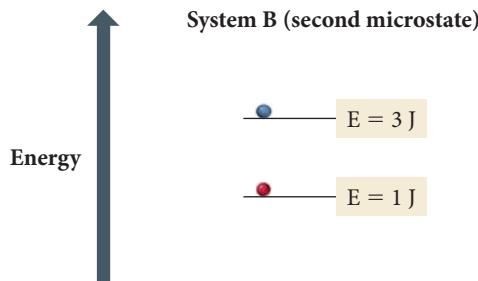
The key to understanding entropy is the quantity  $W$ . What does  $W$ —the number of energetically equivalent ways to arrange the components of the system—signify? Imagine a system of particles such as a fixed amount of an ideal gas. A given set of conditions ( $P$ ,  $V$ , and  $T$ ) defines the *state* (or *macrostate*) of the system. As long as these conditions remain constant, the energy of the system also remains constant. However, exactly where that energy is at any given instant is anything but constant.

At any one instant, a particular gas particle may have lots of kinetic energy. However, after a very short period of time, that particle may have only a little kinetic energy (because it lost its energy through collisions with other particles). The exact internal energy distribution among the particles at any one instant is sometimes referred to as a *microstate*. You can think of a microstate as a snapshot of the system at a given instant in time. The next instant, the snapshot (the microstate) changes. However, the *macrostate*—defined by  $P$ ,  $V$ , and  $T$ —remains constant. A given macrostate can exist as a result of a large number of different microstates. In other words, the snapshot (or microstate) of a given macrostate is generally different from one moment to the next as the energy of the system is constantly redistributing itself among the particles of the system.

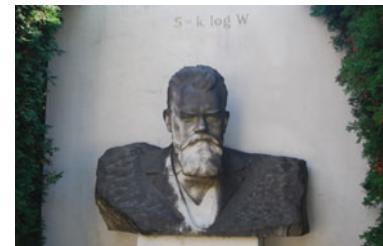
We can conceive of  $W$  in terms of microstates. The quantity,  $W$ , is the number of *possible* microstates that can result in a given macrostate. For example, suppose we have two systems (call them System A and System B), and that each is composed of two particles (one blue and one red). Both systems have a total energy of 4 joules, but System A has only one energy level and System B has two:



Each system has the same total energy (4 J), but System A has only one possible microstate (the red and the blue particle both occupying the 2 J energy level) while System B has a second possible microstate:



In this second microstate for System B, the blue particle has 3 J and the red one has 1 J (as opposed to System B's first microstate, where the energy of the particles is switched). This second microstate is not possible for System A because it has only one energy level. For System A,  $W = 1$ , but for System B,  $W = 2$ . In other words, System B has more microstates that result in the same 4 J macrostate. Since  $W$  is larger for System B than for



▲ Boltzmann's equation is engraved on his tombstone.

System A, System B has greater *entropy*; it has more *energetically equivalent ways to arrange the components of the system*.

We can understand an important aspect of entropy by turning our attention to energy for a moment. The entropy of a state increases with the number of *energetically equivalent* ways to arrange the components of the system to achieve that particular state. This implies that *the state with the highest entropy also has the greatest dispersal of energy*. Returning to our previous example, the energy of System B is dispersed over two energy levels instead of being confined to just one. At the heart of entropy is the concept of energy dispersal or energy randomization. *A state in which a given amount of energy is more highly dispersed (or more highly randomized) has more entropy than a state in which the same energy is more highly concentrated.*

Although we have already alluded to the **second law of thermodynamics**, we can now formally define it:

**For any spontaneous process, the entropy of the universe increases ( $\Delta S_{\text{univ}} > 0$ ).**

*The criterion for spontaneity is the entropy of the universe.* Processes that increase the entropy of the universe—those that result in greater dispersal or randomization of energy—occur spontaneously. Processes that decrease the entropy of the universe do not occur spontaneously.

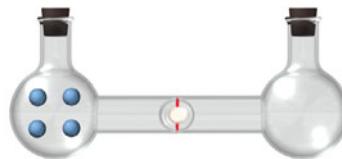
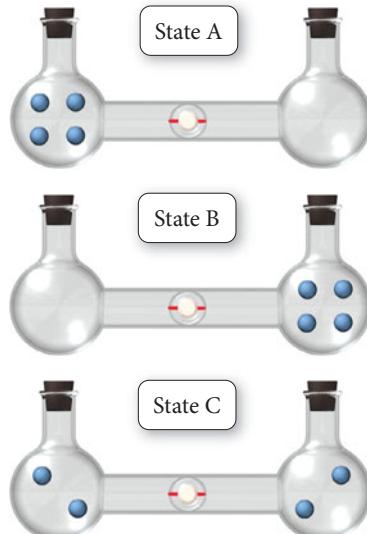
Entropy, like enthalpy, is a *state function*—its value depends only on the state of the system, not on how the system arrived at that state. Therefore, for any process, *the change in entropy is the entropy of the final state minus the entropy of the initial state.*

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

Entropy determines the direction of chemical and physical change. *A chemical system proceeds in a direction that increases the entropy of the universe*—it proceeds in a direction that has the largest number of *energetically equivalent* ways to arrange its components.

To better understand this tendency, let us examine the expansion of an ideal gas into a vacuum (a spontaneous process with no associated change in enthalpy). Consider a flask containing an ideal gas that is connected to another, evacuated, flask by a tube equipped with a stopcock. When the stopcock is opened, the gas spontaneously expands into the evacuated flask. Since the gas is expanding into a vacuum, the pressure against which it expands is zero, and therefore the work ( $w = -P_{\text{ext}} \Delta V$ ) is also zero.

However, even though the total energy of the gas does not change during the expansion, the entropy does change. To picture this, consider a simplified system containing only four gas atoms.



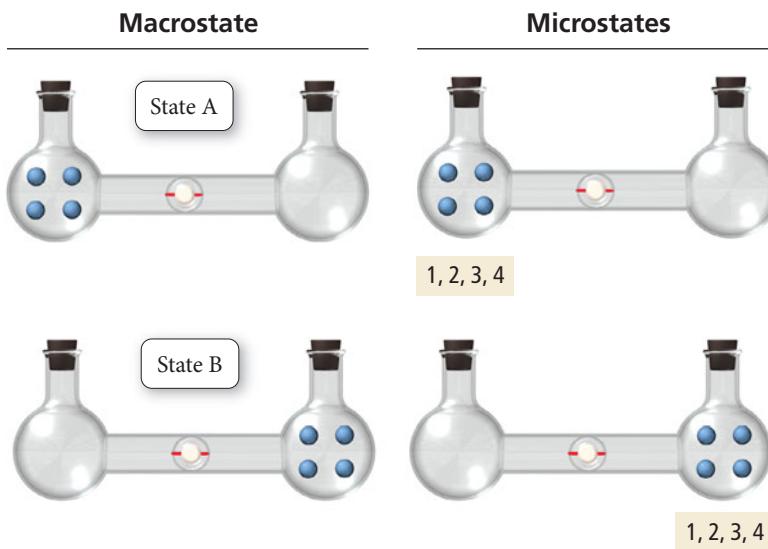
When the stopcock is opened, several possible energetically equivalent final states may result, each with the four atoms distributed in a different way. For example, there could be three atoms in the flask on the left and one in the flask on the right, or vice versa. For simplicity, we consider only the possibilities shown at left: state A, state B, and state C.

Since the energy of any one atom is the same in either flask, and since the atoms do not interact, states A, B, and C are energetically equivalent.

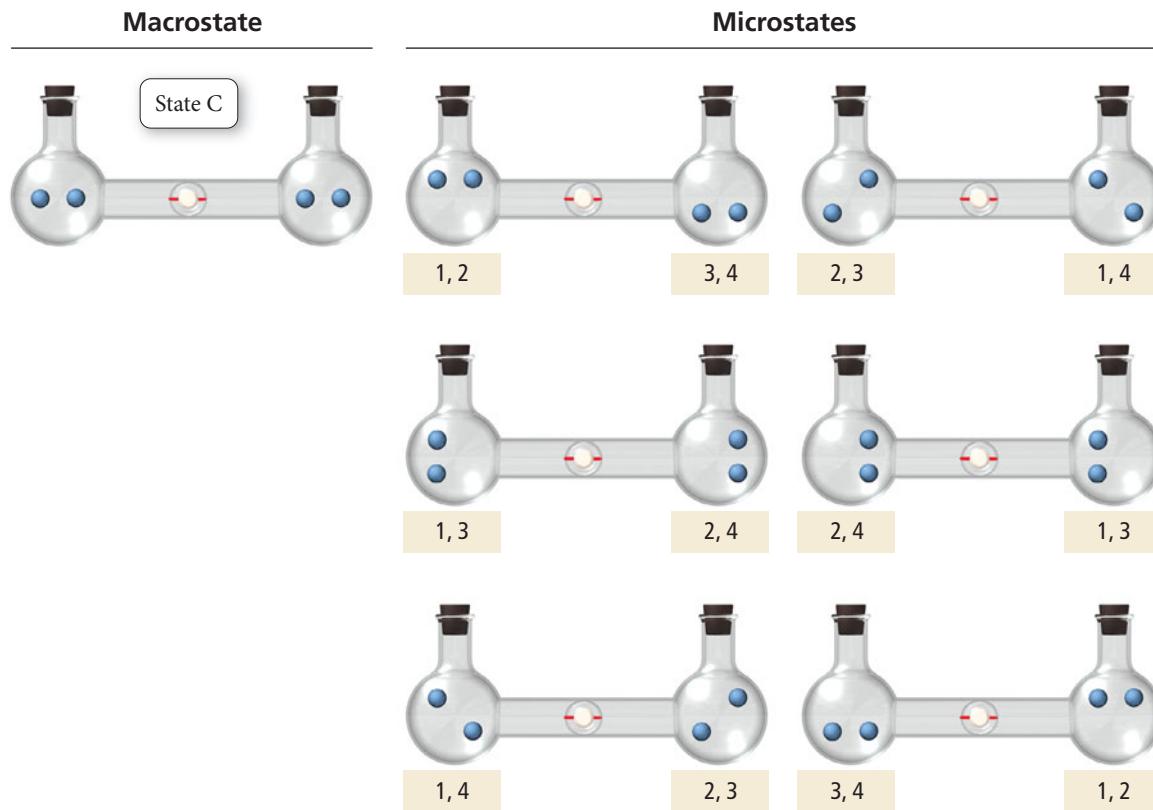
Now we ask the following question for each state: how many microstates give rise to the same macrostate? To keep track of the microstates we label the atoms 1–4. Although they have different numbered labels, since the atoms are all the same, there is externally no difference between them. For states A and B, only one microstate results in the specified macrostate—atoms 1–4 on the left side or the right side, respectively.

| See the discussion of state functions in Section 6.3.

| See the discussion of work done by an expanding gas in Section 6.4.



For state C, however, six different possible microstates all result in the same macrostate (two atoms on each side).



This means that if the atoms are just randomly moving between the two flasks, the statistical probability of finding the atoms in state C is six times greater than the probability of finding the atoms in state A or state B. Consequently, even for a simple system consisting of only four atoms, the atoms are most likely to be found in state C. State C has the greatest entropy—it has the greatest number of energetically equivalent ways to distribute its components.

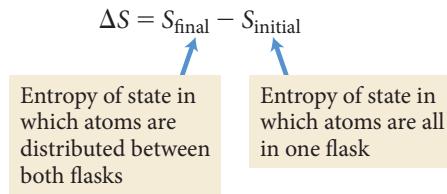
As the number of atoms increases, the number of microstates that leads to the atoms being equally distributed between the two flasks increases dramatically. For example, with 10 atoms, the number of microstates leading to an equal distribution of atoms between two flasks is 252 and with 20 atoms the number of microstates is 184,756. Yet, the number of microstates that leads to all of the atoms being only in the left flask

In these drawings, the exact location of an atom within a flask is insignificant. The significant aspect is whether the atom is in the left flask or the right flask.

For  $n$  particles, the number of ways to put  $r$  particles in one flask and  $n-r$  particles in the other flask is  $n!/(n-r)!r!$ . For 10 atoms,  $n = 10$  and  $r = 5$ .

(or all only in the right flask) does not increase—it is always only 1. In other words, the arrangement in which the atoms are equally distributed between the two flasks has a much larger number of possible microstates and therefore much greater entropy. The system thus tends toward that state.

The *change in entropy* in transitioning from a state in which all of the atoms are in the left flask to the state in which the atoms are evenly distributed between both flasks is *positive* because the final state has a greater entropy than the initial state:



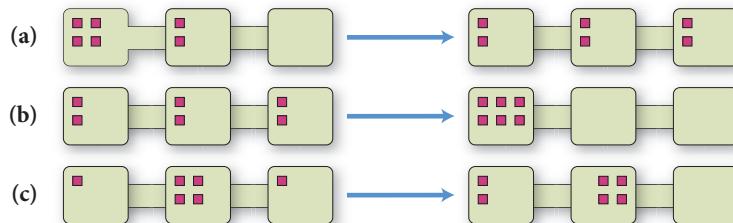
Since  $S_{\text{final}}$  is greater than  $S_{\text{initial}}$ ,  $\Delta S$  is positive and the process is spontaneous according to the second law. Notice that when the atoms are confined to one flask, their energy is also confined to that one flask; however, when the atoms are evenly distributed between both flasks, their energy is spread out over a greater volume. As the gas expands into the empty flask, energy is dispersed.

The second law explains many phenomena not explained by the first law. In Chapter 6, we learned that heat travels from a substance at higher temperature to one at lower temperature. For example, if we drop an ice cube into water, heat travels from the water to the ice cube—the water cools and the ice warms (and eventually melts). Why? The first law would not prohibit some heat from flowing the other way—from the ice to the water. The ice could lose 10 J of heat (cooling even more) and the water could gain 10 J of heat (warming even more). The first law of thermodynamics would not be violated by such a heat transfer. Imagine putting ice into water only to have the water get warmer as it absorbed thermal energy from the ice! It will never happen because heat transfer from cold to hot violates the second law of thermodynamics. According to the second law, energy is dispersed, not concentrated. The transfer of heat from a substance of higher temperature to one of lower temperature results in greater energy randomization—the energy that was concentrated in the hot substance becomes dispersed between the two substances. The second law accounts for this pervasive tendency.



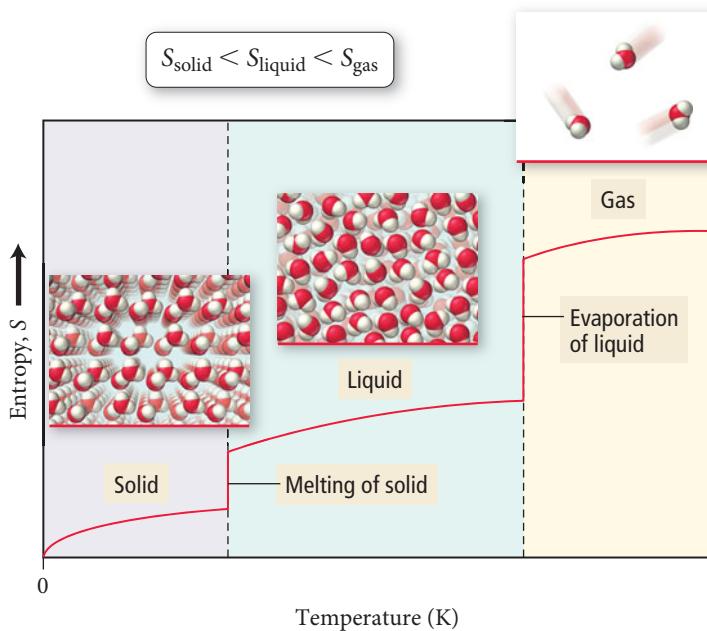
### Conceptual Connection 17.2 Entropy

Consider these three changes in the possible distributions of six gaseous particles within three interconnected boxes. Which change has a positive  $\Delta S$ ?



### The Entropy Change Associated with a Change in State

The entropy of a sample of matter *increases* as it changes state from a solid to a liquid or from a liquid to a gas (Figure 17.5 ▶). We can informally think of this increase in entropy by analogy with macroscopic disorder. The gaseous state is more disorderly than

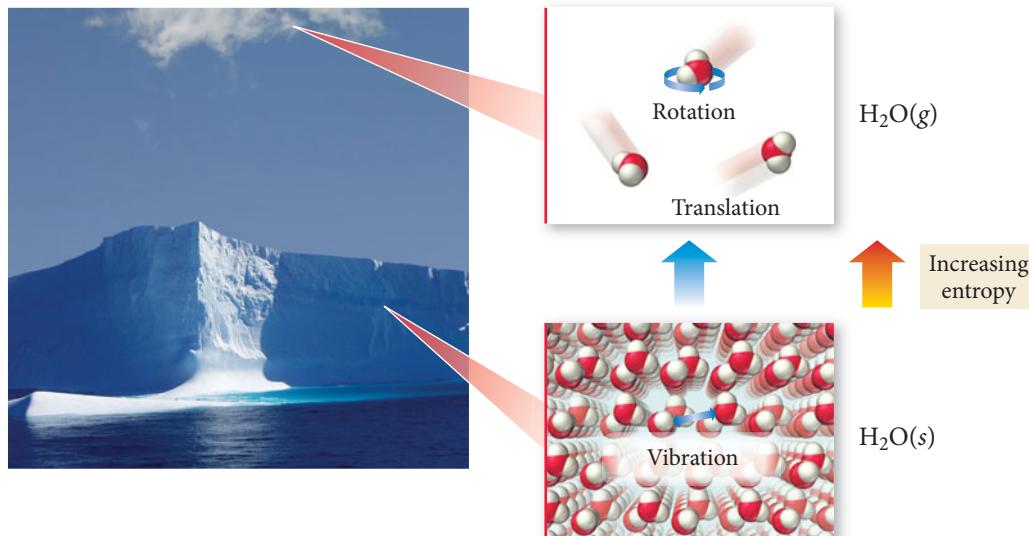


◀ FIGURE 17.5 Entropy and State Change Entropy increases when matter changes from a solid to a liquid and from a liquid to a gas.

the liquid state, which is in turn more disorderly than the solid state. More formally, however, the differences in entropy are related to the number of energetically equivalent ways of arranging the particles in each state—there are more in the gas than in the liquid, and more in the liquid than in the solid.

A gas has more energetically equivalent configurations because it has more ways to distribute its energy than a solid. The energy in a molecular solid consists largely of the vibrations between its molecules. If the same substance is vaporized, however, the energy can take the form of straight-line motions of the molecules (called translational energy) and rotations of the molecules (called rotational energy). In other words, when a solid vaporizes into a gas, there are new “places” to put energy (Figure 17.6 ▼). The gas thus has more possible microstates (more energetically equivalent configurations) than the solid and therefore a greater entropy.

### Additional “Places” for Energy



▲ FIGURE 17.6 “Places” for Energy In the solid state, energy is contained largely in the vibrations between molecules. In the gas state, energy can be contained in both the straight-line motion of molecules (translational energy) and the rotation of molecules (rotational energy).

We can now predict the sign of  $\Delta S$  for processes involving changes of state (or phase). In general, entropy increases ( $\Delta S > 0$ ) for each of the following:

- the phase transition from a solid to a liquid
- the phase transition from a solid to a gas
- the phase transition from a liquid to a gas
- an increase in the number of moles of a gas during a chemical reaction

### EXAMPLE 17.1 Predicting the Sign of Entropy Change

Predict the sign of  $\Delta S$  for each process:

- (a)  $\text{H}_2\text{O}(g) \longrightarrow \text{H}_2\text{O}(l)$
- (b) Solid carbon dioxide sublimes.
- (c)  $2 \text{ N}_2\text{O}(g) \longrightarrow 2 \text{ N}_2(g) + \text{O}_2(g)$

#### SOLUTION

- (a) Since a gas has a greater entropy than a liquid, the entropy decreases and  $\Delta S$  is negative.
- (b) Since a solid has a lower entropy than a gas, the entropy increases and  $\Delta S$  is positive.
- (c) Since the number of moles of gas increases, the entropy increases and  $\Delta S$  is positive.

#### FOR PRACTICE 17.1

Predict the sign of  $\Delta S$  for each process:

- (a) the boiling of water
- (b)  $\text{I}_2(g) \longrightarrow \text{I}_2(s)$
- (c)  $\text{CaCO}_3(s) \longrightarrow \text{CaO}(s) + \text{CO}_2(g)$

## 17.4 Heat Transfer and Changes in the Entropy of the Surroundings

We have now seen that the criterion for spontaneity is an increase in the entropy of the universe. However, you can probably think of several spontaneous processes in which entropy seems to decrease. For example, when water freezes at temperatures below 0 °C, the entropy of the water decreases, yet the process is spontaneous. Similarly, when water vapor in air condenses into fog on a cold night, the entropy of the water also decreases. Why are these processes spontaneous?

To answer this question, we must return to the second law: for any spontaneous process, the entropy of the universe increases ( $\Delta S_{\text{univ}} > 0$ ). Even though the entropy of the water decreases during freezing and condensation, the entropy of the universe must somehow increase in order for these processes to be spontaneous. In Chapter 6, we distinguished between a thermodynamic system and its surroundings. The same distinction is useful in our discussion of entropy. For the freezing of water, let us consider the system to be the water. The surroundings are then the rest of the universe. Accordingly,  $\Delta S_{\text{sys}}$  is the entropy change for the water itself,  $\Delta S_{\text{surr}}$  is the entropy change for the surroundings, and  $\Delta S_{\text{univ}}$  is the entropy change for the universe. The entropy change for the universe is the sum of the entropy changes for the system and the surroundings:

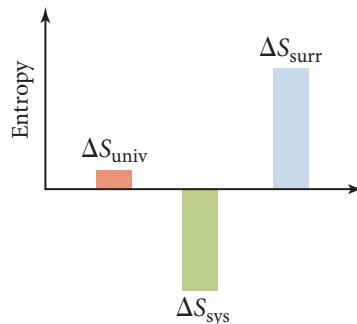
$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

The second law states that the entropy of the universe must increase ( $\Delta S_{\text{univ}} > 0$ ) for a process to be spontaneous. The entropy of the system can decrease ( $\Delta S_{\text{sys}} < 0$ ) as long as the entropy of the surroundings increases by a greater amount ( $\Delta S_{\text{surr}} > -\Delta S_{\text{sys}}$ ), so that the overall entropy of the universe undergoes a net increase.

For liquid water freezing or water vapor condensing, we know that the change in entropy for the system ( $\Delta S_{\text{sys}}$ ) is negative because the water becomes more orderly in both cases.

For  $\Delta S_{\text{univ}}$  to be positive, therefore,  $\Delta S_{\text{surr}}$  must be positive and greater in absolute value (or magnitude) than  $\Delta S_{\text{sys}}$  as shown graphically here:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$



But why does the freezing of ice or the condensation of water increase the entropy of the surroundings? Because both processes are *exothermic*: they give off heat to the surroundings. Because we think of entropy as the dispersal or randomization of energy, *the release of heat energy by the system disperses that energy into the surroundings, increasing the entropy of the surroundings*. The freezing of water below 0 °C and the condensation of water vapor on a cold night both increase the entropy of the universe because the heat given off to the surroundings increases the entropy of the surroundings to a sufficient degree to overcome the entropy decrease in the water.

