

**One molecule of nonsaline substance (held in the solvent) dissolved in 100 molecules of any volatile liquid decreases the vapor pressure of this liquid by a nearly constant fraction, nearly 0.0105.**

—FRANÇOIS-MARIE RAOULT (1830–1901)

CHAPTER

# 14

## Solutions

We learned in Chapter 1 that most of the matter we encounter is in the form of mixtures. In this chapter, we focus on homogeneous mixtures, known as solutions.

Solutions are mixtures in which atoms and molecules intermingle on the molecular and atomic scale. Common examples of solutions include ocean water, gasoline, and air. Why do solutions form? How are their properties different from the properties of the pure substances that compose them? As you read this chapter, keep in mind the large number of solutions that surround you at every moment, including those that exist within your own body.



Drinking seawater causes dehydration because seawater draws water out of body tissues.

- 14.1** Thirsty Solutions: Why You Shouldn't Drink Seawater 579
- 14.2** Types of Solutions and Solubility 581
- 14.3** Energetics of Solution Formation 586
- 14.4** Solution Equilibrium and Factors Affecting Solubility 589
- 14.5** Expressing Solution Concentration 594

- 14.6** Colligative Properties: Vapor Pressure Lowering, Freezing Point Depression, Boiling Point Elevation, and Osmotic Pressure 601
- 14.7** Colligative Properties of Strong Electrolyte Solutions 613
- 14.8** Colloids 616

#### LEARNING OUTCOMES 621

### 14.1

## Thirsty Solutions: Why You Shouldn't Drink Seawater

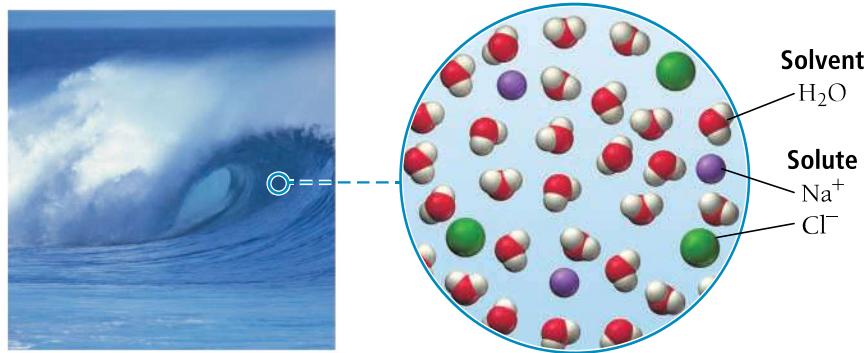
In the popular novel *Life of Pi* by Yann Martel, the main character (whose name is Pi) is stranded on a lifeboat with a Bengal tiger in the middle of the Pacific Ocean for 227 days. Pi survives in part by rigging a solar still to distill seawater for drinking. However, in the first three days of his predicament (before he rigs the still), he becomes severely dehydrated from lack of water. He is surrounded by seawater, but drinking *that* water would only have made his condition worse. Why? Seawater actually draws water

In some cases, the concepts of solute and solvent are not useful. For example, a homogeneous mixture of water and ethanol can contain equal amounts of both components, and neither component can then be identified as the solvent.

*out of the body* as it passes through the stomach and intestines, resulting in diarrhea and further dehydration. We can think of seawater as a *thirsty solution*—one that draws more water to itself. Consequently, seawater should never be consumed as drinking water.

Seawater is a **solution**, a homogeneous mixture of two or more substances or components, as shown in Figure 14.1▼. The majority component in a solution is typically called the **solvent**, and the minority component is called the **solute**. In seawater, water is the solvent, and sodium chloride is the primary solute. Solutions form in part because of the intermolecular forces we discussed in Chapter 12. In most solutions, the particles of the solute interact with the particles of the solvent through intermolecular forces.

► **FIGURE 14.1 A Typical Solution** In seawater, sodium chloride is the primary solute. Water is the solvent.

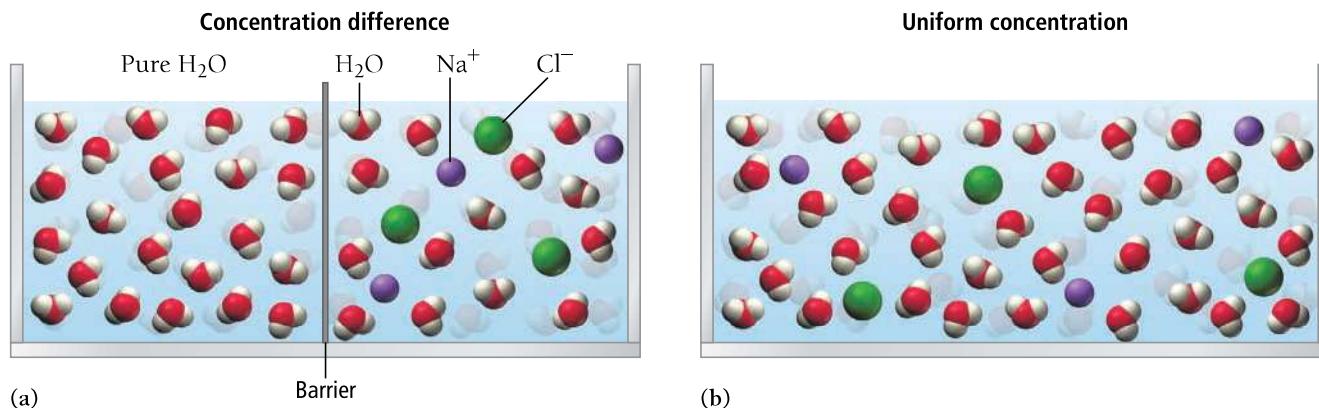


The reason that seawater draws water to itself is related to nature's tendency toward spontaneous mixing, which we discuss in more detail later in this chapter and in Chapter 19. For now, we simply observe that unless the mixing process is highly unfavorable energetically, substances tend to combine into uniform mixtures and do not separate into pure substances. For example, suppose pure water and a sodium chloride solution are in separate compartments with a removable barrier between them, as shown in Figure 14.2(a)▼. If we remove the barrier, the two liquids spontaneously mix, eventually forming a more dilute sodium chloride solution of uniform concentration, as shown in Figure 14.2(b)▼. The tendency toward mixing results in a uniform concentration of the final solution.

Seawater is a *thirsty solution* because of this tendency toward mixing. As seawater moves through the intestine, it flows past cells that line the digestive tract. These cells consist of largely fluid interiors surrounded by membranes. Cellular fluids themselves contain dissolved ions, including sodium and chloride, but the fluids in the cells are more dilute than seawater. Nature's tendency toward mixing (which tends to produce

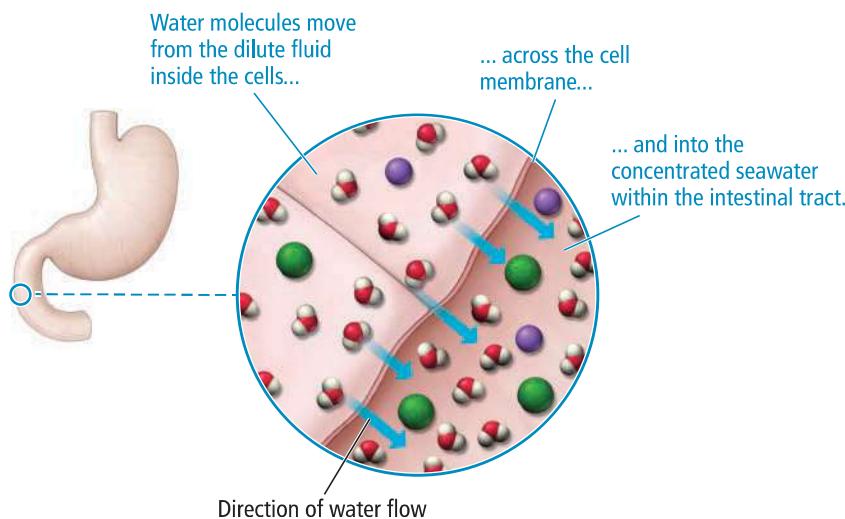
## Spontaneous Mixing

When the barrier that separates pure water and a sodium chloride solution is removed, spontaneous mixing occurs, producing a solution of uniform concentration.



▲ **FIGURE 14.2 The Tendency to Mix** (a) A barrier separates pure water and a sodium chloride solution. (b) When the barrier is removed, the two liquids spontaneously mix, producing a single solution of uniform concentration.

solutions of uniform concentration), together with the selective permeability of the cell membranes (which allows water to flow in and out, but restricts the flow of dissolved solids), cause a *flow of solvent out of the body's cells into the seawater*. In this way, the two solutions become more similar in concentration (as though they had mixed). The solution in the intestine becomes somewhat more dilute than it was, and the solution in the cells becomes somewhat more concentrated. The accumulation of extra fluid in the intestines causes diarrhea, and the decreased fluid in the cells causes dehydration. If Pi had drunk the seawater instead of constructing the solar still, neither he nor his companion, the large Bengal tiger, would have survived their ordeal.

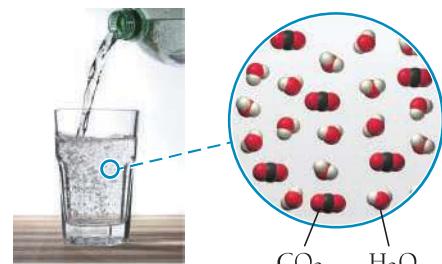


► Seawater is a more concentrated solution than the fluids in body cells. As a result, when seawater flows through the digestive tract, it draws water out of the surrounding tissues.

## 14.2

## Types of Solutions and Solubility

A solution may be composed of a solid and a liquid (such as the salt and water that are the primary components of seawater), but it may also be composed of a gas and a liquid, two different liquids, or other combinations (see Table 14.1). In **aqueous solutions**, water is the solvent, and a solid, liquid, or gas is the solute. For example, sugar water and salt water are both aqueous solutions. Similarly, ethyl alcohol—the alcohol in alcoholic beverages—readily mixes with water to form a solution, and carbon dioxide dissolves in water to form the aqueous solution that we know as club soda.



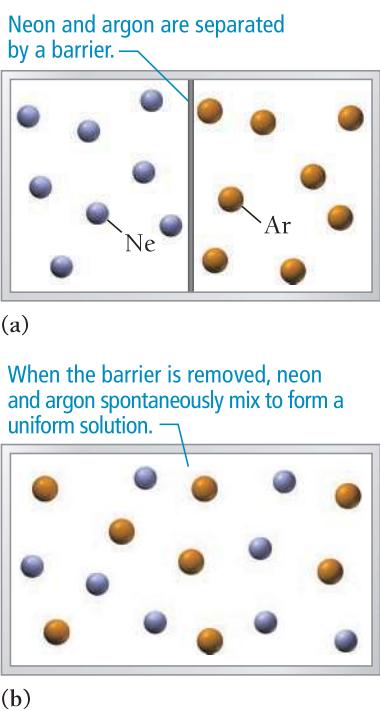
▲ Club soda is a solution of carbon dioxide and water.

**TABLE 14.1 ■ Common Types of Solutions**

Solution Phase	Solute Phase	Solvent Phase	Example
Gaseous solution	Gas	Gas	Air (mainly oxygen and nitrogen)
Liquid solution	Gas	Liquid	Club soda (CO <sub>2</sub> and water)
	Liquid	Liquid	Vodka (ethanol and water)
	Solid	Liquid	Seawater (salt and water)
Solid solution	Solid	Solid	Brass (copper and zinc) and other alloys

You probably know from experience that a particular solvent, such as water, does not dissolve all possible solutes. For example, you cannot clean your greasy hands with water alone because the water does not dissolve the grease. However, another solvent, such as paint thinner, can easily dissolve the grease. The grease is *insoluble* in water but *soluble* in the paint thinner. The **solubility** of a substance is the amount of the substance that dissolves in a given amount of solvent. The solubility of sodium chloride in water at 25 °C is 36 g NaCl per 100 g water, whereas the solubility of grease in water is nearly zero. The solubility of one substance in another depends both on the tendency toward mixing that we discussed in Section 14.1 and on the types of intermolecular forces that we discussed in Chapter 12.

The general solubilities of a number of ionic compounds are described by the solubility rules in Section 5.4.



**▲ FIGURE 14.3** Spontaneous Mixing of Two Ideal Gases  
**(a)** A barrier separates neon and argon. **(b)** When the barrier is removed, the two gases spontaneously mix to form a uniform solution.

The potential energy of the gas particles does not change upon mixing because the gas is ideal; the particles do not exert any attractive or repulsive forces on each other, so mixing does not change their potential energy.

#### ANSWER NOW!



#### 14.1 Cc Conceptual Connection

#### MIXING OF IDEAL GASES

Which statement is true?

- (a)** Ideal gases mix because mixing decreases their potential energy.
- (b)** Ideal gases mix because mixing increases their potential energy.
- (c)** Ideal gases mix because mixing decreases their entropy.
- (d)** Ideal gases mix because mixing increases their entropy.

#### The Effect of Intermolecular Forces

We have just seen that, in the absence of intermolecular forces, two substances spontaneously mix to form a homogeneous solution. We know from Chapter 12, however, that solids and liquids exhibit a number of different types of intermolecular forces, including dispersion forces, dipole-dipole forces, hydrogen bonding, and ion-dipole forces (Figure 14.4►). These forces may promote the formation of a solution or prevent it, depending on the nature of the forces in the particular combination of solute and solvent.

Intermolecular forces exist between (a) the solvent and solute particles, (b) the solvent particles themselves, and (c) the solute particles themselves, as shown in Figure 14.5►.

#### Nature's Tendency toward Mixing: Entropy

So far in this book, we have seen that many physical systems tend toward lower *potential energy*. For example, two particles with opposite charges (such as a proton and an electron or a cation and an anion) move toward each other because their potential energy decreases as their separation decreases according to Coulomb's law. The formation of a solution, however, *does not necessarily* lower the potential energy of its constituent particles. The clearest example of this phenomenon is the formation of a homogeneous mixture (a *solution*) of two ideal gases. Suppose that we enclose neon and argon in a container with a removable barrier between them, as shown in Figure 14.3(a)◀. As soon as we remove the barrier, the neon and argon mix together to form a solution, as shown in Figure 14.3(b)◀. *Why?*

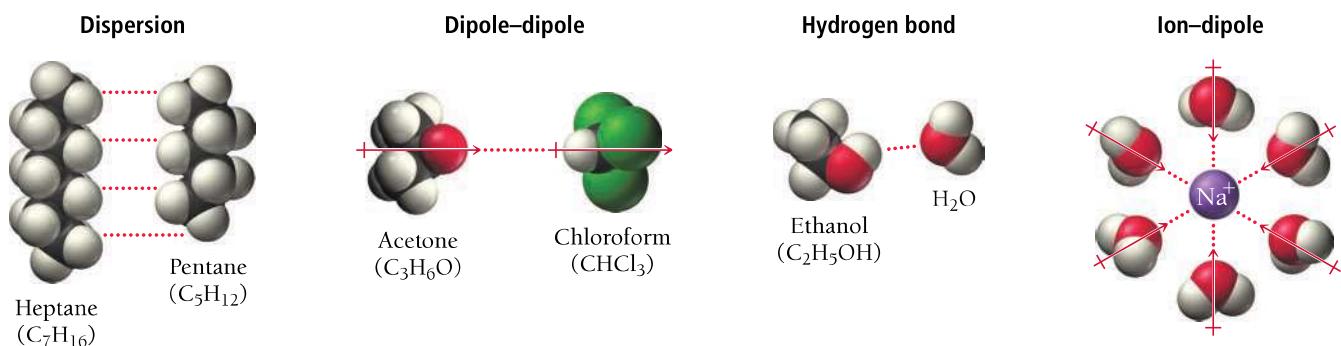
At low pressures and moderate temperatures, both neon and argon behave as ideal gases—they do not interact with each other in any way (that is, there are no significant intermolecular forces between their constituent particles). When the barrier is removed, the two gases mix, but their potential energy remains unchanged. In other words, we *cannot think of the mixing of two ideal gases as lowering their potential energy*. Rather, the tendency to mix is related to a concept called *entropy*.

**Entropy** is a measure of *energy randomization* or *energy dispersal* in a system. Recall that a gas at any temperature above 0 K has kinetic energy due to the motion of its atoms. When neon and argon are confined to their individual compartments, their kinetic energies are also confined to those compartments. When the barrier between the compartments is removed, each gas—along with its kinetic energy—becomes *spread out* or *dispersed* over a larger volume. Thus, the mixture of the two gases has greater energy dispersal, or greater *entropy*, than the separated components.

*The pervasive tendency for energy to spread out, or disperse, whenever it is not restrained from doing so* is the reason that two ideal gases mix. Another common example of the tendency toward energy dispersal is the transfer of thermal energy from hot to cold. When we heat one end of an iron rod, the thermal energy added to the end of the rod spontaneously spreads along the rod's entire length. In contrast to the mixing of two ideal gases—where the kinetic energy of the particles becomes dispersed over a larger volume because the particles themselves become dispersed—the thermal energy in the rod, initially concentrated in relatively fewer particles, becomes dispersed by being distributed over a larger number of particles. The tendency for energy to disperse is why thermal energy flows from the hot end of the rod to the cold one, and not the other way around. Imagine a metal rod that became spontaneously hotter on one end and ice cold on the other—this does not happen because energy does not spontaneously concentrate itself. In Chapter 19, we will see that the dispersal of energy is actually the fundamental criterion that ultimately determines the spontaneity of any process.

## Intermolecular Forces

These forces may contribute to or oppose the formation of a solution.



▲ FIGURE 14.4 Intermolecular Forces Involved in Solutions

*Solvent–solute interactions:*

The interactions between a solvent particle and a solute particle.

*Solvent–solvent interactions:*

The interactions between a solvent particle and another solvent particle.

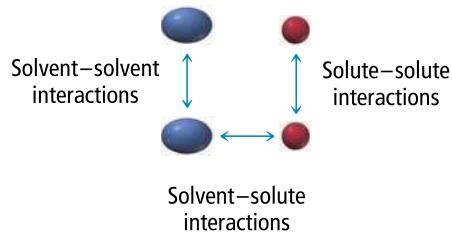
*Solute–solute interactions:*

The interactions between a solute particle and another solute particle.

As Table 14.2 indicates, a solution always forms if the solvent–solute interactions are comparable to, or stronger than, the solvent–solvent interactions and the solute–solute interactions. For example, consider mixing the hydrocarbons pentane ( $C_5H_{12}$ ) and heptane ( $C_7H_{16}$ ). The intermolecular forces present *within* pentane (that is, the pentane–pentane attractions) and within heptane (the heptane–heptane attractions) are dispersion forces. Similarly, the intermolecular forces present *between* heptane and pentane (the pentane–heptane attractions) are also dispersion forces. All three interactions are of similar magnitude, so the two substances are soluble in each other in all proportions—they are said to be **miscible**. The formation of the solution is driven by the tendency toward mixing, or toward greater entropy, that we just discussed.

## Solution Interactions

The relative strengths of these three interactions determine whether a solution forms:



▲ FIGURE 14.5 Forces in a Solution

TABLE 14.2 ■ Relative Interactions and Solution Formation

Solvent–solute interactions	>	Solvent–solvent and solute–solute interactions	Solution forms
Solvent–solute interactions	=	Solvent–solvent and solute–solute interactions	Solution forms
Solvent–solute interactions	<	Solvent–solvent and solute–solute interactions	Solution may or may not form, depending on relative disparity

A solution sometimes forms even when solvent–solute interactions are weak. For example, if solvent molecules and solute molecules each interact more strongly with molecules of their own kind than with molecules of the other kind, then a solution may still form, depending on the relative disparities between the interactions. If the disparity is small, the tendency to mix results in the formation of a solution even though the process is energetically uphill. If the disparity is large, however, a solution does not form. For example, consider mixing hexane and water. The water molecules have strong hydrogen-bonding attractions to each other but cannot form hydrogen bonds with hexane. The energy required to pull water molecules away from one another is too great, and too little energy is returned when

**TABLE 14.3 ■ Common Laboratory Solvents**

Common Polar Solvents	Common Nonpolar Solvents
Water ( $\text{H}_2\text{O}$ )	Hexane ( $\text{C}_6\text{H}_{14}$ )
Acetone ( $\text{CH}_3\text{COCH}_3$ )	Diethyl ether ( $(\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3)^*$ )
Methanol ( $\text{CH}_3\text{OH}$ )	Toluene ( $\text{C}_7\text{H}_8$ )
Ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ )	Carbon tetrachloride ( $\text{CCl}_4$ )

\*Diethyl ether has a small dipole moment and can be considered intermediate between polar and nonpolar.

## ANSWER NOW!


**14.2**  
**Cc**  
 Conceptual Connection

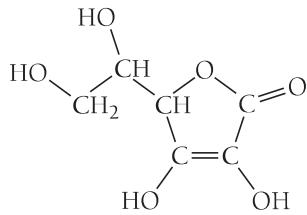
**SOLUTION FORMATION** If the solvent–solute interactions in a mixture are comparable in strength to the solvent–solvent interactions and the solute–solute interactions, what can you conclude about solution formation in this mixture?

- (a) A homogeneous solution forms.
- (b) A homogeneous solution does not form.
- (c) The formation of a homogeneous solution is uncertain.

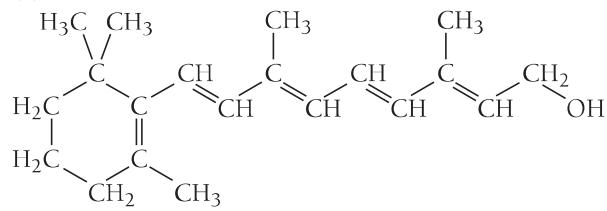
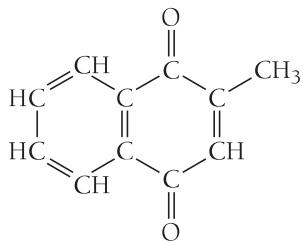
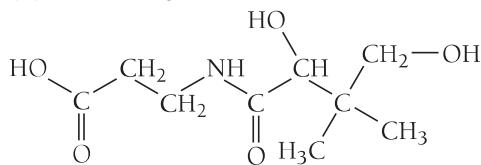
**EXAMPLE 14.1** Solubility

Vitamins are often categorized as either fat-soluble or water-soluble. Water-soluble vitamins, on one hand, dissolve in body fluids and are easily eliminated in the urine, so there is little danger of overconsumption. Fat-soluble vitamins, on the other hand, can accumulate in the body's fatty deposits. Overconsumption of a fat-soluble vitamin can be dangerous to your health. Examine the structure of the vitamins shown here and classify each as either fat-soluble or water-soluble.