Even though (as we saw earlier) enthalpy by itself cannot determine spontaneity, the increase in the entropy of the surroundings caused by the release of heat explains why exothermic processes are so often spontaneous.

#### **Summarizing Entropy Changes in the Surroundings:**

- ▶ An exothermic process increases the entropy of the surroundings.
- ▶ An endothermic process decreases the entropy of the surroundings.

#### **The Temperature Dependence of $\Delta S_{\text{surr}}$**

We have just seen how the freezing of water increases the entropy of the surroundings by dispersing heat energy into the surroundings. Yet we know that the freezing of water is not spontaneous at all temperatures. The freezing of water becomes *nonspontaneous* above 0 °C. Why? Because the magnitude of the increase in the entropy of the surroundings due to the dispersal of energy into the surroundings is *temperature dependent*.

The greater the temperature, the smaller the increase in entropy for a given amount of energy dispersed into the surroundings. Recall that the units of entropy are joules per kelvin: energy units divided by temperature units. *Entropy is a measure of energy dispersal (joules) per unit temperature (kelvins)*. The higher the temperature, the lower the amount of entropy for a given amount of energy dispersed. We can understand the temperature dependence of entropy changes due to heat flow with a simple analogy. Imagine that you have \$1000 to give away. If you gave the \$1000 to a rich man, the impact on his net worth would be negligible (because he already has so much money). If you gave the same \$1000 to a poor man, however, his net worth would change substantially (because he has so little money). Similarly, if you disperse 1000 J of energy into surroundings that are hot, the entropy increase is small (because the impact of the 1000 J is small on surroundings that already contain a lot of energy). If you disperse the same 1000 J of energy into surroundings that are cold, however, the entropy increase is large (because the impact of the 1000 J is great on surroundings that contain little energy). For this same reason, the impact of the heat released to the surroundings by the freezing of water depends on the temperature of the surroundings—the higher the temperature, the smaller the impact.

We can now understand why water spontaneously freezes at low temperature but not at high temperature. For the freezing of liquid water into ice, the change in entropy of the system is negative at all temperatures:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

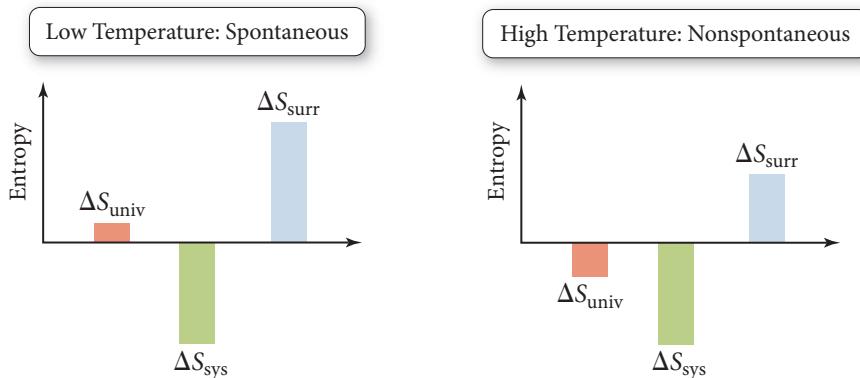
Negative

Positive and large at low temperature

Positive and small at high temperature

At low temperatures, the decrease in entropy of the system is overcome by the large increase in the entropy of the surroundings (a positive quantity), resulting in a positive  $\Delta S_{\text{univ}}$  and a spontaneous process. At high temperatures, on the other hand, the decrease in entropy of the system is not overcome by the increase in entropy of the surroundings (because the magnitude of the positive  $\Delta S_{\text{surr}}$  is smaller at higher temperatures), resulting in a negative  $\Delta S_{\text{univ}}$ ; therefore, the freezing of water is not spontaneous at high temperature as shown graphically here:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \quad (\text{for water freezing})$$



## Quantifying Entropy Changes in the Surroundings

We have seen that when a system exchanges heat with the surroundings, it changes the entropy of the surroundings. At constant pressure, we can use  $q_{\text{sys}}$  to quantify the change in *entropy* for the surroundings ( $\Delta S_{\text{surr}}$ ). In general,

- a process that emits heat into the surroundings ( $q_{\text{sys}}$  negative) *increases* the entropy of the surroundings (positive  $\Delta S_{\text{surr}}$ ).
- a process that absorbs heat from the surroundings ( $q_{\text{sys}}$  positive) *decreases* the entropy of the surroundings (negative  $\Delta S_{\text{surr}}$ ).
- the magnitude of the change in entropy of the surroundings is proportional to the magnitude of  $q_{\text{sys}}$ .

We can summarize these three points with the proportionality:

$$\Delta S_{\text{surr}} \propto -q_{\text{sys}} \quad [17.1]$$

We have also seen that, for a given amount of heat exchanged with the surroundings, the magnitude of  $\Delta S_{\text{surr}}$  is inversely proportional to the temperature. In general, the higher the temperature, the lower the magnitude of  $\Delta S_{\text{surr}}$  for a given amount of heat exchanged:

$$\Delta S_{\text{surr}} \propto \frac{1}{T} \quad [17.2]$$

Combining the proportionalities in Equations 17.1 and 17.2, we get the following general expression at constant temperature:

$$\Delta S_{\text{surr}} = \frac{-q_{\text{sys}}}{T}$$

For any chemical or physical process occurring at constant temperature and pressure, the entropy change of the surroundings is equal to the energy dispersed into the surroundings ( $-q_{\text{sys}}$ ) divided by the temperature of the surroundings in kelvins.

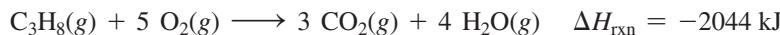
This equation provides insight into why exothermic processes have a tendency to be spontaneous at low temperatures—they increase the entropy of the surroundings. As temperature increases, however, a given negative  $q$  produces a smaller positive  $\Delta S_{\text{surr}}$ ; thus, exothermicity becomes less of a determining factor for spontaneity as temperature increases.

Under conditions of constant pressure  $q_{\text{sys}} = \Delta H_{\text{sys}}$ ; therefore,

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T} \quad (\text{constant } P, T) \quad [17.3]$$

### EXAMPLE 17.2 Calculating Entropy Changes in the Surroundings

Consider the combustion of propane gas:



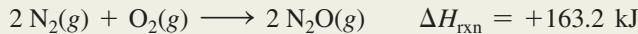
- (a) Calculate the entropy change in the surroundings associated with this reaction occurring at 25 °C.
- (b) Determine the sign of the entropy change for the system.
- (c) Determine the sign of the entropy change for the universe. Will the reaction be spontaneous?

#### SOLUTION

|  |   |           |           |
|--|---|-----------|-----------|
| <p>(a) The entropy change of the surroundings is given by Equation 17.3. Substitute the value of <math>\Delta H_{\text{rxn}}</math> and the temperature in kelvins and calculate <math>\Delta S_{\text{surr}}</math>.</p>  | $T = 273 + 25 = 298 \text{ K}$ $\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{rxn}}}{T}$ $= \frac{-(-2044 \text{ kJ})}{298 \text{ K}}$ $= +6.86 \text{ kJ/K}$ $= +6.86 \times 10^3 \text{ J/K}$   |           |           |
| <p>(b) Determine the number of moles of gas on each side of the reaction. An increase in the number of moles of gas implies a positive <math>\Delta S_{\text{sys}}</math>.</p>   | $\text{C}_3\text{H}_8(g) + 5 \text{ O}_2(g) \longrightarrow 3 \text{ CO}_2(g) + 4 \text{ H}_2\text{O}(g)$ <table style="margin-left: auto; margin-right: auto;"> <tr> <td style="text-align: center;">6 mol gas</td> <td style="text-align: center;">7 mol gas</td> </tr> </table> <p><math>\Delta S_{\text{sys}}</math> is positive.</p> | 6 mol gas | 7 mol gas |
| 6 mol gas  | 7 mol gas   |           |           |
| <p>(c) The change in entropy of the universe is the sum of the entropy changes of the system and the surroundings. If the entropy changes of the system and surroundings are both the same sign, the entropy change for the universe also has the same sign.</p> | $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$  <p>Therefore, <math>\Delta S_{\text{univ}}</math> is positive and the reaction is spontaneous.</p>   |           |           |

#### FOR PRACTICE 17.2

Consider the reaction between nitrogen and oxygen gas to form dinitrogen monoxide:



- (a) Calculate the entropy change in the surroundings associated with this reaction occurring at 25 °C.
- (b) Determine the sign of the entropy change for the system.
- (c) Determine the sign of the entropy change for the universe. Will the reaction be spontaneous?

#### FOR MORE PRACTICE 17.2

A reaction has  $\Delta H_{\text{rxn}} = -107 \text{ kJ}$  and  $\Delta S_{\text{rxn}} = 285 \text{ J/K}$ . At what temperature is the change in entropy for the reaction equal to the change in entropy for the surroundings?



### Conceptual Connection 17.3 Entropy and Biological Systems

Do biological systems contradict the second law of thermodynamics? By taking energy from their surroundings and synthesizing large, complex biological molecules, plants and animals tend to concentrate energy, not disperse it. How can this be so?

## 17.5 Gibbs Free Energy

Equation 17.3 establishes a relationship between the enthalpy change in a system and the entropy change in the surroundings. Recall that for any process the entropy change of the universe is the sum of the entropy change of the system and the entropy change of the surroundings:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \quad [17.4]$$

Combining Equation 17.4 with Equation 17.3 gives us the following relationship at constant temperature and pressure:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} \quad [17.5]$$

Using Equation 17.5, we can calculate  $\Delta S_{\text{univ}}$  while focusing only on the *system*. If we multiply Equation 17.5 by  $-T$ , we arrive at the expression:

$$\begin{aligned} -T\Delta S_{\text{univ}} &= -T\Delta S_{\text{sys}} + T \frac{\Delta H_{\text{sys}}}{T} \\ &= \Delta H_{\text{sys}} - T\Delta S_{\text{sys}} \end{aligned} \quad [17.6]$$

If we drop the subscript *sys*—from now on  $\Delta H$  and  $\Delta S$  without subscripts mean  $\Delta H_{\text{sys}}$  and  $\Delta S_{\text{sys}}$ —we get the expression:

$$-T\Delta S_{\text{univ}} = \Delta H - T\Delta S \quad [17.7]$$

The right hand side of Equation 17.7 represents the change in a thermodynamic function called *Gibbs free energy*. The formal definition of **Gibbs free energy ( $G$ )** is:

$$G = H - TS \quad [17.8]$$

where  $H$  is enthalpy,  $T$  is the temperature in kelvins, and  $S$  is entropy. The *change* in Gibbs free energy, symbolized by  $\Delta G$ , is expressed as follows (at constant temperature):

$$\Delta G = \Delta H - T\Delta S \quad [17.9]$$

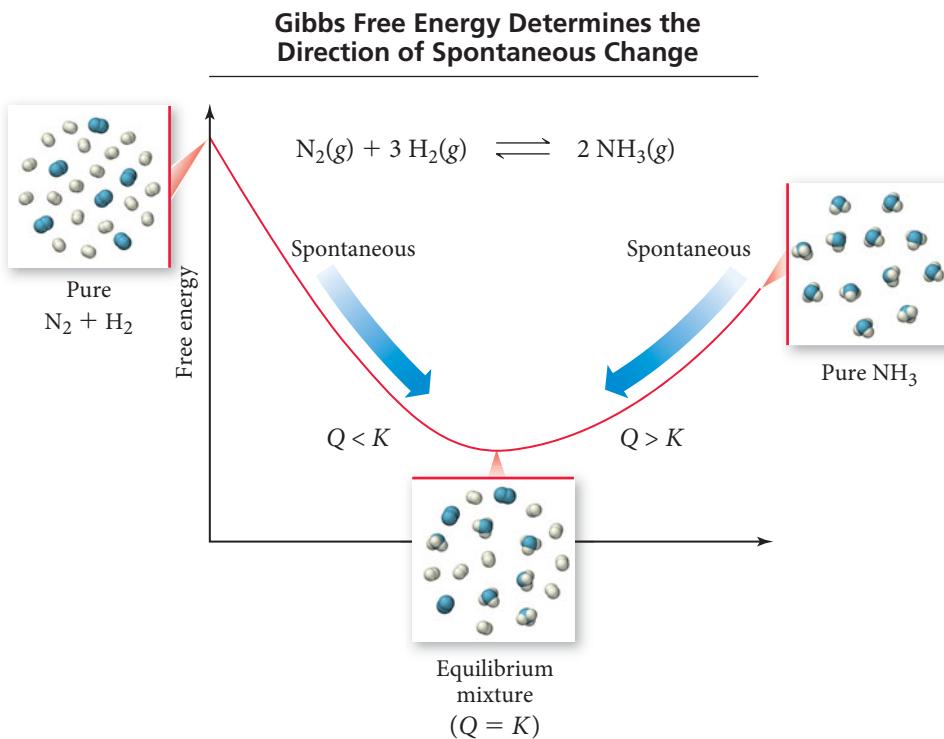
If we combine Equations 17.7 and 17.9, we have an equation that makes clear the significance of  $\Delta G$ :

$$\Delta G = -T\Delta S_{\text{univ}} \quad (\text{constant } T, P) \quad [17.10]$$

*The change in Gibbs free energy for a process occurring at constant temperature and pressure is proportional to the negative of  $\Delta S_{\text{univ}}$ .* Since  $\Delta S_{\text{univ}}$  is a criterion for spontaneity,  $\Delta G$  is also a criterion for spontaneity (although opposite in sign). In fact, Gibbs free energy is also called *chemical potential* because it is analogous to mechanical potential energy discussed earlier. Just as mechanical systems tend toward lower potential energy, so chemical systems tend toward lower Gibbs free energy (toward lower chemical potential) (Figure 17.7 ►).

#### Summarizing Gibbs Free Energy (at Constant Temperature and Pressure):

- ▶  $\Delta G$  is proportional to the negative of  $\Delta S_{\text{univ}}$ .
- ▶ A decrease in Gibbs free energy ( $\Delta G < 0$ ) corresponds to a spontaneous process.
- ▶ An increase in Gibbs free energy ( $\Delta G > 0$ ) corresponds to a nonspontaneous process.

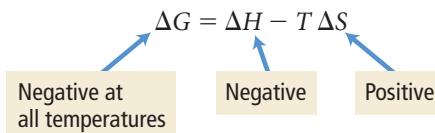


**◀ FIGURE 17.7 Gibbs Free Energy** Gibbs free energy is also called chemical potential because it determines the direction of spontaneous change for chemical systems.

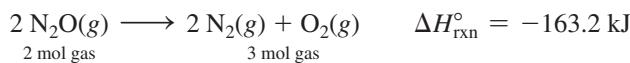
Notice that we can calculate changes in Gibbs free energy solely with reference to the system. So, to determine whether a process is spontaneous, we only have to find the change in *entropy* for the system ( $\Delta S$ ) and the change in *enthalpy* for the system ( $\Delta H$ ). We can then predict the spontaneity of the process at any temperature. In Chapter 6, we learned how to calculate changes in enthalpy ( $\Delta H$ ) for chemical reactions. In Section 17.6, we learn how to calculate changes in entropy ( $\Delta S$ ) for chemical reactions. We can then use those two quantities to calculate changes in free energy ( $\Delta G$ ) for chemical reactions and predict their spontaneity (Section 17.7). Before we move on to these matters, however, let us examine some examples that demonstrate how  $\Delta H$ ,  $\Delta S$ , and  $T$  affect the spontaneity of chemical processes.

## The Effect of $\Delta H$ , $\Delta S$ , and $T$ on Spontaneity

**Case 1:  $\Delta H$  Negative,  $\Delta S$  Positive** If a reaction is exothermic ( $\Delta H < 0$ ), and if the change in entropy for the reaction is positive ( $\Delta S > 0$ ), then the change in free energy is negative at all temperatures and the reaction is spontaneous at all temperatures.



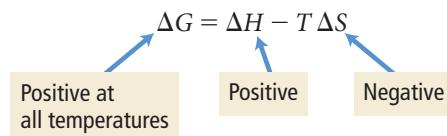
As an example, consider the dissociation of  $\text{N}_2\text{O}$ :



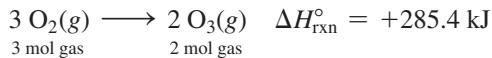
The change in *enthalpy* is negative—heat is emitted, increasing the entropy of the surroundings. The change in *entropy* for the reaction is positive, which means that the entropy of the system increases. (We can see that the change in entropy is positive from the balanced equation—the number of moles of gas increases.) Since the entropy of both the system and the surroundings increases, the entropy of the universe must also increase, making the reaction spontaneous at all temperatures.

Recall from Chapter 6 that  $\Delta H^{\circ}$  represents the standard enthalpy change. The definition of the standard state was first given in Section 6.9 and is summarized in Section 17.6.

**Case 2:  $\Delta H$  Positive,  $\Delta S$  Negative** If a reaction is endothermic ( $\Delta H > 0$ ), and if the change in entropy for the reaction is negative ( $\Delta S < 0$ ), then the change in free energy is positive at all temperatures and the reaction is nonspontaneous at all temperatures.

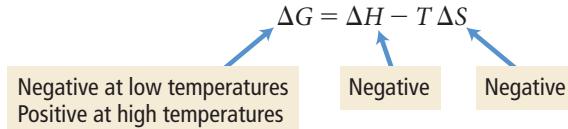


As an example, consider the formation of ozone from oxygen:

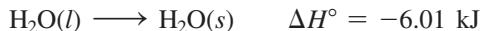


The change in *enthalpy* is positive—heat is therefore absorbed, *decreasing* the entropy of the surroundings. The change in *entropy* is negative, which means that the entropy of the system decreases. (We can see that the change in entropy is negative from the balanced equation—the number of moles of gas decreases.) Since the entropy of both the system and the surroundings decreases, the entropy of the universe must also decrease, making the reaction nonspontaneous at all temperatures.

**Case 3:  $\Delta H$  Negative,  $\Delta S$  Negative** If a reaction is exothermic ( $\Delta H < 0$ ), and if the change in entropy for the reaction is negative ( $\Delta S < 0$ ), then the sign of the change in free energy depends on temperature. The reaction is spontaneous at low temperature, but nonspontaneous at high temperature.



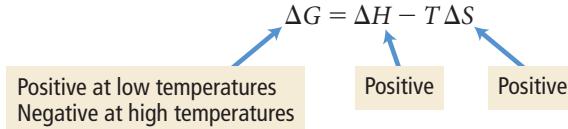
As an example, consider the freezing of liquid water to form ice:



The change in *enthalpy* is negative—heat is emitted, increasing the entropy of the surroundings. The change in *entropy* is negative, which means that the entropy of the system decreases. (We can see that the change in entropy is negative from the balanced equation—a liquid turns into a solid.)

Unlike the two previous cases, where the changes in *entropy* of the system and of the surroundings had the same sign, the changes here are opposite in sign. Therefore, the sign of the change in free energy depends on the relative magnitudes of the two changes. At a low enough temperature, the heat emitted into the surroundings causes a large entropy change in the surroundings, making the process spontaneous. At high temperature, the same amount of heat is dispersed into warmer surroundings, so the positive entropy change in the surroundings is smaller, resulting in a nonspontaneous process.

**Case 4:  $\Delta H$  Positive,  $\Delta S$  Positive** If a reaction is endothermic ( $\Delta H > 0$ ), and if the change in entropy for the reaction is positive ( $\Delta S > 0$ ), then the sign of the change in free energy again depends on temperature. The reaction is nonspontaneous at low temperature but spontaneous at high temperature.



As an example, consider the vaporizing of liquid water to gaseous water:



The change in *enthalpy* is positive—heat is absorbed from the surroundings, so the entropy of the surroundings decreases. The change in *entropy* is positive, which means that the entropy of the system increases. (We can see that the change in entropy is

**TABLE 17.1** The Effect of  $\Delta H$ ,  $\Delta S$ , and  $T$  on Spontaneity

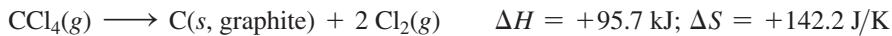
| $\Delta H$ | $\Delta S$ | Low Temperature                   | High Temperature                  | Example   |
|------------|------------|-----------------------------------|-----------------------------------|---|
| —          | +          | Spontaneous ( $\Delta G < 0$ )    | Spontaneous ( $\Delta G < 0$ )    | $2 \text{N}_2\text{O}(g) \longrightarrow 2 \text{N}_2(g) + \text{O}_2(g)$ |
| +          | —          | Nonspontaneous ( $\Delta G > 0$ ) | Nonspontaneous ( $\Delta G > 0$ ) | $3 \text{O}_2(g) \longrightarrow 2 \text{O}_3(g)$                         |
| —          | —          | Spontaneous ( $\Delta G < 0$ )    | Nonspontaneous ( $\Delta G > 0$ ) | $\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(s)$             |
| +          | +          | Nonspontaneous ( $\Delta G > 0$ ) | Spontaneous ( $\Delta G < 0$ )    | $\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(g)$             |

positive from the balanced equation—a liquid turns into a gas.) The changes in entropy of the system and the surroundings again have opposite signs, only this time the entropy of the surroundings decreases while the entropy of the system increases. In cases such as this, high temperature favors spontaneity because the absorption of heat from the surroundings has less effect on the entropy of the surroundings as temperature increases.

The results of this section are summarized in Table 17.1. Notice that when  $\Delta H$  and  $\Delta S$  have opposite signs, the spontaneity of the reaction does not depend on temperature. *When  $\Delta H$  and  $\Delta S$  have the same sign, however, the spontaneity does depend on temperature.* The temperature at which the reaction changes from being spontaneous to being nonspontaneous (or vice versa) is the temperature at which  $\Delta G$  changes sign, which can be found by setting  $\Delta G = 0$  and solving for  $T$ , as shown in part b of Example 17.3.

### EXAMPLE 17.3 Computing Gibbs Free Energy Changes and Predicting Spontaneity from $\Delta H$ and $\Delta S$

Consider the reaction for the decomposition of carbon tetrachloride gas:



- (a) Calculate  $\Delta G$  at 25 °C and determine whether the reaction is spontaneous.
- (b) If the reaction is not spontaneous at 25 °C, determine at what temperature (if any) the reaction becomes spontaneous.

#### SOLUTION

- (a) Use Equation 17.9 to calculate  $\Delta G$  from the given values of  $\Delta H$  and  $\Delta S$ . The temperature must be in kelvins. Be sure to express both  $\Delta H$  and  $\Delta S$  in the same units (usually joules).

$$T = 273 + 25 = 298 \text{ K}$$

$$\begin{aligned} \Delta G &= \Delta H - T\Delta S \\ &= 95.7 \times 10^3 \text{ J} - (298 \text{ K})142.2 \text{ J/K} \\ &= 95.7 \times 10^3 \text{ J} - 42.4 \times 10^3 \text{ J} \\ &= +53.3 \times 10^3 \text{ J} \end{aligned}$$

The reaction is not spontaneous.