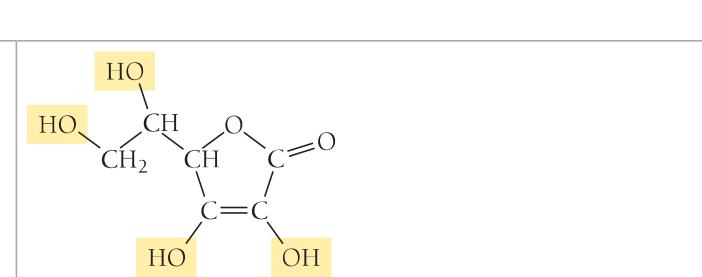
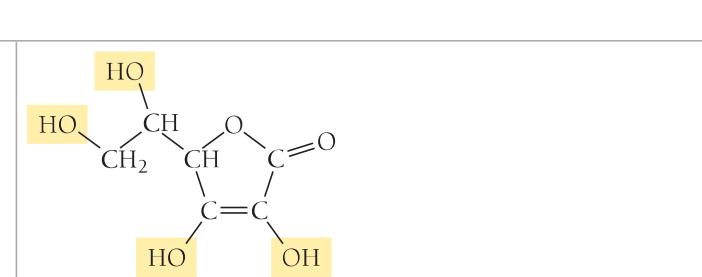
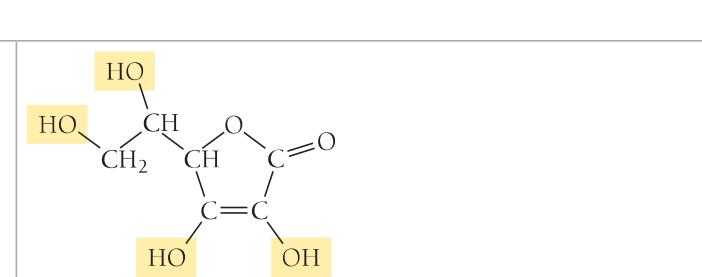
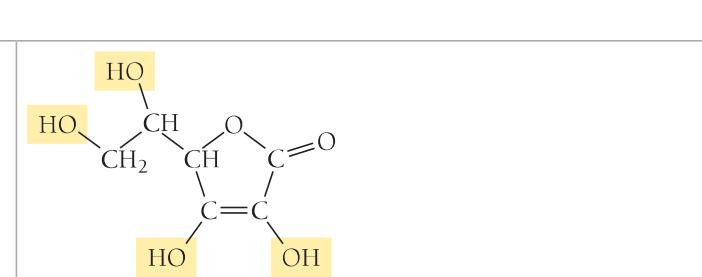
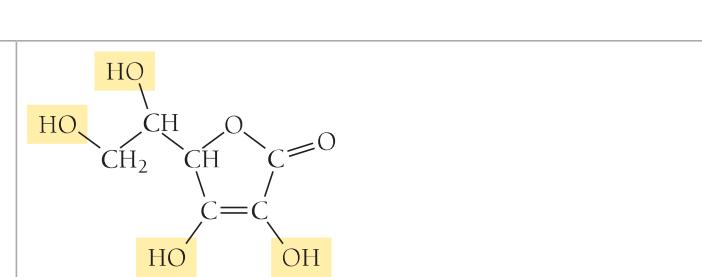
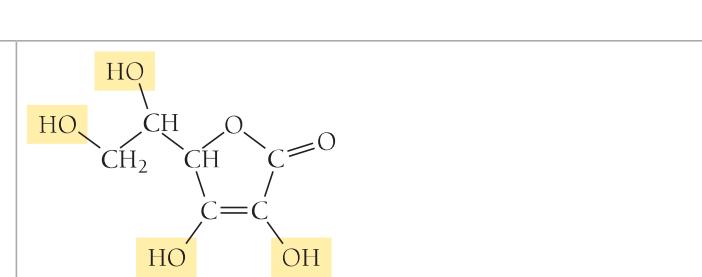
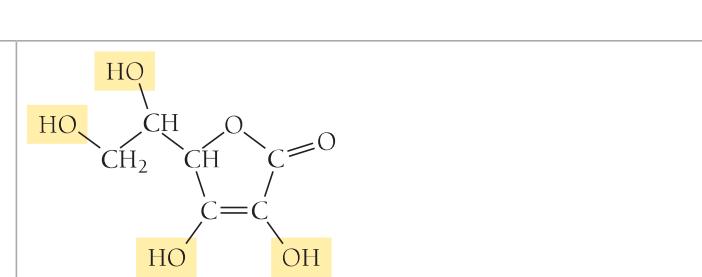
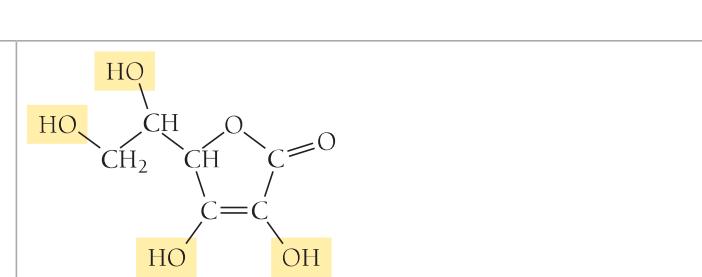
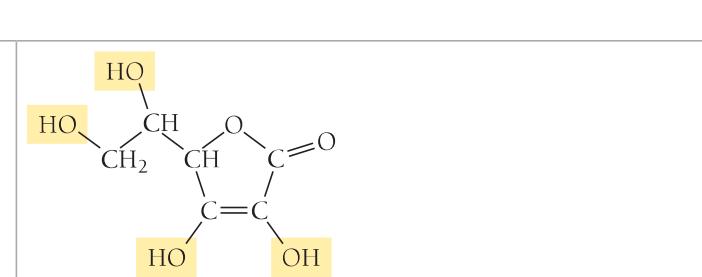
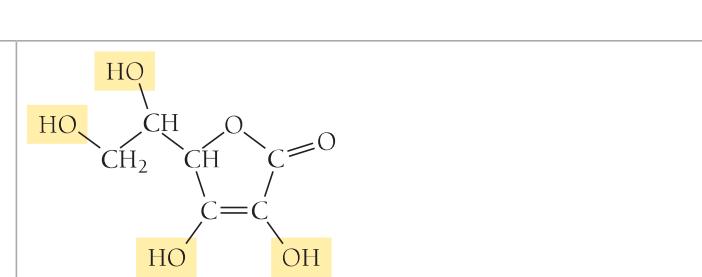
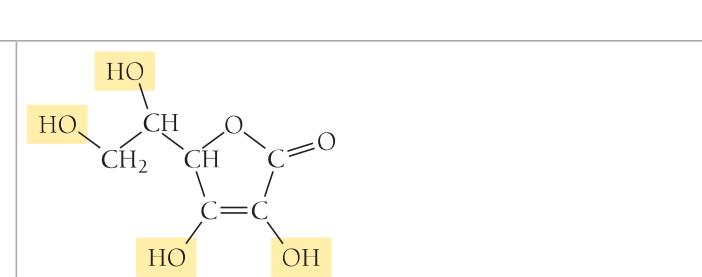
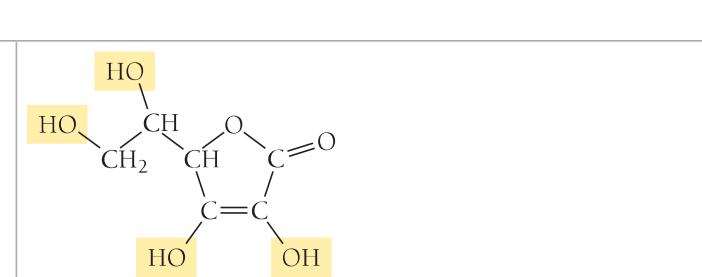
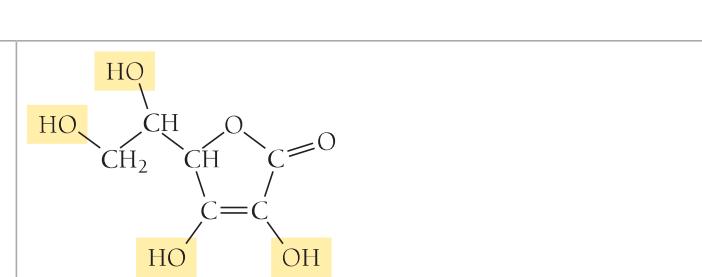
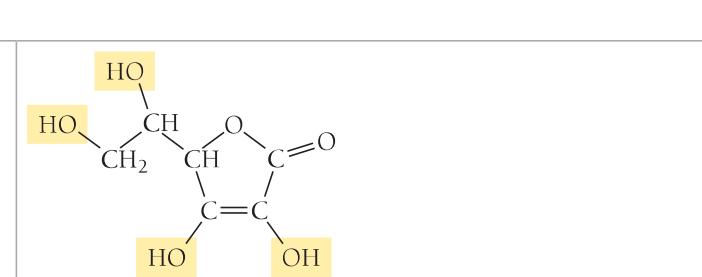
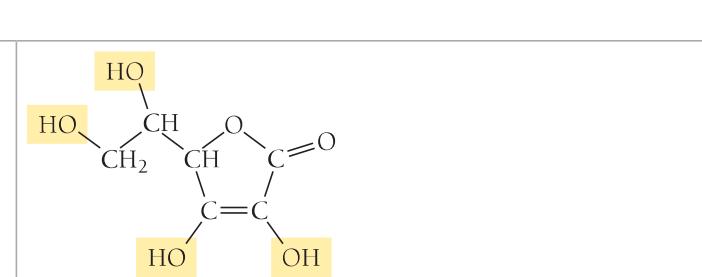
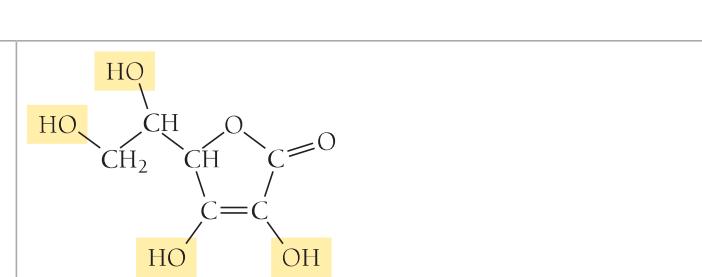
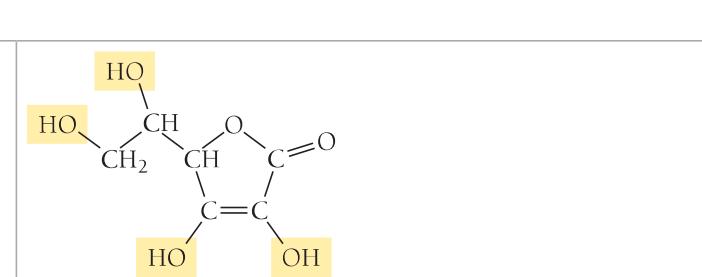
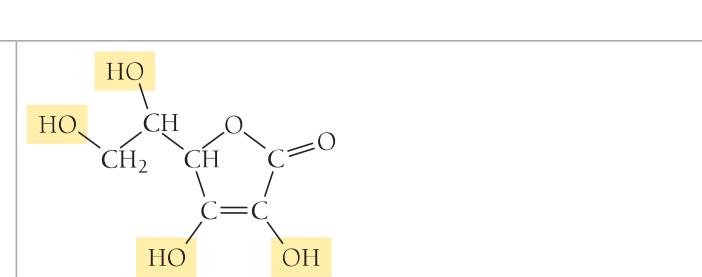
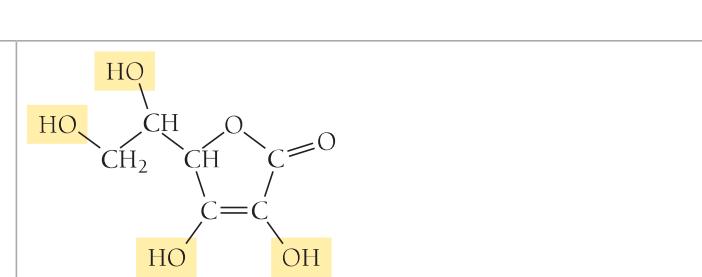
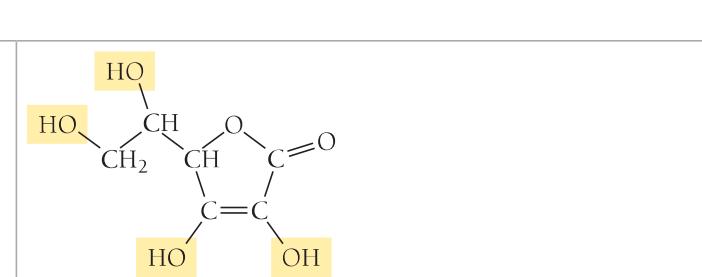
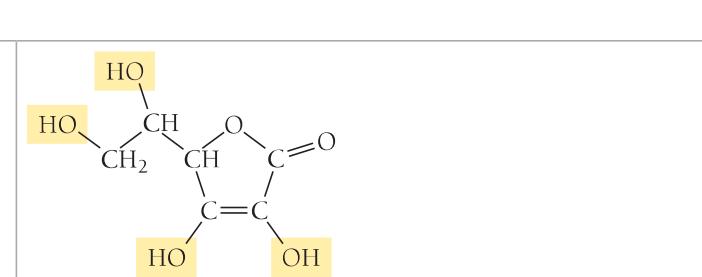
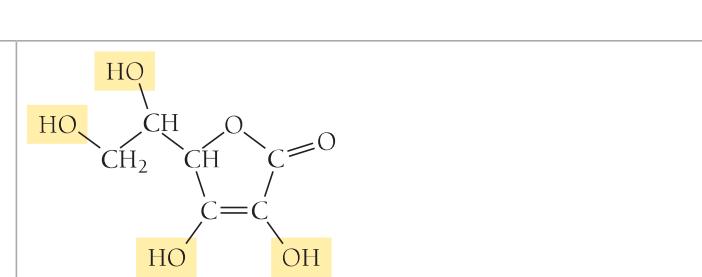
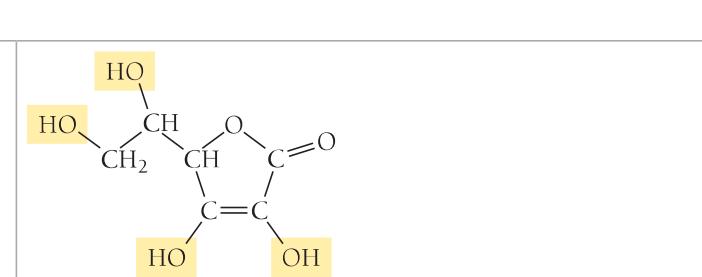
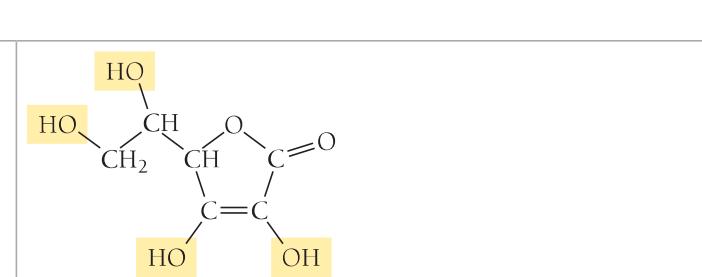
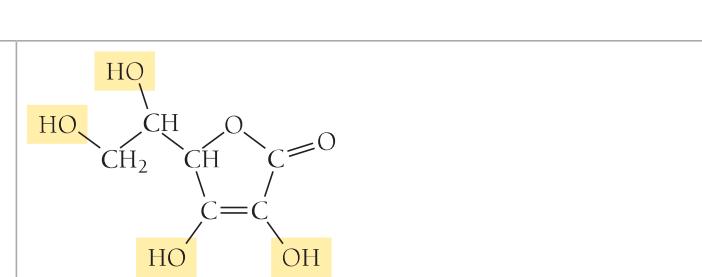
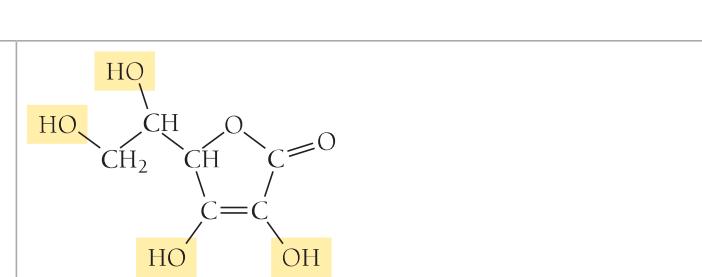
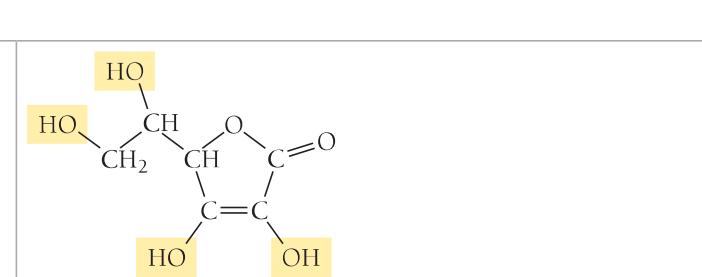
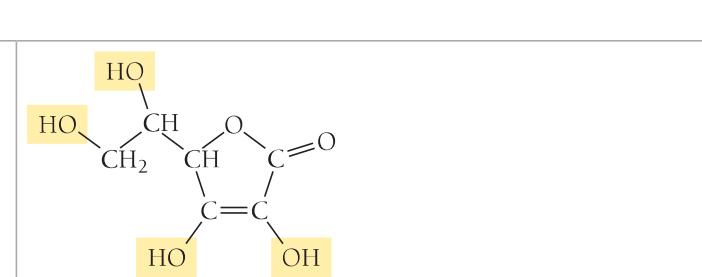
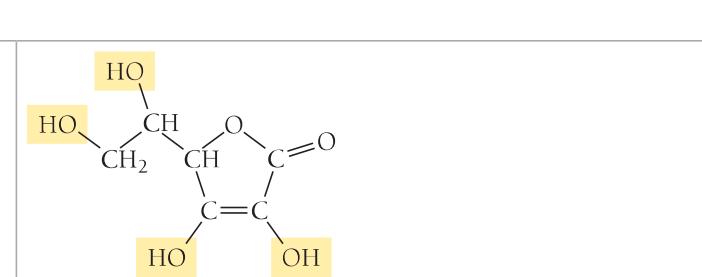
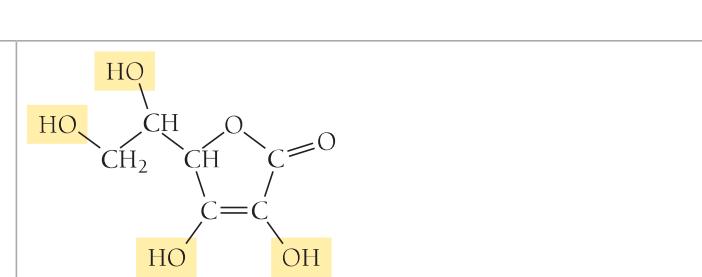
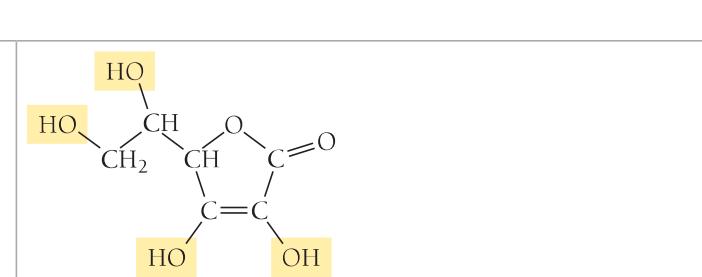
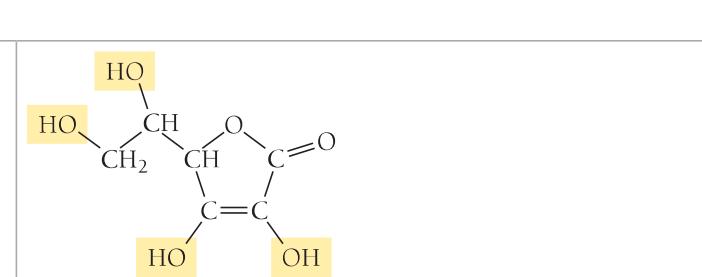
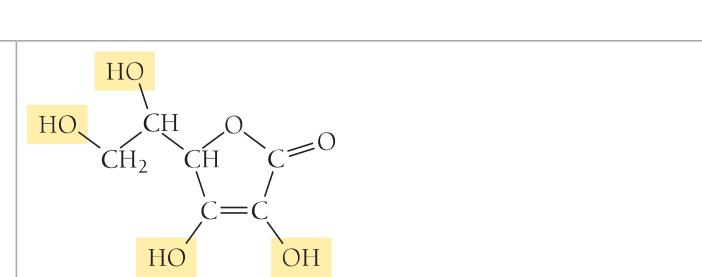
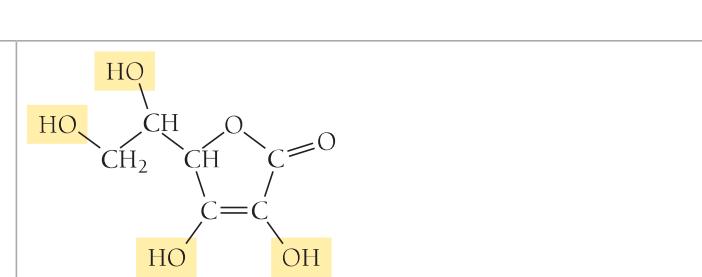
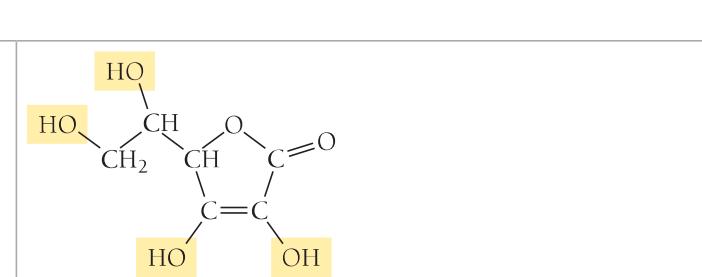
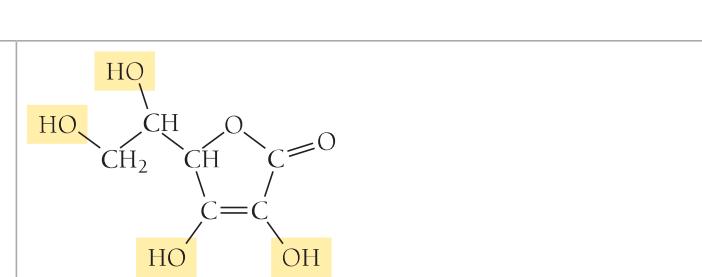
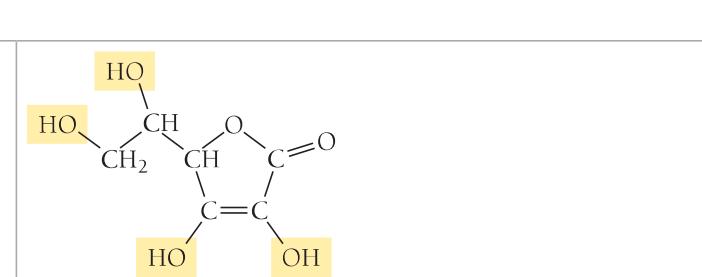
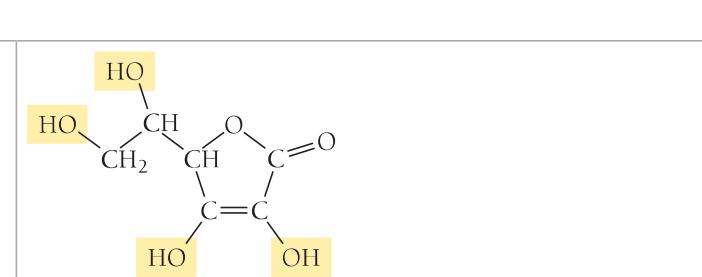
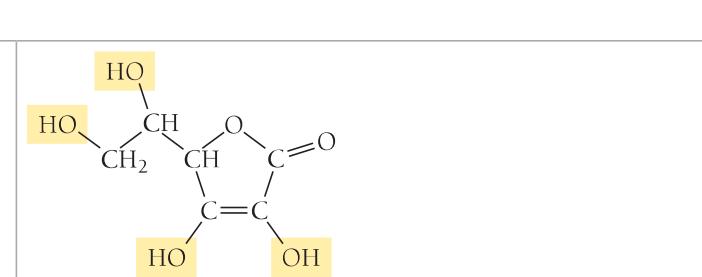
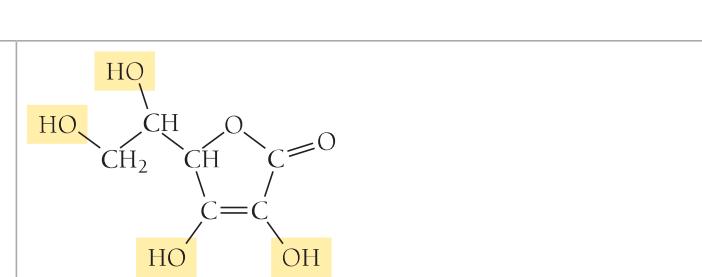
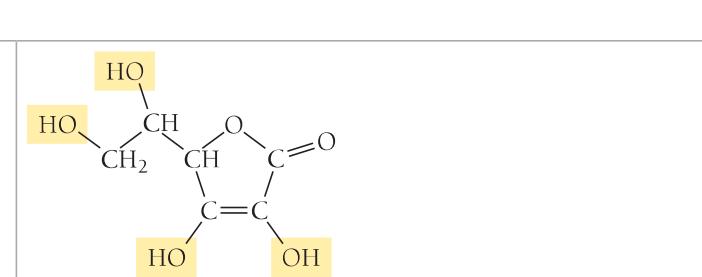
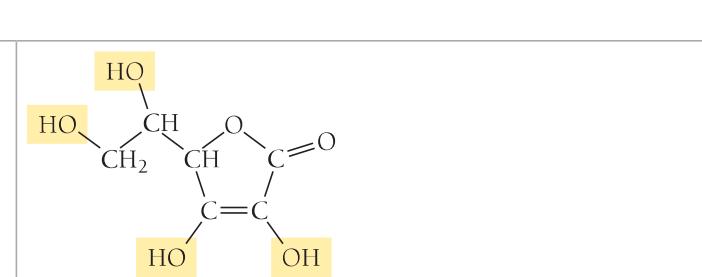
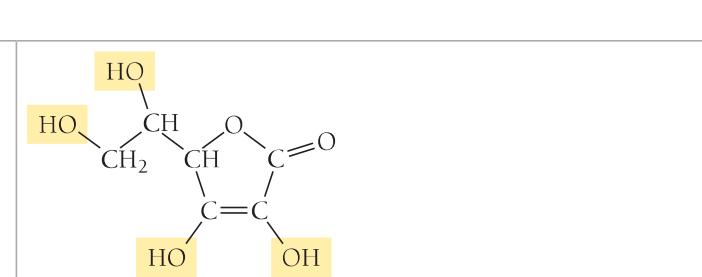
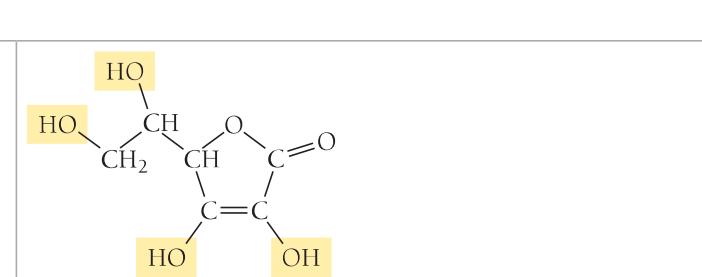
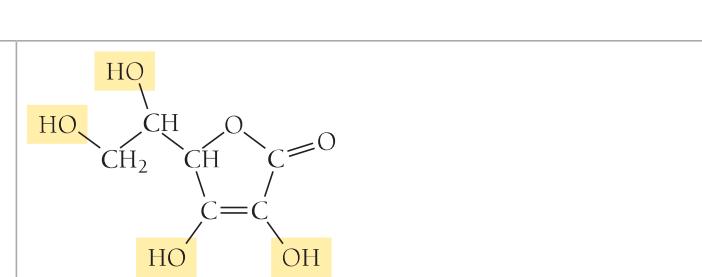
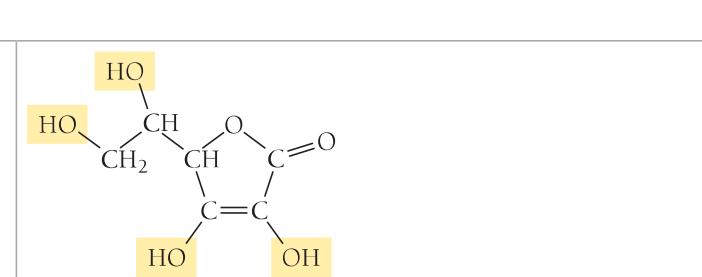
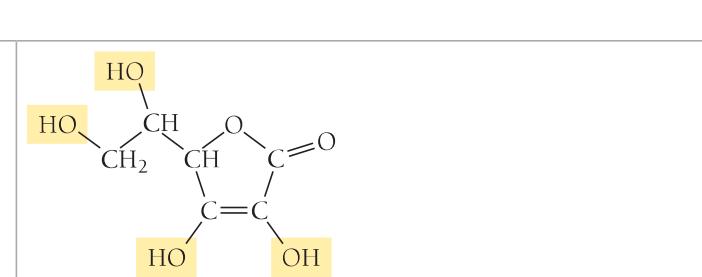
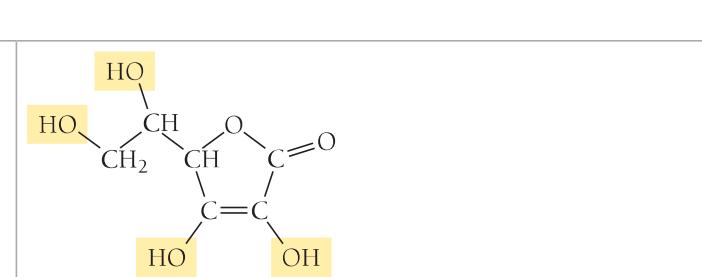
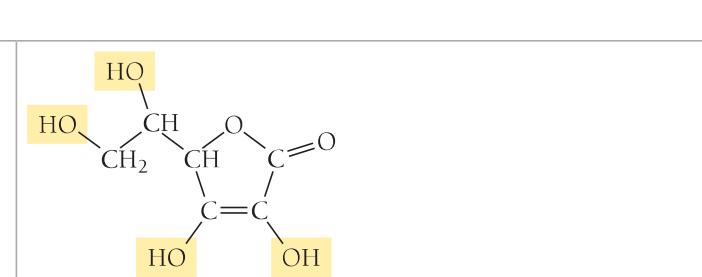
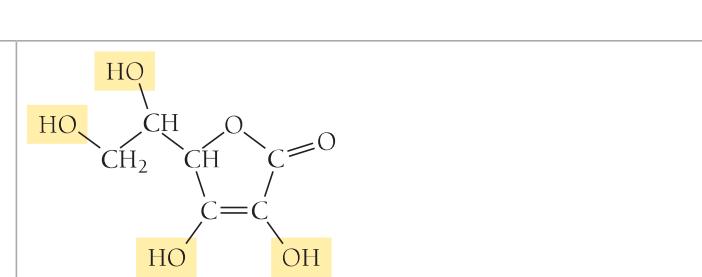
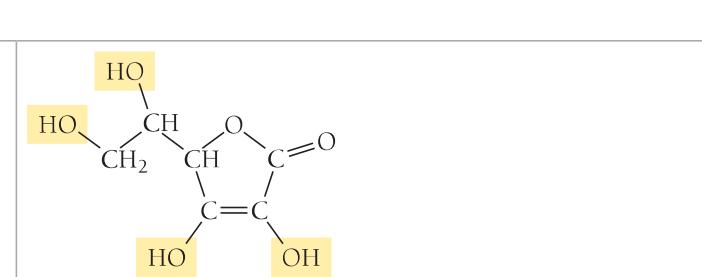
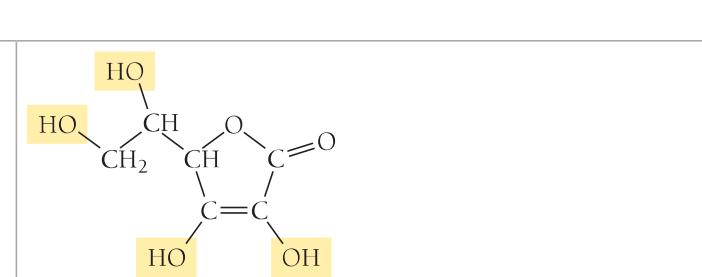
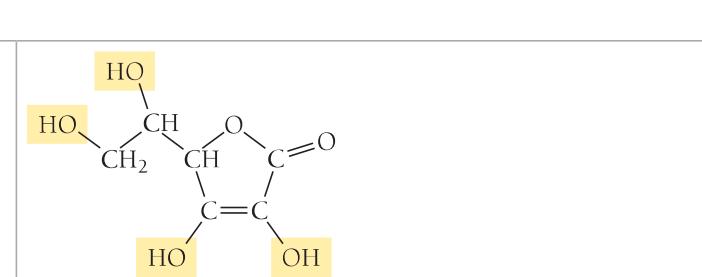
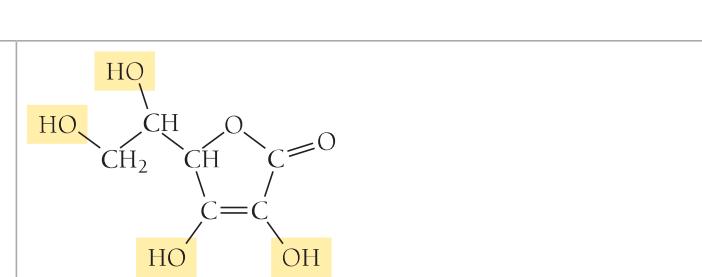
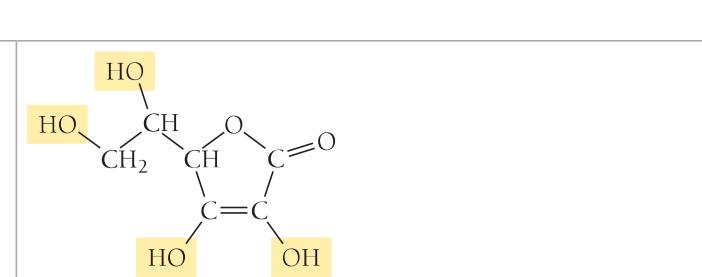
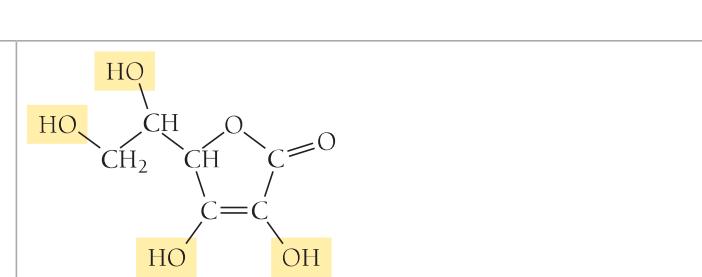
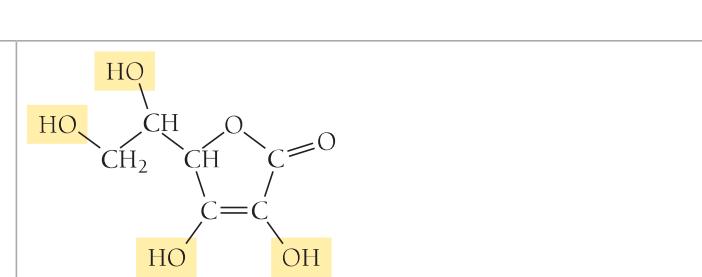
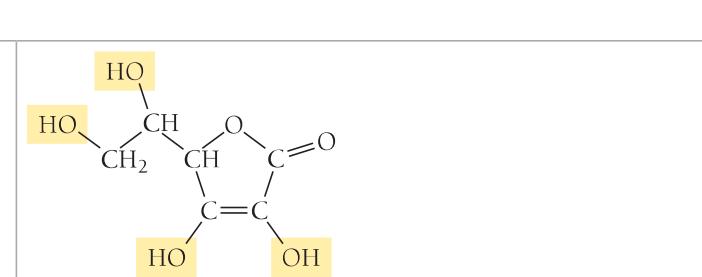
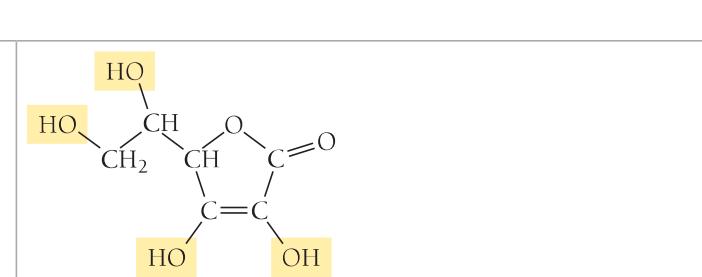
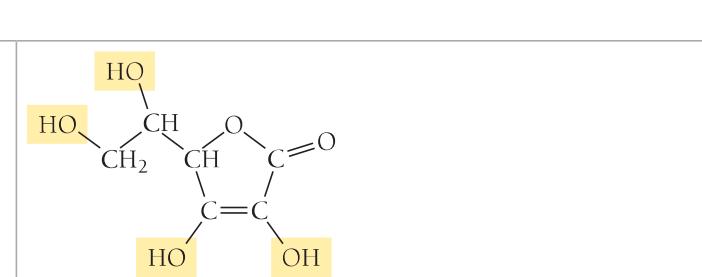
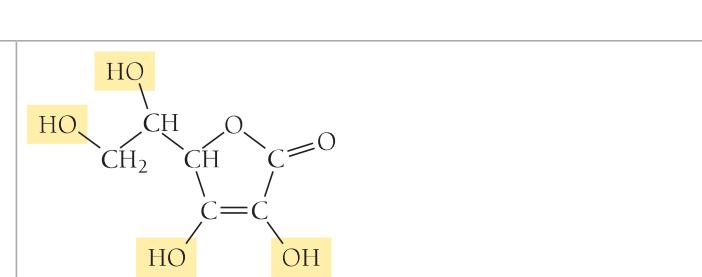
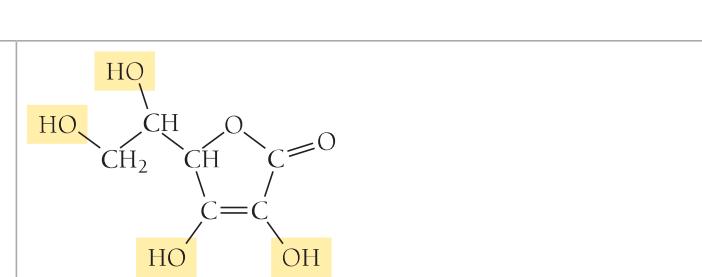
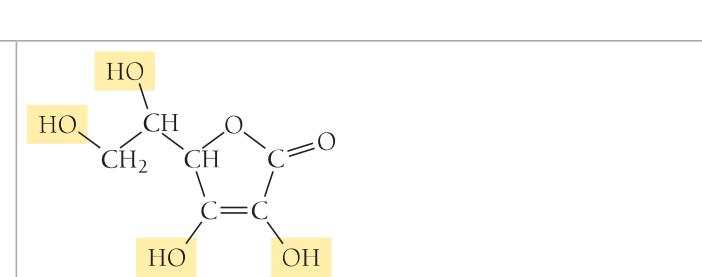
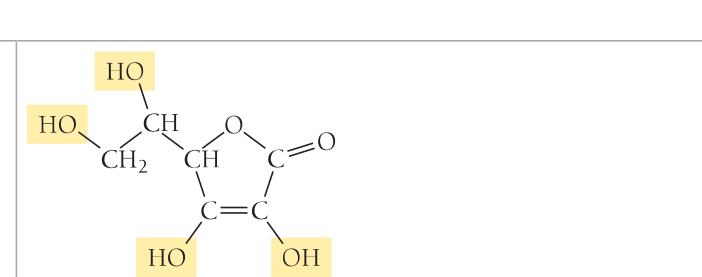
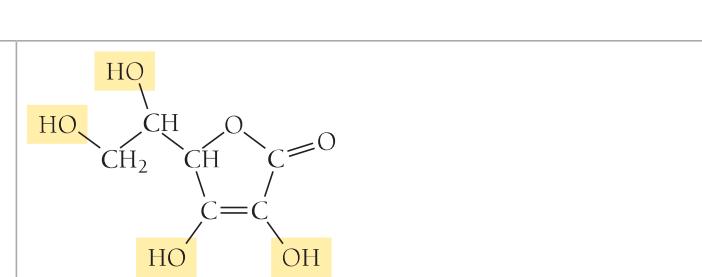
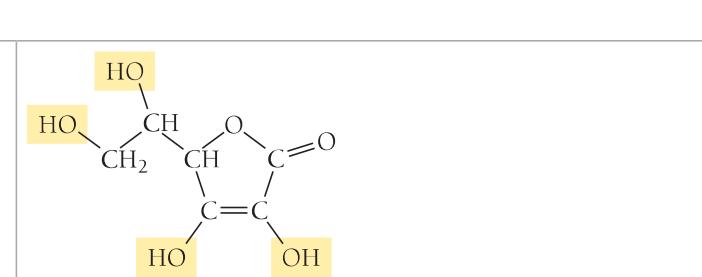
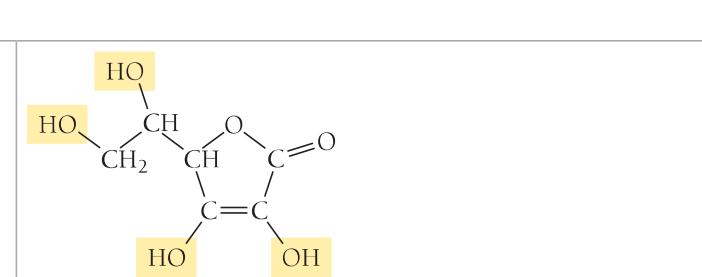
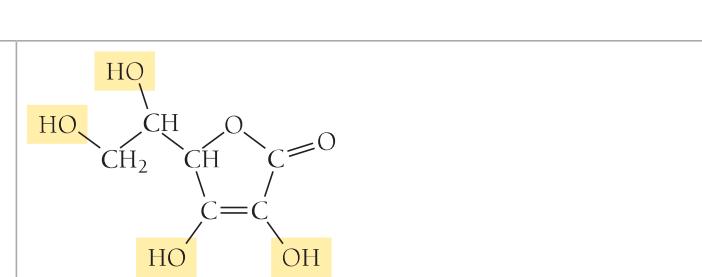
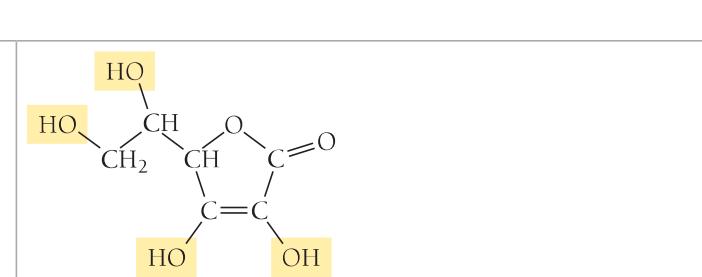
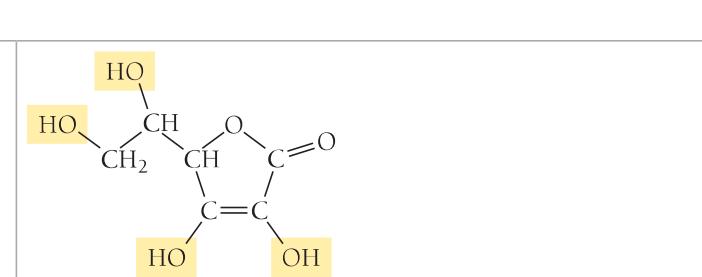
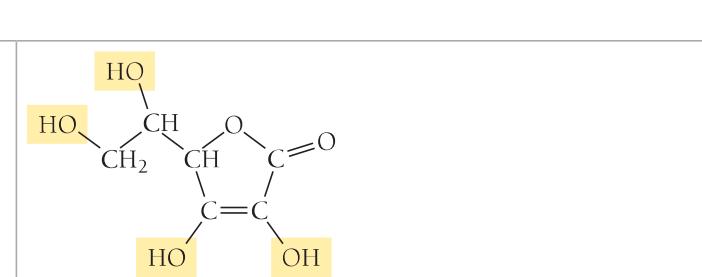
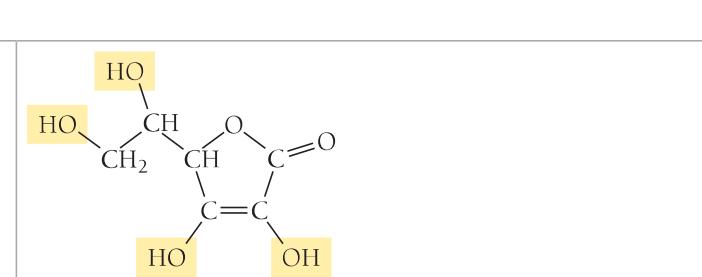
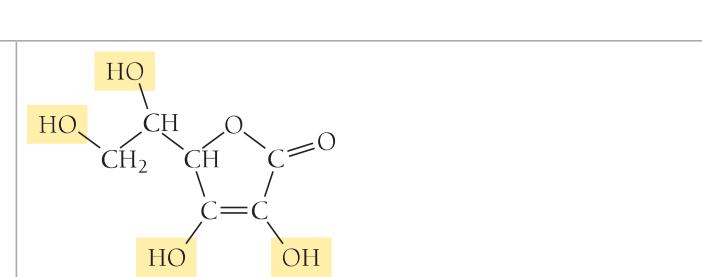
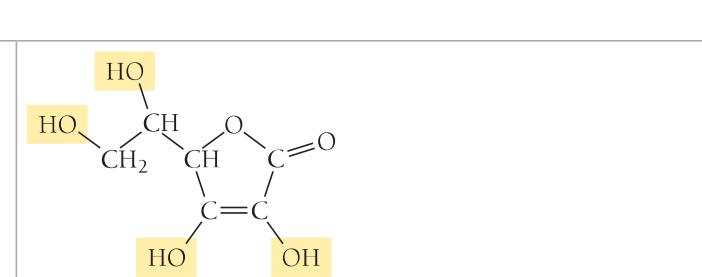
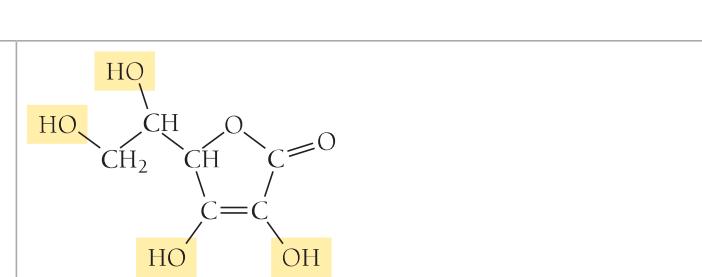
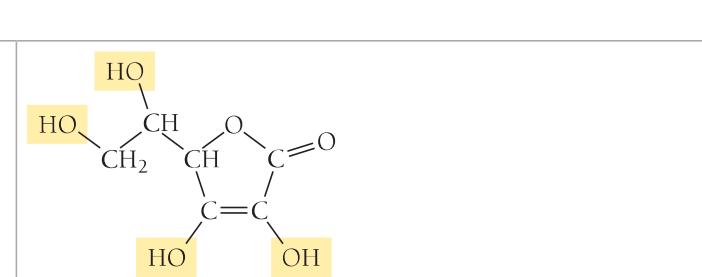
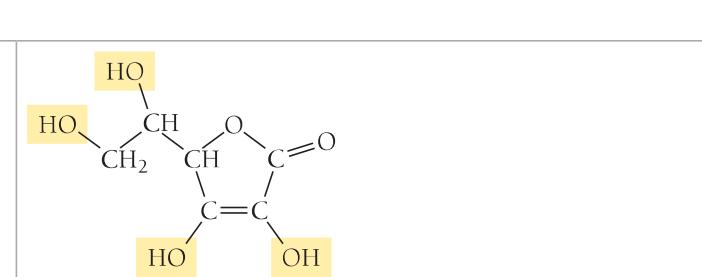
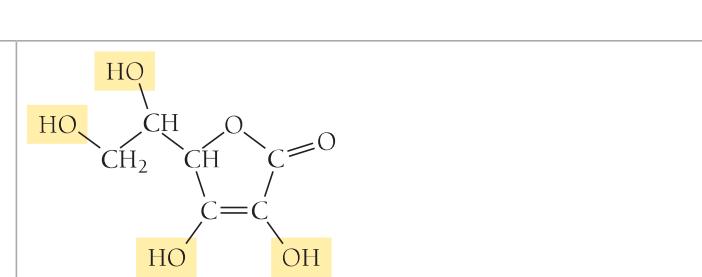
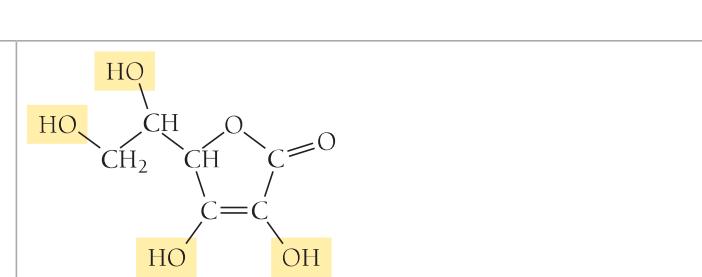
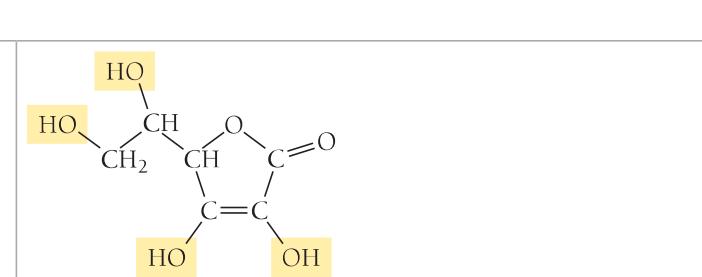
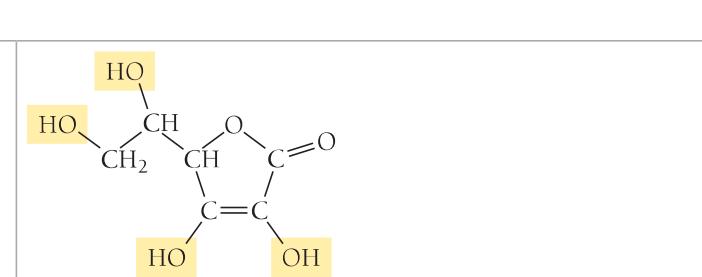
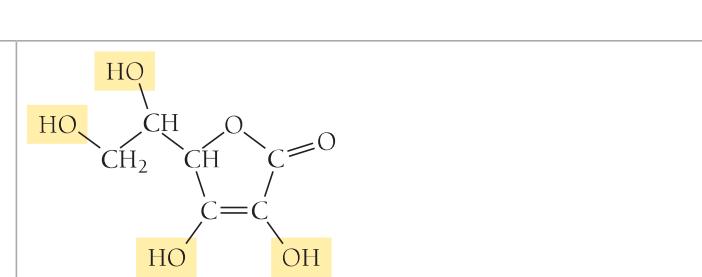
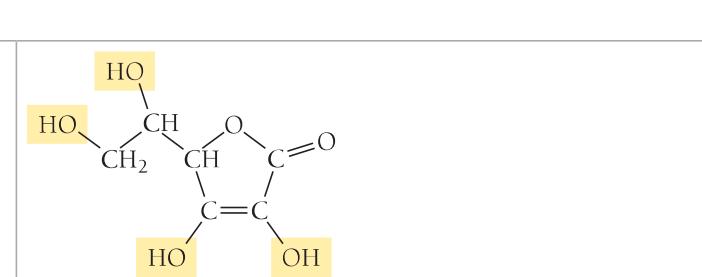
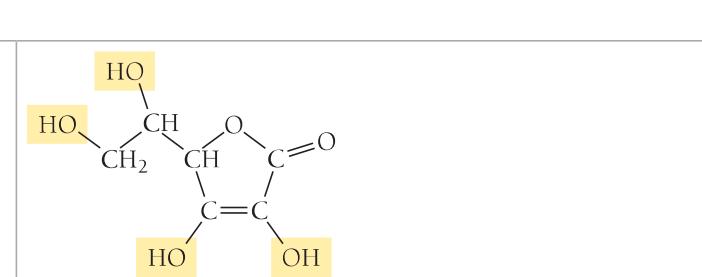
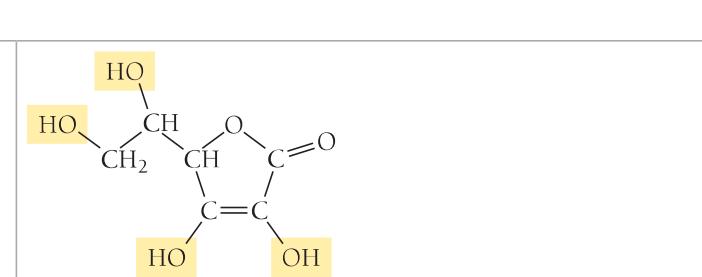
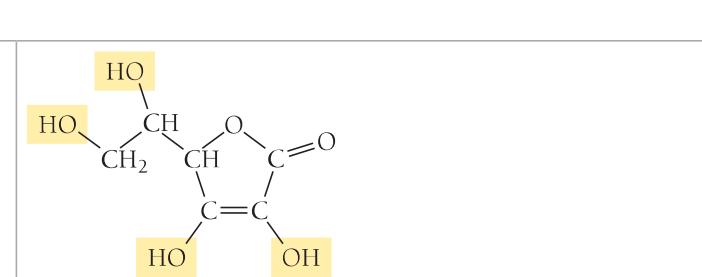
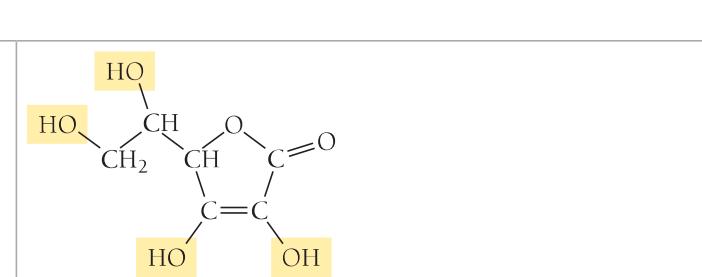
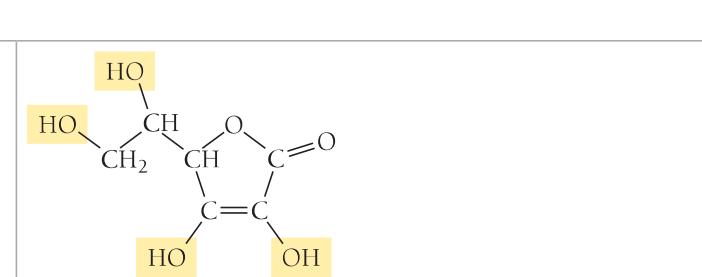