- (b) Since  $\Delta S$  is positive,  $\Delta G$  becomes more negative with increasing temperature. To determine the temperature at which the reaction becomes spontaneous, use Equation 17.9 to find the temperature at which  $\Delta G$  changes from positive to negative (set  $\Delta G = 0$  and solve for  $T$ ). The reaction is spontaneous above this temperature.

$$\Delta G = \Delta H - T \Delta S$$

$$0 = 95.7 \times 10^3 \text{ J} - (T)142.2 \text{ J/K}$$

$$\begin{aligned} T &= \frac{95.7 \times 10^3 \text{ J}}{142.2 \text{ J/K}} \\ &= 673 \text{ K} \end{aligned}$$

#### FOR PRACTICE 17.3

Consider the reaction:



Calculate  $\Delta G$  at 25 °C and determine whether the reaction is spontaneous. Does  $\Delta G$  become more negative or more positive as the temperature increases?

## Conceptual Connection 17.4 $\Delta H$ , $\Delta S$ , and $\Delta G$

Which statement is true regarding the sublimation of dry ice (solid CO<sub>2</sub>)?

- (a)  $\Delta H$  is positive,  $\Delta S$  is positive, and  $\Delta G$  is positive at low temperature and negative at high temperature.
- (b)  $\Delta H$  is negative,  $\Delta S$  is negative, and  $\Delta G$  is negative at low temperature and positive at high temperature.
- (c)  $\Delta H$  is negative,  $\Delta S$  is positive, and  $\Delta G$  is negative at all temperatures.
- (d)  $\Delta H$  is positive,  $\Delta S$  is negative, and  $\Delta G$  is positive at all temperatures.

## 17.6 Entropy Changes in Chemical Reactions: Calculating $\Delta S_{\text{rxn}}^{\circ}$

In Chapter 6, we learned how to calculate standard changes in enthalpy ( $\Delta H_{\text{rxn}}^{\circ}$ ) for chemical reactions. We now turn to calculating standard changes in *entropy* for chemical reactions. Recall from Section 6.9 that the standard enthalpy change for a reaction ( $\Delta H_{\text{rxn}}^{\circ}$ ) is the change in enthalpy for a process in which all reactants and products are in their standard states. Recall also the definition of the standard state:

- *For a Gas:* The standard state for a gas is the pure gas at a pressure of exactly 1 atm.
- *For a Liquid or Solid:* The standard state for a liquid or solid is the pure substance in its most stable form at a pressure of 1 atm and at the temperature of interest (often taken to be 25 °C).
- *For a Substance in Solution:* The standard state for a substance in solution is a concentration of 1 M.

We now define the **standard entropy change for a reaction** ( $\Delta S_{\text{rxn}}^{\circ}$ ) as the change in *entropy* for a process in which all reactants and products are in their standard states. Since entropy is a function of state, the standard change in entropy is therefore the standard entropy of the products minus the standard entropy of the reactants:

$$\Delta S_{\text{rxn}}^{\circ} = S_{\text{products}}^{\circ} - S_{\text{reactants}}^{\circ}$$

But how do we find the standard entropies of the reactants and products? Recall from Chapter 6 that we defined *standard molar enthalpies of formation* ( $\Delta H_f^{\circ}$ ) to use in calculating  $\Delta H_{\text{rxn}}^{\circ}$ . We now need to define **standard molar entropies** ( $S^{\circ}$ ) to use in calculating  $\Delta S_{\text{rxn}}^{\circ}$ .

### Standard Molar Entropies ( $S^{\circ}$ ) and the Third Law of Thermodynamics

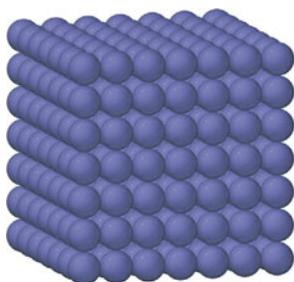
In Chapter 6, we defined a *relative zero* for enthalpy. To do this, we assigned a value of zero to the standard enthalpy of formation for an element in its standard state. This was necessary because absolute values of enthalpy cannot be determined. In other words, for enthalpy, there is no absolute zero against which to measure all other values; therefore, we always have to rely on enthalpy changes from an arbitrarily assigned standard (the elements in their standard states and most stable forms). For entropy, however, *there is an absolute zero*. The absolute zero of entropy is established by the **third law of thermodynamics**, which states:

**The entropy of a perfect crystal at absolute zero (0 K) is zero.**

A perfect crystal at a temperature of absolute zero has only one possible way ( $W = 1$ ) to arrange its components (Figure 17.8 ▲). Based on Boltzmann's definition of entropy ( $S = k \ln W$ ), its entropy is zero ( $S = k \ln 1 = 0$ ).

We can measure all entropy values against the absolute zero of entropy as defined by the third law. Table 17.2 lists values of standard entropies at 25 °C for selected substances. A more complete list can be found in Appendix II B. Standard entropy values are listed in units of joules per mole per kelvin (J/mol · K). The units of mole in the

Perfect crystal at 0 K  
 $W = 1$      $S = 0$



▲ FIGURE 17.8 Zero Entropy  
 A perfect crystal at 0 K has only one possible way to arrange its components.

**TABLE 17.2 Standard Molar Entropy Values ( $S^{\circ}$ ) for Selected Substances at 298 K**

| Substance    | $S^{\circ}$ (J/mol·K) | Substance      | $S^{\circ}$ (J/mol·K) | Substance     | $S^{\circ}$ (J/mol·K) |
|--------------|-----------------------|----------------|-----------------------|---------------|-----------------------|
| <b>Gases</b> |                       | <b>Liquids</b> |                       | <b>Solids</b> |                       |
| $H_2(g)$     | 130.7                 | $H_2O(l)$      | 70.0                  | $MgO(s)$      | 27.0                  |
| $Ar(g)$      | 154.8                 | $CH_3OH(l)$    | 126.8                 | $Fe(s)$       | 27.3                  |
| $CH_4(g)$    | 186.3                 | $Br_2(l)$      | 152.2                 | $Li(s)$       | 29.1                  |
| $H_2O(g)$    | 188.8                 | $C_6H_6(l)$    | 173.4                 | $Cu(s)$       | 33.2                  |
| $N_2(g)$     | 191.6                 |                |                       | $Na(s)$       | 51.3                  |
| $NH_3(g)$    | 192.8                 |                |                       | $K(s)$        | 64.7                  |
| $F_2(g)$     | 202.8                 |                |                       | $NaCl(s)$     | 72.1                  |
| $O_2(g)$     | 205.2                 |                |                       | $CaCO_3(s)$   | 91.7                  |
| $Cl_2(g)$    | 223.1                 |                |                       | $FeCl_3(s)$   | 142.3                 |
| $C_2H_4(g)$  | 219.3                 |                |                       |               |                       |

denominator is required because *entropy is an extensive property*—it depends on the amount of the substance.

At 25 °C, the standard entropy of any substance is the energy dispersed into one mole of that substance at 25 °C, which depends on the number of “places” to put energy within the substance. The factors that affect the number of “places” to put energy—and therefore the standard entropy—include the state of the substance, the molar mass of the substance, the particular allotrope, its molecular complexity, and its extent of dissolution. Let’s examine each of these separately.

**Relative Standard Entropies: Gases, Liquids, and Solids** As we saw in Section 17.3, the entropy of a gas is generally greater than the entropy of a liquid, which is in turn greater than the entropy of a solid. We can see these trends in the tabulated values of standard entropies. For example, consider the relative standard entropies of liquid water and gaseous water at 25 °C:

| $S^{\circ}$ (J/mol·K) |       |
|-----------------------|-------|
| $H_2O(l)$             | 70.0  |
| $H_2O(g)$             | 188.8 |

Gaseous water has a much greater standard entropy because, as we discussed in Section 17.3, it has more energetically equivalent ways to arrange its components, which in turn results in greater energy dispersal at 25 °C.

**Relative Standard Entropies: Molar Mass** Consider the standard entropies of the noble gases at 25 °C:

| $S^{\circ}$ (J/mol·K) |       |  |
|-----------------------|-------|--|
| $He(g)$               | 126.2 |  |
| $Ne(g)$               | 146.1 |  |
| $Ar(g)$               | 154.8 |  |
| $Kr(g)$               | 163.8 |  |
| $Xe(g)$               | 169.4 |  |

Some elements exist in two or more forms, called *allotropes*, within the same state.

The more massive the noble gas, the greater its entropy at 25 °C. A complete explanation of why entropy increases with increasing molar mass is beyond the scope of this book. Briefly, the energy states associated with the motion of heavy atoms are more closely spaced than those of lighter atoms. The more closely spaced energy states allow for greater dispersal of energy at a given temperature and therefore greater entropy. This trend holds only for elements in the same state. (The effect of a state change—from a liquid to a gas, for example—is far greater than the effect of molar mass.)

**Relative Standard Entropies: Allotropes** As mentioned previously, some elements can exist in two or more forms—called *allotropes*—in the same state of matter. For example, the allotropes of carbon include diamond and graphite—both solid forms of carbon. Since the arrangement of atoms within these forms is different, their standard molar entropies are different:

| S° (J/mol·K)   |     |  |
|----------------|-----|--|
| C(s, diamond)  | 2.4 |  |
| C(s, graphite) | 5.7 |  |

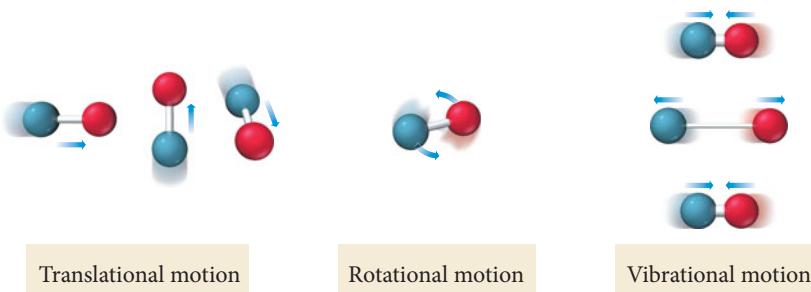
In diamond the atoms are constrained by chemical bonds in a highly restricted three-dimensional crystal structure. In graphite the atoms bond together in sheets, but the sheets have freedom to slide past each other. The less constrained structure of graphite results in more “places” to put energy and therefore greater entropy compared to diamond.

**Relative Standard Entropies: Molecular Complexity** For a given state of matter, entropy generally increases with increasing molecular complexity. For example, consider the standard entropies of the argon and nitrogen monoxide gas:

|       | Molar Mass (g/mol) | S°(J/mol·K) |
|-------|--------------------|-------------|
| Ar(g) | 39.948             | 154.8       |
| NO(g) | 30.006             | 210.8       |

Ar has a greater molar mass than NO, yet it has less entropy at 25 °C. Why? Molecules generally have more “places” to put energy than do atoms. In a gaseous sample of argon, the only form that energy can take is the translational motion of the atoms. In a gaseous sample of NO, on the other hand, energy can take the form of translational motion, rotational motion, and (at high enough temperatures) vibrational motions of the molecules (Figure 17.9 ►). Therefore, for a given state, molecules will generally have a greater entropy than free atoms. Similarly, more complex molecules will generally have more entropy than simpler ones. For example, consider the standard entropies of carbon monoxide and ethene gas:

|                                   | Molar Mass (g/mol) | S°(J/mol·K) |
|-----------------------------------|--------------------|-------------|
| CO(g)                             | 28.01              | 197.7       |
| C <sub>2</sub> H <sub>4</sub> (g) | 28.05              | 219.3       |



**◀ FIGURE 17.9 “Places” for Energy in Gaseous NO** Energy can be contained in translational motion, rotational motion, and (at high enough temperatures) vibrational motion.

These two substances have nearly the same molar mass, but the greater complexity of  $C_2H_4$  results in a greater molar entropy. When molecular complexity and molar mass both increase (as is often the case), molar entropy also increases, as demonstrated by the oxides of nitrogen:

| $S^\circ(J/mol \cdot K)$                     |
|--|
| NO(g)      210.8                             |
| NO <sub>2</sub> (g)      240.1               |
| N <sub>2</sub> O <sub>4</sub> (g)      304.4 |

The increasing molecular complexity as you move down this list, as well as the increasing molar mass, results in more “places” to put energy and therefore greater entropy.

**Relative Standard Entropies: Dissolution** The dissolution of a crystalline solid into solution usually results in an increase in entropy. For example, consider the standard entropies of solid and aqueous potassium chlorate:

| $S^\circ(J/mol \cdot K)$          |
|-----------------------------------|
| KClO <sub>3</sub> (s)      143.1  |
| KClO <sub>3</sub> (aq)      265.7 |

The standard entropies for aqueous solutions are for the solution in its standard state, which is defined as having a concentration of 1 M.

When solid potassium chlorate dissolves in water, the energy that was concentrated within the crystal becomes dispersed throughout the entire solution. The greater energy dispersal results in greater entropy.

## Conceptual Connection 17.5 Standard Entropies

Arrange these gases in order of increasing standard molar entropy: SO<sub>3</sub>, Kr, Cl<sub>2</sub>.

**Calculating the Standard Entropy Change ( $\Delta S_{rxn}^\circ$ ) for a Reaction** Since entropy is a state function, and since standard entropies for many common substances are tabulated, we can calculate the standard entropy change for a chemical reaction by calculating the difference in entropy between the products and the reactants. More specifically,

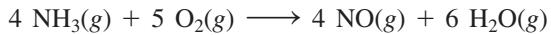
**To calculate  $\Delta S_{rxn}^\circ$ , subtract the standard entropies of the reactants multiplied by their stoichiometric coefficients from the standard entropies of the products multiplied by their stoichiometric coefficients. In the form of an equation:**

$$\Delta S_{rxn}^\circ = \sum n_p S^\circ(\text{products}) - \sum n_r S^\circ(\text{reactants}) \quad [17.11]$$

In Equation 17.11,  $n_p$  represents the stoichiometric coefficients of the products,  $n_r$  represents the stoichiometric coefficients of the reactants, and  $S^\circ$  represents the standard entropies. Keep in mind when using this equation that, *unlike enthalpies of formation, which are zero for elements in their standard states, standard entropies are always nonzero at 25 °C*. Example 17.4 demonstrates the application of Equation 17.11.

### EXAMPLE 17.4 Calculating Standard Entropy Changes ( $\Delta S_{\text{rxn}}^{\circ}$ )

Calculate  $\Delta S_{\text{rxn}}^{\circ}$  for the balanced chemical equation:



#### SOLUTION

Begin by looking up the standard entropy for each reactant and product in Appendix IIB. Always note the correct state—(g), (l), (aq), or (s)—for each reactant and product.

Calculate  $\Delta S_{\text{rxn}}^{\circ}$  by substituting the appropriate values into Equation 17.11. Remember to include the stoichiometric coefficients in your calculation.

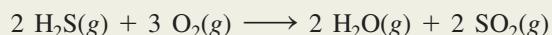
| Reactant or product     | $S^{\circ}$ (in J/mol·K) |
|-------------------------|--------------------------|
| $\text{NH}_3(g)$        | 192.8                    |
| $\text{O}_2(g)$         | 205.2                    |
| $\text{NO}(g)$          | 210.8                    |
| $\text{H}_2\text{O}(g)$ | 188.8                    |

$$\begin{aligned}\Delta S_{\text{rxn}}^{\circ} &= \sum n_p S^{\circ}(\text{products}) - \sum n_r S^{\circ}(\text{reactants}) \\ &= [4(S_{\text{NO}(g)}^{\circ}) + 6(S_{\text{H}_2\text{O}(g)}^{\circ})] - [4(S_{\text{NH}_3(g)}^{\circ}) + 5(S_{\text{O}_2(g)}^{\circ})] \\ &= [4(210.8 \text{ J/K}) + 6(188.8 \text{ J/K})] - [4(192.8 \text{ J/K}) + 5(205.2 \text{ J/K})] \\ &= 1976.0 \text{ J/K} - 1797.2 \text{ J/K} \\ &= 178.8 \text{ J/K}\end{aligned}$$

**CHECK** Notice that  $\Delta S_{\text{rxn}}^{\circ}$  is positive, as you would expect for a reaction in which the number of moles of gas increases.

#### FOR PRACTICE 17.4

Calculate  $\Delta S_{\text{rxn}}^{\circ}$  for the balanced chemical equation:



## 17.7 Free Energy Changes in Chemical Reactions: Calculating $\Delta G_{\text{rxn}}^{\circ}$

In the previous section, we learned how to calculate the standard change in entropy for a chemical reaction ( $\Delta S_{\text{rxn}}^{\circ}$ ). However, the criterion for spontaneity at standard conditions is the **standard change in free energy** ( $\Delta G_{\text{rxn}}^{\circ}$ ). In this section, we examine three methods to calculate the standard change in free energy for a reaction ( $\Delta G_{\text{rxn}}^{\circ}$ ). In the first method, we calculate  $\Delta H_{\text{rxn}}^{\circ}$  and  $\Delta S_{\text{rxn}}^{\circ}$  from tabulated values of  $\Delta H_f^{\circ}$  and  $S^{\circ}$ , and then use the relationship  $\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T\Delta S_{\text{rxn}}^{\circ}$  to calculate  $\Delta G_{\text{rxn}}^{\circ}$ . In the second method, we use tabulated values of free energies of formation to calculate  $\Delta G_{\text{rxn}}^{\circ}$  directly. In the third method, we determine the free energy change for a stepwise reaction from the free energy changes of each of the steps. At the end of this section, we discuss what is “free” about free energy. Remember that  $\Delta G_{\text{rxn}}^{\circ}$  is extremely useful because it tells us about the spontaneity of a process at standard conditions. The more negative  $\Delta G_{\text{rxn}}^{\circ}$  is, the more spontaneous the process (the further it will go toward products to reach equilibrium).

### Calculating Standard Free Energy Changes with $\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T\Delta S_{\text{rxn}}^{\circ}$

In Chapter 6 (Section 6.9), we learned how to use tabulated values of standard enthalpies of formation to calculate  $\Delta H_{\text{rxn}}^{\circ}$ . In the previous section, we learned how to use tabulated values of standard entropies to calculate  $\Delta S_{\text{rxn}}^{\circ}$ . We can use these calculated values of

$\Delta H_{\text{rxn}}^{\circ}$  and  $\Delta S_{\text{rxn}}^{\circ}$  to determine the standard free energy change for a reaction by using the equation:

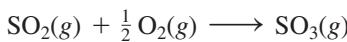
$$\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T\Delta S_{\text{rxn}}^{\circ} \quad [17.12]$$

Since tabulated values of standard enthalpies of formation ( $\Delta H_f^{\circ}$ ) and standard entropies ( $S^{\circ}$ ) are usually applicable at 25 °C, the equation should (strictly speaking) be valid only when  $T = 298$  K (25 °C). However, the changes in  $\Delta H_{\text{rxn}}^{\circ}$  and  $\Delta S_{\text{rxn}}^{\circ}$  over a limited temperature range are small when compared to the changes in the value of the temperature itself. Therefore, we can use Equation 17.12 to estimate changes in free energy at temperatures other than 25 °C.

### EXAMPLE 17.5 Calculating the Standard Change in Free Energy for a Reaction Using $\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T\Delta S_{\text{rxn}}^{\circ}$



One of the possible initial steps in the formation of acid rain is the oxidation of the pollutant SO<sub>2</sub> to SO<sub>3</sub> by the reaction:



Calculate  $\Delta G_{\text{rxn}}^{\circ}$  at 25 °C and determine whether the reaction is spontaneous.

#### SOLUTION

Begin by looking up (in Appendix IIB) the standard enthalpy of formation and the standard entropy for each reactant and product.

| Reactant or product | $\Delta H_f^{\circ}$ (kJ/mol) | $S^{\circ}$ (J/mol · K) |
|---------------------|-------------------------------|-------------------------|
| SO <sub>2</sub> (g) | -296.8                        | 248.2                   |
| O <sub>2</sub> (g)  | 0                             | 205.2                   |
| SO <sub>3</sub> (g) | -395.7                        | 256.8                   |

Calculate  $\Delta H_{\text{rxn}}^{\circ}$  using Equation 6.15.

$$\begin{aligned} \Delta H_{\text{rxn}}^{\circ} &= \sum n_p \Delta H_f^{\circ}(\text{products}) - \sum n_r \Delta H_f^{\circ}(\text{reactants}) \\ &= [\Delta H_f^{\circ}, \text{SO}_3(g)] - [\Delta H_f^{\circ}, \text{SO}_2(g) + \frac{1}{2}(\Delta H_f^{\circ}, \text{O}_2(g))] \\ &= -395.7 \text{ kJ} - (-296.8 \text{ kJ} + 0.0 \text{ kJ}) \\ &= -98.9 \text{ kJ} \end{aligned}$$

Calculate  $\Delta S_{\text{rxn}}^{\circ}$  using Equation 17.11.

$$\begin{aligned} \Delta S_{\text{rxn}}^{\circ} &= \sum n_p S^{\circ}(\text{products}) - \sum n_r S^{\circ}(\text{reactants}) \\ &= [S^{\circ}_{\text{SO}_3(g)}] - [S^{\circ}_{\text{SO}_2(g)} + \frac{1}{2}(S^{\circ}_{\text{O}_2(g)})] \\ &= 256.8 \text{ J/K} - [248.2 \text{ J/K} + \frac{1}{2}(205.2 \text{ J/K})] \\ &= -94.0 \text{ J/K} \end{aligned}$$

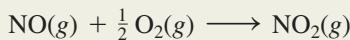
Calculate  $\Delta G_{\text{rxn}}^{\circ}$  using the calculated values of  $\Delta H_{\text{rxn}}^{\circ}$  and  $\Delta S_{\text{rxn}}^{\circ}$  and Equation 17.12. Convert the temperature to kelvins.

$$\begin{aligned} T &= 25 + 273 = 298 \text{ K} \\ \Delta G_{\text{rxn}}^{\circ} &= \Delta H_{\text{rxn}}^{\circ} - T\Delta S_{\text{rxn}}^{\circ} \\ &= -98.9 \times 10^3 \text{ J} - 298 \text{ K}(-94.0 \text{ J/K}) \\ &= -70.9 \times 10^3 \text{ J} \\ &= -70.9 \text{ kJ} \end{aligned}$$

The reaction is spontaneous at this temperature because  $\Delta G_{\text{rxn}}^{\circ}$  is negative.

#### FOR PRACTICE 17.5

Consider the oxidation of NO to NO<sub>2</sub>:



Calculate  $\Delta G_{\text{rxn}}^{\circ}$  at 25 °C and determine whether the reaction is spontaneous at standard conditions.