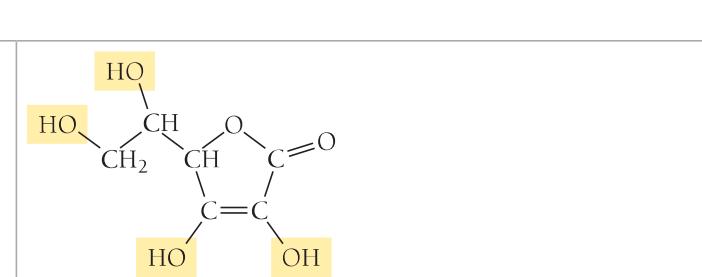
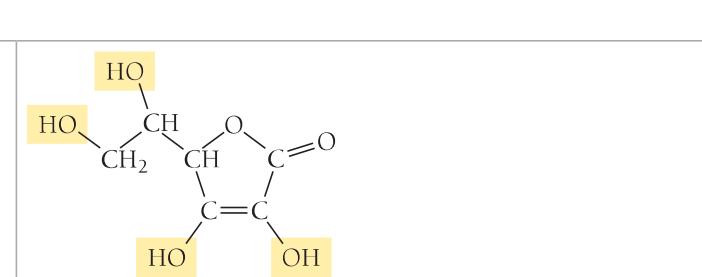
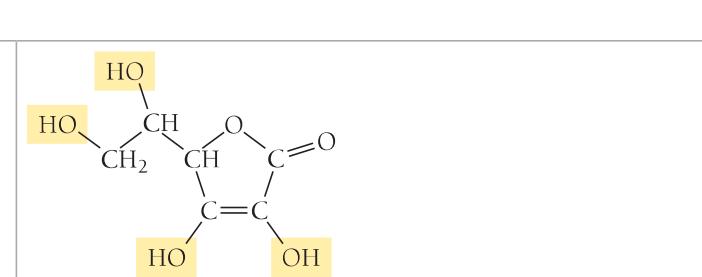
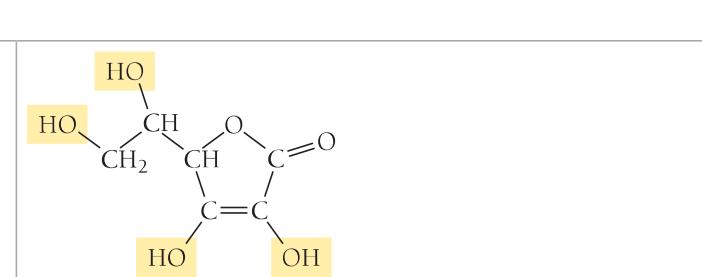
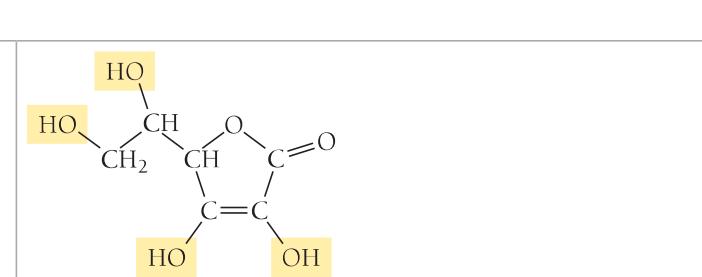
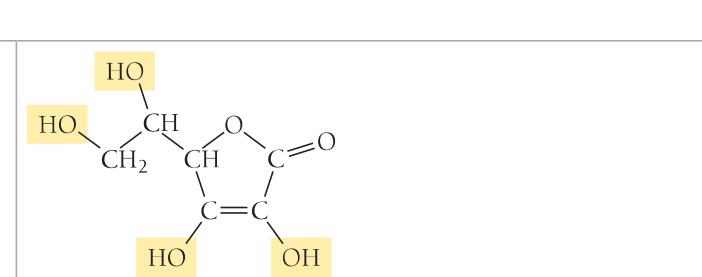
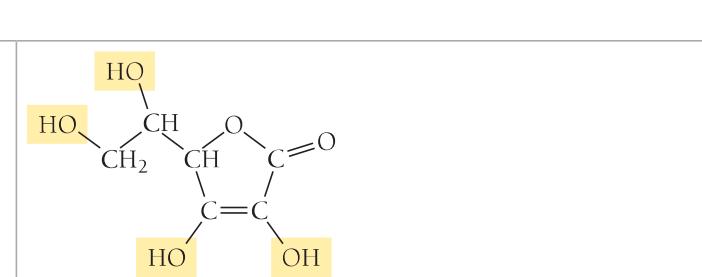
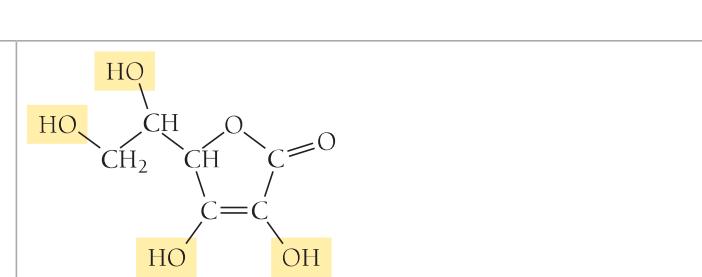
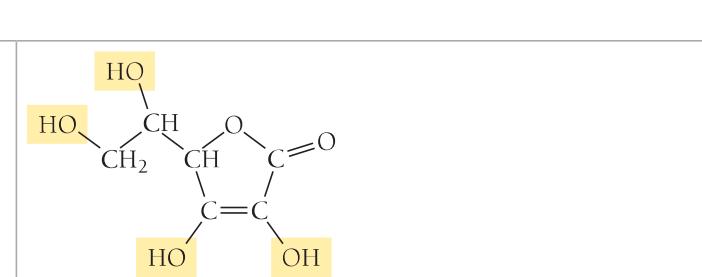
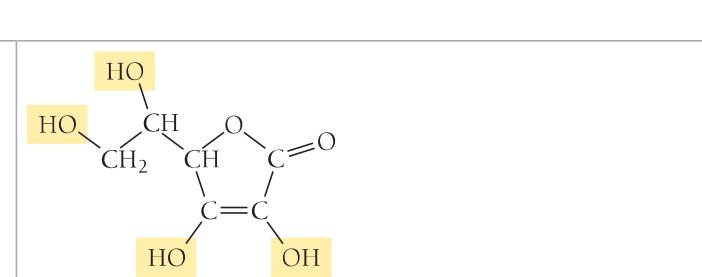
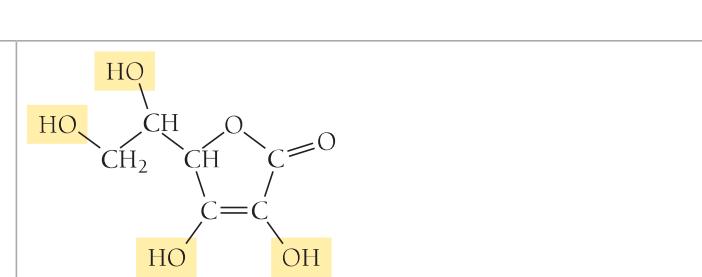
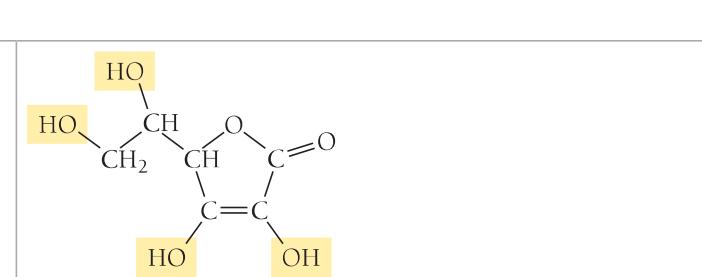
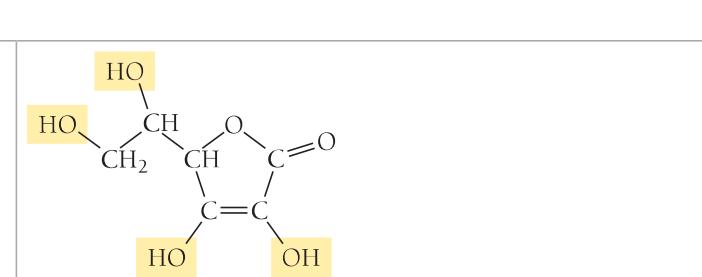
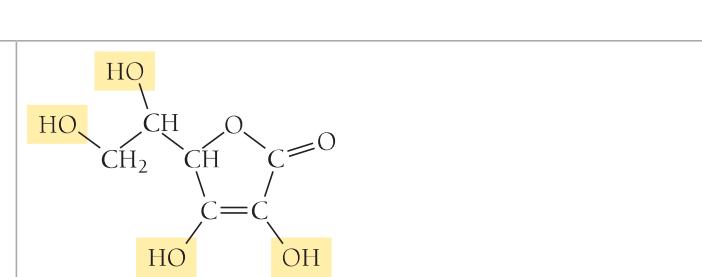
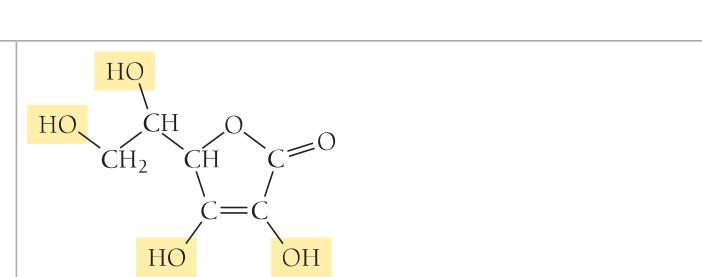
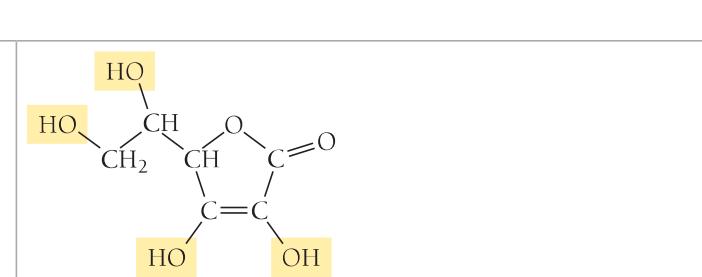
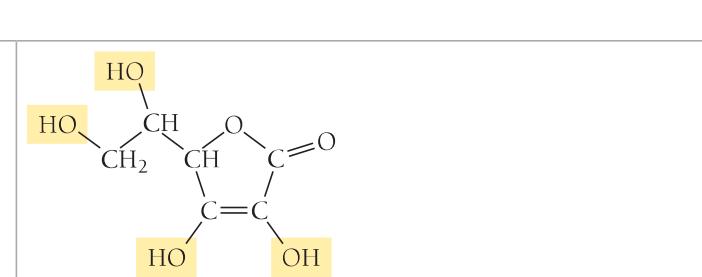
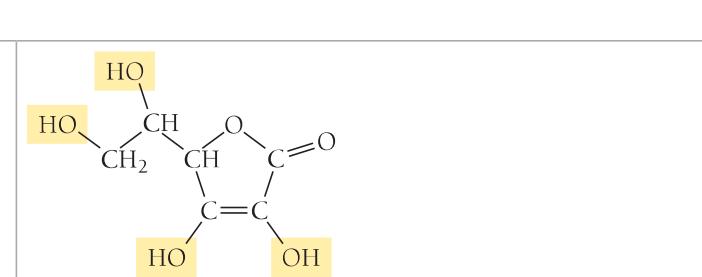
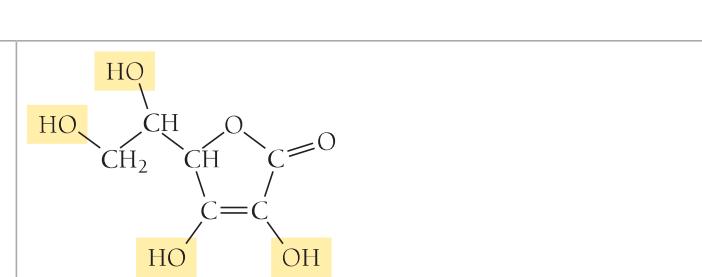
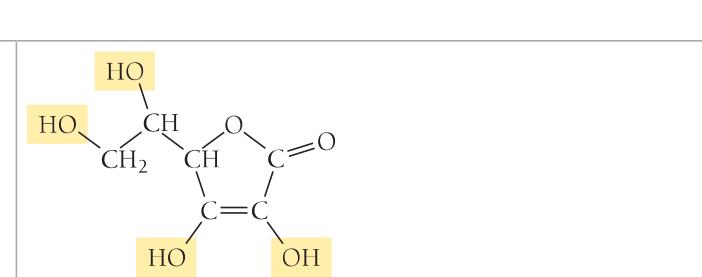
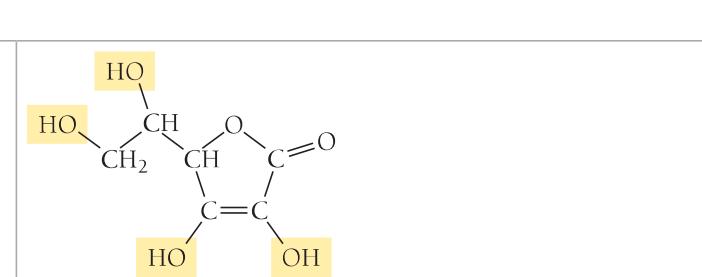
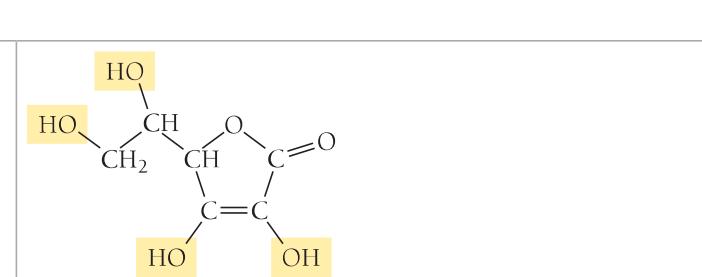
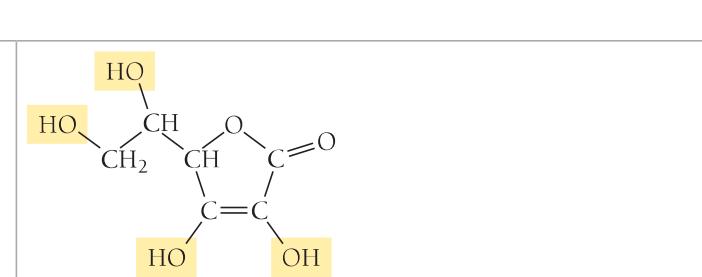
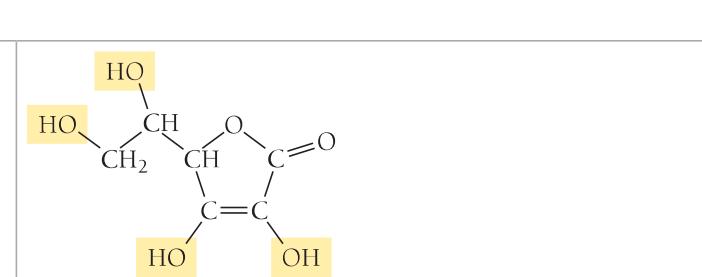
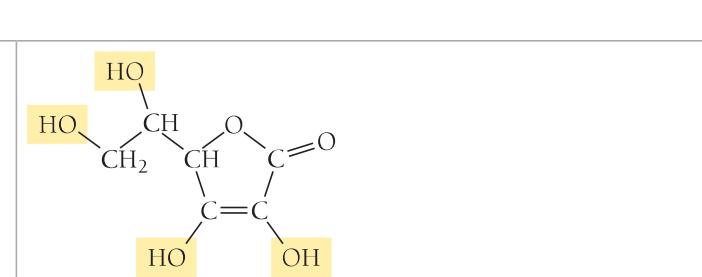
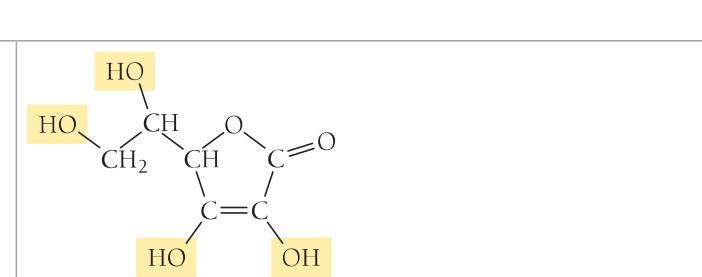
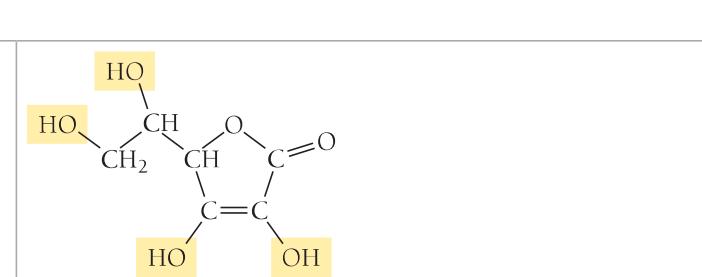
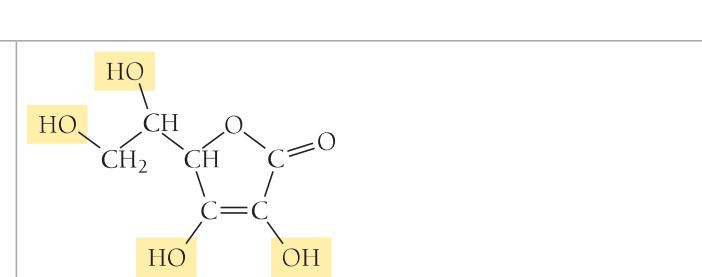
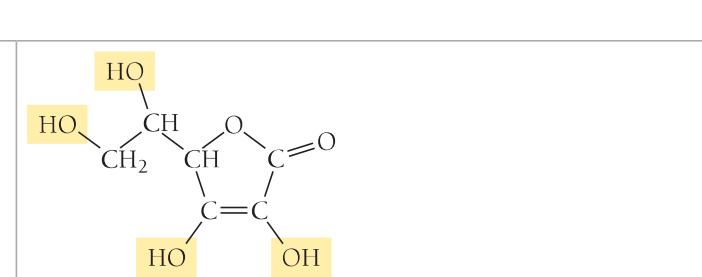
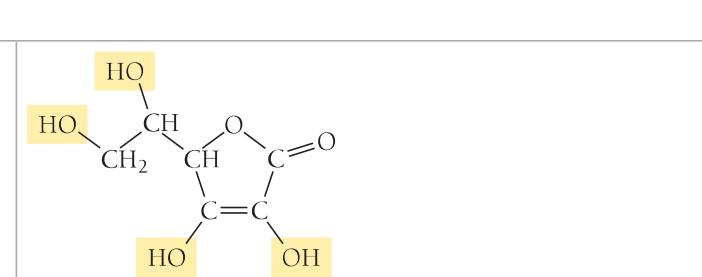
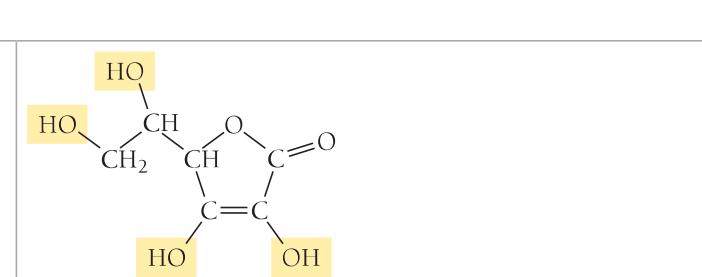
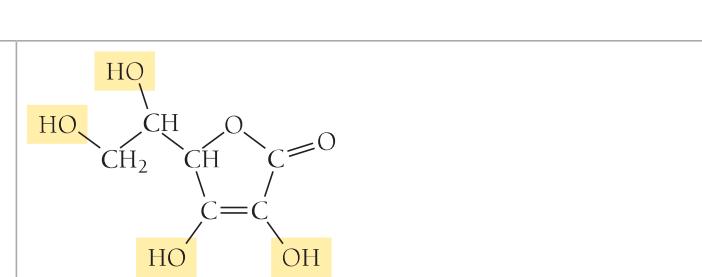
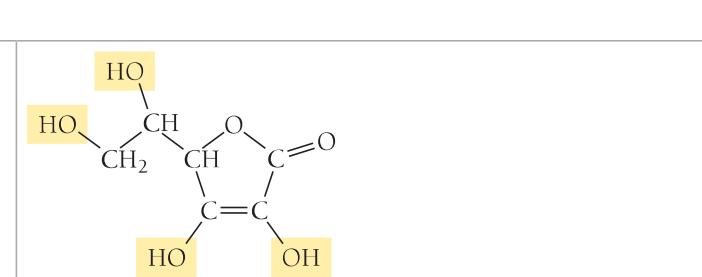
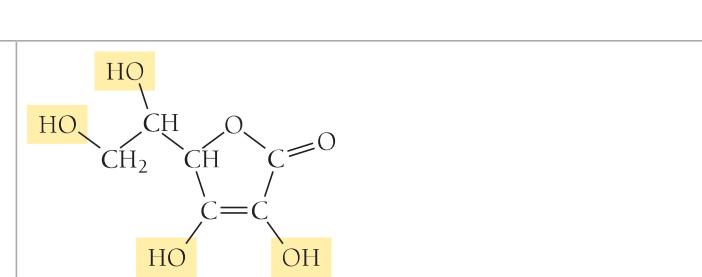
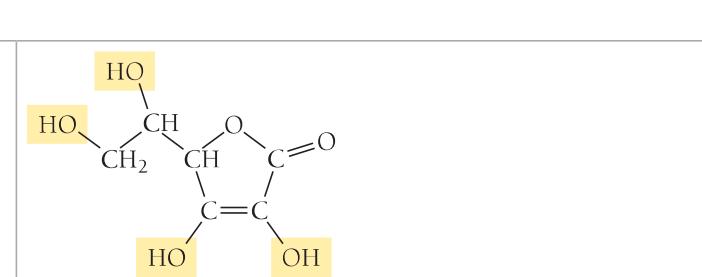
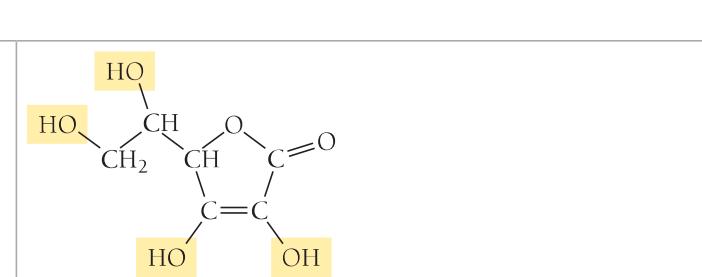
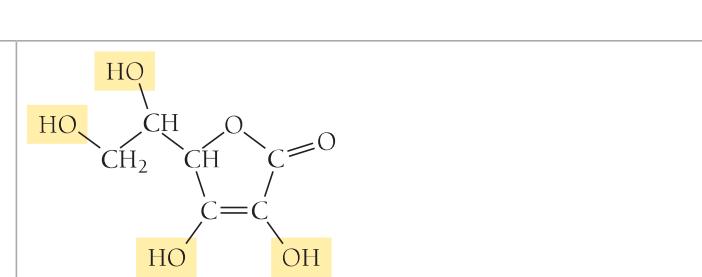
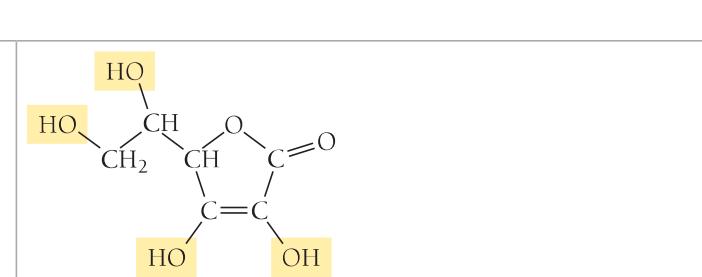
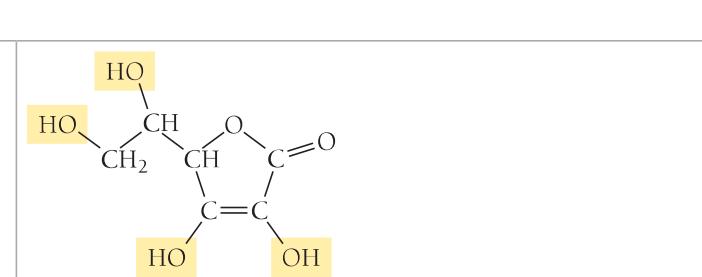
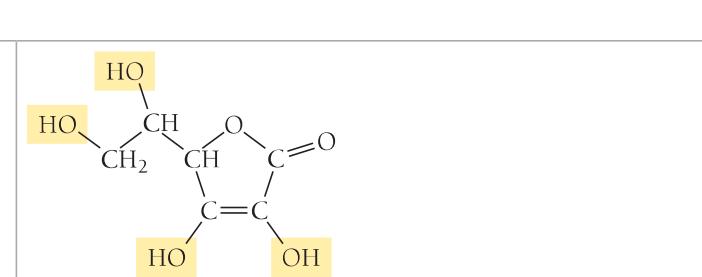
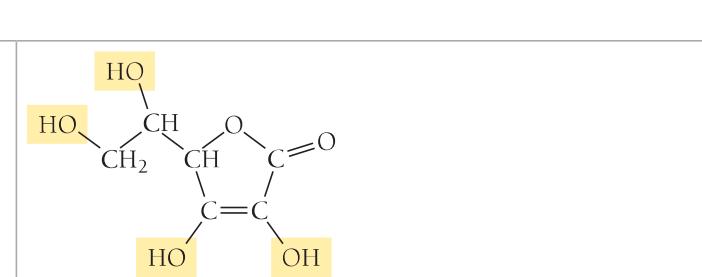
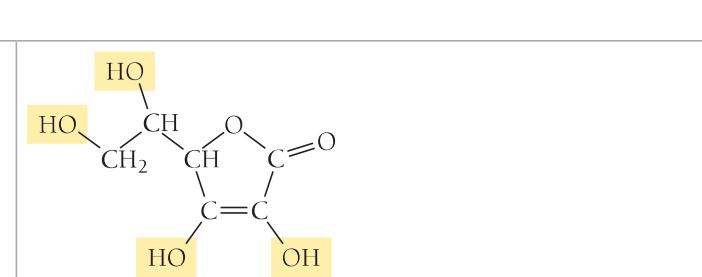
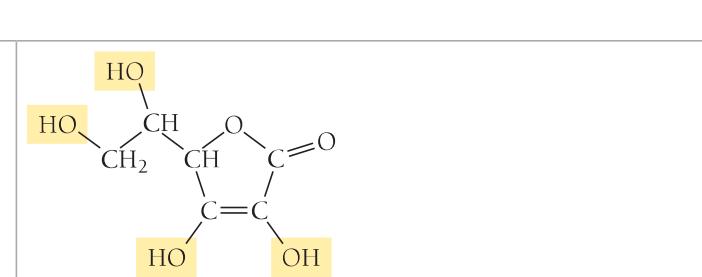
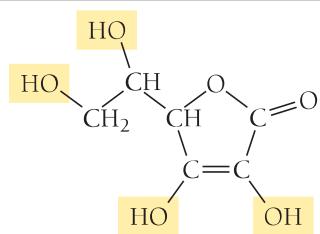
## (a) Vitamin C