**EXAMPLE 17.6** Estimating the Standard Change in Free Energy for a Reaction at a Temperature Other than 25 °C  
Using  $\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ}$

For the reaction in Example 17.5, estimate the value of  $\Delta G_{\text{rxn}}^{\circ}$  at 125 °C. Is the reaction more or less spontaneous at this elevated temperature; that is, is the value of  $\Delta G_{\text{rxn}}^{\circ}$  more negative (more spontaneous) or more positive (less spontaneous)?

**SOLUTION**

Estimate  $\Delta G_{\text{rxn}}^{\circ}$  at the new temperature using the calculated values of  $\Delta H_{\text{rxn}}^{\circ}$  and  $\Delta S_{\text{rxn}}^{\circ}$  from Example 17.5. For  $T$ , convert the given temperature to kelvins. Make sure to use the same units for  $\Delta H_{\text{rxn}}^{\circ}$  and  $\Delta S_{\text{rxn}}^{\circ}$  (usually joules).

$$T = 125 + 273 = 398 \text{ K}$$

$$\begin{aligned}\Delta G_{\text{rxn}}^{\circ} &= \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ} \\ &= -98.9 \times 10^3 \text{ J} - 398 \text{ K}(-94.0 \text{ J/K}) \\ &= -61.5 \times 10^3 \text{ J} \\ &= -61.5 \text{ kJ}\end{aligned}$$

Since the value of  $\Delta G_{\text{rxn}}^{\circ}$  at this elevated temperature is less negative (or more positive) than the value of  $\Delta G_{\text{rxn}}^{\circ}$  at 25 °C (which is  $-70.9 \text{ kJ}$ ), the reaction is less spontaneous.

**FOR PRACTICE 17.6**

For the reaction in For Practice 17.5, calculate the value of  $\Delta G_{\text{rxn}}^{\circ}$  at  $-55 \text{ }^{\circ}\text{C}$ . Is the reaction more spontaneous (more negative  $\Delta G_{\text{rxn}}^{\circ}$ ) or less spontaneous (more positive  $\Delta G_{\text{rxn}}^{\circ}$ ) at the lower temperature?

### Calculating $\Delta G_{\text{rxn}}^{\circ}$ with Tabulated Values of Free Energies of Formation

Because  $\Delta G_{\text{rxn}}^{\circ}$  is the *change* in free energy for a chemical reaction—the difference in free energy between the products and the reactants—and because free energy is a state function, we can calculate  $\Delta G_{\text{rxn}}^{\circ}$  by subtracting the free energies of the reactants of the reaction from the free energies of the products of the reaction. Also, since we are interested only in *changes* in free energy (and not in absolute values of free energy), we are free to define the *zero* of free energy as conveniently as possible. By analogy with our definition of enthalpies of formation, we define the **free energy of formation** ( $\Delta G_f^{\circ}$ ) as follows:

**The free energy of formation ( $\Delta G_f^{\circ}$ ) is the change in free energy when 1 mol of a compound in its standard state forms from its constituent elements in their standard states. The free energy of formation of pure elements in their standard states is zero.**

We can measure all changes in free energy relative to pure elements in their standard states. To calculate  $\Delta G_{\text{rxn}}^{\circ}$ , we subtract the free energies of formation of the reactants multiplied by their stoichiometric coefficients from the free energies of formation of the products multiplied by their stoichiometric coefficients. In the form of an equation:

$$\Delta G_{\text{rxn}}^{\circ} = \sum n_p \Delta G_f^{\circ}(\text{products}) - \sum n_r \Delta G_f^{\circ}(\text{reactants}) \quad [17.13]$$

In Equation 17.13,  $n_p$  represents the stoichiometric coefficients of the products,  $n_r$  represents the stoichiometric coefficients of the reactants, and  $\Delta G_f^{\circ}$  represents the standard free energies of formation. Table 17.3 lists  $\Delta G_f^{\circ}$  values for selected substances. You can find a more complete list in Appendix IIB. Notice that, by definition, *elements* have standard free energies of formation of zero. Notice also that most *compounds* have negative standard free energies of formation. This means that those compounds spontaneously form from their elements in their standard states. Compounds with positive free energies of formation do not spontaneously form from their elements and are therefore less common.

Example 17.7 demonstrates the calculation of  $\Delta G_{\text{rxn}}^{\circ}$  from  $\Delta G_f^{\circ}$  values. This method of calculating  $\Delta G_{\text{rxn}}^{\circ}$  works only at the temperature for which the free energies of

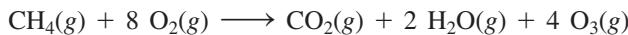
**TABLE 17.3 Standard Molar Free Energies of Formation ( $\Delta G_f^{\circ}$ ) for Selected Substances at 298 K**

| Substance        | $\Delta G_f^{\circ}$ (kJ/mol) | Substance               | $\Delta G_f^{\circ}$ (kJ/mol) |
|------------------|-------------------------------|-------------------------|-------------------------------|
| $\text{H}_2(g)$  | 0                             | $\text{CH}_4(g)$        | -50.5                         |
| $\text{O}_2(g)$  | 0                             | $\text{H}_2\text{O}(g)$ | -228.6                        |
| $\text{N}_2(g)$  | 0                             | $\text{H}_2\text{O}(l)$ | -237.1                        |
| C(s, graphite)   | 0                             | $\text{NH}_3(g)$        | -16.4                         |
| C(s, diamond)    | 2.900                         | $\text{NO}(g)$          | +87.6                         |
| $\text{CO}(g)$   | -137.2                        | $\text{NO}_2(g)$        | +51.3                         |
| $\text{CO}_2(g)$ | -394.4                        | $\text{NaCl}(s)$        | -384.1                        |

formation are tabulated, namely, 25 °C. To estimate  $\Delta G_{\text{rxn}}^{\circ}$  at other temperatures we must use  $\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ}$ , as demonstrated previously.

### EXAMPLE 17.7 Calculating $\Delta G_{\text{rxn}}^{\circ}$ from Standard Free Energies of Formation

Ozone in the lower atmosphere is a pollutant that can form by the following reaction involving the oxidation of unburned hydrocarbons:



Use the standard free energies of formation to determine  $\Delta G_{\text{rxn}}^{\circ}$  for this reaction at 25 °C.

#### SOLUTION

Begin by looking up (in Appendix IIB) the standard free energies of formation for each reactant and product. Remember that the standard free energy of formation of a pure element in its standard state is zero.

| Reactant/product        | $\Delta G_f^{\circ}$ (in kJ/mol) |
|-------------------------|----------------------------------|
| $\text{CH}_4(g)$        | -50.5                            |
| $\text{O}_2(g)$         | 0.0                              |
| $\text{CO}_2(g)$        | -394.4                           |
| $\text{H}_2\text{O}(g)$ | -228.6                           |
| $\text{O}_3(g)$         | 163.2                            |

Calculate  $\Delta G_{\text{rxn}}^{\circ}$  by substituting into Equation 17.13.

$$\begin{aligned}\Delta G_{\text{rxn}}^{\circ} &= \sum n_p \Delta G_f^{\circ}(\text{products}) - \sum n_r \Delta G_f^{\circ}(\text{reactants}) \\ &= [\Delta G_f^{\circ}, \text{CO}_2(g) + 2(\Delta G_f^{\circ}, \text{H}_2\text{O}(g)) + 4(\Delta G_f^{\circ}, \text{O}_3(g))] - [\Delta G_f^{\circ}, \text{CH}_4(g) + 8(\Delta G_f^{\circ}, \text{O}_2(g))] \\ &= [-394.4 \text{ kJ} + 2(-228.6 \text{ kJ}) + 4(163.2 \text{ kJ})] - [-50.5 \text{ kJ} + 8(0.0 \text{ kJ})] \\ &= -198.8 \text{ kJ} + 50.5 \text{ kJ} \\ &= -148.3 \text{ kJ}\end{aligned}$$

#### FOR PRACTICE 17.7

One of the reactions that occurs within a catalytic converter in the exhaust pipe of a car is the simultaneous oxidation of carbon monoxide and reduction of NO (both of which are harmful pollutants).



Use standard free energies of formation to determine  $\Delta G_{\text{rxn}}^{\circ}$  for this reaction at 25 °C. Is the reaction spontaneous at standard conditions?

#### FOR MORE PRACTICE 17.7

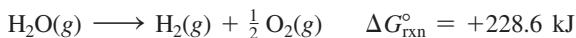
In For Practice 17.7, you calculated  $\Delta G_{\text{rxn}}^{\circ}$  for the simultaneous oxidation of carbon monoxide and reduction of NO using standard free energies of formation. Calculate  $\Delta G_{\text{rxn}}^{\circ}$  for that reaction again at 25 °C, only this time use  $\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ}$ . How do the two values compare? Use your results to calculate  $\Delta G_{\text{rxn}}^{\circ}$  at 500.0 K and explain why you could not calculate  $\Delta G_{\text{rxn}}^{\circ}$  at 500.0 K using tabulated standard free energies of formation.



## Chemistry in Your Day

### Making a Nonspontaneous Process Spontaneous

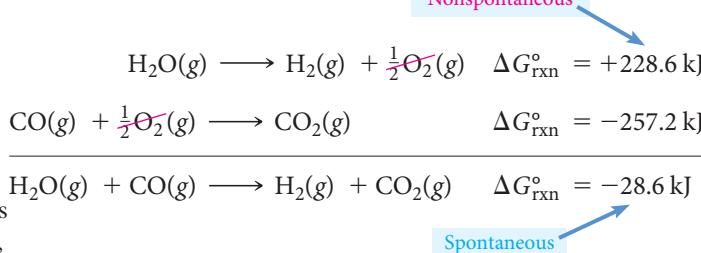
A process that is nonspontaneous can be made spontaneous by coupling it with another process that is highly spontaneous. For example, hydrogen gas is a potential future fuel because it can be used in a fuel cell (a type of battery in which the reactants are constantly supplied—see Chapter 18) to generate electricity. The main problem with switching to hydrogen is securing a source. Where can we get the huge amounts of hydrogen gas that would be needed to meet our world's energy needs? Earth's oceans and lakes, of course, contain vast amounts of hydrogen. But that hydrogen is locked up in water molecules, and the decomposition of water into hydrogen and oxygen has a positive  $\Delta G_{\text{rxn}}^{\circ}$  and is therefore nonspontaneous:



To obtain hydrogen from water, we need to find another reaction with a highly negative  $\Delta G_{\text{rxn}}^{\circ}$  that can couple with the decomposition reaction to give an overall reaction with a negative  $\Delta G_{\text{rxn}}^{\circ}$ . For example, the oxidation of carbon monoxide to carbon dioxide has a large negative  $\Delta G_{\text{rxn}}^{\circ}$  and is highly spontaneous:

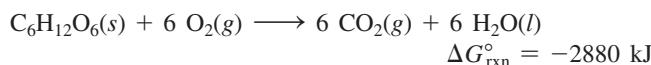


If we add the two reactions together, we get a negative  $\Delta G_{\text{rxn}}^{\circ}$ :



The reaction between water and carbon monoxide is thus a spontaneous way to generate hydrogen gas.

The coupling of nonspontaneous reactions with highly spontaneous ones is also important in biological systems. The synthesis reactions that create the complex biological molecules (such as proteins and DNA) needed by living organisms, for example, are themselves nonspontaneous. Living systems grow and reproduce by coupling these nonspontaneous reactions to highly spontaneous ones. The main spontaneous reaction that ultimately drives the nonspontaneous ones is the metabolism of food. The oxidation of glucose, for example, is highly spontaneous:



Spontaneous reactions such as these ultimately drive the nonspontaneous reactions necessary to sustain life.

### Calculating $\Delta G_{\text{rxn}}^{\circ}$ for a Stepwise Reaction from the Changes in Free Energy for Each of the Steps

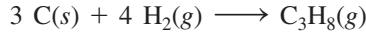
Recall from Section 6.8 that since enthalpy is a state function, we can calculate  $\Delta H_{\text{rxn}}^{\circ}$  for a stepwise reaction from the sum of the changes in enthalpy for each step (according to Hess's law). Since free energy is also a state function, the same relationships that we covered in Chapter 6 for enthalpy also apply to free energy:

1. If a chemical equation is multiplied by some factor, then  $\Delta G_{\text{rxn}}$  is also multiplied by the same factor.
2. If a chemical equation is reversed, then  $\Delta G_{\text{rxn}}$  changes sign.
3. If a chemical equation can be expressed as the sum of a series of steps, then  $\Delta G_{\text{rxn}}$  for the overall equation is the sum of the free energies of reactions for each step.

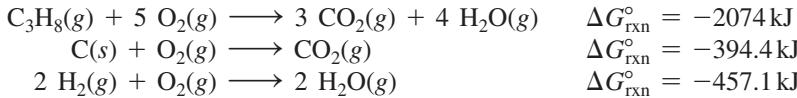
The following example illustrates the use of these relationships to calculate  $\Delta G_{\text{rxn}}^{\circ}$  for a stepwise reaction.

#### EXAMPLE 17.8 Calculating $\Delta G_{\text{rxn}}^{\circ}$ for a Stepwise Reaction

Find  $\Delta G_{\text{rxn}}^{\circ}$  for the reaction.



Use the following reactions with known  $\Delta G^{\circ}$ 's:



#### SOLUTION

To work this problem, manipulate the reactions with known  $\Delta G_{\text{rxn}}^{\circ}$ 's in such a way as to get the reactants of interest on the left, the products of interest on the right, and other species to cancel.

|  |  |
|--|--|
| Since the first reaction has $\text{C}_3\text{H}_8$ as a reactant, and the reaction of interest has $\text{C}_3\text{H}_8$ as a product, reverse the first reaction and change the sign of $\Delta G_{\text{rxn}}^{\circ}$ .   | $3 \text{ CO}_2(g) + 4 \text{ H}_2\text{O}(g) \longrightarrow \text{C}_3\text{H}_8(g) + 5 \text{ O}_2(g) \quad \Delta G_{\text{rxn}}^{\circ} = +2074 \text{ kJ}$   |
| The second reaction has C as a reactant and $\text{CO}_2$ as a product, as required in the reaction of interest. However, the coefficient for C is 1, and in the reaction of interest, the coefficient for C is 3. Therefore, multiply this equation and its $\Delta G_{\text{rxn}}^{\circ}$ by 3. | $3 \times [\text{C}(s) + \text{O}_2(g) \longrightarrow \text{CO}_2(g)] \quad \Delta G_{\text{rxn}}^{\circ} = 3 \times (-394.4 \text{ kJ}) \\ = -1183 \text{ kJ}$   |
| The third reaction has $\text{H}_2(g)$ as a reactant, as required. However, the coefficient for $\text{H}_2$ is 2, and in the reaction of interest, the coefficient for $\text{H}_2$ is 4. Multiply this reaction and its $\Delta G_{\text{rxn}}^{\circ}$ by 2.                                    | $2 \times [2 \text{ H}_2(g) + \text{O}_2(g) \longrightarrow 2 \text{ H}_2\text{O}(g)] \quad \Delta G_{\text{rxn}}^{\circ} = 2 \times (-457.1 \text{ kJ}) \\ = -914.2 \text{ kJ}$   |
| Lastly, rewrite the three reactions after multiplying through by the indicated factors and show how they sum to the reaction of interest. $\Delta G_{\text{rxn}}^{\circ}$ for the reaction of interest is then the sum of the $\Delta G$ 's for the steps.   | $\begin{array}{l} \cancel{3 \text{ CO}_2(g)} + \cancel{4 \text{ H}_2\text{O}(g)} \longrightarrow \text{C}_3\text{H}_8(g) + \cancel{5 \text{ O}_2(g)} \\ \quad \quad \quad \Delta G_{\text{rxn}}^{\circ} = +2074 \text{ kJ} \\ \cancel{3 \text{ C}(s)} + \cancel{3 \text{ O}_2(g)} \longrightarrow \cancel{3 \text{ CO}_2(g)} \\ \quad \quad \quad \Delta G_{\text{rxn}}^{\circ} = -1183 \text{ kJ} \\ \cancel{4 \text{ H}_2(g)} + \cancel{2 \text{ O}_2(g)} \longrightarrow \cancel{4 \text{ H}_2\text{O}(g)} \\ \quad \quad \quad \Delta G_{\text{rxn}}^{\circ} = -914.2 \text{ kJ} \\ \hline 3 \text{ C}(s) + 4 \text{ H}_2(g) \longrightarrow \text{C}_3\text{H}_8(g) & \Delta G_{\text{rxn}}^{\circ} = -23 \text{ kJ} \end{array}$ |

**FOR PRACTICE 17.8**  
Find  $\Delta G_{\text{rxn}}^{\circ}$  for the reaction:

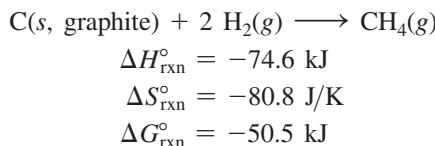
$$\text{N}_2\text{O}(g) + \text{NO}_2(g) \longrightarrow 3 \text{ NO}(g)$$

Use the following reactions with known  $\Delta G$  values:

|   |   |
|---|---|
| $2 \text{ NO}(g) + \text{O}_2(g) \longrightarrow 2 \text{ NO}_2(g)$         | $\Delta G_{\text{rxn}}^{\circ} = -71.2 \text{ kJ}$  |
| $\text{N}_2(g) + \text{O}_2(g) \longrightarrow 2 \text{ NO}(g)$             | $\Delta G_{\text{rxn}}^{\circ} = +175.2 \text{ kJ}$ |
| $2 \text{ N}_2\text{O}(g) \longrightarrow 2 \text{ N}_2(g) + \text{O}_2(g)$ | $\Delta G_{\text{rxn}}^{\circ} = -207.4 \text{ kJ}$ |

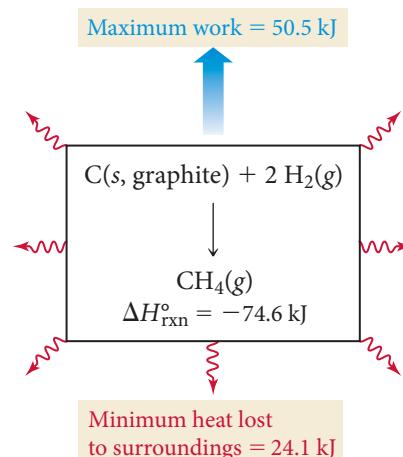
## Why Free Energy Is “Free”

We often want to use the energy released by a chemical reaction to do work. For example, in an automobile, we use the energy released by the combustion of gasoline to move the car forward. The change in free energy of a chemical reaction represents the maximum amount of energy available, or *free*, to do work (if  $\Delta G_{\text{rxn}}^{\circ}$  is negative). For many reactions, the amount of free energy change is less than the change in enthalpy for the reaction. Consider the reaction between carbon and hydrogen occurring at 25 °C:



The reaction is exothermic and gives off 74.6 kJ of heat energy. However, the maximum amount of energy available for useful work is only 50.5 kJ (Figure 17.10 ▶). Why? We can see that the change in entropy of the *system* is negative. Nevertheless, the reaction is spontaneous. This is possible only if some of the emitted heat goes to increase the entropy of the surroundings by an amount sufficient to make the change in entropy of the *universe* positive. The amount of energy available to do work (the free energy) is what remains after accounting for the heat that must be lost to the surroundings.

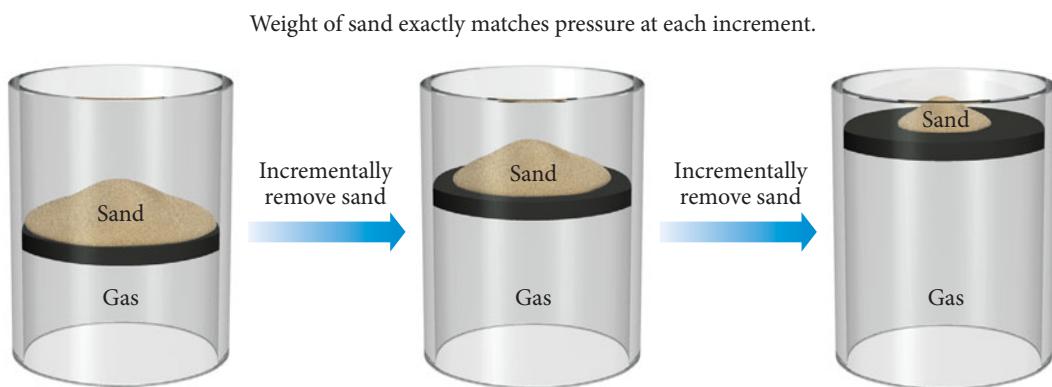
The change in free energy for a chemical reaction represents a *theoretical limit* as to how much work can be done by the reaction. In a *real* reaction, the amount of energy available to do work is even *less* than  $\Delta G_{\text{rxn}}^{\circ}$  because additional energy is lost to the



▲ FIGURE 17.10 Free Energy

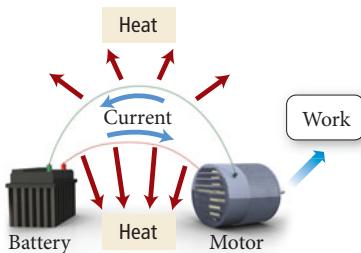
Although the reaction produces 74.6 kJ of heat, only a maximum of 50.5 kJ is available to do work. The rest of the energy is lost to the surroundings.

### Reversible Process



**▲ FIGURE 17.11 A Reversible Process** In a reversible process, the free energy is drawn out in infinitesimally small increments that exactly match the amount of energy that the process is producing in that increment. In this case, grains of sand are removed one at a time, resulting in a series of small expansions in which the weight of sand almost exactly matches the pressure of the expanding gas. This process is close to reversible—each sand grain would need to have an infinitesimally small mass for the process to be fully reversible.

More formally, a **reversible reaction** is one that will change direction upon an infinitesimally small change in a variable (such as temperature or pressure) related to the reaction.



**▲ FIGURE 17.12 Energy Loss in a Battery**

When current is drawn from a battery to do work, some energy is lost as heat due to resistance in the wire. Consequently, the quantity of energy required to recharge the battery will be more than the quantity of work done.

surroundings as heat. A reaction that achieves the theoretical limit with respect to free energy is called a **reversible reaction**. A reversible reaction occurs infinitesimally slowly, and the free energy can only be drawn out in infinitesimally small increments that exactly match the amount of energy that the reaction is producing during that increment (Figure 17.11 ▲).

All real reactions are **irreversible reactions** and therefore do not achieve the theoretical limit of available free energy. Let's return to our discharging battery from the opening section of this chapter as an example of this concept. A battery contains chemical reactants configured in such a way that, upon spontaneous reaction, they produce an electrical current. The free energy released by the reaction is then harnessed to do work. For example, an electric motor can be wired to the battery. Flowing electrical current makes the motor turn (Figure 17.12 ▲). Owing to resistance in the wire, the flowing electrical current will also produce some heat, which is lost to the surroundings and is not available to do work. The amount of free energy lost as heat can be lowered by slowing down the rate of current flow. The slower the rate of current flow, the less free energy is lost as heat and the more is available to do work. However, only in the theoretical case of infinitesimally slow current flow will the maximum amount of work (equal to  $\Delta G_{rxn}^\circ$ ) be done. Any real rate of current flow will result in some loss of energy as heat. This lost energy is the “heat tax” that we discussed in the opening section of this chapter. Recharging the battery will necessarily require more energy than was obtained as work because some of the energy was lost as heat.

If the change in free energy of a chemical reaction is positive, then  $\Delta G_{rxn}^\circ$  represents the minimum amount of energy required to make the reaction occur. Again,  $\Delta G_{rxn}^\circ$  represents a theoretical limit. Making a real nonspontaneous reaction occur always requires more energy than the theoretical limit.

## 17.8 Free Energy Changes for Nonstandard States: The Relationship between $\Delta G_{rxn}^\circ$ and $\Delta G_{rxn}$

We have learned how to calculate the *standard* free energy change for a reaction ( $\Delta G_{rxn}^\circ$ ). However, the standard free energy change applies only to a very narrow set of conditions, namely, those conditions in which the reactants and products are in their standard states. Consider the standard free energy change for the evaporation of liquid water to gaseous water:



The standard free energy change for this process is positive, so the process is nonspontaneous. But you know that if you spill water onto the floor under ordinary conditions, it spontaneously evaporates. Why? *Because ordinary conditions are not standard conditions* and  $\Delta G_{rxn}^\circ$  applies only to standard conditions. For a gas (such as the water vapor in the reaction just given), standard conditions are those in which the pure gas is present at a partial pressure of 1 atmosphere. In a flask containing liquid water and water vapor under standard conditions ( $P_{H_2O} = 1 \text{ atm}$ ) at 25 °C the water would not vaporize. In fact, since  $\Delta G_{rxn}^\circ$  is negative for the reverse reaction, the reaction would spontaneously occur in reverse—water vapor would condense.

In open air under ordinary circumstances, the partial pressure of water vapor is much less than 1 atm. The conditions are not standard, and therefore the value of  $\Delta G_{rxn}^\circ$  does not apply. For nonstandard conditions, we must calculate  $\Delta G_{rxn}$  (as opposed to  $\Delta G_{rxn}^\circ$ ) to predict spontaneity.



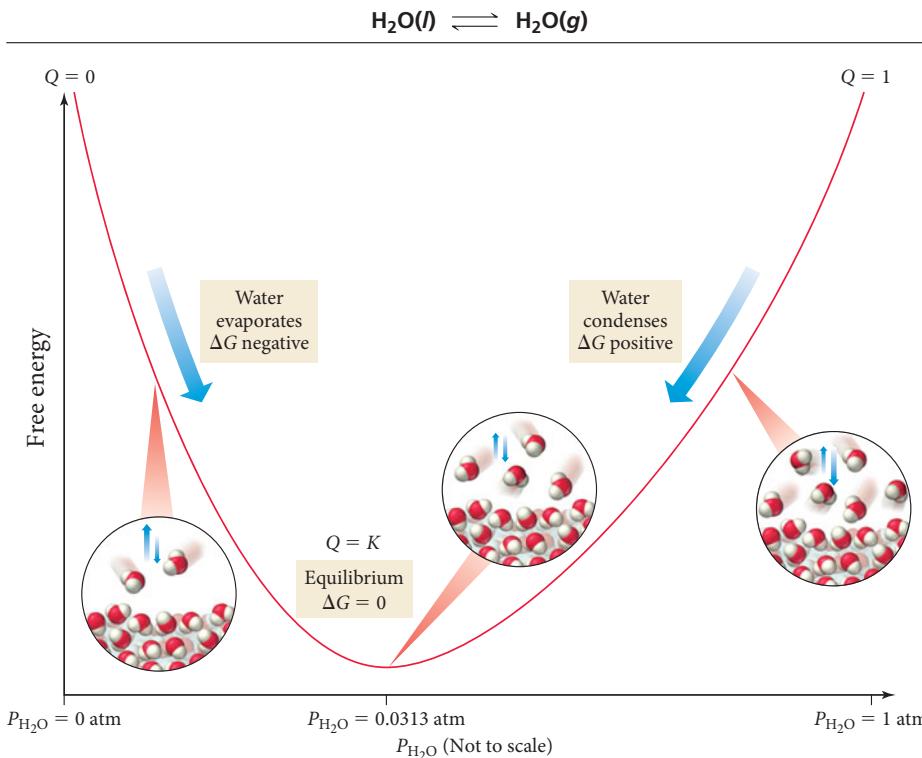
▲ Spilled water spontaneously evaporates even though  $\Delta G^\circ$  for the vaporization of water is positive. Why?

## The Free Energy Change of a Reaction under Nonstandard Conditions

We can calculate the **free energy change of a reaction under nonstandard conditions** ( $\Delta G_{rxn}$ ) from  $\Delta G_{rxn}^\circ$  using the relationship:

$$\Delta G_{rxn} = \Delta G_{rxn}^\circ + RT \ln Q \quad [17.14]$$

where  $Q$  is the reaction quotient (defined in Section 14.7),  $T$  is the temperature in kelvins, and  $R$  is the gas constant in the appropriate units (8.314 J/mol · K). In Equation 17.14 and all subsequent thermodynamic equations, use  $Q_p$  for reactions involving gases, and use  $Q_c$  for reactions involving substances dissolved in solution. We can demonstrate the use of this equation by applying it to the liquid–vapor water equilibrium under several different conditions, as shown in Figure 17.13 ▼. Note that by the law of mass action, for this equilibrium,  $Q = P_{H_2O}$  (where the pressure is expressed in atmospheres):



▲ FIGURE 17.13 Free Energy versus Pressure for Water The free energy change for the vaporization of water is a function of pressure.

**Standard Conditions** Under standard conditions,  $P_{\text{H}_2\text{O}} = 1 \text{ atm}$  and therefore  $Q = 1$ . Substituting, we get the expression:

$$\begin{aligned}\Delta G_{\text{rxn}} &= \Delta G_{\text{rxn}}^\circ + RT \ln Q \\ &= +8.59 \text{ kJ/mol} + RT \ln(1) \\ &= +8.59 \text{ kJ/mol}\end{aligned}$$

Under standard conditions,  $Q$  will always be equal to 1, and since  $\ln(1) = 0$ , the value of  $\Delta G_{\text{rxn}}$  will therefore be equal to  $\Delta G_{\text{rxn}}^\circ$ , as expected. For the liquid–vapor water equilibrium, because  $\Delta G_{\text{rxn}}^\circ > 0$ , the reaction is not spontaneous in the forward direction but is spontaneous in the reverse direction. As stated previously, under standard conditions water vapor condenses into liquid water.

**Equilibrium Conditions** At  $25.00^\circ\text{C}$ , liquid water is in equilibrium with water vapor at a pressure of  $0.0313 \text{ atm}$ ; therefore,  $Q = K_p = 0.0313$ . Substituting:

$$\begin{aligned}\Delta G_{\text{rxn}} &= \Delta G_{\text{rxn}}^\circ + RT \ln(0.0313) \\ &= +8.59 \text{ kJ/mol} + 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} (298.15 \text{ K}) \ln(0.0313) \\ &= +8.59 \text{ kJ/mol} + (-8.59 \times 10^3 \text{ J/mol}) \\ &= +8.59 \text{ kJ/mol} - 8.59 \text{ kJ/mol} \\ &= 0\end{aligned}$$

Under equilibrium conditions, the value of  $RT \ln Q$  is always equal in magnitude but opposite in sign to the value of  $\Delta G_{\text{rxn}}^\circ$ . Therefore, the value of  $\Delta G_{\text{rxn}}$  is zero. Because  $\Delta G_{\text{rxn}} = 0$ , the reaction is not spontaneous in either direction, as expected for a reaction at equilibrium.

A water partial pressure of  $5.00 \times 10^{-3}$  atm corresponds to a relative humidity of 16% at  $25^\circ\text{C}$ .

**Other Nonstandard Conditions** To calculate the value of  $\Delta G_{\text{rxn}}$  under any other set of non-standard conditions, calculate  $Q$  and substitute the value into Equation 17.14. For example, the partial pressure of water vapor in the air on a dry (nonhumid) day might be  $5.00 \times 10^{-3} \text{ atm}$ , so  $Q = 5.00 \times 10^{-3}$ . Substituting:

$$\begin{aligned}\Delta G_{\text{rxn}} &= \Delta G_{\text{rxn}}^\circ + RT \ln(5.00 \times 10^{-3}) \\ &= +8.59 \text{ kJ/mol} + 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} (298 \text{ K}) \ln(5.00 \times 10^{-3}) \\ &= +8.59 \text{ kJ/mol} + (-13.1 \times 10^3 \text{ J/mol}) \\ &= +8.59 \text{ kJ/mol} - 13.1 \text{ kJ/mol} \\ &= -4.5 \text{ kJ/mol}\end{aligned}$$

Under these conditions, the value of  $\Delta G_{\text{rxn}} < 0$ , so the reaction is spontaneous in the forward direction, consistent with our experience of water evaporating when spilled on the floor.

### EXAMPLE 17.9 Calculating $\Delta G_{\text{rxn}}$ under Nonstandard Conditions

Consider the reaction at  $298 \text{ K}$ :



Calculate  $\Delta G_{\text{rxn}}$  under these conditions:

$$P_{\text{NO}} = 0.100 \text{ atm}; \quad P_{\text{O}_2} = 0.100 \text{ atm}; \quad P_{\text{NO}_2} = 2.00 \text{ atm}$$

Is the reaction more or less spontaneous under these conditions than under standard conditions?

#### SOLUTION

Use the law of mass action to calculate  $Q$ .

$$Q = \frac{P_{\text{NO}_2}^2}{P_{\text{NO}}^2 P_{\text{O}_2}} = \frac{(2.00)^2}{(0.100)^2 (0.100)} = 4.00 \times 10^3$$

Substitute  $Q$ ,  $T$ , and  $\Delta G_{\text{rxn}}^{\circ}$  into Equation 17.14 to calculate  $\Delta G_{\text{rxn}}$ . (Since the units of  $R$  include joules, write  $\Delta G_{\text{rxn}}^{\circ}$  in joules.)

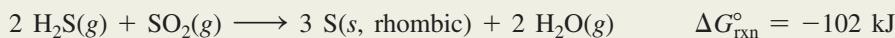
$$\begin{aligned}\Delta G_{\text{rxn}} &= \Delta G_{\text{rxn}}^{\circ} + RT \ln Q \\ &= -71.2 \times 10^3 \text{ J} + 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} (298 \text{ K}) \ln(4.00 \times 10^3) \\ &= -71.2 \times 10^3 \text{ J} + 20.5 \times 10^3 \text{ J} \\ &= -50.7 \times 10^3 \text{ J} \\ &= -50.7 \text{ kJ}\end{aligned}$$

The reaction is spontaneous under these conditions, but less spontaneous than it would be under standard conditions (because  $\Delta G_{\text{rxn}}$  is less negative than  $\Delta G_{\text{rxn}}^{\circ}$ ).

**CHECK** The calculated result is consistent with what you would expect based on Le Châtelier's principle; increasing the concentration of the products and decreasing the concentration of the reactants relative to standard conditions should make the reaction less spontaneous than it was under standard conditions.

### FOR PRACTICE 17.9

Consider the reaction at 298 K:



Calculate  $\Delta G_{\text{rxn}}$  under these conditions:

$$P_{\text{H}_2\text{S}} = 2.00 \text{ atm}; \quad P_{\text{SO}_2} = 1.50 \text{ atm}; \quad P_{\text{H}_2\text{O}} = 0.0100 \text{ atm}$$

Is the reaction more or less spontaneous under these conditions than under standard conditions?



### Conceptual Connection 17.6 Free Energy Changes and Le Châtelier's Principle

According to Le Châtelier's principle and the dependence of free energy on reactant and product concentrations, which statement is true? (Assume that both the reactants and products are gaseous.)

- (a) A high concentration of reactants relative to products results in a more spontaneous reaction than one in which the reactants and products are in their standard states.
- (b) A high concentration of products relative to reactants results in a more spontaneous reaction than one in which the reactants and products are in their standard states.
- (c) A reaction in which the reactants are in standard states, but in which no products have formed, has a  $\Delta G_{\text{rxn}}$  that is more positive than  $\Delta G_{\text{rxn}}^{\circ}$ .

## 17.9 Free Energy and Equilibrium: Relating $\Delta G_{\text{rxn}}^{\circ}$ to the Equilibrium Constant ( $K$ )

We have discussed throughout this chapter that  $\Delta G_{\text{rxn}}^{\circ}$  determines the spontaneity of a reaction when the reactants and products are in their standard states. In Chapter 14, we learned that the equilibrium constant ( $K$ ) determines how far a reaction goes toward products, a measure of spontaneity. Therefore, as you might expect, the standard free energy change of a reaction and the equilibrium constant are related—the equilibrium constant becomes larger as the standard free energy change becomes more negative. In other words, if the reactants in a particular reaction undergo a large *negative* free energy change as they become products, then the reaction has a large equilibrium constant, with products strongly favored at equilibrium. If, on the other hand, the reactants in a particular reaction undergo a large *positive* free energy change as they become products, then the reaction has

a small equilibrium constant, with reactants strongly favored at equilibrium. We can derive a relationship between  $\Delta G_{\text{rxn}}^\circ$  and  $K$  from Equation 17.14. We know that at equilibrium  $Q = K$  and  $\Delta G_{\text{rxn}} = 0$ . Making these substitutions:

$$\Delta G_{\text{rxn}} = \Delta G_{\text{rxn}}^\circ + RT \ln Q$$

$$0 = \Delta G_{\text{rxn}}^\circ + RT \ln K$$

$$\Delta G_{\text{rxn}}^\circ = -RT \ln K$$

[17.15]

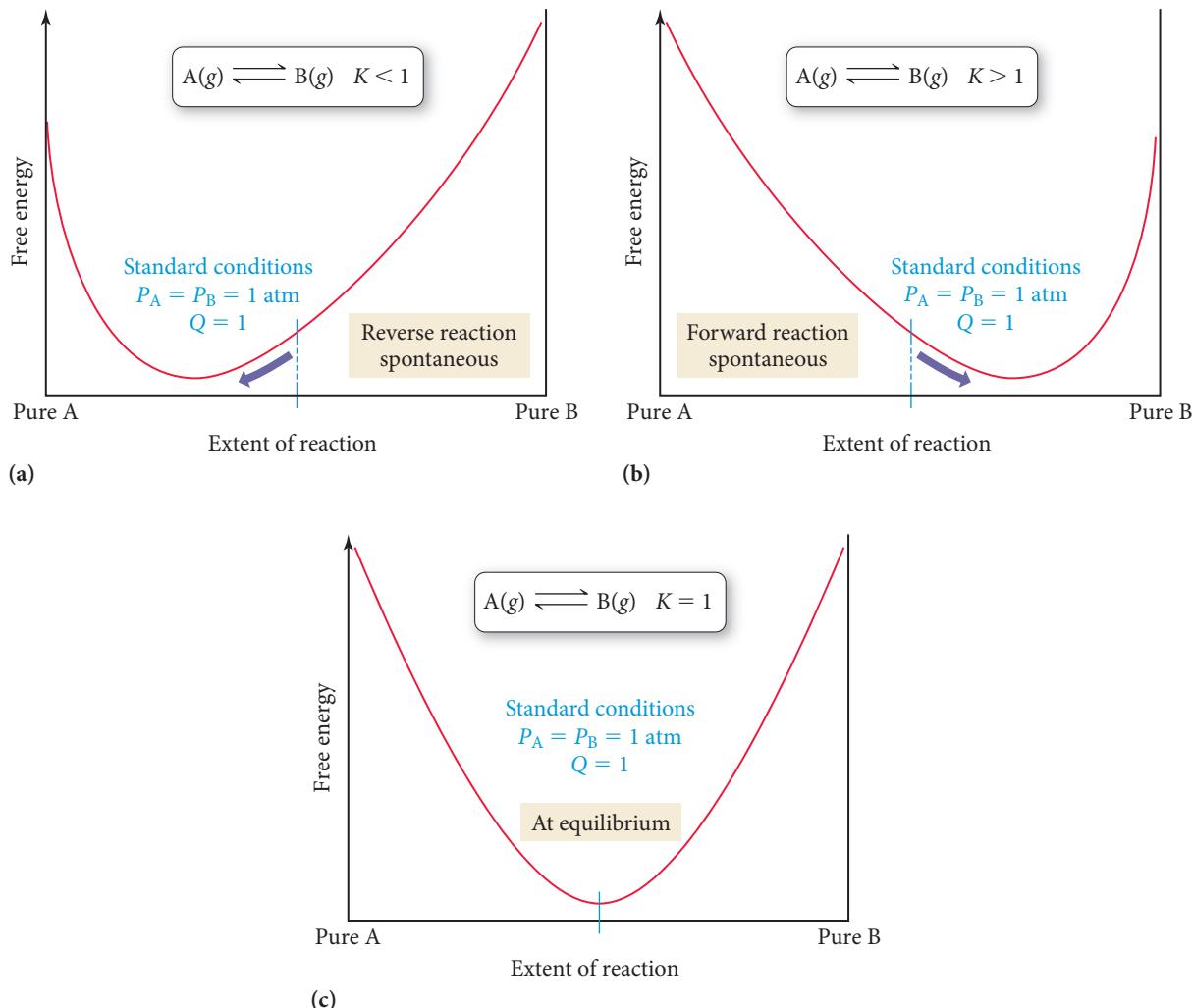
The relationship between  $\Delta G_{\text{rxn}}^\circ$  and  $K$  is logarithmic—small changes in  $\Delta G_{\text{rxn}}^\circ$  have a large effect on  $K$ .

In Equation 17.15 and all subsequent thermodynamic equations, use  $K_p$  for reactions involving gases, and use  $K_c$  for reactions involving substances dissolved in solution.

We can better understand the relationship between  $\Delta G_{\text{rxn}}^\circ$  and  $K$  by considering the following ranges of values for  $K$ , as summarized in Figure 17.14 ▶.

- When  $K < 1$ ,  $\ln K$  is negative and  $\Delta G_{\text{rxn}}^\circ$  is positive. Under standard conditions (when  $Q = 1$ ) the reaction is spontaneous in the reverse direction.
- When  $K > 1$ ,  $\ln K$  is positive and  $\Delta G_{\text{rxn}}^\circ$  is negative. Under standard conditions (when  $Q = 1$ ) the reaction is spontaneous in the forward direction.
- When  $K = 1$ ,  $\ln K$  is zero and  $\Delta G_{\text{rxn}}^\circ$  is zero. The reaction happens to be at equilibrium under standard conditions.

### Free Energy and the Equilibrium Constant



▲ FIGURE 17.14 Free Energy and the Equilibrium Constant (a) Free energy curve for a reaction with a small equilibrium constant. (b) Free energy curve for a reaction with a large equilibrium constant. (c) Free energy curve for a reaction in which  $K = 1$ .

**EXAMPLE 17.10** The Equilibrium Constant and  $\Delta G_{\text{rxn}}^{\circ}$ 

Use tabulated free energies of formation to calculate the equilibrium constant for the reaction at 298 K:

**SOLUTION**

Look up (in Appendix IIB) the standard free energies of formation for each reactant and product.

| Reactant or product       | $\Delta G_f^{\circ}$ (in kJ/mol) |
|---------------------------|----------------------------------|
| $\text{N}_2\text{O}_4(g)$ | 99.8                             |
| $\text{NO}_2(g)$          | 51.3                             |

Calculate  $\Delta G_{\text{rxn}}^{\circ}$  by substituting into Equation 17.13.

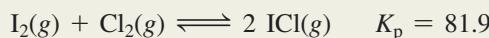
$$\begin{aligned}\Delta G_{\text{rxn}}^{\circ} &= \sum n_p \Delta G_f^{\circ}(\text{products}) - \sum n_r \Delta G_f^{\circ}(\text{reactants}) \\ &= 2[\Delta G_f^{\circ}, \text{NO}_2(g)] - \Delta G_f^{\circ}, \text{N}_2\text{O}_4(g) \\ &= 2(51.3 \text{ kJ}) - 99.8 \text{ kJ} \\ &= 2.8 \text{ kJ}\end{aligned}$$

Calculate  $K$  from  $\Delta G_{\text{rxn}}^{\circ}$  by solving Equation 17.15 for  $K$  and substituting the values of  $\Delta G_{\text{rxn}}^{\circ}$  and temperature.

$$\begin{aligned}\Delta G_{\text{rxn}}^{\circ} &= -RT \ln K \\ \ln K &= \frac{-\Delta G_{\text{rxn}}^{\circ}}{RT} \\ &= \frac{-2.8 \times 10^3 \text{ J/mol}}{8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} (298 \text{ K})} \\ &= -1.13 \\ K &= e^{-1.13} \\ &= 0.32\end{aligned}$$

**FOR PRACTICE 17.10**

Calculate  $\Delta G_{\text{rxn}}^{\circ}$  at 298 K for the reaction:



**Conceptual Connection 17.7**  $K$  and  $\Delta G_{\text{rxn}}^{\circ}$ 

The reaction  $\text{A}(g) \rightleftharpoons \text{B}(g)$  has an equilibrium constant that is less than one. What can you conclude about  $\Delta G_{\text{rxn}}^{\circ}$  for the reaction?

- (a)  $\Delta G_{\text{rxn}}^{\circ} = 0$       (b)  $\Delta G_{\text{rxn}}^{\circ} < 0$       (c)  $\Delta G_{\text{rxn}}^{\circ} > 0$

**The Temperature Dependence of the Equilibrium Constant**

We now have an equation that relates the standard free energy change for a reaction ( $\Delta G_{\text{rxn}}^{\circ}$ ) to the equilibrium constant for a reaction ( $K$ ):

$$\Delta G_{\text{rxn}}^{\circ} = -RT \ln K \quad [17.16]$$

We also have an equation for how the free energy change for a reaction ( $\Delta G_{\text{rxn}}^{\circ}$ ) depends on temperature ( $T$ ):

$$\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ} \quad [17.17]$$

We can combine these two equations to obtain an equation for how the equilibrium constant depends on temperature. Combining Equations 17.16 and 17.17, we get:

$$-RT \ln K = \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ} \quad [17.18]$$

We can then divide both sides of Equation 17.18 by the quantity  $RT$ :

$$-\ln K = \frac{\Delta H_{rxn}^{\circ}}{RT} - \frac{T \Delta S_{rxn}^{\circ}}{RT}$$

Cancelling and rearranging, we get this important result:

$$\ln K = -\frac{\Delta H_{rxn}^{\circ}}{R} \left( \frac{1}{T} \right) + \frac{\Delta S_{rxn}^{\circ}}{R} \quad [17.19]$$

$$y = mx + b$$

Equation 17.19 is in the form of a straight line. A plot of the natural log of the equilibrium constant ( $\ln K$ ) versus the inverse of the temperature in kelvins ( $1/T$ ) yields a straight line with a slope of  $-\Delta H_{rxn}^{\circ}/R$  and a  $y$ -intercept of  $\Delta S_{rxn}^{\circ}/R$ . Such a plot is useful for obtaining thermodynamic data (namely,  $\Delta H_{rxn}^{\circ}$  and  $\Delta S_{rxn}^{\circ}$ ) from measurements of  $K$  as a function of temperature. However, since  $\Delta H_{rxn}^{\circ}$  and  $\Delta S_{rxn}^{\circ}$  can themselves be slightly temperature dependent, this analysis works only over a relatively limited temperature range. The equation can also be expressed in a two-point form:

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H_{rxn}^{\circ}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad [17.20]$$

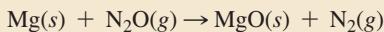
We can use this equation to find  $\Delta H_{rxn}^{\circ}$  from a measurement of the equilibrium constant at two different temperatures or to find the equilibrium constant at some other temperature if we know the equilibrium constant at a given temperature and  $\Delta H_{rxn}^{\circ}$ .