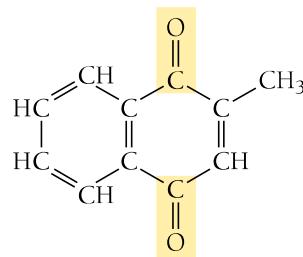
## (c) Vitamin A

(b) Vitamin K<sub>3</sub>(d) Vitamin B<sub>5</sub>**SOLUTION**

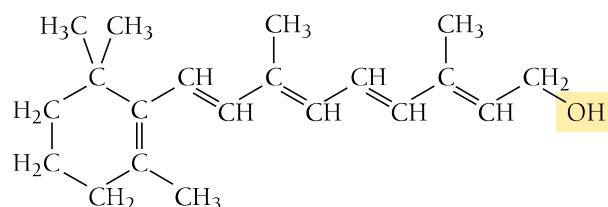
- (a) The four —OH bonds in vitamin C make it highly polar and allow it to hydrogen-bond with water. Vitamin C is water-soluble.



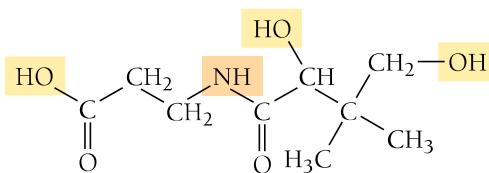
- (b)** The C—C bonds in vitamin K<sub>3</sub> are nonpolar and the C—H bonds are nearly so. The C=O bonds are polar, but the bond dipoles oppose and largely cancel each other, so the molecule is dominated by the nonpolar bonds. Vitamin K<sub>3</sub> is fat-soluble.



- (c)** The C—C bonds in vitamin A are nonpolar, and the C—H bonds are nearly so. The one polar —OH bond may increase its water solubility slightly, but overall vitamin A is nonpolar and therefore fat-soluble.



- (d)** The three —OH bonds and one —NH bond in vitamin B<sub>5</sub> make it highly polar and allow it to hydrogen-bond with water. Vitamin B<sub>5</sub> is water-soluble.



**FOR PRACTICE 14.1** Determine whether each compound is soluble in hexane.

- (a)** water (H<sub>2</sub>O)      **(b)** propane (CH<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub>)      **(c)** ammonia (NH<sub>3</sub>)      **(d)** hydrogen chloride (HCl)

**SOLUBILITY** Consider the table listing the solubilities of several alcohols in water and in hexane. Which statement best describes the observed trend in terms of intermolecular forces?

### 14.3 Cc Conceptual Connection

ANSWER NOW!



Alcohol	Space-Filling Model	Solubility in H <sub>2</sub> O (mol alcohol/100 g H <sub>2</sub> O)	Solubility in Hexane (C <sub>6</sub> H <sub>14</sub> ) (mol alcohol/100 g C <sub>6</sub> H <sub>14</sub> )
Methanol (CH <sub>3</sub> OH)		Miscible	0.12
Ethanol (CH <sub>3</sub> CH <sub>2</sub> OH)		Miscible	Miscible
Propanol (CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH)		Miscible	Miscible
Butanol (CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH)		0.11	Miscible
Pentanol (CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH)		0.030	Miscible

—Continued on the next page

Continued—

- (a) As you move down the list, molecules become more polar, less soluble in water, and more soluble in hexane.
- (b) As you move down the list, molecules become more polar, more soluble in water, and less soluble in hexane.
- (c) As you move down the list, molecules become less polar, less soluble in water, and more soluble in hexane.
- (d) As you move down the list, molecules become less polar, more soluble in water, and less soluble in hexane.

### 14.3

## Energetics of Solution Formation

Although forming a solution does not involve a chemical reaction, it can produce an energy change—just like the chemical reactions discussed in Chapter 7. This section explores the factors that determine if energy is absorbed or released when a solution is formed.

The energy changes that occur when a solution forms depend on the magnitude of the interactions between the solute and solvent particles. For example, when we dissolve sodium hydroxide in water, heat is evolved—the solution process is *exothermic*. In contrast, when we dissolve ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) in water, heat is absorbed—this solution process is *endothermic*. Other solutions, such as sodium chloride in water, barely absorb or evolve heat upon formation. What causes these different behaviors?

### Energy Changes in Solution Formation

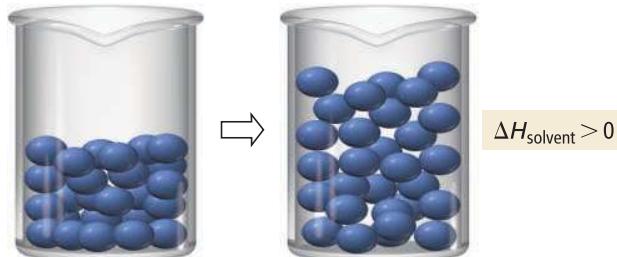
We can understand the energy changes associated with solution formation by envisioning the process as occurring in three steps, each with an associated change in enthalpy:

- 1 Separating the solute into its constituent particles.



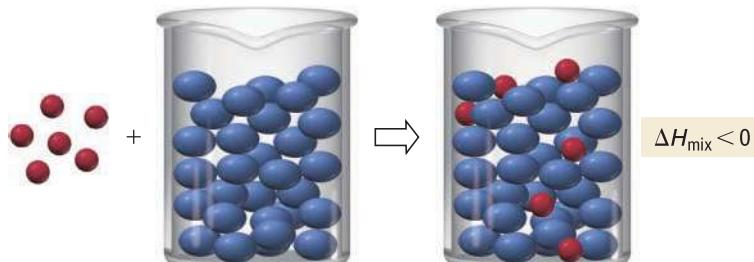
This step is always endothermic (positive  $\Delta H$ ) because energy is required to overcome the forces that hold the solute particles together.

- 2 Separating the solvent particles from each other to make room for the solute particles.



This step is also endothermic because energy is required to overcome the intermolecular forces among the solvent particles.

- 3 Mixing the solute particles with the solvent particles.



This step is exothermic because energy is released as the solute particles interact (through intermolecular forces) with the solvent particles.

According to Hess's law, the overall enthalpy change upon solution formation, called the **enthalpy of solution** ( $\Delta H_{\text{soln}}$ ), is the sum of the changes in enthalpy for each step:

$$\Delta H_{\text{soln}} = \Delta H_{\text{solute}} + \Delta H_{\text{solvent}} + \Delta H_{\text{mix}}$$

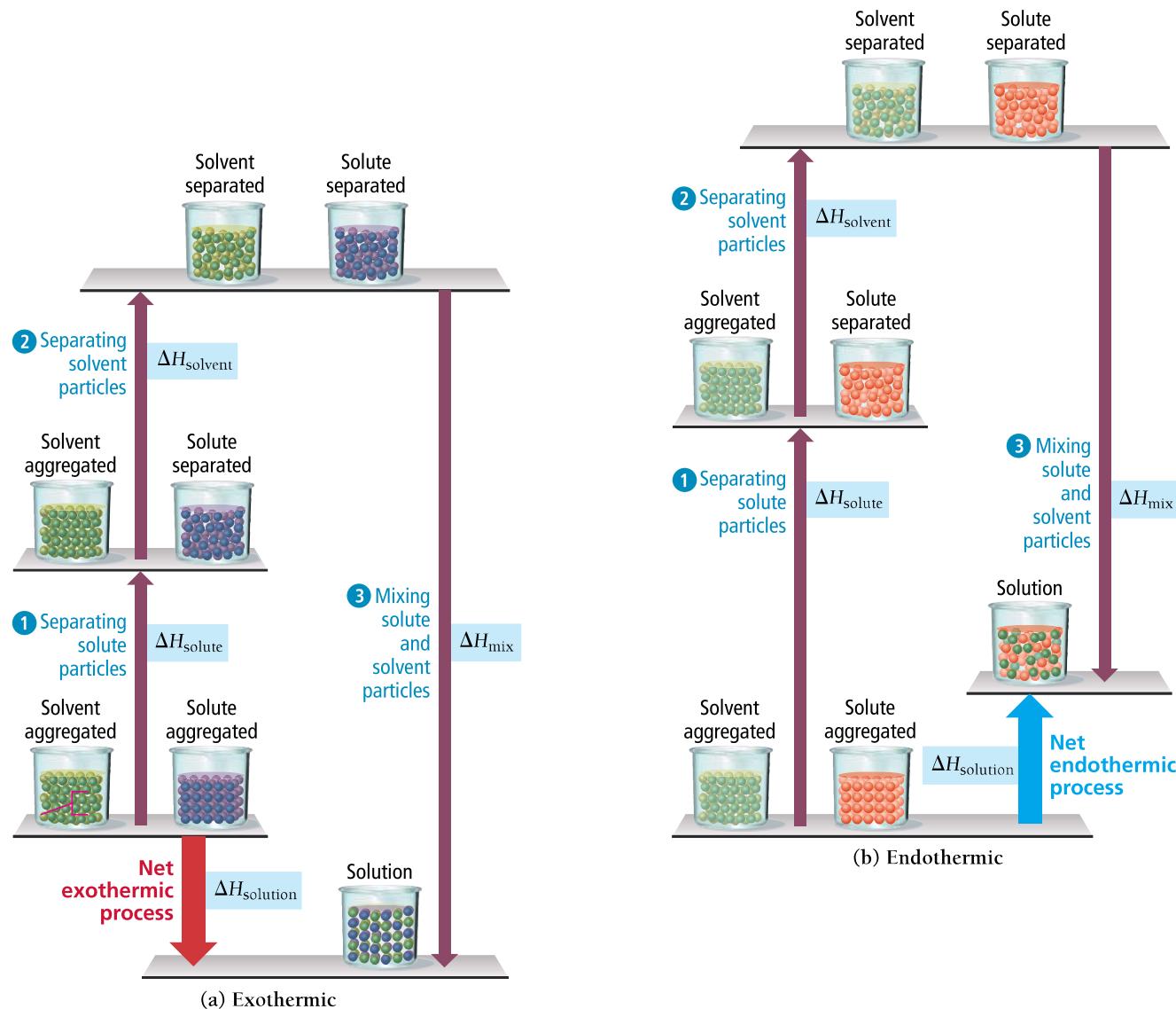
endothermic (+)      endothermic (+)      exothermic (-)

Since the first two terms are endothermic (positive  $\Delta H$ ) and the third term is exothermic (negative  $\Delta H$ ), the overall sign of  $\Delta H_{\text{soln}}$  depends on the magnitudes of the individual terms, as shown in Figure 14.6▼.

- $\Delta H_{\text{soln}} \approx 0$  If the sum of the endothermic terms is approximately equal in magnitude to the exothermic term, then  $\Delta H_{\text{soln}}$  is about zero. The increasing entropy upon mixing drives the formation of a solution while the overall energy of the system remains nearly constant.
- $\Delta H_{\text{soln}} < 0$  If the sum of the endothermic terms is smaller in magnitude than the exothermic term, then  $\Delta H_{\text{soln}}$  is negative and the solution process is exothermic. In this case, both the tendency toward lower energy and the tendency toward greater entropy drive the formation of a solution.
- $\Delta H_{\text{soln}} > 0$  If the sum of the endothermic terms is greater in magnitude than the exothermic term, then  $\Delta H_{\text{soln}}$  is positive and the solution process is endothermic. As long as  $\Delta H_{\text{soln}}$  is not too large, the tendency toward greater entropy still drives the formation of a solution. However, if  $\Delta H_{\text{soln}}$  is too large, a solution does not form.