## CHAPTER IN REVIEW

### Self Assessment Quiz

- Q1.** Which reaction is most likely to have a positive  $\Delta S_{sys}^{\circ}$ ?
- $\text{SiO}_2(s) + 3 \text{C}(s) \rightarrow \text{SiC}(s) + 2 \text{CO}(g)$
  - $6 \text{CO}_2(g) + 6 \text{H}_2\text{O}(g) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6(s) + 6 \text{O}_2(g)$
  - $\text{CO}(g) + \text{Cl}_2(g) \rightarrow \text{COCl}_2(g)$
  - $3 \text{NO}_2(g) + \text{H}_2\text{O}(l) \rightarrow 2 \text{HNO}_3(l) + \text{NO}(g)$
- Q2.** The sign of  $\Delta H_{rxn}$  and  $\Delta S_{rxn}$  for several different reactions are given. In which case is the reaction spontaneous at all temperatures?
- $\Delta H_{rxn} < 0; \Delta S_{rxn} < 0$
  - $\Delta H_{rxn} > 0; \Delta S_{rxn} > 0$
  - $\Delta H_{rxn} < 0; \Delta S_{rxn} > 0$
  - $\Delta H_{rxn} > 0; \Delta S_{rxn} < 0$
- Q3.** Arrange the gases— $\text{F}_2$ ,  $\text{Ar}$ , and  $\text{CH}_3\text{F}$ —in order of increasing standard entropy ( $S^{\circ}$ ) at 298 K.
- $\text{F}_2 < \text{Ar} < \text{CH}_3\text{F}$
  - $\text{CH}_3\text{F} < \text{F}_2 < \text{Ar}$
  - $\text{CH}_3\text{F} < \text{Ar} < \text{F}_2$
  - $\text{Ar} < \text{F}_2 < \text{CH}_3\text{F}$
- Q4.** A reaction has a  $\Delta H_{rxn} = 54.2 \text{ kJ}$ . Calculate the change in entropy for the surroundings ( $\Delta S_{surv}$ ) for the reaction at 25.0 °C. (Assume constant pressure and temperature.)
- $2.17 \times 10^3 \text{ J/K}$
  - $-2.17 \times 10^3 \text{ J/K}$
  - $-182 \text{ J/K}$
  - $182 \text{ J/K}$
- Q5.** A reaction has  $\Delta H_{rxn}^{\circ} = -255 \text{ kJ}$  and  $\Delta S_{rxn}^{\circ} = 211 \text{ J/K}$ . Calculate  $\Delta G_{rxn}^{\circ}$  at 55 °C.
- $11.9 \times 10^3 \text{ kJ}$
  - $69.5 \times 10^3 \text{ kJ}$
  - $-267 \text{ kJ}$
  - $-324 \text{ kJ}$
- Q6.** Use standard entropies to calculate  $\Delta S_{rxn}^{\circ}$  for the balanced chemical equation:
- $$2 \text{PCl}_3(l) + \text{O}_2(g) \rightarrow 2 \text{POCl}_3(l)$$
- | Substance          | $S^{\circ} (\text{J/mol} \cdot \text{K})$ |
|--------------------|---|
| $\text{POCl}_3(l)$ | 222.5                                     |
| $\text{POCl}_3(g)$ | 325.5                                     |
| $\text{PCl}_3(l)$  | 217.1                                     |
| $\text{PCl}_3(g)$  | 311.8                                     |
| $\text{O}_2(g)$    | 205.2                                     |
- $-194.4 \text{ J/K}$
  - $-199.8 \text{ J/K}$
  - $10.8 \text{ J/K}$
  - $1084.4 \text{ J/K}$

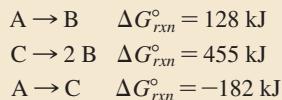
- Q7.** Use standard free energies of formation to calculate  $\Delta G_{rxn}^\circ$  for the balanced chemical equation:



| Substance               | $\Delta G_{rxn}^\circ(\text{kJ/mol})$ |
|-------------------------|---------------------------------------|
| $\text{N}_2\text{O}(g)$ | 103.7                                 |
| $\text{MgO}(s)$         | -569.3                                |

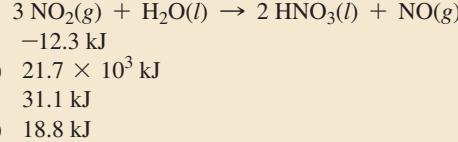
- a) 673.0 kJ  
 b) -673.0 kJ  
 c) -465.6 kJ  
 d) 465.6 kJ

- Q8.** Find  $\Delta G_{rxn}^\circ$  for the reaction  $2 \text{A} + \text{B} \rightarrow 2 \text{C}$  from the given data.



- a) -401 kJ  
 b) 509 kJ  
 c) 401 kJ  
 d) -509 kJ

- Q9.** The following reaction has a  $\Delta G_{rxn}^\circ = 9.4 \text{ kJ}$  at  $25^\circ\text{C}$ . Find  $\Delta G_{rxn}$  when  $P_{\text{NO}_2} = 0.115 \text{ atm}$  and  $P_{\text{NO}} = 9.7 \text{ atm}$  at  $25^\circ\text{C}$ .

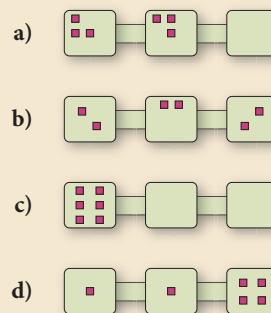


- Q10.** The reaction  $\text{A}(g) \rightleftharpoons \text{B}(g)$  has an equilibrium constant of  $K_p = 2.3 \times 10^{-5}$ . What can you conclude about the sign of  $\Delta G_{rxn}^\circ$  for the reaction?
- a)  $\Delta G_{rxn}^\circ = 0$   
 b)  $\Delta G_{rxn}^\circ$  is negative  
 c)  $\Delta G_{rxn}^\circ$  is positive  
 d) Nothing can be concluded about the sign of  $\Delta G_{rxn}^\circ$  for the reaction.

- Q11.** A reaction has an equilibrium constant of  $K_p = 0.018$  at  $25^\circ\text{C}$ . Find  $\Delta G_{rxn}$  for the reaction at this temperature.

- a) -835 J  
 b) -4.32 kJ  
 c) -9.95 kJ  
 d) 9.96 kJ

- Q12.** Which distribution of six particles into three interconnected boxes has the highest entropy?



- Q13.** Which process results in the increase in entropy of the universe?

- a) the cooling of a hot cup of coffee in room temperature air  
 b) the evaporation of water from a desk at room temperature  
 c) the melting of snow above  $0^\circ\text{C}$   
 d) all of the above

- Q14.** Under which set of conditions is  $\Delta G_{rxn}$  for the reaction  $\text{A}(g) \rightarrow \text{B}(g)$  most likely to be negative?

- a)  $P_A = 10.0 \text{ atm}; P_B = 10.0 \text{ atm}$   
 b)  $P_A = 10.0 \text{ atm}; P_B = 0.010 \text{ atm}$   
 c)  $P_A = 0.010 \text{ atm}; P_B = 10.0 \text{ atm}$   
 d)  $P_A = 0.010 \text{ atm}; P_B = 0.010 \text{ atm}$

- Q15.** Which statement is true for the freezing of liquid water below  $0^\circ\text{C}$ ?

- a)  $\Delta H$  is positive;  $\Delta S$  is negative;  $\Delta G$  is negative  
 b)  $\Delta H$  is negative;  $\Delta S$  is negative;  $\Delta G$  is negative  
 c)  $\Delta H$  is positive;  $\Delta S$  is positive;  $\Delta G$  is positive  
 d)  $\Delta H$  is positive;  $\Delta S$  is negative;  $\Delta G$  is positive

Answers: 1. (a) 2. (c) 3. (d) 4. (c) 5. (d) 6. (a) 7. (b) 8. (d) 9. (c) 10. (c) 11. (d) 12. (b) 13. (d) 14. (b) 15. (b)

## Key Terms

### Section 17.2

spontaneous process (814)

### Section 17.3

entropy ( $S$ ) (818)  
 second law of thermodynamics (820)

### Section 17.5

Gibbs free energy ( $G$ ) (828)

### Section 17.6

standard entropy change for a reaction ( $\Delta S_{rxn}^\circ$ ) (832)

standard molar entropies ( $S^\circ$ ) (832)  
 third law of thermodynamics (832)

### Section 17.7

standard free energy change ( $\Delta G_{rxn}^\circ$ ) (836)  
 free energy of formation ( $\Delta G_f^\circ$ ) (838)

reversible reaction (842)

irreversible reaction (842)

### Section 17.8

free energy change of a reaction under nonstandard conditions ( $\Delta G_{rxn}$ ) (843)

## Key Concepts

### Nature's Heat Tax: You Can't Win and You Can't Break Even (17.1)

- The first law of thermodynamics states that energy can be neither created nor destroyed.
- The second law implies that for every energy transaction, some energy is lost to the surroundings; this lost energy is nature's heat tax.

### Spontaneous and Nonspontaneous Processes (17.2)

- Both spontaneous and nonspontaneous processes can occur, but only spontaneous processes can take place without outside intervention.
- Thermodynamics is the study of the *spontaneity* of reactions, *not* to be confused with kinetics, the study of the *rate* of reactions.

### Entropy and the Second Law of Thermodynamics (17.3)

- The second law of thermodynamics states that for *any* spontaneous process, the entropy of the universe increases.
- Entropy ( $S$ ) is proportional to the number of energetically equivalent ways in which the components of a system can be arranged and is a measure of energy dispersal per unit temperature.

### Heat Transfer and Changes in the Entropy of the Surroundings (17.4)

- For a process to be spontaneous, the total entropy of the universe (system plus surroundings) must increase.
- The entropy of the surroundings increases when the change in *enthalpy* of the system ( $\Delta H_{\text{sys}}$ ) is negative (i.e., for exothermic reactions).
- The change in entropy of the surroundings for a given  $\Delta H_{\text{sys}}$  depends inversely on temperature—the greater the temperature, the lower the magnitude of  $\Delta S_{\text{surr}}$ .

### Gibbs Free Energy (17.5)

- Gibbs free energy,  $G$ , is a thermodynamic function that is proportional to the negative of the change in the entropy of the universe. A negative  $\Delta G$  represents a spontaneous reaction and a positive  $\Delta G$  represents a nonspontaneous reaction.
- We can calculate the value of  $\Delta G$  for a reaction from the values of  $\Delta H$  and  $\Delta S$  for the *system* using the equation  $\Delta G = \Delta H - T\Delta S$ .

### Entropy Changes in Chemical Reactions: Calculating $\Delta S_{\text{rxn}}^{\circ}$ (17.6)

- We calculate the standard change in entropy for a reaction similarly to the way we calculate the standard change in enthalpy for

a reaction: by subtracting the sum of the standard entropies of the reactants multiplied by their stoichiometric coefficients from the sum of the standard entropies of the products multiplied by their stoichiometric coefficients.

- Standard entropies are *absolute*: an entropy of zero is established by the third law of thermodynamics as the entropy of a perfect crystal at absolute zero.
- The entropy of a substance at a given temperature depends on factors that affect the number of energetically equivalent arrangements of the substance; these include the state, size, and molecular complexity of the substance.

### Free Energy Changes in Chemical Reactions: Calculating $\Delta G_{\text{rxn}}^{\circ}$ (17.7)

- There are three ways to calculate  $\Delta G_{\text{rxn}}^{\circ}$ : (1) from  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$ , (2) from free energies of formations (only at 25 °C), and (3) from the  $\Delta G^{\circ}$ 's of reactions that sum to the reaction of interest.
- The magnitude of a negative  $\Delta G_{\text{rxn}}^{\circ}$  represents the theoretical amount of energy available to do work, while a positive  $\Delta G_{\text{rxn}}^{\circ}$  represents the minimum amount of energy required to make a nonspontaneous process occur.

### Free Energy Changes for Nonstandard States: The Relationship between $\Delta G_{\text{rxn}}^{\circ}$ and $\Delta G_{\text{rxn}}$ (17.8)

- The value of  $\Delta G_{\text{rxn}}^{\circ}$  applies only to standard conditions, and most real conditions are not standard.
- Under nonstandard conditions, we can calculate  $\Delta G_{\text{rxn}}$  from the equation  $\Delta G_{\text{rxn}} = \Delta G_{\text{rxn}}^{\circ} + RT \ln Q$ .

### Free Energy and Equilibrium: Relating $\Delta G_{\text{rxn}}^{\circ}$ to the Equilibrium Constant ( $K$ ) (17.9)

- Under standard conditions, the free energy change for a reaction is directly proportional to the negative of the natural log of the equilibrium constant,  $K$ ; the more negative the free energy change (i.e., the more spontaneous the reaction), the larger the equilibrium constant.
- We can use the temperature dependence of  $\Delta G_{\text{rxn}}^{\circ}$ , as given by  $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ , to derive an expression for the temperature dependence of the equilibrium constant.

## Key Equations and Relationships

### The Definition of Entropy (17.3)

$$S = k \ln W \quad k = 1.38 \times 10^{-23} \text{ J/K}$$

### Change in Entropy (17.3)

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

### Change in the Entropy of the Universe (17.4)

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

### Change in the Entropy of the Surroundings (17.4)

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T} \text{ (constant } T, P\text{)}$$

### Change in Gibbs Free Energy (17.5)

$$\Delta G = \Delta H - T\Delta S$$

### The Relationship between Spontaneity and $\Delta H$ , $\Delta S$ , and $T$ (17.5)

| $\Delta H$ | $\Delta S$ | Low Temperature | High Temperature |
|------------|------------|-----------------|------------------|
| —          | +          | Spontaneous     | Spontaneous      |
| +          | —          | Nonspontaneous  | Nonspontaneous   |
| —          | —          | Spontaneous     | Nonspontaneous   |
| +          | +          | Nonspontaneous  | Spontaneous      |

### Standard Change in Entropy (17.6)

$$\Delta S_{\text{rxn}}^{\circ} = \sum n_p S^{\circ}(\text{products}) - \sum n_r S^{\circ}(\text{reactants})$$

### Methods for Calculating the Free Energy of Formation ( $\Delta G_{\text{rxn}}^{\circ}$ ) (17.7)

1.  $\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ}$
- 2.

$$\Delta G_{\text{rxn}}^{\circ} = \sum n_p \Delta G_f^{\circ}(\text{products}) - \sum n_r \Delta G_f^{\circ}(\text{reactants})$$

$$3. \Delta G_{\text{rxn}(\text{overall})}^{\circ} = \Delta G_{\text{rxn}(\text{step 1})}^{\circ} + \Delta G_{\text{rxn}(\text{step 2})}^{\circ} + \Delta G_{\text{rxn}(\text{step 3})}^{\circ} + \dots$$

### The Relationship between $\Delta G_{\text{rxn}}^{\circ}$ and $\Delta G_{\text{rxn}}$ (17.8)

$$\Delta G_{\text{rxn}} = \Delta G_{\text{rxn}}^{\circ} + RT \ln Q \quad R = 8.314 \text{ J/mol} \cdot \text{K}$$

### The Relationship between $\Delta G_{\text{rxn}}^{\circ}$ and $K$ (17.9)

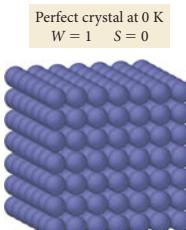
$$\Delta G_{\text{rxn}}^{\circ} = -RT \ln K$$

### The Temperature Dependence of the Equilibrium Constant (17.9)

$$\ln K = -\frac{\Delta H_{\text{rxn}}^{\circ}}{R} \left( \frac{1}{T} \right) + \frac{\Delta S_{\text{rxn}}^{\circ}}{R}$$

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H_{\text{rxn}}^{\circ}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

## Key Learning Outcomes

| Chapter Objectives   | Assessment  |
|--|---|
| Predicting the Sign of Entropy Change (17.3)   | Example 17.1 For Practice 17.1 Exercises 27–28, 31–34, 37–38  |
| Calculating Entropy Changes in the Surroundings (17.4)   | Example 17.2 For Practice 17.2 For More Practice 17.2 Exercises 33–36   |
| Computing Gibbs Free Energy Changes and Predicting Spontaneity from $\Delta H$ and $\Delta S$ (17.5)   | Example 17.3 For Practice 17.3 Exercises 39–44  |
| Computing Standard Entropy Changes ( $\Delta S_{\text{rxn}}^{\circ}$ ) (17.6)  | Example 17.4 For Practice 17.4 Exercises 51–52<br> |
| Calculating the Standard Change in Free Energy for a Reaction using $\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ}$ (17.7) | Examples 17.5, 17.6 For Practice 17.5, 17.6 Exercises 55–58, 61–62  |
| Calculating $\Delta G_{\text{rxn}}^{\circ}$ from Standard Free Energies of Formation (17.7)  | Example 17.7 For Practice 17.7 For More Practice 17.7 Exercises 59–60   |
| Determining $\Delta G_{\text{rxn}}^{\circ}$ for a Stepwise Reaction (17.7)   | Example 17.8 For Practice 17.8 Exercises 63–64  |
| Calculating $\Delta G_{\text{rxn}}$ under Nonstandard Conditions (17.8)  | Example 17.9 For Practice 17.9 Exercises 65–72  |
| Relating the Equilibrium Constant and $\Delta G_{\text{rxn}}^{\circ}$ (17.9)   | Example 17.10 For Practice 17.10 Exercises 73–76  |

## EXERCISES

### Review Questions

1. What is the first law of thermodynamics and how does it relate to energy use?
2. What is nature's "heat tax" and how does it relate to energy use?
3. What is a perpetual motion machine? Can such a machine exist given the laws of thermodynamics?
4. Is it more efficient to heat your home with a natural gas furnace or an electric furnace? Explain.
5. What is a spontaneous process? Provide an example.
6. Explain the difference between the spontaneity of a reaction (which depends on thermodynamics) and the speed at which the reaction occurs (which depends on kinetics). Can a catalyst make a nonspontaneous reaction spontaneous?
7. What is the precise definition of entropy? What is the significance of entropy being a state function?
8. Why does the entropy of a gas increase when it expands into a vacuum?
9. Explain the difference between macrostates (external arrangements of particles) and microstates (internal arrangements of particles).
10. Based on its fundamental definition, explain why entropy is a measure of energy dispersion.
11. Provide the definition of the second law of thermodynamics. How does the second law explain why heat travels from a substance at higher temperature to one at lower temperature?
12. What happens to the entropy of a sample of matter when it changes state from a solid to a liquid? From a liquid to a gas?
13. Explain why water spontaneously freezes to form ice below 0 °C even though the entropy of the water decreases during the state transition. Why is the freezing of water not spontaneous above 0 °C?
14. Why do exothermic processes tend to be spontaneous at low temperatures? Why does their tendency toward spontaneity decrease with increasing temperature?
15. What is the significance of the change in Gibbs free energy ( $\Delta G$ ) for a reaction?
16. Predict the spontaneity of a reaction (and the temperature dependence of the spontaneity) for each possible combination of signs for  $\Delta H$  and  $\Delta S$  (for the system).
  - $\Delta H$  negative,  $\Delta S$  positive
  - $\Delta H$  positive,  $\Delta S$  negative
  - $\Delta H$  negative,  $\Delta S$  negative
  - $\Delta H$  positive,  $\Delta S$  positive
17. State the third law of thermodynamics and explain its significance.
18. Why is the standard entropy of a substance in the gas state greater than its standard entropy in the liquid state?
19. How does the standard entropy of a substance depend on its molar mass? On its molecular complexity?
20. How can you calculate the standard entropy change for a reaction from tables of standard entropies?
21. What are three different methods to calculate  $\Delta G^\circ$  for a reaction? Which method would you choose to calculate  $\Delta G^\circ$  for a reaction at a temperature other than 25 °C?
22. Why is free energy "free"?
23. Explain the difference between  $\Delta G^\circ$  and  $\Delta G$ .
24. Why does water spilled on the floor evaporate even though  $\Delta G^\circ$  for the evaporation process is positive at room temperature?
25. How do you calculate the change in free energy for a reaction under nonstandard conditions?
26. How does the value of  $\Delta G^\circ$  for a reaction relate to the equilibrium constant for the reaction? What does a negative  $\Delta G^\circ$  for a reaction imply about  $K$  for the reaction? A positive  $\Delta G^\circ$ ?

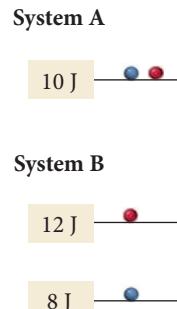
### Problems by Topic

#### Entropy, the Second Law of Thermodynamics, and the Direction of Spontaneous Change

27. Which of these processes is spontaneous?
  - the combustion of natural gas
  - the extraction of iron metal from iron ore
  - a hot drink cooling to room temperature
  - drawing heat energy from the ocean's surface to power a ship
28. Which of these processes are nonspontaneous? Are the nonspontaneous processes impossible?
  - a bike going up a hill
  - a meteor falling to Earth
  - obtaining hydrogen gas from liquid water
  - a ball rolling down a hill

29. Suppose that two systems, each composed of two particles represented by circles, have 20 J of total energy. Which system, A or B, has the greatest entropy? Why?
 

**System A**

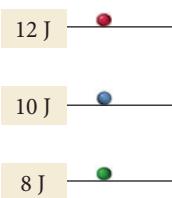


30. Suppose two systems, each composed of three particles represented by circles, have 30 J of total energy. How many energetically equivalent ways can you distribute the particles in each system? Which system has greater entropy?

System A



System B



31. Without doing any calculations, determine the sign of  $\Delta S_{\text{sys}}$  for each chemical reaction.

- $2 \text{KClO}_3(s) \longrightarrow 2 \text{KCl}(s) + 3 \text{O}_2(g)$
  - $\text{CH}_2=\text{CH}_2(g) + \text{H}_2(g) \longrightarrow \text{CH}_3\text{CH}_3(g)$
  - $\text{Na}(s) + 1/2 \text{Cl}_2(g) \longrightarrow \text{NaCl}(s)$
  - $\text{N}_2(g) + 3 \text{H}_2(g) \longrightarrow 2 \text{NH}_3(g)$
32. Without doing any calculations, determine the sign of  $\Delta S_{\text{sys}}$  for each chemical reaction.
- $\text{Mg}(s) + \text{Cl}_2(g) \longrightarrow \text{MgCl}_2(s)$
  - $2 \text{H}_2\text{S}(g) + 3 \text{O}_2(g) \longrightarrow 2 \text{H}_2\text{O}(g) + 2 \text{SO}_2(g)$
  - $2 \text{O}_3(g) \longrightarrow 3 \text{O}_2(g)$
  - $\text{HCl}(g) + \text{NH}_3(g) \longrightarrow \text{NH}_4\text{Cl}(s)$

33. Without doing any calculations, determine the sign of  $\Delta S_{\text{sys}}$  and  $\Delta S_{\text{surr}}$  for each chemical reaction. In addition, predict under what temperatures (all temperatures, low temperatures, or high temperatures), if any, the reaction is spontaneous.

- $\text{C}_3\text{H}_8(g) + 5 \text{O}_2(g) \longrightarrow 3 \text{CO}_2(g) + 4 \text{H}_2\text{O}(g)$   
 $\Delta H_{\text{rxn}}^\circ = -2044 \text{ kJ}$
- $\text{N}_2(g) + \text{O}_2(g) \longrightarrow 2 \text{NO}(g)$   
 $\Delta H_{\text{rxn}}^\circ = +182.6 \text{ kJ}$
- $2 \text{N}_2(g) + \text{O}_2(g) \longrightarrow 2 \text{N}_2\text{O}(g)$   
 $\Delta H_{\text{rxn}}^\circ = +163.2 \text{ kJ}$
- $4 \text{NH}_3(g) + 5 \text{O}_2(g) \longrightarrow 4 \text{NO}(g) + 6 \text{H}_2\text{O}(g)$   
 $\Delta H_{\text{rxn}}^\circ = -906 \text{ kJ}$

34. Without doing any calculations, determine the sign of  $\Delta S_{\text{sys}}$  and  $\Delta S_{\text{surr}}$  for each chemical reaction. In addition, predict under what temperatures (all temperatures, low temperatures, or high temperatures), if any, the reaction is spontaneous.

- $2 \text{CO}(g) + \text{O}_2(g) \longrightarrow 2 \text{CO}_2(g)$   
 $\Delta H_{\text{rxn}}^\circ = -566.0 \text{ kJ}$
- $2 \text{NO}_2(g) \longrightarrow 2 \text{NO}(g) + \text{O}_2(g)$   
 $\Delta H_{\text{rxn}}^\circ = +113.1 \text{ kJ}$
- $2 \text{H}_2(g) + \text{O}_2(g) \longrightarrow 2 \text{H}_2\text{O}(g)$   
 $\Delta H_{\text{rxn}}^\circ = -483.6 \text{ kJ}$
- $\text{CO}_2(g) \longrightarrow \text{C}(s) + \text{O}_2(g)$   
 $\Delta H_{\text{rxn}}^\circ = +393.5 \text{ kJ}$

35. Calculate  $\Delta S_{\text{surr}}$  at the indicated temperature for each reaction.
- $\Delta H_{\text{rxn}}^\circ = -385 \text{ kJ}; 298 \text{ K}$
  - $\Delta H_{\text{rxn}}^\circ = -385 \text{ kJ}; 77 \text{ K}$
  - $\Delta H_{\text{rxn}}^\circ = +114 \text{ kJ}; 298 \text{ K}$
  - $\Delta H_{\text{rxn}}^\circ = +114 \text{ kJ}; 77 \text{ K}$

36. A reaction has  $\Delta H_{\text{rxn}}^\circ = -112 \text{ kJ}$  and  $\Delta S_{\text{rxn}}^\circ = 354 \text{ J/K}$ . At what temperature is the change in entropy for the reaction equal to the change in entropy for the surroundings?

37. Given the values of  $\Delta H_{\text{rxn}}^\circ$ ,  $\Delta S_{\text{rxn}}^\circ$ , and  $T$ , determine  $\Delta S_{\text{univ}}$  and predict whether or not each reaction is spontaneous.
- $\Delta H_{\text{rxn}}^\circ = +115 \text{ kJ}; \Delta S_{\text{rxn}}^\circ = -263 \text{ J/K}; T = 298 \text{ K}$
  - $\Delta H_{\text{rxn}}^\circ = -115 \text{ kJ}; \Delta S_{\text{rxn}}^\circ = +263 \text{ J/K}; T = 298 \text{ K}$
  - $\Delta H_{\text{rxn}}^\circ = -115 \text{ kJ}; \Delta S_{\text{rxn}}^\circ = -263 \text{ J/K}; T = 298 \text{ K}$
  - $\Delta H_{\text{rxn}}^\circ = -115 \text{ kJ}; \Delta S_{\text{rxn}}^\circ = -263 \text{ J/K}; T = 615 \text{ K}$

38. Given the values of  $\Delta H_{\text{rxn}}$ ,  $\Delta S_{\text{rxn}}$ , and  $T$ , determine  $\Delta S_{\text{univ}}$  and predict whether or not each reaction is spontaneous.

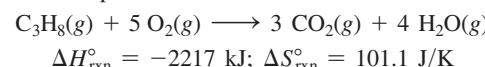
- $\Delta H_{\text{rxn}}^\circ = -95 \text{ kJ}; \Delta S_{\text{rxn}}^\circ = -157 \text{ J/K}; T = 298 \text{ K}$
- $\Delta H_{\text{rxn}}^\circ = -95 \text{ kJ}; \Delta S_{\text{rxn}}^\circ = -157 \text{ J/K}; T = 855 \text{ K}$
- $\Delta H_{\text{rxn}}^\circ = +95 \text{ kJ}; \Delta S_{\text{rxn}}^\circ = -157 \text{ J/K}; T = 298 \text{ K}$
- $\Delta H_{\text{rxn}}^\circ = -95 \text{ kJ}; \Delta S_{\text{rxn}}^\circ = +157 \text{ J/K}; T = 398 \text{ K}$

### Standard Entropy Changes and Gibbs Free Energy

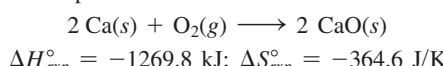
39. Calculate the change in Gibbs free energy for each of the sets of  $\Delta H_{\text{rxn}}$ ,  $\Delta S_{\text{rxn}}$ , and  $T$  given in Problem 37. Predict whether or not each reaction is spontaneous at the temperature indicated.

40. Calculate the change in Gibbs free energy for each of the sets of  $\Delta H_{\text{rxn}}$ ,  $\Delta S_{\text{rxn}}$ , and  $T$  given in Problem 38. Predict whether or not each reaction is spontaneous at the temperature indicated.

41. Calculate the free energy change for this reaction at 25 °C. Is the reaction spontaneous?



42. Calculate the free energy change for this reaction at 25 °C. Is the reaction spontaneous?



43. Fill in the blanks in the table. Both  $\Delta H$  and  $\Delta S$  refer to the system.

| $\Delta H$ | $\Delta S$ | $\Delta G$            | Low Temperature | High Temperature |
|------------|------------|-----------------------|-----------------|------------------|
| —          | +          | —                     | Spontaneous     | _____            |
| —          | —          | Temperature dependent | _____           | _____            |
| +          | +          | _____                 | _____           | Spontaneous      |
| _____      | —          | _____                 | Nonspontaneous  | Nonspontaneous   |

44. Predict the conditions (high temperature, low temperature, all temperatures, or no temperatures) under which each reaction is spontaneous.

- $\text{H}_2\text{O}(g) \longrightarrow \text{H}_2\text{O}(l)$
- $\text{CO}_2(s) \longrightarrow \text{CO}_2(g)$
- $\text{H}_2(g) \longrightarrow 2 \text{H}(g)$
- $2 \text{NO}_2(g) \longrightarrow 2 \text{NO}(g) + \text{O}_2(g)$  (endothermic)

45. How does the molar entropy of a substance change with increasing temperature?

46. What is the molar entropy of a pure crystal at 0 K? What is the significance of the answer to this question?

47. For each pair of substances, choose the one that you expect to have the higher standard molar entropy ( $S^\circ$ ) at 25 °C. Explain the reasons for your choices.

- |   |   |
|---|---|
| a. $\text{CO}(g); \text{CO}_2(g)$                         | b. $\text{CH}_3\text{OH}(l); \text{CH}_3\text{OH}(g)$ |
| c. $\text{Ar}(g); \text{CO}_2(g)$                         | d. $\text{CH}_4(g); \text{SiH}_4(g)$                  |
| e. $\text{NO}_2(g); \text{CH}_3\text{CH}_2\text{CH}_3(g)$ | f. $\text{NaBr}(s); \text{NaBr}(aq)$                  |

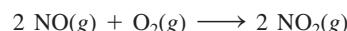
48. For each pair of substances, choose the one that you expect to have the higher standard molar entropy ( $S^\circ$ ) at 25 °C. Explain the reasons for your choices.

- |  |  |
|--|--|
| a. $\text{NaNO}_3(s); \text{NaNO}_3(aq)$ | b. $\text{CH}_4(g); \text{CH}_3\text{CH}_3(g)$                       |
| c. $\text{Br}_2(l); \text{Br}_2(g)$      | d. $\text{Br}_2(g); \text{F}_2(g)$                                   |
| e. $\text{PCl}_3(g); \text{PCl}_5(g)$    | f. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3(g); \text{SO}_2(g)$ |

- 49.** Rank each set of substances in order of increasing standard molar entropy ( $S^\circ$ ). Explain your reasoning.
- $\text{NH}_3(g)$ ;  $\text{Ne}(g)$ ;  $\text{SO}_2(g)$ ;  $\text{CH}_3\text{CH}_2\text{OH}(g)$ ;  $\text{He}(g)$
  - $\text{H}_2\text{O}(s)$ ;  $\text{H}_2\text{O}(l)$ ;  $\text{H}_2\text{O}(g)$
  - $\text{CH}_4(g)$ ;  $\text{CF}_4(g)$ ;  $\text{CCl}_4(g)$
- 50.** Rank each set of substances in order of increasing standard molar entropy ( $S^\circ$ ). Explain your reasoning.
- $\text{I}_2(g)$ ;  $\text{F}_2(g)$ ;  $\text{Br}_2(g)$ ;  $\text{Cl}_2(g)$
  - $\text{H}_2\text{O}(g)$ ;  $\text{H}_2\text{O}_2(g)$ ;  $\text{H}_2\text{S}(g)$
  - $\text{C(s, graphite)}$ ;  $\text{C(s, diamond)}$ ;  $\text{C(s, amorphous)}$
- 51.** Use data from Appendix IIB to calculate  $\Delta S_{\text{rxn}}^\circ$  for each of the reactions. In each case, try to rationalize the sign of  $\Delta S_{\text{rxn}}^\circ$ .
- $\text{C}_2\text{H}_4(g) + \text{H}_2(g) \longrightarrow \text{C}_2\text{H}_6(g)$
  - $\text{C(s)} + \text{H}_2\text{O}(g) \longrightarrow \text{CO(g)} + \text{H}_2(g)$
  - $\text{CO(g)} + \text{H}_2\text{O}(g) \longrightarrow \text{H}_2(g) + \text{CO}_2(g)$
  - $2 \text{H}_2\text{S}(g) + 3 \text{O}_2(g) \longrightarrow 2 \text{H}_2\text{O}(l) + 2 \text{SO}_2(g)$
- 52.** Use data from Appendix IIB to calculate  $\Delta S_{\text{rxn}}^\circ$  for each of the reactions. In each case, try to rationalize the sign of  $\Delta S_{\text{rxn}}^\circ$ .
- $3 \text{NO}_2(g) + \text{H}_2\text{O}(l) \longrightarrow 2 \text{HNO}_3(aq) + \text{NO}(g)$
  - $\text{Cr}_2\text{O}_3(s) + 3 \text{CO}(g) \longrightarrow 2 \text{Cr}(s) + 3 \text{CO}_2(g)$
  - $\text{SO}_2(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{SO}_3(g)$
  - $\text{N}_2\text{O}_4(g) + 4 \text{H}_2(g) \longrightarrow \text{N}_2(g) + 4 \text{H}_2\text{O}(g)$
- 53.** Find  $\Delta S^\circ$  for the formation of  $\text{CH}_2\text{Cl}_2(g)$  from its gaseous elements in their standard states. Rationalize the sign of  $\Delta S^\circ$ .
- 54.** Find  $\Delta S^\circ$  for the reaction between nitrogen gas and fluorine gas to form nitrogen trifluoride gas. Rationalize the sign of  $\Delta S^\circ$ .
- 55.** Methanol burns in oxygen to form carbon dioxide and water. Write a balanced equation for the combustion of liquid methanol and calculate  $\Delta H_{\text{rxn}}^\circ$ ,  $\Delta S_{\text{rxn}}^\circ$ , and  $\Delta G_{\text{rxn}}^\circ$  at 25 °C. Is the combustion of methanol spontaneous?
- 56.** In photosynthesis, plants form glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) and oxygen from carbon dioxide and water. Write a balanced equation for photosynthesis and calculate  $\Delta H_{\text{rxn}}^\circ$ ,  $\Delta S_{\text{rxn}}^\circ$ , and  $\Delta G_{\text{rxn}}^\circ$  at 25 °C. Is photosynthesis spontaneous?
- 57.** For each reaction, calculate  $\Delta H_{\text{rxn}}^\circ$ ,  $\Delta S_{\text{rxn}}^\circ$ , and  $\Delta G_{\text{rxn}}^\circ$  at 25 °C and state whether or not the reaction is spontaneous. If the reaction is not spontaneous, would a change in temperature make it spontaneous? If so, should the temperature be raised or lowered from 25 °C?
- $\text{N}_2\text{O}_4(g) \longrightarrow 2 \text{NO}_2(g)$
  - $\text{NH}_4\text{Cl}(s) \longrightarrow \text{HCl}(g) + \text{NH}_3(g)$
  - $3 \text{H}_2(g) + \text{Fe}_2\text{O}_3(s) \longrightarrow 2 \text{Fe}(s) + 3 \text{H}_2\text{O}(g)$
  - $\text{N}_2(g) + 3 \text{H}_2(g) \longrightarrow 2 \text{NH}_3(g)$
- 58.** For each reaction, calculate  $\Delta H_{\text{rxn}}^\circ$ ,  $\Delta S_{\text{rxn}}^\circ$ , and  $\Delta G_{\text{rxn}}^\circ$  at 25 °C and state whether or not the reaction is spontaneous. If the reaction is not spontaneous, would a change in temperature make it spontaneous? If so, should the temperature be raised or lowered from 25 °C?
- $2 \text{CH}_4(g) \longrightarrow \text{C}_2\text{H}_6(g) + \text{H}_2(g)$
  - $2 \text{NH}_3(g) \longrightarrow \text{N}_2\text{H}_4(g) + \text{H}_2(g)$
  - $\text{N}_2(g) + \text{O}_2(g) \longrightarrow 2 \text{NO}(g)$
  - $2 \text{KClO}_3(s) \longrightarrow 2 \text{KCl}(s) + 3 \text{O}_2(g)$
- 59.** Use standard free energies of formation to calculate  $\Delta G^\circ$  at 25 °C for each reaction in Problem 57. How do the values of  $\Delta G^\circ$  calculated this way compare to those calculated from  $\Delta H^\circ$  and  $\Delta S^\circ$ ? Which of the two methods could be used to determine how  $\Delta G^\circ$  changes with temperature?
- 60.** Use standard free energies of formation to calculate  $\Delta G^\circ$  at 25 °C for each reaction in Problem 58. How well do the values of  $\Delta G^\circ$  calculated this way compare to those calculated from

$\Delta H^\circ$  and  $\Delta S^\circ$ ? Which of the two methods could be used to determine how  $\Delta G^\circ$  changes with temperature?

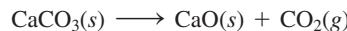
- 61.** Consider the reaction:



Estimate  $\Delta G^\circ$  for this reaction at each temperature and predict whether or not the reaction is spontaneous. (Assume that  $\Delta H^\circ$  and  $\Delta S^\circ$  do not change too much within the given temperature range.)

- a. 298 K      b. 715 K      c. 855 K

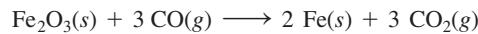
- 62.** Consider the reaction:



Estimate  $\Delta G^\circ$  for this reaction at each temperature and predict whether or not the reaction is spontaneous. (Assume that  $\Delta H^\circ$  and  $\Delta S^\circ$  do not change too much within the given temperature range.)

- a. 298 K      b. 1055 K      c. 1455 K

- 63.** Determine  $\Delta G^\circ$  for the reaction:



Use the following reactions with known  $\Delta G_{\text{rxn}}^\circ$  values:

$$\begin{aligned} 2 \text{Fe}(s) + \frac{3}{2}\text{O}_2(g) &\longrightarrow \text{Fe}_2\text{O}_3(s) & \Delta G_{\text{rxn}}^\circ = -742.2 \text{ kJ} \\ \text{CO}(g) + \frac{1}{2}\text{O}_2(g) &\longrightarrow \text{CO}_2(g) & \Delta G_{\text{rxn}}^\circ = -257.2 \text{ kJ} \end{aligned}$$

- 64.** Calculate  $\Delta G_{\text{rxn}}^\circ$  for the reaction:



Use the following reactions and given  $\Delta G_{\text{rxn}}^\circ$  values:

$$\begin{aligned} \text{Ca}(s) + \text{CO}_2(g) + \frac{1}{2}\text{O}_2(g) &\longrightarrow \text{CaCO}_3(s) & \Delta G_{\text{rxn}}^\circ = -734.4 \text{ kJ} \\ 2 \text{Ca}(s) + \text{O}_2(g) &\longrightarrow 2 \text{CaO}(s) & \Delta G_{\text{rxn}}^\circ = -1206.6 \text{ kJ} \end{aligned}$$

### Free Energy Changes, Nonstandard Conditions, and the Equilibrium Constant

- 65.** Consider the sublimation of iodine at 25.0 °C:



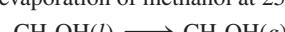
- a. Find  $\Delta G_{\text{rxn}}^\circ$  at 25.0 °C.  
b. Find  $\Delta G_{\text{rxn}}$  at 25.0 °C under the following nonstandard conditions:

i.  $P_{\text{I}_2} = 1.00 \text{ mmHg}$

ii.  $P_{\text{I}_2} = 0.100 \text{ mmHg}$

- c. Explain why iodine spontaneously sublimes in open air at 25.0 °C.

- 66.** Consider the evaporation of methanol at 25.0 °C:



- a. Find  $\Delta G_f^\circ$  at 25.0 °C.  
b. Find  $\Delta G_f$  at 25.0 °C under the following nonstandard conditions:

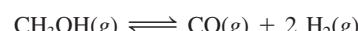
i.  $P_{\text{CH}_3\text{OH}} = 150.0 \text{ mmHg}$

ii.  $P_{\text{CH}_3\text{OH}} = 100.0 \text{ mmHg}$

iii.  $P_{\text{CH}_3\text{OH}} = 10.0 \text{ mmHg}$

- c. Explain why methanol spontaneously evaporates in open air at 25.0 °C.

- 67.** Consider the reaction:



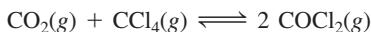
Calculate  $\Delta G$  for this reaction at 25 °C under the following conditions:

$P_{\text{CH}_3\text{OH}} = 0.855 \text{ atm}$

$P_{\text{CO}} = 0.125 \text{ atm}$

$P_{\text{H}_2} = 0.183 \text{ atm}$

68. Consider the reaction:



Calculate  $\Delta G$  for this reaction at 25 °C under the following conditions:

$$P_{\text{CO}_2} = 0.112 \text{ atm}$$

$$P_{\text{CCl}_4} = 0.174 \text{ atm}$$

$$P_{\text{COCl}_2} = 0.744 \text{ atm}$$

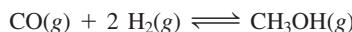
69. Use data from Appendix IIB to calculate the equilibrium constants at 25 °C for each reaction.

- a.  $2 \text{ CO}(g) + \text{O}_2(g) \rightleftharpoons 2 \text{ CO}_2(g)$
- b.  $2 \text{ H}_2\text{S}(g) \rightleftharpoons 2 \text{ H}_2(g) + \text{S}_2(g)$

70. Use data from Appendix IIB to calculate the equilibrium constants at 25 °C for each reaction.  $\Delta G_f^\circ$  for  $\text{BrCl}(g)$  is  $-1.0 \text{ kJ/mol}$ .

- a.  $2 \text{ NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)$
- b.  $\text{Br}_2(g) + \text{Cl}_2(g) \rightleftharpoons 2 \text{ BrCl}(g)$

71. Consider the reaction:



$$K_p = 2.26 \times 10^4 \text{ at } 25 \text{ }^\circ\text{C}$$

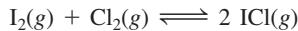
Calculate  $\Delta G_{\text{rxn}}$  for the reaction at 25 °C under each of the following conditions:

- a. standard conditions

- b. at equilibrium

- c.  $P_{\text{CH}_3\text{OH}} = 1.0 \text{ atm}$ ;  $P_{\text{CO}} = P_{\text{H}_2} = 0.010 \text{ atm}$

72. Consider the reaction:



$$K_p = 81.9 \text{ at } 25 \text{ }^\circ\text{C}$$

Calculate  $\Delta G_{\text{rxn}}$  for the reaction at 25 °C under each of the following conditions:

- a. standard conditions

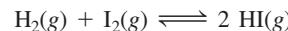
- b. at equilibrium

- c.  $P_{\text{ICl}} = 2.55 \text{ atm}$ ;  $P_{\text{I}_2} = 0.325 \text{ atm}$ ;  $P_{\text{Cl}_2} = 0.221 \text{ atm}$

73. Estimate the value of the equilibrium constant at 525 K for each reaction in Problem 69.

74. Estimate the value of the equilibrium constant at 655 K for each reaction in Problem 70. ( $\Delta H_f^\circ$  for  $\text{BrCl}$  is 14.6 kJ/mol.)

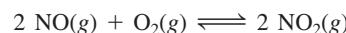
75. Consider the reaction:



The following data show the equilibrium constant for this reaction measured at several different temperatures. Use the data to find  $\Delta H_{\text{rxn}}^\circ$  and  $\Delta S_{\text{rxn}}^\circ$  for the reaction.

| Temperature | $K_p$                |
|-------------|----------------------|
| 150 K       | $1.4 \times 10^{-6}$ |
| 175 K       | $4.6 \times 10^{-4}$ |
| 200 K       | $3.6 \times 10^{-2}$ |
| 225 K       | 1.1                  |
| 250 K       | 15.5                 |

76. Consider the reaction:



The following data show the equilibrium constant for this reaction measured at several different temperatures. Use the data to find  $\Delta H_{\text{rxn}}^\circ$  and  $\Delta S_{\text{rxn}}^\circ$  for the reaction.

| Temperature | $K_p$                |
|-------------|----------------------|
| 170 K       | $3.8 \times 10^{-3}$ |
| 180 K       | 0.34                 |
| 190 K       | 18.4                 |
| 200 K       | 681                  |

77. The change in enthalpy ( $\Delta H_{\text{rxn}}^\circ$ ) for a reaction is  $-25.8 \text{ kJ/mol}$ . The equilibrium constant for the reaction is  $1.4 \times 10^3$  at 298 K. What is the equilibrium constant for the reaction at 655 K?