▼ FIGURE 14.6 Energetics of the Solution Process (a) When  $\Delta H_{\text{mix}}$  is greater in magnitude than the sum of  $\Delta H_{\text{solute}}$  and  $\Delta H_{\text{solvent}}$ , the heat of solution is negative (exothermic). (b) When  $\Delta H_{\text{mix}}$  is smaller in magnitude than the sum of  $\Delta H_{\text{solute}}$  and  $\Delta H_{\text{solvent}}$ , the heat of solution is positive (endothermic).

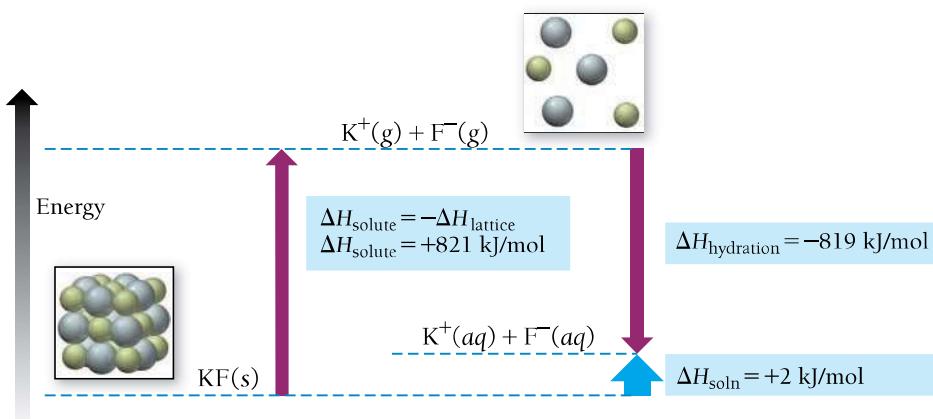
## Energetics of Solution Formation



## Aqueous Solutions and Heats of Hydration

Many common solutions, such as the seawater mentioned in Section 14.1, contain an ionic compound dissolved in water. In these aqueous solutions,  $\Delta H_{\text{solvent}}$  and  $\Delta H_{\text{mix}}$  can be combined into a single term called the **heat of hydration** ( $\Delta H_{\text{hydration}}$ ) (Figure 14.7▼).

### Heat of Hydration

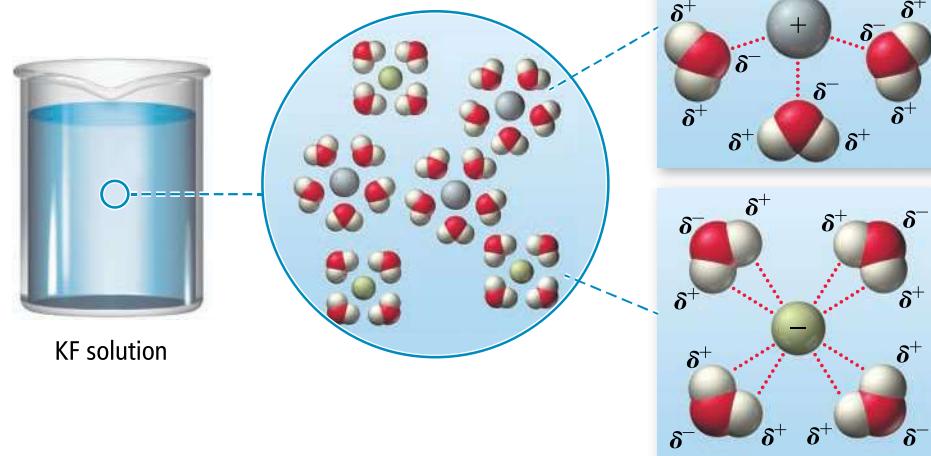


**► FIGURE 14.7 Heat of Hydration and Heat of Solution** The heat of hydration is the heat emitted when 1 mol of gaseous solute ions is dissolved in water. The sum of the negative of the lattice energy (which is  $\Delta H_{\text{solute}}$ ) and the heat of hydration is the heat of solution.

**► FIGURE 14.8 Ion-Dipole Interactions**

### Ion-Dipole Interactions

Ion-dipole interactions, such as those between potassium or fluoride ions and polar water molecules, cause the heat of hydration to be largely negative (exothermic).



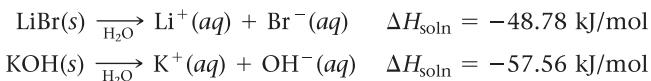
The heat of hydration is the enthalpy change that occurs when 1 mol of the gaseous solute ions is dissolved in water. Because the ion-dipole interactions that occur between a dissolved ion and the surrounding water molecules (Figure 14.8▲) are much stronger than the hydrogen bonds in water,  $\Delta H_{\text{hydration}}$  is always largely negative (exothermic) for ionic compounds. Using the heat of hydration, we can write the enthalpy of solution as a sum of just two terms, one endothermic and one exothermic:

$$\Delta H_{\text{soln}} = \Delta H_{\text{solute}} + \underbrace{\Delta H_{\text{solvent}} + \Delta H_{\text{mix}}}_{\substack{\text{endothermic} \\ \text{(positive)}}} + \underbrace{\Delta H_{\text{hydration}}}_{\substack{\text{exothermic} \\ \text{(negative)}}}$$

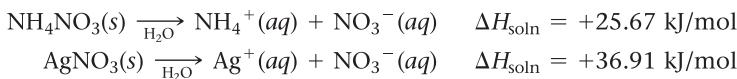
For ionic compounds,  $\Delta H_{\text{solute}}$ , the energy required to separate the solute into its constituent particles, is the negative of the solute's lattice energy ( $\Delta H_{\text{solute}} = -\Delta H_{\text{lattice}}$ ),

discussed in Section 10.4. For ionic aqueous solutions, then, the overall enthalpy of solution depends on the relative magnitudes of  $\Delta H_{\text{solute}}$  and  $\Delta H_{\text{hydration}}$ , with three possible scenarios (in each case we refer to the *magnitude (absolute value)* of  $\Delta H$ ):

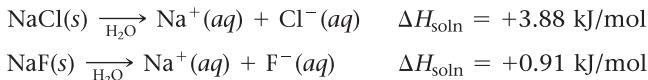
- $|\Delta H_{\text{solute}}| < |\Delta H_{\text{hydration}}|$ . EXOTHERMIC SOLUTION PROCESS** The amount of energy required to separate the solute into its constituent ions is less than the energy given off when the ions are hydrated.  $\Delta H_{\text{soln}}$  is therefore negative, and the solution process is exothermic. Solutes with negative enthalpies of solution include lithium bromide and potassium hydroxide. When these solutes dissolve in water, the resulting solutions feel warm to the touch:



- $|\Delta H_{\text{solute}}| > |\Delta H_{\text{hydration}}|$ . ENDOOTHERMIC SOLUTION PROCESS** The amount of energy required to separate the solute into its constituent ions is greater than the energy given off when the ions are hydrated.  $\Delta H_{\text{soln}}$  is therefore positive, and the solution process is endothermic (if a solution forms at all). Solutes that form aqueous solutions with positive enthalpies of solution include ammonium nitrate and silver nitrate. When these solutes dissolve in water, the resulting solutions feel cool to the touch:



- $|\Delta H_{\text{solute}}| \approx |\Delta H_{\text{hydration}}|$ .** The amount of energy required to separate the solute into its constituent ions is roughly equal to the energy given off when the ions are hydrated.  $\Delta H_{\text{soln}}$  is therefore approximately zero, and the solution process is neither appreciably exothermic nor appreciably endothermic. Solutes with enthalpies of solution near zero include sodium chloride and sodium fluoride. When these solutes dissolve in water, the resulting solutions do not undergo a noticeable change in temperature:



## ENERGETICS OF AQUEOUS SOLUTION FORMATION

The enthalpy of solution for cesium fluoride is  $-36.8 \text{ kJ/mol}$ . What can you conclude about the relative magnitudes of  $\Delta H_{\text{solute}}$  and  $\Delta H_{\text{hydration}}$ ?

- (a)  $|\Delta H_{\text{solute}}| > |\Delta H_{\text{hydration}}|$
- (b)  $|\Delta H_{\text{solute}}| < |\Delta H_{\text{hydration}}|$
- (c)  $|\Delta H_{\text{solute}}| = |\Delta H_{\text{hydration}}|$

14.4



Conceptual  
Connection

ANSWER NOW!



14.4

## Solution Equilibrium and Factors Affecting Solubility

The dissolution of a solute in a solvent is an equilibrium process similar to the equilibrium process associated with a phase change (discussed in Chapter 12). Imagine, from a molecular viewpoint, the dissolution of a solid solute such as sodium chloride in a liquid solvent such as water (Figure 14.9▼). Initially, water molecules rapidly solvate sodium cations and chloride anions, resulting in a noticeable decrease in the amount of

WATCH NOW!

KEY CONCEPT VIDEO 14.4

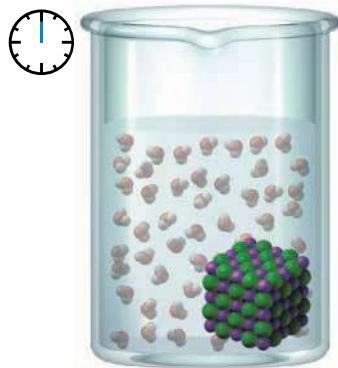
Solution Equilibrium and the Factors Affecting Solubility

## Solution Equilibrium

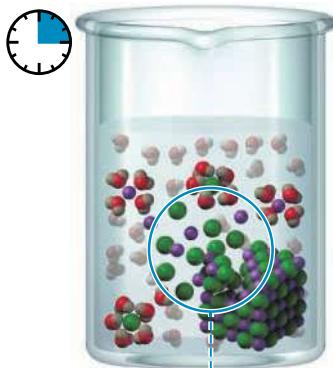
Sodium chloride is added to water.

The sodium and chloride ions dissolve in the water, but as the solution becomes more concentrated, some of the ions begin to recrystallize.

When the rate of dissolution equals the rate of recrystallization, dynamic equilibrium has been reached.

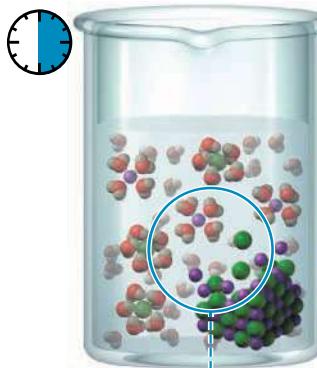


(a) Initial



Rate of dissolution &gt; Rate of recrystallization

(b) Dissolving



Rate of dissolution = Rate of recrystallization

(c) Dynamic equilibrium

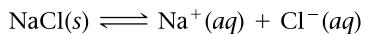
▲ FIGURE 14.9 Dissolution of NaCl

solid sodium chloride in the water. Over time, however, the concentration of dissolved sodium chloride in the solution increases. This dissolved sodium chloride then begins to recrystallize as solid sodium chloride. Initially, the rate of dissolution far exceeds the rate of recrystallization, but as the concentration of dissolved sodium chloride increases, the rate of recrystallization also increases. Eventually, the rates of dissolution and recrystallization become equal—**dynamic equilibrium** has been reached.



▲ FIGURE 14.10 Precipitation from a Supersaturated Solution

**Solution** When a small piece of solid sodium acetate is added to a supersaturated sodium acetate solution, the excess solid precipitates out of the solution.



A solution in which the dissolved solute is in dynamic equilibrium with the solid (undissolved) solute is a **saturated solution**. If you add additional solute to a saturated solution, it will not dissolve. A solution containing less than the equilibrium amount of solute is an **unsaturated solution**. If you add additional solute to an unsaturated solution, it will dissolve.

Under certain circumstances, a **supersaturated solution**—one containing more than the equilibrium amount of solute—may form. Supersaturated solutions are unstable, and the excess solute normally precipitates

out of the solution. However, in some cases, if left undisturbed, a supersaturated solution can exist for an extended period of time. For example, in a common classroom demonstration, a tiny piece of solid sodium acetate is added to a supersaturated solution of sodium acetate. This triggers the precipitation of the solute, which crystallizes out of solution in a dramatic and often beautiful way (Figure 14.10◀).

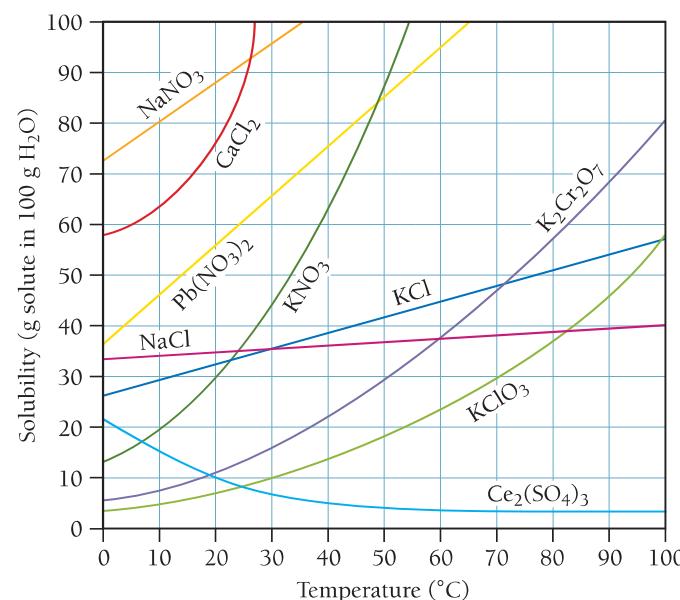
## The Temperature Dependence of the Solubility of Solids

The solubility of solids in water can be highly dependent on temperature. Have you ever noticed how much more sugar you can dissolve in hot tea than in cold tea? Although exceptions exist, *the solubility of most solids in water increases with increasing temperature*, as shown in Figure 14.11▶. For example, the solubility of potassium nitrate ( $\text{KNO}_3$ ) at room temperature is about 37 g  $\text{KNO}_3$  per 100 g of water. At 50 °C, the solubility rises to 88 g  $\text{KNO}_3$  per 100 g of water.

A common way to purify a solid is through a technique called **recrystallization**. In this technique, enough solid is added to water (or some other solvent) to create a saturated solution at an elevated temperature. As the solution cools, it becomes supersaturated and the excess solid precipitates out of solution. If the solution cools slowly, the solid forms crystals as it comes out of solution. The crystalline structure tends to reject impurities, resulting in a purer solid.

You can use the temperature dependence of the solubility of solids to make rock candy. Prepare a saturated sucrose (table sugar) solution at an elevated temperature, and allow a string or stick to dangle into the solution for several days. As the solution cools and the solvent evaporates, the solution becomes supersaturated and sugar crystals grow on the string or stick. After several days, beautiful edible crystals or “rocks” of sugar cover the string.

In the case of sugar dissolving in water, the higher temperature increases both *how fast* the sugar dissolves and *how much* sugar dissolves.



▲ FIGURE 14.11 Solubility and Temperature The solubility of most solids increases with increasing temperature.

## Factors Affecting the Solubility of Gases in Water

Solutions of gases dissolved in water are common. Club soda, for example, is a solution of carbon dioxide and water, and most liquids exposed to air contain dissolved gases from air. Fish and other aquatic animals depend on the oxygen dissolved in lake or ocean water for life, and our blood contains dissolved nitrogen, oxygen, and carbon dioxide. Even tap water contains dissolved gases. The solubility of a gas in a liquid is affected by both temperature and pressure.

### The Effect of Temperature

You can observe the effect of temperature on the solubility of a gas in water by heating ordinary tap water on a stove. Before the water reaches its boiling point, small bubbles develop in the water. These bubbles are the dissolved air (mostly nitrogen and oxygen) coming out of solution. (Once the water boils, the bubbling becomes more vigorous—these larger bubbles are composed of water vapor.) The dissolved air comes out of the heated solution because—unlike solids, whose solubility generally increases with increasing temperature—the solubility of gases in water decreases with increasing temperature.

The inverse relationship between gas solubility and temperature is the reason that warm soda pop bubbles more than cold soda pop when you open it and warm beer goes flat faster than cold beer. More carbon dioxide comes out of these solutions at room



▲ Rock candy is formed by the recrystallization of sugar.

**SOLUBILITY AND TEMPERATURE** A solution is saturated in both nitrogen gas and potassium bromide at 75 °C. When the solution is cooled to room temperature, what is most likely to happen?

- (a) Some nitrogen gas bubbles out of solution.
- (b) Some potassium bromide precipitates out of solution.
- (c) Some nitrogen gas bubbles out of solution, and some potassium bromide precipitates out of solution.
- (d) Nothing happens.

**14.5**  
**Cc**  
Conceptual Connection

ANSWER NOW!





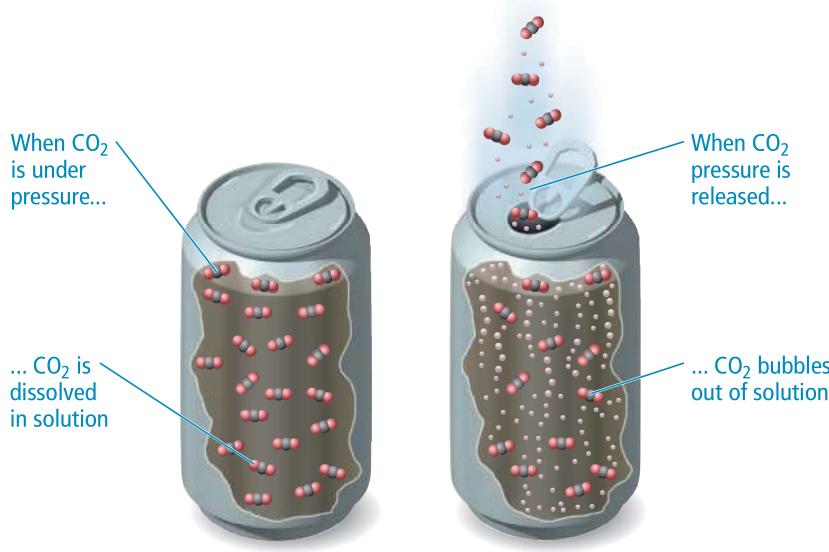
Cold soda pop      Warm soda pop

▲ Warm soda pop bubbles more than cold soda pop because carbon dioxide is less soluble in the warm solution.

temperature than at a lower temperature because the gas is less soluble at room temperature. The decreasing solubility of gases with increasing temperature is also the reason that fish don't bite much in a warm lake. The warm temperature results in a lower oxygen concentration. With lower oxygen levels, the fish become lethargic and do not strike as aggressively at the lure or bait you cast their way.

### The Effect of Pressure

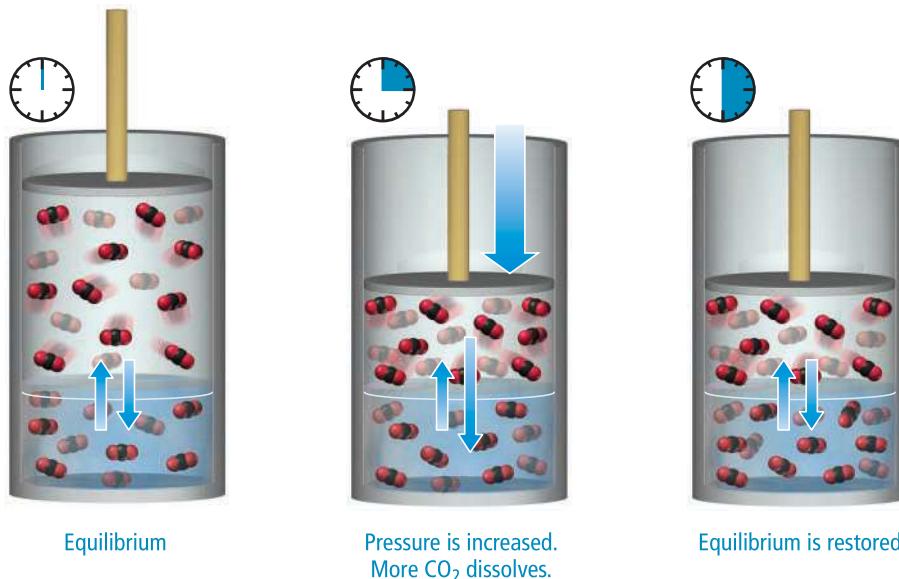
The solubility of gases also depends on pressure. The higher the pressure of a gas above a liquid, the more soluble the gas is in the liquid. In a sealed can of soda pop, for example, the carbon dioxide is maintained in solution by a high pressure of carbon dioxide within the can. When the can is opened, this pressure is released and the solubility of carbon dioxide decreases, resulting in bubbling as shown in Figure 14.12▼.



#### ► FIGURE 14.12 Soda Fizz

The bubbling that occurs when a can of soda is opened results from the reduced pressure of carbon dioxide over the liquid. At lower pressure, the carbon dioxide is less soluble and bubbles out of solution.

The increased solubility of a gas in a liquid can be understood by considering cylinders containing water and carbon dioxide gas:



The first cylinder represents an equilibrium between gaseous and dissolved carbon dioxide—the rate of carbon dioxide molecules entering solution exactly equals the rate of molecules leaving the solution. Now imagine decreasing the volume, as we have done in the second cylinder. The pressure of carbon dioxide increases, causing the rate of

molecules entering the solution to rise. The number of molecules in solution increases until equilibrium is established again, as shown in the third cylinder. However, the amount of carbon dioxide in solution in the third cylinder is greater.

We quantify the solubility of gases with increasing pressure with **Henry's law**:

$$S_{\text{gas}} = k_H P_{\text{gas}}$$

where  $S_{\text{gas}}$  is the solubility of the gas (usually in M),  $k_H$  is a constant of proportionality (called the *Henry's law constant*) that depends on the specific solute and solvent and also on temperature, and  $P_{\text{gas}}$  is the partial pressure of the gas (usually in atm). The equation shows that the solubility of a gas in a liquid is directly proportional to the pressure of the gas above the liquid. Table 14.4 lists the Henry's law constants for several common gases.

**TABLE 14.4 ■ Henry's Law Constants for Several Gases in Water at 25 °C**

Gas	$k_H$ (M/atm)
O <sub>2</sub>	$1.3 \times 10^{-3}$
N <sub>2</sub>	$6.1 \times 10^{-4}$
CO <sub>2</sub>	$3.4 \times 10^{-2}$
NH <sub>3</sub>	$5.8 \times 10^1$
He	$3.7 \times 10^{-4}$

## HENRY'S LAW

Examine the Henry's law constants in Table 14.4. Why is the constant for ammonia larger than the others?

- (a) Because ammonia is polar and the other substances in the table are nonpolar.
- (b) Because ammonia has the highest molar mass of the substances listed in the table.
- (c) Because ammonia is nonpolar and the other substances in the table are polar.

ANSWER NOW!



Conceptual  
Connection



WATCH NOW!

INTERACTIVE WORKED EXAMPLE 14.2

### EXAMPLE 14.2 Henry's Law

What pressure of carbon dioxide is required to keep the carbon dioxide concentration in a bottle of club soda at 0.12 M at 25 °C?



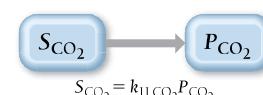
**SORT** You are given the desired solubility of carbon dioxide and asked to find the pressure required to achieve this solubility.

**GIVEN:**  $S_{\text{CO}_2} = 0.12 \text{ M}$

**FIND:**  $P_{\text{CO}_2}$

**STRATEGIZE** Use Henry's law to find the required pressure from the solubility. You will need the Henry's law constant for carbon dioxide, which is listed in Table 14.4.