78. A reaction has an equilibrium constant of  $8.5 \times 10^3$  at 298 K. At 755 K, the equilibrium constant is 0.65. Find  $\Delta H_{\text{rxn}}^\circ$  for the reaction.

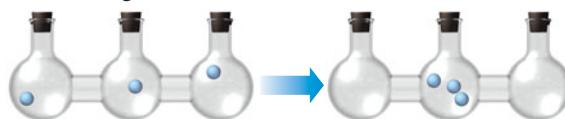
## Cumulative Problems

79. Determine the sign of  $\Delta S_{\text{sys}}$  for each process:

- a. water boiling

- b. water freezing

- c.

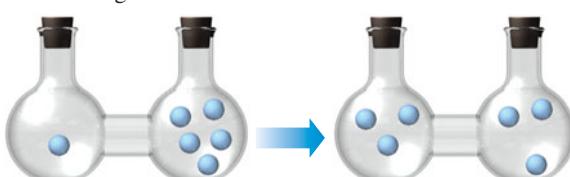


80. Determine the sign of  $\Delta S_{\text{sys}}$  for each process:

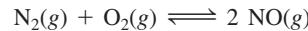
- a. dry ice subliming

- b. dew forming

- c.



81. Our atmosphere is composed primarily of nitrogen and oxygen, which coexist at 25 °C without reacting to any significant extent. However, the two gases can react to form nitrogen monoxide according to the reaction:



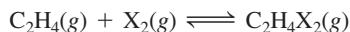
- a. Calculate  $\Delta G^\circ$  and  $K_p$  for this reaction at 298 K. Is the reaction spontaneous?

- b. Estimate  $\Delta G^\circ$  at 2000 K. Does the reaction become more spontaneous as temperature increases?

82. Nitrogen dioxide, a pollutant in the atmosphere, can combine with water to form nitric acid. One of the possible reactions is shown here. Calculate  $\Delta G^\circ$  and  $K_p$  for this reaction at 25 °C and comment on the spontaneity of the reaction.



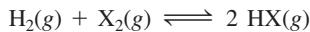
83. Ethene ( $C_2H_4$ ) can be halogenated by the reaction:



where  $X_2$  can be  $Cl_2$ ,  $Br_2$ , or  $I_2$ . Use the thermodynamic data given to calculate  $\Delta H^\circ$ ,  $\Delta S^\circ$ ,  $\Delta G^\circ$ , and  $K_p$  for the halogenation reaction by each of the three halogens at 25 °C. Which reaction is most spontaneous? Least spontaneous? What is the main factor responsible for the difference in the spontaneity of the three reactions? Does higher temperature make the reactions more spontaneous or less spontaneous?

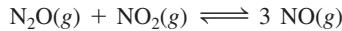
| Compound        | $\Delta H_f^\circ$ (kJ/mol) | $S^\circ$ (J/mol·K) |
|-----------------|-----------------------------|---------------------|
| $C_2H_4Cl_2(g)$ | -129.7                      | 308.0               |
| $C_2H_4Br_2(g)$ | +38.3                       | 330.6               |
| $C_2H_4I_2(g)$  | +66.5                       | 347.8               |

84.  $H_2$  reacts with the halogens ( $X_2$ ) according to the reaction:



where  $X_2$  can be  $Cl_2$ ,  $Br_2$ , or  $I_2$ . Use the thermodynamic data in Appendix IIB to calculate  $\Delta H^\circ$ ,  $\Delta S^\circ$ ,  $\Delta G^\circ$ , and  $K_p$  for the reaction between hydrogen and each of the three halogens. Which reaction is most spontaneous? Least spontaneous? What is the main factor responsible for the difference in the spontaneity of the three reactions? Does higher temperature make the reactions more spontaneous or less spontaneous?

85. Consider this reaction occurring at 298 K:



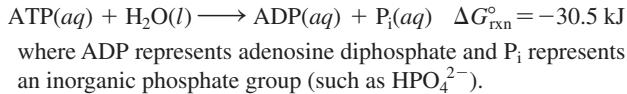
- Show that the reaction is not spontaneous under standard conditions by calculating  $\Delta G_{rxn}^\circ$ .
- If a reaction mixture contains only  $N_2O$  and  $NO_2$  at partial pressures of 1.0 atm each, the reaction will be spontaneous until some  $NO$  forms in the mixture. What maximum partial pressure of  $NO$  builds up before the reaction ceases to be spontaneous?
- Can the reaction be made more spontaneous by an increase or decrease in temperature? If so, what temperature is required to make the reaction spontaneous under standard conditions?

86. Consider this reaction occurring at 298 K:



- Show that the reaction is not spontaneous under standard conditions by calculating  $\Delta G_{rxn}^\circ$ .
- If  $BaCO_3$  is placed in an evacuated flask, what is the partial pressure of  $CO_2$  when the reaction reaches equilibrium?
- Can the reaction be made more spontaneous by an increase or decrease in temperature? If so, at what temperature is the partial pressure of carbon dioxide 1.0 atm?

87. Living organisms use energy from the metabolism of food to create an energy-rich molecule called adenosine triphosphate (ATP). The ATP then acts as an energy source for a variety of reactions that the living organism must carry out to survive. ATP provides energy through its hydrolysis, which can be symbolized as follows:



- Calculate the equilibrium constant,  $K$ , for the given reaction at 298 K.

b. The free energy obtained from the oxidation (reaction with oxygen) of glucose ( $C_6H_{12}O_6$ ) to form carbon dioxide and water can be used to re-form ATP by driving the given reaction in reverse. Calculate the standard free energy change for the oxidation of glucose and estimate the maximum number of moles of ATP that can be formed by the oxidation of one mole of glucose.

88. The standard free energy change for the hydrolysis of ATP was given in Problem 87. In a particular cell, the concentrations of ATP, ADP, and  $P_i$  are 0.0031 M, 0.0014 M, and 0.0048 M, respectively. Calculate the free energy change for the hydrolysis of ATP under these conditions. (Assume a temperature of 298 K.)

89. These reactions are important in catalytic converters in automobiles. Calculate  $\Delta G^\circ$  for each at 298 K. Predict the effect of increasing temperature on the magnitude of  $\Delta G^\circ$ .

- $2 CO(g) + 2 NO(g) \longrightarrow N_2(g) + 2 CO_2(g)$
- $5 H_2(g) + 2 NO(g) \longrightarrow 2 NH_3(g) + 2 H_2O(g)$
- $2 H_2(g) + 2 NO(g) \longrightarrow N_2(g) + 2 H_2O(g)$
- $2 NH_3(g) + 2 O_2(g) \longrightarrow N_2O(g) + 3 H_2O(g)$

90. Calculate  $\Delta G^\circ$  at 298 K for these reactions and predict the effect on  $\Delta G^\circ$  of lowering the temperature.

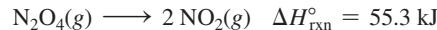
- $NH_3(g) + HBr(g) \longrightarrow NH_4Br(s)$
  - $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$
  - $CH_4(g) + 3 Cl_2(g) \longrightarrow CHCl_3(g) + 3 HCl(g)$
- ( $\Delta G_f^\circ$  for  $CHCl_3(g)$  is -70.4 kJ/mol.)

91. All the oxides of nitrogen have positive values of  $\Delta G_f^\circ$  at 298 K, but only one common oxide of nitrogen has a positive  $\Delta S_f^\circ$ . Identify that oxide of nitrogen without reference to thermodynamic data and explain.

92. The values of  $\Delta G_f^\circ$  for the hydrogen halides become less negative with increasing atomic number. The  $\Delta G_f^\circ$  of HI is slightly positive. On the other hand, the trend in  $\Delta S_f^\circ$  is to become more positive with increasing atomic number. Explain.

93. Consider the reaction  $X_2(g) \longrightarrow 2 X(g)$ . When a vessel initially containing 755 torr of  $X_2$  comes to equilibrium at 298 K, the equilibrium partial pressure of  $X$  is 103 torr. The same reaction is repeated with an initial partial pressure of 748 torr of  $X_2$  at 755 K; the equilibrium partial pressure of  $X$  is 532 torr. Find  $\Delta H^\circ$  for the reaction.

94. Dinitrogen tetroxide decomposes to nitrogen dioxide:



At 298 K, a reaction vessel initially contains 0.100 atm of  $N_2O_4$ . When equilibrium is reached, 58% of the  $N_2O_4$  has decomposed to  $NO_2$ . What percentage of  $N_2O_4$  decomposes at 388 K? Assume that the initial pressure of  $N_2O_4$  is the same (0.100 atm).

95. Indicate and explain the sign of  $\Delta S_{univ}$  for each process.

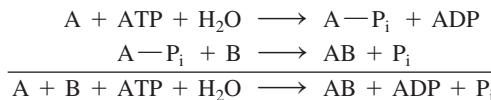
- $2 H_2(g) + O_2(g) \longrightarrow 2 H_2O(l)$  at 298 K
- the electrolysis of  $H_2O(l)$  to  $H_2(g)$  and  $O_2(g)$  at 298 K
- the growth of an oak tree from a little acorn

96. The Haber process is very important for agriculture because it converts  $N_2(g)$  from the atmosphere into bound nitrogen, which can be taken up and used by plants. The Haber process reaction is  $N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$ . The reaction is exothermic but is carried out at relatively high temperatures. Why?

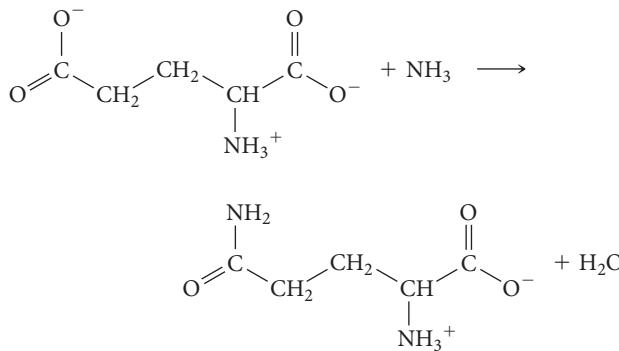
97. A metal salt with the formula  $\text{MCl}_2$  crystallizes from water to form a solid with the composition  $\text{MCl}_2 \cdot 6 \text{H}_2\text{O}$ . The equilibrium vapor pressure of water above this solid at 298 K is 18.3 mmHg. What is the value of  $\Delta G$  for the reaction  $\text{MCl}_2 \cdot 6 \text{H}_2\text{O}(s) \rightleftharpoons \text{MCl}_2(s) + 6 \text{H}_2\text{O}(g)$  when the pressure

## Challenge Problems

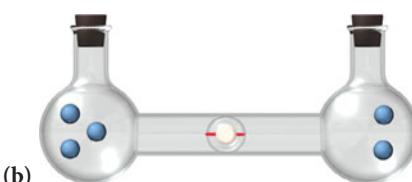
99. Review the box in this chapter entitled *Chemistry in Your Day: Making a Nonspontaneous Process Spontaneous*. The hydrolysis of ATP, shown in Problem 87, is often used to drive non-spontaneous processes—such as muscle contraction and protein synthesis—in living organisms. The nonspontaneous process to be driven must be coupled to the ATP hydrolysis reaction. For example, suppose the nonspontaneous process is  $A + B \longrightarrow AB$  ( $\Delta G^\circ$  positive). The coupling of a nonspontaneous reaction such as this one to the hydrolysis of ATP is often accomplished by the mechanism:



As long as  $\Delta G_{\text{rxn}}$  for the nonspontaneous reaction is less than 30.5 kJ, the reaction can be made spontaneous by coupling in this way to the hydrolysis of ATP. Suppose that ATP is to drive the reaction between glutamate and ammonia to form glutamine:

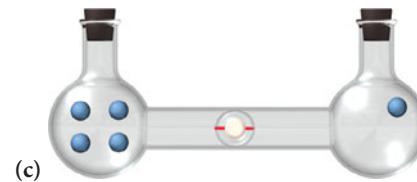


- a. Calculate  $K$  for the reaction between glutamate and ammonia. (The standard free energy change for the reaction is +14.2 kJ/mol. Assume a temperature of 298 K.)  
 b. Write a set of reactions such as those given showing how the glutamate and ammonia reaction can couple with the hydrolysis of ATP. What is  $\Delta G_{\text{rxn}}^\circ$  and  $K$  for the coupled reaction?  
 100. Calculate the entropy of each state and rank the states in order of increasing entropy.



of water vapor is 18.3 mmHg? When the pressure of water vapor is 760 mmHg?

98. The solubility of  $\text{AgCl}(s)$  in water at 25 °C is  $1.33 \times 10^{-5}$  mol/L and its  $\Delta H^\circ$  of solution is 65.7 kJ/mol. What is its solubility at 50.0 °C?



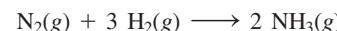
101. Suppose we redefine the standard state as  $P = 2$  atm. Find the new standard  $\Delta G_f^\circ$  values of each substance.

- a.  $\text{HCl}(g)$   
 b.  $\text{N}_2\text{O}(g)$   
 c.  $\text{H}(g)$

Explain the results in terms of the relative entropies of reactants and products of each reaction.

102. The  $\Delta G$  for the freezing of  $\text{H}_2\text{O}(l)$  at -10 °C is -210 J/mol, and the heat of fusion of ice at this temperature is 5610 J/mol. Find the entropy change of the universe when 1 mol of water freezes at -10 °C.

103. Consider the reaction that occurs during the Haber process:



The equilibrium constant is  $3.9 \times 10^5$  at 300 K and  $1.2 \times 10^{-1}$  at 500 K. Calculate  $\Delta H_{\text{rxn}}^\circ$  and  $\Delta S_{\text{rxn}}^\circ$  for this reaction.

104. The salt ammonium nitrate can follow three modes of decomposition: (a) to  $\text{HNO}_3(g)$  and  $\text{NH}_3(g)$ , (b) to  $\text{N}_2\text{O}(g)$  and  $\text{H}_2\text{O}(g)$ , and (c) to  $\text{N}_2(g)$ ,  $\text{O}_2(g)$ , and  $\text{H}_2\text{O}(g)$ . Calculate  $\Delta G_{\text{rxn}}^\circ$  for each mode of decomposition at 298 K. Explain in light of these results how it is still possible to use ammonium nitrate as a fertilizer and the precautions that should be taken when it is used.

105. Given the data, calculate  $\Delta S_{\text{vap}}$  for each of the first four liquids. ( $\Delta S_{\text{vap}} = \Delta H_{\text{vap}}/T$ , where  $T$  is in K)

| Compound                          | Name          | BP (°C) | $\Delta H_{\text{vap}}(\text{kJ/mol})$ at BP |
|-----------------------------------|---------------|---------|--|
| $\text{C}_4\text{H}_{10}\text{O}$ | Diethyl ether | 34.6    | 26.5   |
| $\text{C}_3\text{H}_6\text{O}$    | Acetone       | 56.1    | 29.1   |
| $\text{C}_6\text{H}_6\text{O}$    | Benzene       | 79.8    | 30.8   |
| $\text{CHCl}_3$                   | Chloroform    | 60.8    | 29.4   |
| $\text{C}_2\text{H}_5\text{OH}$   | Ethanol       | 77.8    | 38.6   |
| $\text{H}_2\text{O}$              | Water         | 100     | 40.7   |

All four values should be close to each other. Predict whether the last two liquids in the table have  $\Delta S_{\text{vap}}$  in this same range. If not, predict whether it is larger or smaller and explain. Verify your prediction.

## Conceptual Problems

**106.** Which is more efficient, a butane lighter or an electric lighter (such as can be found in most automobiles)? Explain.

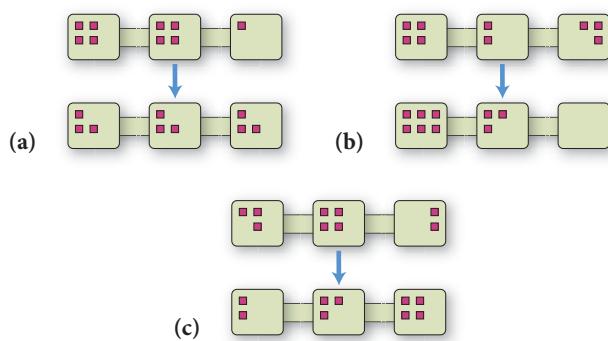
**107.** Which statement is true?

- A spontaneous reaction is always a fast reaction.
- A spontaneous reaction is always a slow reaction.
- The spontaneity of a reaction is not necessarily related to the speed of a reaction.

**108.** Which process is necessarily driven by an increase in the entropy of the surroundings?

- the condensation of water
- the sublimation of dry ice
- the freezing of water

**109.** Consider the changes in the distribution of nine particles into three interconnected boxes shown here. Which has the most negative  $\Delta S$ ?



**110.** Which statement is true?

- A reaction in which the entropy of the system increases can be spontaneous only if it is exothermic.
- A reaction in which the entropy of the system increases can be spontaneous only if it is endothermic.
- A reaction in which the entropy of the system decreases can be spontaneous only if it is exothermic.

**111.** Which process is spontaneous at 298 K?

- $\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(g, 1 \text{ atm})$
- $\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(g, 0.10 \text{ atm})$
- $\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(g, 0.010 \text{ atm})$

**112.** The free energy change of the reaction  $\text{A}(g) \longrightarrow \text{B}(g)$  is zero under certain conditions. The *standard* free energy change of the reaction is  $-42.5 \text{ kJ}$ . Which statement must be true about the reaction?

- The concentration of the product is greater than the concentration of the reactant.
- The reaction is at equilibrium.
- The concentration of the reactant is greater than the concentration of the product.

**113.** The reaction  $\text{A}(g) \rightleftharpoons \text{B}(g)$  has an equilibrium constant of 5.8 and under certain conditions has  $Q = 336$ . What can you conclude about the sign of  $\Delta G_{\text{rxn}}^{\circ}$  and  $\Delta G_{\text{rxn}}$  for this reaction under these conditions?

## Answers to Conceptual Connections

### Nature's Heat Tax and Diet

**17.1** A person subsisting on a vegetarian diet eats fruits and vegetables, metabolizing the energy-containing molecules of these foods directly. A person subsisting on a meat-based diet eats the meat of animals such as cows and metabolizes energy-containing molecules that were part of the animals. A cow synthesized its energy-containing molecules from compounds that it obtained by eating and digesting plants. Since breaking down and resynthesizing biological molecules requires energy—and since the cow also needs to extract some of the energy in its food to live—a meat-based diet necessitates additional energy transactions in the overall process of obtaining energy for life. Due to nature's heat tax, the meat-based diet is less efficient than the vegetarian diet.

### Entropy

**17.2** (a) The more spread out the particles are between the three boxes, the greater the entropy. Therefore, the entropy change is positive only in scheme (a).

### Entropy and Biological Systems

**17.3** Biological systems do not violate the second law of thermodynamics. The key to understanding this concept is realizing that entropy changes in the system can be negative as long as the entropy change of the universe is positive. Biological systems can decrease their own entropy, but only at the expense of creating more entropy in the surroundings (which they do primarily by emitting the heat they generate by their metabolic processes). Thus, for any biological process,  $\Delta S_{\text{univ}}$  is positive.

### $\Delta H$ , $\Delta S$ , and $\Delta G$

**17.4** (a) Sublimation is endothermic (it requires energy to overcome the intermolecular forces that hold solid carbon dioxide together), so  $\Delta H$  is positive. The number of moles of gas increases when the solid turns into a gas, so the entropy of the carbon dioxide increases and  $\Delta S$  is positive. Since  $\Delta G = \Delta H - T\Delta S$ ,  $\Delta G$  is positive at low temperature and negative at high temperature.

**Standard Entropies**

**17.5**  $\text{Kr} < \text{Cl}_2 < \text{SO}_3$ . Because Krypton is a monoatomic gas, it has the least entropy. Because  $\text{SO}_3$  is the most complex molecule, it has the most entropy. The molar masses of the three gases vary slightly, but not enough to overcome the differences in molecular complexity.

**Free Energy Changes and Le Châtelier's Principle**

**17.6** (a) A high concentration of reactants relative to products will lead to  $Q < 1$ , making the term  $RT \ln Q$  in Equation 17.14 negative.  $\Delta G_{\text{rxn}}$  is more negative than  $\Delta G_{\text{rxn}}^\circ$  and the reaction is more spontaneous.

**K and  $\Delta G_{\text{rxn}}^\circ$** 

**17.7** (c) Since the equilibrium constant is less than 1, the reaction proceeds toward reactants under standard conditions (when  $Q = 1$ ). Therefore,  $\Delta G_{\text{rxn}}^\circ$  is positive.

# 18

# Electrochemistry

*One day sir, you may tax it.*

—Michael Faraday (1791–1867)

*[In response to Mr. Gladstone, the British chancellor of the exchequer, when asked about the practical worth of electricity.]*

|                              |   |     |
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**T**HIS CHAPTER'S OPENING QUOTE FROM MICHAEL FARADAY illustrates an important aspect of basic research (research for the sake of understanding how nature works). The chancellor of the exchequer (the British cabinet minister responsible for all financial matters) wanted to know how Michael Faraday's apparently esoteric investigations of electricity would ever be useful to the empire. Faraday responded in a way that the chancellor would understand—he pointed out the eventual financial payoff. Today, of course, electricity is a fundamental form of energy, powering our entire economy. Although basic research does not always lead to useful applications, much of the technology our society relies on has grown out of basic research. The history of modern science shows that you must first understand nature (the goal of basic research) before you can harness its power. In this chapter, we discuss oxidation–reduction reactions (first introduced in Chapter 4) and how we can exploit them to generate electricity. The applications range from the batteries that power flashlights to the fuel cells that may one day power our homes and automobiles.



## 18.1 Pulling the Plug on the Power Grid

The power grid distributes centrally generated electricity throughout the country to homes and businesses. When you turn on a light or electrical appliance, electricity flows from the grid, through the wires in your home, to the light or appliance. The electrical energy is converted into light within the lightbulb or into work within the appliance. The average U.S. household consumes about 1000 kilowatt-hours (kWh) of electricity per month. The local electrical utility, of course, monitors your electricity use and bills you for it.

In the future, you may have the option of disconnecting from the power grid. Several innovative companies are developing small, fuel-cell power plants—each no bigger than a refrigerator—to sit next to homes and quietly generate enough electricity to meet each household's power needs. The heat produced by a fuel cell's operation can be recaptured and used to heat water or the space within the home, eliminating the need for a hot-water

*The smartphone shown here is powered by a hydrogen–oxygen fuel cell, a device that generates electricity from the reaction between hydrogen and oxygen to form water.*

**The kilowatt-hour is a unit of energy first introduced in Section 6.2.**