**CONCEPTUAL PLAN**



**RELATIONSHIPS USED**

$$S_{\text{gas}} = k_H P_{\text{gas}} \text{ (Henry's law)}$$

$$k_{\text{H, CO}_2} = 3.4 \times 10^{-2} \text{ M/atm} \text{ (from Table 14.4)}$$

**SOLVE** Solve the Henry's law equation for  $P_{\text{CO}_2}$  and substitute the other quantities to calculate it.

**SOLUTION**

$$S_{\text{CO}_2} = k_{\text{H, CO}_2} P_{\text{CO}_2}$$

$$P_{\text{CO}_2} = \frac{S_{\text{CO}_2}}{k_{\text{H, CO}_2}}$$

$$= \frac{0.12 \text{ M}}{3.4 \times 10^{-2} \frac{\text{M}}{\text{atm}}}$$

$$= 3.5 \text{ atm}$$

**CHECK** The answer is in the correct units and seems reasonable. A small answer (for example, less than 1 atm) would be suspect because you know that the soda is under a pressure greater than atmospheric pressure when you open it. A very large answer (for example, over 100 atm) would be suspect because an ordinary can or bottle probably could not sustain such high pressures without bursting.

**FOR PRACTICE 14.2** Determine the solubility of oxygen in water at 25 °C exposed to air at 1.0 atm. Assume a partial pressure for oxygen of 0.21 atm.

**WATCH NOW!****KEY CONCEPT VIDEO 14.5**

 Solution Concentration:  
Molarity, Molality, Parts by  
Mass and Volume, Mole  
Fraction

**14.5****Expressing Solution Concentration**

As we have seen, the amount of solute in a solution is an important property of the solution. For example, the amount of sodium chloride in a solution determines whether or not the solution will cause dehydration if consumed. A **dilute solution** contains small quantities of solute relative to the amount of solvent. Drinking

**CHEMISTRY IN THE ENVIRONMENT****Lake Nyos**

**M**ost people living near Lake Nyos in the West African country of Cameroon began August 22, 1986, like any other day. Unfortunately, their day ended in tragedy. On that evening, a large cloud of carbon dioxide gas burped



▲ Lake Nyos, in Cameroon, has a deceptively peaceful appearance; in the summer of 1986, more than 1700 people died around its shores.

up from the depths of Lake Nyos, killing over 1700 people and about 3000 cattle. Two years before, a similar tragedy had occurred in Lake Monoun, just 60 miles away, killing 37 people.



▲ A plumbing system slowly vents carbon dioxide from Lake Nyos.

Today, scientists have taken steps to prevent these lakes from accumulating the carbon dioxide that caused the disasters.

Lake Nyos is a water-filled volcanic crater. Some 50 miles beneath the surface of the lake, molten volcanic rock (magma) produces carbon dioxide gas that seeps into the lake. The carbon dioxide forms a solution with the lake water. The high pressure at the bottom of the deep lake allows the solution to become highly concentrated in carbon dioxide. The 1986 disaster occurred because over time—either because of the high concentration itself or because of some other natural trigger such as a landslide or small earthquake—some gaseous carbon dioxide escaped. The rising bubbles disrupted the stratified layers of lake water, causing water at the bottom of the lake to rise to a region of lower pressure. The drop in pressure decreased the solubility of the carbon dioxide, so more carbon dioxide bubbles formed. This in turn caused more churning and still more carbon dioxide release. The result was a massive cloud of carbon dioxide gas that escaped from the lake. Since carbon dioxide is heavier than air, the carbon dioxide traveled down the sides of the volcano and into the nearby valley, displacing air and asphyxiating many of the local residents.

In an effort to keep these events from recurring, scientists have constructed a piping system that slowly vents carbon dioxide from the lake bottom, preventing the buildup that led to the tragedy.



**QUESTION** Suppose that the water pressure at the bottom of Lake Nyos is 25 atm. What is the solubility of carbon dioxide at that depth?



a dilute sodium chloride solution does not cause dehydration. A **concentrated solution** contains large quantities of solute relative to the amount of solvent. Drinking a concentrated sodium chloride solution does cause dehydration. Common ways of reporting solution concentration include molarity, molality, parts by mass, parts by volume, mole fraction, and mole percent, as summarized in Table 14.5. We have seen two of these units before: molarity in Section 5.2, and mole fraction in Section 6.6. In the following section, we review the terms we have already covered and introduce the new ones.

**TABLE 14.5 ■ Solution Concentration Terms**

Unit	Definition	Units
Molarity (M)	$\frac{\text{amount solute (in mol)}}{\text{volume solution (in L)}}$	$\frac{\text{mol}}{\text{L}}$
Molality (m)	$\frac{\text{amount solute (in mol)}}{\text{mass solvent (in kg)}}$	$\frac{\text{mol}}{\text{kg}}$
Mole fraction ( $\chi$ )	$\frac{\text{amount solute (in mol)}}{\text{total amount of solute and solvent (in mol)}}$	None
Mole percent (mol %)	$\frac{\text{amount solute (in mol)}}{\text{total amount of solute and solvent (in mol)}} \times 100\%$	%
Parts by mass	$\frac{\text{mass solute}}{\text{mass solution}} \times \text{multiplication factor}$	
Percent by mass (%)	Multiplication factor = 100	%
Parts per million by mass (ppm)	Multiplication factor = $10^6$	ppm
Parts per billion by mass (ppb)	Multiplication factor = $10^9$	ppb
Parts by volume (%), ppm, ppb)	$\frac{\text{volume solute}}{\text{volume solution}} \times \text{multiplication factor}^*$	

\*Multiplication factors for parts by volume are identical to those for parts by mass.

## Molarity

The **molarity (M)** of a solution is the amount of solute (in moles) divided by the volume of solution (in liters):

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

Note that molarity is moles of solute per liter of *solution*, not per liter of solvent. To make a solution of a specified molarity, we usually put the solute into a flask and then add water (or another solvent) to the desired volume of solution, as shown in Figure 14.13▶. Molarity is a convenient unit to use when making, diluting, and transferring solutions because it specifies the amount of solute per unit of solution.

Molarity depends on volume, and because volume varies with temperature, molarity also varies with temperature. For example, a 1 M aqueous solution at room temperature is slightly less than 1 M at an elevated temperature because the volume of the solution is slightly greater at the elevated temperature.

**► FIGURE 14.13** Preparing**a Solution of Known**

**Concentration** To make a 1 M NaCl solution, we add 1 mol of the solid to a flask and dilute with water to make 1 L of solution.

Molality is abbreviated with a lowercase italic *m*, and molarity is abbreviated with a capital M.

**ANSWER NOW!**

## 14.7 Cc Conceptual Connection

**MOLALITY** If you combine 25.0 g of a solute that has a mass of 25.0 g/mol with 100.0 g of a solvent, what is the molality of the resulting solution?

- (a) 0.25 *m*      (b) 10.0 *m*      (c) 1.0 *m*      (d) 8.0 *m*

**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 concentration of the solution determines the best parts by mass unit (and therefore the multiplication factor) to use. 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.

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.

## 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:



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



### WATCH NOW!

### INTERACTIVE WORKED EXAMPLE 14.3

#### EXAMPLE 14.3 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.

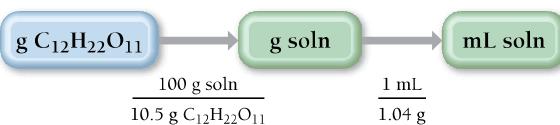
**GIVEN:** 78.5 g  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$   
10.5%  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  by mass  
density = 1.04 g/mL

**FIND:** mL

—Continued on the next page

Continued—

**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.

**CONCEPTUAL PLAN****RELATIONSHIPS USED**

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

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

**SOLVE** Begin with 78.5 g C<sub>12</sub>H<sub>22</sub>O<sub>11</sub> 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 ≈ 10 × 78.5).

**FOR PRACTICE 14.3** What mass of sucrose (C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>), 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 14.3** 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 × 10<sup>2</sup> mg of chlorobenzene? (Assume a density of 1.00 g/mL.)

**Mole Fraction and Mole Percent**

The mole fraction can also be defined for the solvent:

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

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 × 100 percent

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



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 named the Stockholm Convention on Persistent Organic Pollutants was signed in 2001. It targeted 12 such substances referred to as the “dirty dozen” (Table 14.6).

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 nonpolar, these chemicals are stored and concentrated in the

**TABLE 14.6 ■ 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



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



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.

For example, the use of DDT nearly drove the bald eagle (whose egg shells were greatly weakened by eating fish contaminated with DDT) to extinction. In 1963, the population dwindled to less than 500 nesting pairs. Fortunately, nearly all



▲ The bald eagle was nearly driven to extinction by human use of DDT. Bald eagles eat fish, which became contaminated due to bioamplification. The DDT consumed with the fish caused the eagle's egg shells to become fragile. The DDT ban has allowed the bald eagle population to recover.

intentional production of DDT (and the other chemicals on this list) has been banned. The bald eagle population has recovered to an estimated 10,000 nesting pairs. The recovery has been so strong that the bald eagle has been removed from both the endangered and threatened species lists.

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 14.7 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.

**TABLE 14.7 ■ 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 chemical in Table 14.7 at the MCL is present in 715 L of water, the approximate amount of water consumed by an adult in one year.



### WATCH NOW!

### INTERACTIVE WORKED EXAMPLE 14.4



## EXAMPLE 14.4 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. Calculate the concentration of the solution 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.

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

$$\begin{aligned} \text{Molarity (M)} &= \frac{\text{amount solute (in mol)}}{\text{volume solution (in L)}} \\ &= \frac{0.2771 \text{ mol } C_2H_6O_2}{0.515 \text{ L solution}} \\ &= 0.538 \text{ M} \end{aligned}$$

—Continued on the next page

Continued—

<p><b>(b)</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.</p>	$\text{Molality } (m) = \frac{\text{amount solute (in mol)}}{\text{mass solvent (in kg)}}$ $= \frac{0.2771 \text{ mol C}_2\text{H}_6\text{O}_2}{0.500 \text{ kg H}_2\text{O}}$ $= 0.554 \text{ m}$
<p><b>(c)</b> 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%.</p>	$\text{Percent by mass} = \frac{\text{mass solute}}{\text{mass solution}} \times 100\%$ $= \frac{17.2 \text{ g}}{17.2 \text{ g} + 5.00 \times 10^2 \text{ g}} \times 100\%$ $= 3.33\%$
<p><b>(d)</b> 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.</p>	$\text{mol H}_2\text{O} = 5.00 \times 10^2 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}}$ $= 27.75 \text{ mol H}_2\text{O}$ $\chi_{\text{solute}} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}}$ $= \frac{0.2771 \text{ mol}}{0.2771 \text{ mol} + 27.75 \text{ mol}}$ $= 9.89 \times 10^{-3}$
<p><b>(e)</b> To calculate mole percent, multiply the mole fraction by 100%.</p>	$\text{mol \%} = \chi_{\text{solute}} \times 100\%$ $= 0.989\%$

**FOR PRACTICE 14.4** A solution is prepared by dissolving 50.4 g sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) 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

### WATCH NOW!

### INTERACTIVE WORKED EXAMPLE 14.5

## EXAMPLE 14.5 Converting between Concentration Units

What is the molarity of a 6.56% by mass glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) solution? (The density of the solution is 1.03 g/mL.)



<p><b>SORT</b> 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.</p>	<p><b>GIVEN:</b> 6.56% <math>\text{C}_6\text{H}_{12}\text{O}_6</math> density = 1.03 g/mL</p> <p><b>FIND:</b> M</p>
<p><b>STRATEGIZE</b> 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 <math>\text{C}_6\text{H}_{12}\text{O}_6</math> to mol <math>\text{C}_6\text{H}_{12}\text{O}_6</math>. Convert the denominator from g solution to mL of solution and then to L solution. Divide the numerator (now in mol) by the denominator (now in L) to obtain molarity.</p>	<p><b>CONCEPTUAL PLAN</b></p>

	<b>RELATIONSHIPS USED</b>
	$\frac{6.56 \text{ g C}_6\text{H}_{12}\text{O}_6}{100 \text{ g soln}}$ (percent by mass written as ratio)
	$\frac{1 \text{ mol}}{180.16 \text{ g C}_6\text{H}_{12}\text{O}_6}$ (from molar mass of glucose)
	$\frac{1 \text{ mL}}{1.03 \text{ g}}$ (from given density of the solution)
<b>SOLVE</b>	Begin with the numerator ( $6.56 \text{ g C}_6\text{H}_{12}\text{O}_6$ ) and use the molar mass to convert to mol $\text{C}_6\text{H}_{12}\text{O}_6$ .
	Convert the denominator (100 g solution) into mL of solution (using the density) and then to L of solution.
	Finally, divide mol $\text{C}_6\text{H}_{12}\text{O}_6$ by L solution to arrive at molarity.
<b>CHECK</b>	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.
<b>FOR PRACTICE 14.5</b>	What is the molarity of a 10.5% by mass glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) solution? (The density of the solution is 1.03 g/mL.)
<b>FOR MORE PRACTICE 14.5</b>	What is the molality of a 10.5% by mass glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) solution? (The density of the solution is 1.03 g/mL.)

**14.6****Colligative Properties: Vapor Pressure Lowering, Freezing Point Depression, Boiling Point Elevation, and Osmotic Pressure**

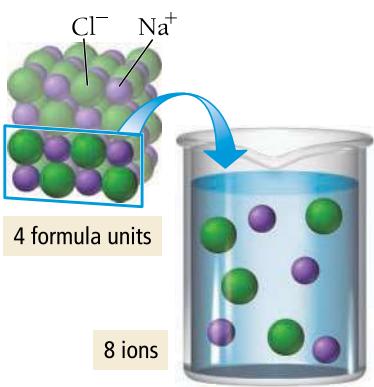
Have you ever wondered why you add salt to the ice in an ice-cream maker? Or why salt is scattered on icy roads in cold climates? Salt lowers the temperature at which a saltwater solution freezes. A salt and water solution remains liquid even below 0 °C. When salt is added to ice in the ice-cream maker, 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

**WATCH NOW!****KEY CONCEPT VIDEO 14.6**

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

**► FIGURE 14.14**  $\text{NaCl}$  in Water

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

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 14.14). For example, when 1 mol of  $\text{NaCl}$  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 nonelectrolyte solutions; we expand the concept to include electrolyte solutions in Section 14.7.

## Vapor Pressure Lowering

Recall from Section 12.5 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). How does a nonvolatile nonelectrolyte solute affect 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.

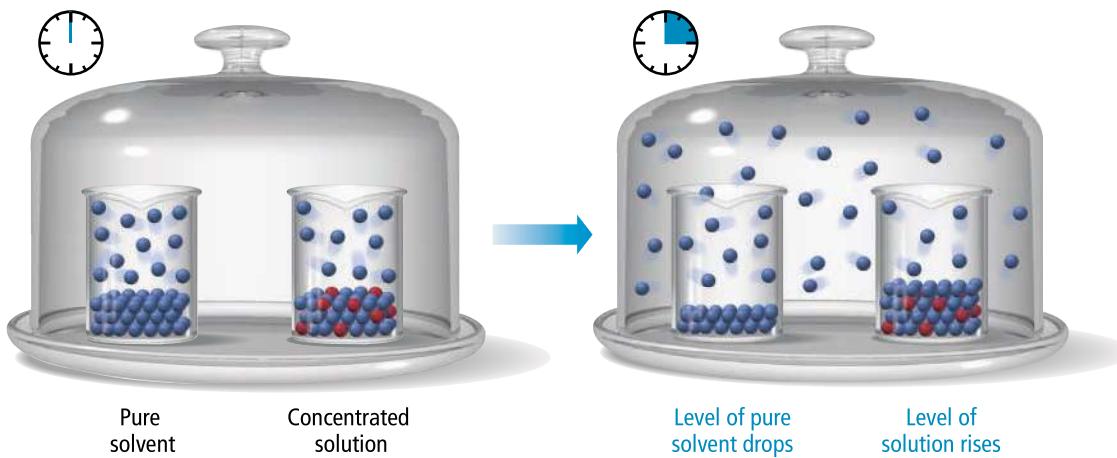
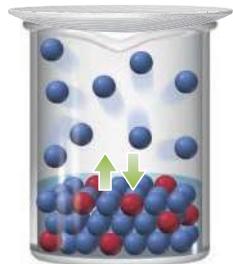
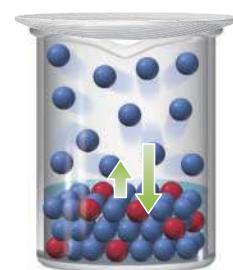
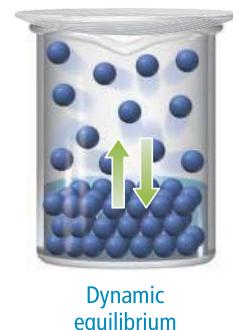
The simplest explanation for why the vapor pressure of a solution is lower than that of the pure solvent is related to the concept of dynamic equilibrium itself. Consider the following representation of a liquid in dynamic equilibrium with its vapor. Here the rate of vaporization is equal to the rate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

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:

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 14.1 and 14.2. 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 0.900 mol of water and 0.100 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:

$$\begin{aligned} P_{\text{solution}} &= \chi_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}^{\circ} \\ &= 0.900(23.8 \text{ torr}) \\ &= 21.4 \text{ torr} \end{aligned}$$

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.

**SOLUTION VAPOR PRESSURE** What is the vapor pressure of a solution in which the mole fraction of the solute is 0.200 and the vapor pressure of the pure solvent is 100.0 torr? (Assume a single nonvolatile, nonelectrolyte solute).

- (a) 20.0 torr      (b) 80.0 torr      (c) 100.0 torr      (d) 120.0 torr

14.8

**Cc**

Conceptual Connection

ANSWER NOW!



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:

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

$$P_{\text{solution}} = (1 - \chi_{\text{solute}}) P_{\text{solvent}}^{\circ}$$

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

$$\Delta P = \chi_{\text{solute}} P_{\text{solvent}}^{\circ}$$

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

WATCH NOW!

## INTERACTIVE WORKED EXAMPLE 14.6

**EXAMPLE 14.6****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 ( $C_{12}H_{22}O_{11}$ ) and 300.0 mL water. The vapor pressure of pure water at 25 °C is 23.8 torr. Assume the density of water is 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.

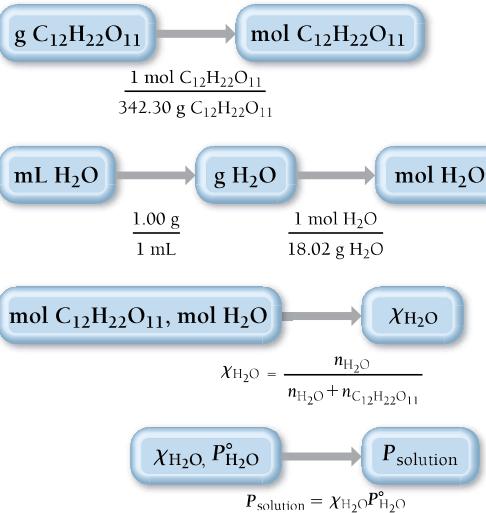
**SOLVE** Calculate the number of moles of each solution component.

Use the number of moles of each component to calculate the mole fraction of the solvent ( $H_2O$ ).

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

**GIVEN:** 99.5 g  $C_{12}H_{22}O_{11}$   
300.0 mL  $H_2O$   
 $P_{H_2O}^\circ = 23.8$  torr at 25 °C  
 $d_{H_2O} = 1.00$  g/mL

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

**CONCEPTUAL PLAN****SOLUTION**

$$99.5 \text{ g } C_{12}H_{22}O_{11} \times \frac{1 \text{ mol } C_{12}H_{22}O_{11}}{342.30 \text{ g } C_{12}H_{22}O_{11}} = 0.2907 \text{ mol } C_{12}H_{22}O_{11}$$

$$300.0 \text{ mL } H_2O \times \frac{1.00 \text{ g}}{1 \text{ mL}} \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 16.65 \text{ mol } H_2O$$

$$\begin{aligned} \chi_{H_2O} &= \frac{n_{H_2O}}{n_{C_{12}H_{22}O_{11}} + n_{H_2O}} \\ &= \frac{16.65 \text{ mol}}{0.2907 \text{ mol} + 16.65 \text{ mol}} \\ &= 0.9828 \end{aligned}$$

$$\begin{aligned} P_{\text{solution}} &= \chi_{H_2O} P_{H_2O}^\circ \\ &= 0.9828 (23.8 \text{ torr}) \\ &= 23.4 \text{ torr} \end{aligned}$$

**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 14.6** Calculate the vapor pressure at 25 °C of a solution containing 55.3 g ethylene glycol ( $HOCH_2CH_2OH$ ) and 285.2 g water. The vapor pressure of pure water at 25 °C is 23.8 torr.

**FOR MORE PRACTICE 14.6** A solution containing ethylene glycol and water has a vapor pressure of 7.88 torr at 10 °C. Pure water has a vapor pressure of 9.21 torr at 10 °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 solution component 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 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:

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

Figure 14.15(a) is a plot of vapor pressure versus solution composition for an ideal two-component solution.

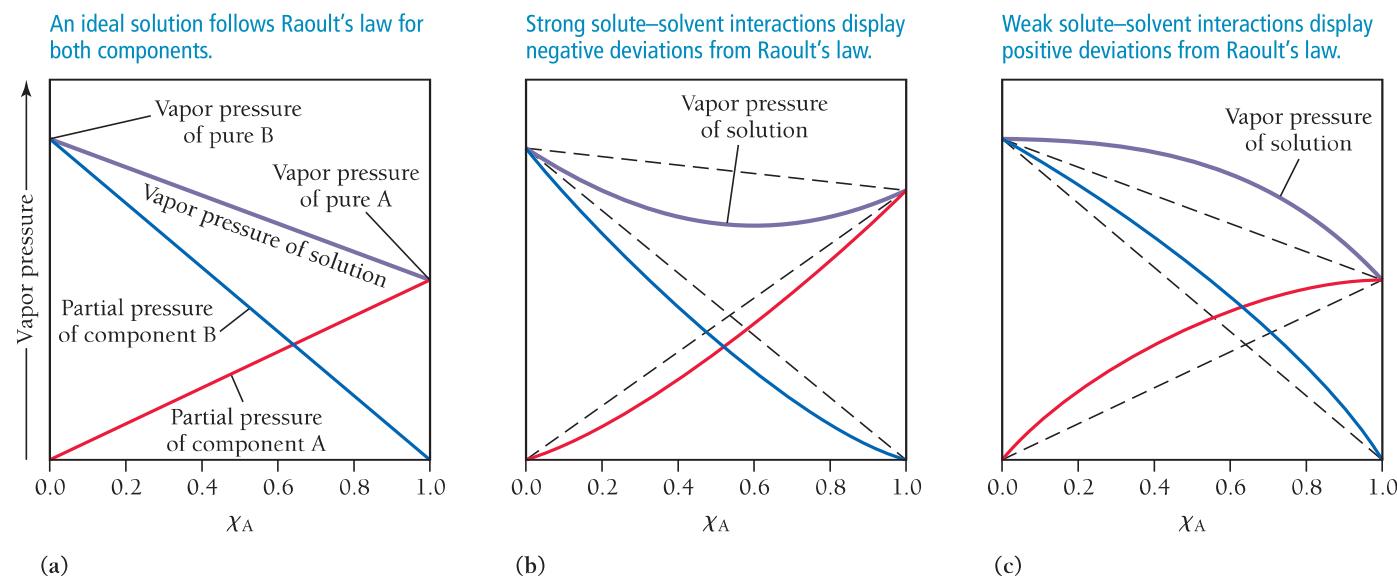
In a nonideal solution, the solute–solvent interactions are either stronger or weaker than the solvent–solvent interactions.

For example, 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 14.15(b).

If, however, 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 14.15(c).

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.

### Deviations from Raoult's Law



**▲ FIGURE 14.15** Behavior of Ideal and Nonideal Solutions (a) Ideal behavior (b) Strong solute-solvent interactions (c) Weak solute-solvent interactions (The dashed lines in parts b and c represent ideal behavior.)

**EXAMPLE 14.7** 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 ( $\text{CH}_3\text{COCH}_3$ ). At 35 °C the vapor pressures of pure carbon disulfide and pure acetone are 515 torr and 332 torr, respectively. Assuming ideal behavior, calculate the vapor pressures of each component 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?

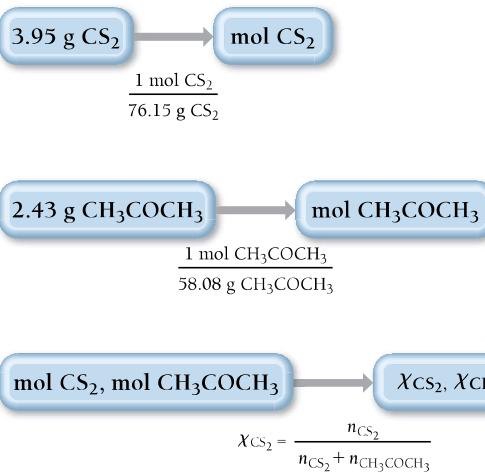
**SORT** You are given the masses and vapor pressures of carbon disulfide and acetone and are asked to find the vapor pressures of each component in the mixture and the total pressure assuming ideal behavior.

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

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

**STRATEGIZE** This problem requires that you use Raoult's law to calculate the partial pressures of each component. In order to use Raoult's law, 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.

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.

**CONCEPTUAL PLAN**


$$\chi_{\text{CS}_2} = \frac{n_{\text{CS}_2}}{n_{\text{CS}_2} + n_{\text{CH}_3\text{COCH}_3}}$$

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

**RELATIONSHIPS USED**

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

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

**SOLVE** Begin by converting the mass of each component to the amounts in moles.

**SOLUTION**

$$3.95 \text{ g } \text{CS}_2 \times \frac{1 \text{ mol } \text{CS}_2}{76.15 \text{ g } \text{CS}_2} = 0.05187 \text{ mol } \text{CS}_2$$

$$2.43 \text{ g } \text{CH}_3\text{COCH}_3 \times \frac{1 \text{ mol } \text{CH}_3\text{COCH}_3}{58.08 \text{ g } \text{CH}_3\text{COCH}_3} = 0.04184 \text{ mol } \text{CH}_3\text{COCH}_3$$

Then calculate the mole fraction of carbon disulfide.

$$\begin{aligned}\chi_{\text{CS}_2} &= \frac{n_{\text{CS}_2}}{n_{\text{CS}_2} + n_{\text{CH}_3\text{COCH}_3}} \\ &= \frac{0.05187 \text{ mol}}{0.05187 \text{ mol} + 0.04184 \text{ mol}} \\ &= 0.5535\end{aligned}$$

Calculate the mole fraction of acetone by subtracting the mole fraction of carbon disulfide from 1.

$$\begin{aligned}\chi_{\text{CH}_3\text{COCH}_3} &= 1 - 0.5535 \\ &= 0.4465\end{aligned}$$

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.

$$\begin{aligned}P_{\text{CS}_2} &= \chi_{\text{CS}_2} P_{\text{CS}_2}^{\circ} \\ &= 0.5535 \text{ (515 torr)} \\ &= 285 \text{ torr} \\ P_{\text{CH}_3\text{COCH}_3} &= \chi_{\text{CH}_3\text{COCH}_3} P_{\text{CH}_3\text{COCH}_3}^{\circ} \\ &= 0.4465 \text{ (332 torr)} \\ &= 148 \text{ torr}\end{aligned}$$

Calculate the total pressure by summing the partial pressures.

$$\begin{aligned}P_{\text{tot}}(\text{ideal}) &= 285 \text{ torr} + 148 \text{ torr} \\ &= 433 \text{ torr}\end{aligned}$$

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.

$$\begin{aligned}P_{\text{tot}}(\text{exp}) &= 645 \text{ torr} \\ P_{\text{tot}}(\text{exp}) &> P_{\text{tot}}(\text{ideal})\end{aligned}$$

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.

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

**FOR PRACTICE 14.7** A solution of benzene ( $\text{C}_6\text{H}_6$ ) and toluene ( $\text{C}_7\text{H}_8$ ) is 25.0% benzene by mass. At  $25^\circ\text{C}$  the vapor pressures of pure benzene and pure toluene 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?

**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?

- (a) Solute–solvent interactions > solute–solute and solvent–solvent interactions
- (b) Solute–solvent interactions = solute–solute and solvent–solvent interactions
- (c) Solute–solute and solvent–solvent interactions > solute–solvent interactions



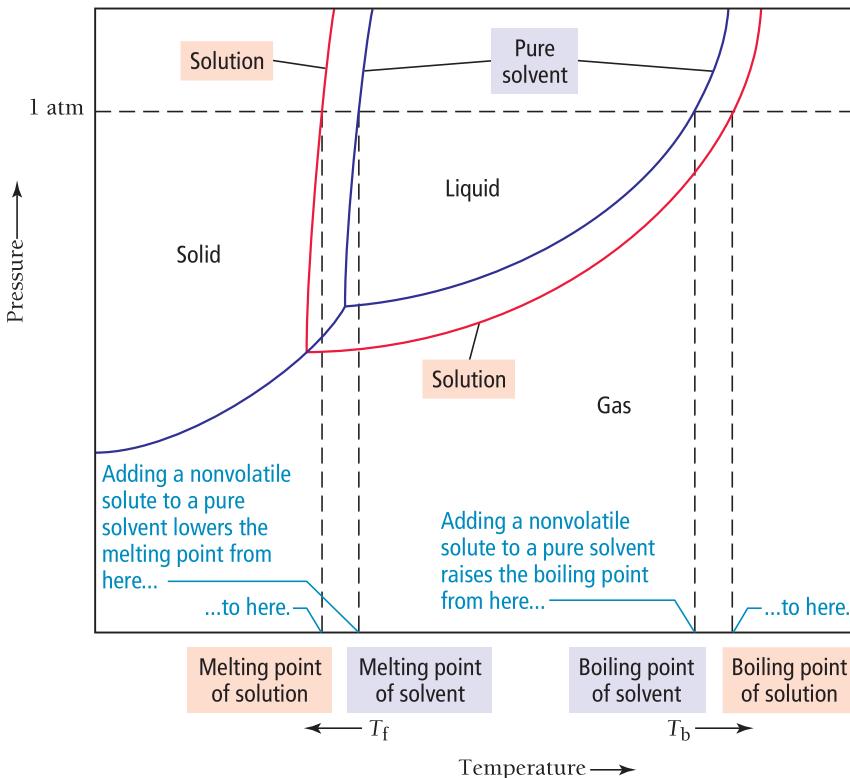
ANSWER NOW!



## 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 and to the left 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**, respectively, 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:

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

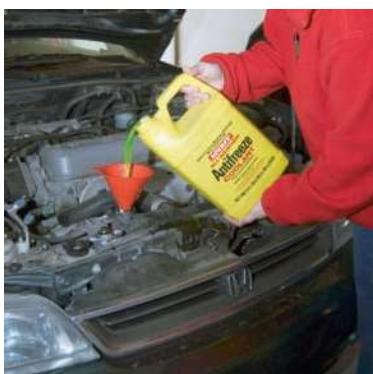
where

- $\Delta T_f$  is the change in temperature of the freezing point in degrees Celsius (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; and
- $K_f$  is the freezing point depression constant for the solvent.

For water,

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

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 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 saltwater 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.



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

**TABLE 14.8 ■ 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

Table 14.8 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 14.8 demonstrates.

### EXAMPLE 14.8 Freezing Point Depression

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

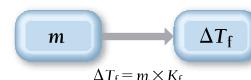
**SORT** You are given the molality of a solution and asked to find its freezing point.

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

**GIVEN:** 1.7 *m* solution

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

**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 14.8** 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 boiling points rise 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 degrees Celsius (relative to the boiling point of the pure solvent);
- *m* is the molality of the solution in moles solute per kilogram solvent; and
- $K_b$  is the boiling point elevation constant for the solvent.

ANSWER NOW!

14.10  
Cc

Conceptual Connection

For water,

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

Calculating the boiling point of a solution involves substituting into the boiling point elevation equation, as Example 14.9 demonstrates.

ANSWER NOW!

**BOILING POINT ELEVATION** Solution A is a  $1.0 \text{ m}$  solution with a nonionic solute and water as the solvent. Solution B is a  $1.0 \text{ m}$  solution with the same nonionic solute and ethanol as the solvent. Which solution has the greater increase in its boiling point (relative to the pure solvent)?

- (a) Solution A      (b) Solution B

WATCH NOW!

INTERACTIVE WORKED EXAMPLE 14.9

**EXAMPLE 14.9** Boiling Point Elevation

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



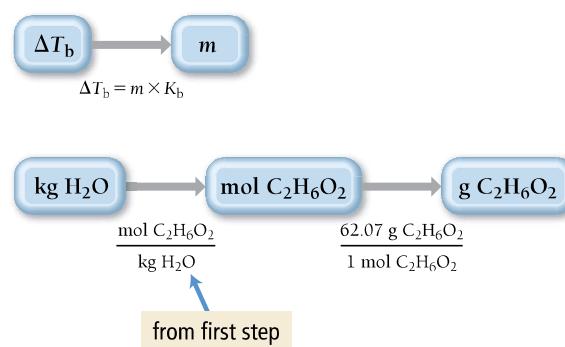
**SORT** You are given the desired boiling point of an ethylene glycol solution containing  $1.0 \text{ kg}$  of water and asked to find the mass of ethylene glycol you need to add to raise the boiling point.

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

**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 =  $62.07 \text{ g/mol}$

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

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

**SOLUTION**

$$\begin{aligned} \Delta T_b &= m \times K_b \\ m &= \frac{\Delta T_b}{K_b} = \frac{5.0 \text{ } ^\circ\text{C}}{0.512 \frac{\text{ } ^\circ\text{C}}{\text{m}}} \\ &= 9.77 \text{ m} \end{aligned}$$

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

**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 14.9** Calculate the boiling point of a  $3.60 \text{ m}$  aqueous sucrose solution.



## CHEMISTRY IN YOUR DAY | Antifreeze in Frogs

**W**ood 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 12.9, 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.

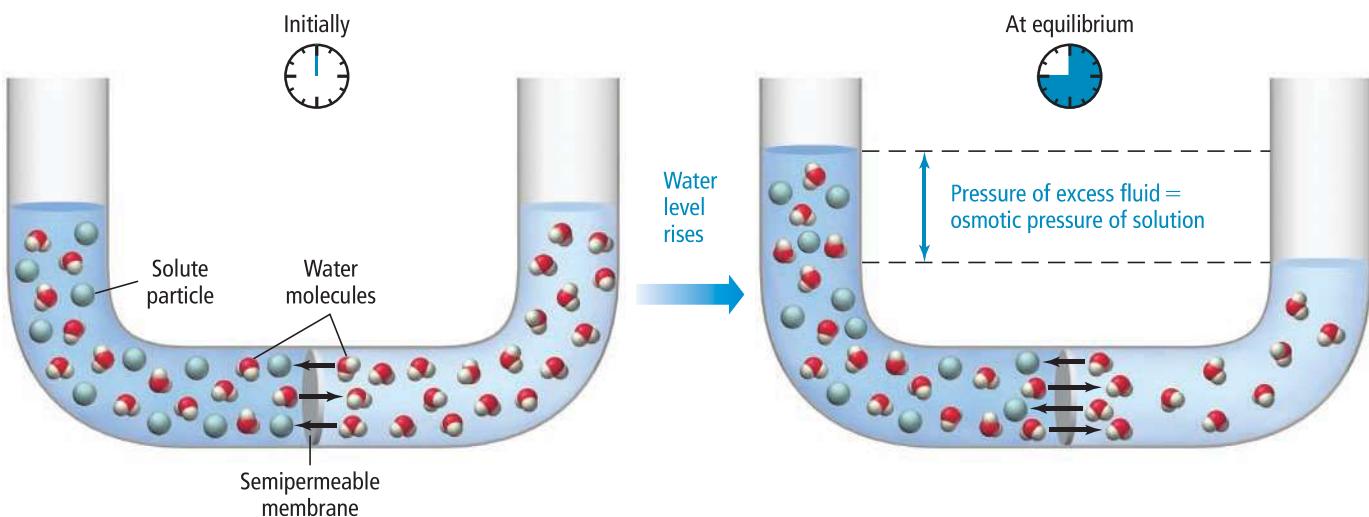
## Osmotic Pressure

The process by which seawater causes dehydration (discussed in Section 14.1) 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 14.16▼ 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 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

### Osmosis and Osmotic Pressure



▲ **FIGURE 14.16** An Osmosis Cell In an osmosis cell, water flows from the pure-water side of the cell through the semipermeable membrane to the saltwater side.

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 side, this process can be opposed and even reversed. 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,  $R$  is the ideal gas constant ( $0.08206 \text{ L} \cdot \text{atm/mol} \cdot \text{K}$ ), and  $T$  is the temperature (in Kelvin).

### EXAMPLE 14.10 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 told 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

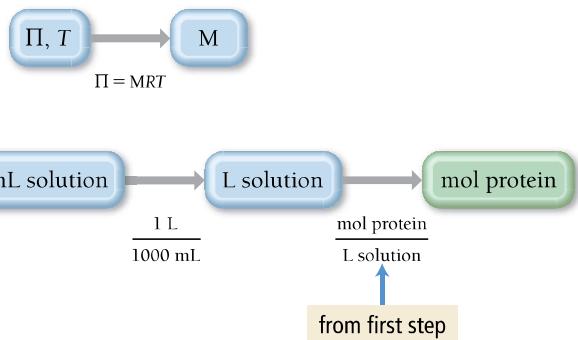
10.0 mL solution

$\Pi = 2.45 \text{ torr}$

$T = 25^\circ\text{C}$

**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

$$\Pi = MRT$$

$$M = \frac{\Pi}{RT} = \frac{2.45 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}}}{0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} (298 \text{ K})} = 1.318 \times 10^{-4} \text{ M}$$

$$10.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{1.318 \times 10^{-4} \text{ mol}}{1 \text{ L}} = 1.318 \times 10^{-6} \text{ mol}$$

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

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

**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 14.10** 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.

## 14.7

### Colligative Properties of Strong Electrolyte Solutions

At the beginning of Section 14.6, we saw that colligative properties depend on the number of dissolved particles and that we must therefore treat electrolytes 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 for a 0.010 *m* NaCl solution the van't Hoff factor is 1.94. The van't Hoff factor approaches the expected value at infinite dilution (as the concentration approaches zero). Table 14.9 lists the actual and expected van't Hoff factors for a number of solutes.

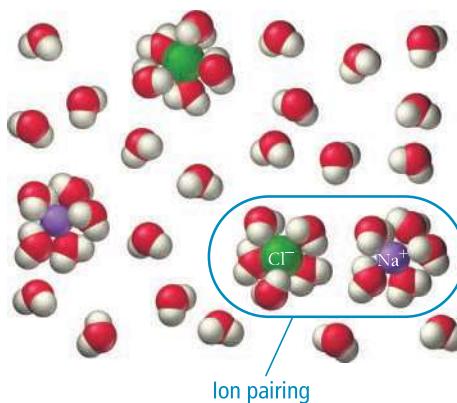
The reason that van't Hoff factors do not exactly equal expected values is that some ions effectively pair in solution. We expect the dissociation of an ionic compound to be complete in solution. In reality, however, the dissociation is not complete—at any moment, some cations pair with anions (Figure 14.17►), 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 14.17 Ion Pairing**  
Hydrated anions and cations may get close enough together to effectively pair, lowering the concentration of particles below what would be expected.

**COLLIGATIVE PROPERTIES** Which aqueous 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  $\text{MgCl}_2$

**14.11**  
**Cc**  
Conceptual Connection

ANSWER NOW!



**EXAMPLE 14.11** Van't Hoff Factor and Freezing Point Depression

The freezing point of an aqueous 0.050  $m$   $\text{CaCl}_2$  solution is  $-0.27^\circ\text{C}$ . 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.

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

**FIND:**  $i$

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

**CONCEPTUAL PLAN**

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

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

**SOLUTION**

$$\begin{aligned} \Delta T_f &= im \times K_f \\ i &= \frac{\Delta T_f}{m \times K_f} \\ &= \frac{0.27^\circ\text{C}}{0.050 \text{ } m \times \frac{1.86^\circ\text{C}}{m}} \\ &= 2.9 \end{aligned}$$

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. Because of ion pairing, the experimental value is slightly less than 3.

**CHECK** The answer has no units, which is 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 14.11** Calculate the freezing point of an aqueous 0.10  $m$   $\text{FeCl}_3$  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 non-electrolyte 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 we demonstrate in Example 14.12.

**WATCH NOW!**

**INTERACTIVE WORKED EXAMPLE 14.12**

**Calculating the Vapor Pressure of a Solution Containing an Ionic Solute****EXAMPLE 14.12**

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

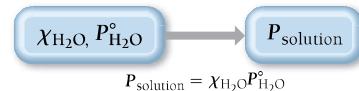
**GIVEN:** 0.102 mol  $\text{Ca}(\text{NO}_3)_2$

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

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

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

**STRATEGIZE** To solve this problem, use Raoult's law as you did in Example 14.6. Calculate  $\chi_{\text{solvent}}$  from the given amounts of solute and solvent.

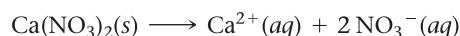
**CONCEPTUAL PLAN**

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

Since 1 mol of calcium nitrate dissociates into 3 mol of dissolved particles, multiply the number of moles of calcium nitrate by 3 when calculating 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**



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

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

**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 14.12** 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. (Assume that the solute completely dissociates.)

## Colligative Properties and Medical Solutions

Doctors and other health care 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 14.18(b)▼). 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 14.18(c)▼).

Normal red blood cells.



(a) Isosmotic solution

Red blood cells in a concentrated solution: water flows out of cells.



(b) Hyperosmotic solution

Red blood cells in pure water: water flows into cells.



(c) Hyposmotic solution

**▲ FIGURE 14.18 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 shrivel. 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 as body fluids.

## 14.8 Colloids

When you mix water and soap together, the resulting mixture has a distinctive haze (Figure 14.19◀). 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 14.10.

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 slowly settles 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 14.20▶. 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 14.21▶. One end of the molecule is ionic and therefore interacts strongly with water molecules via ion-dipole interactions. The other end of the soap molecule is a long, nonpolar, hydrocarbon tail.

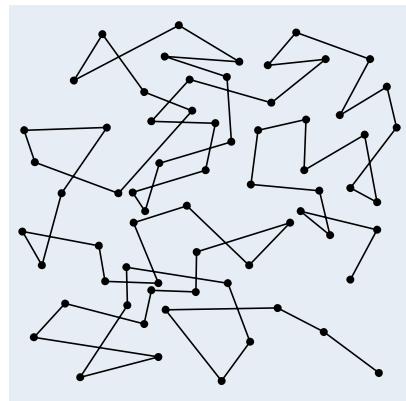


**▲ FIGURE 14.19 A Colloid**  
Soapy water is an example of a colloidal dispersion. The haze is due to the scattering of light by the colloidal particles.

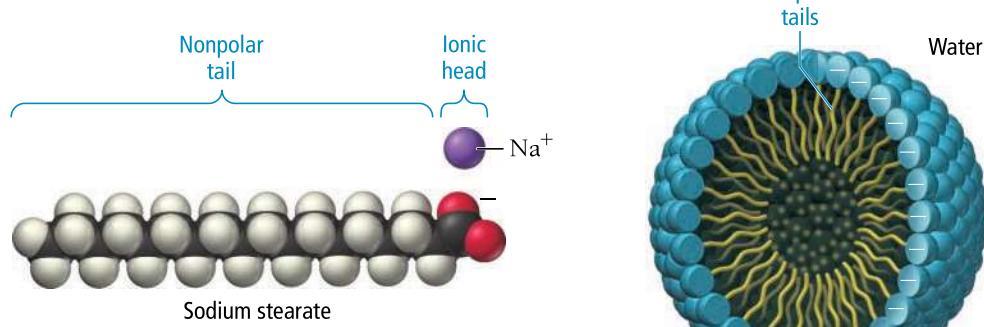
**TABLE 14.10** ■ Types of Colloidal Dispersions

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)

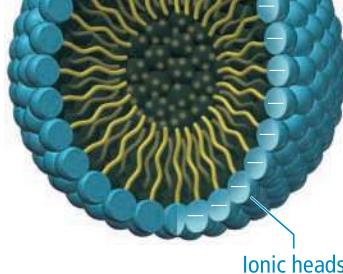
When enough soap is added to water, the soap molecules aggregate in structures called *micelles* (Figure 14.22▼). In a micelle, the nonpolar hydrocarbon tails crowd into the center of a sphere to maximize their interactions with one another. The ionic heads orient toward the surface of the sphere where 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 types of colloids do).



**▲ FIGURE 14.20** **Brownian Motion** A colloidal particle exhibits Brownian motion (Section 2.1), moving in a jerky, haphazard path as it undergoes collisions with molecules in the liquid.



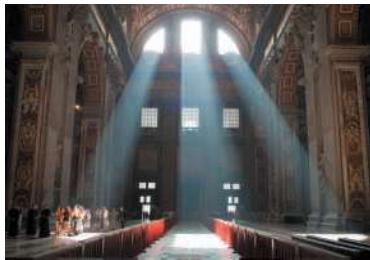
**▲ FIGURE 14.21** **Soap Molecule Structure** A soap molecule has a charged ionic head and a long nonpolar hydrocarbon tail.



**▲ FIGURE 14.22** **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 14.23 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 a noncolloidal solution (right), nor would it be visible in pure water.

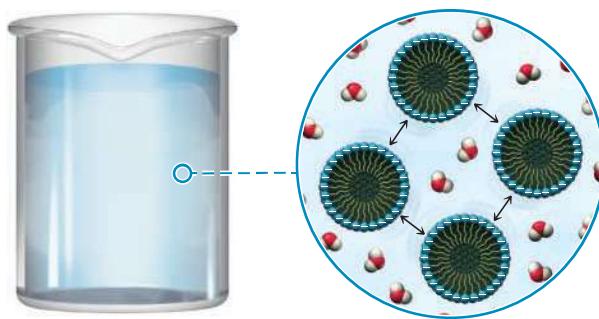


**▲** Light beams are invisible when they are not scattered by colloidal dispersed particles such as dust or mist in the air.

This scattering of light by a colloidal dispersion is known as the **Tyndall effect** (Figure 14.23▲). 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 14.24▼). 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, a solution containing hemoglobin is a colloid. The hemoglobin molecules are so large that they scatter light.



**▲ FIGURE 14.24 Micelle Repulsions** Micelles do not coalesce because the charged surface of one micelle repels the charged surface of another.

# Self-Assessment Quiz



- Q1.** Which compound do you expect to be most soluble in octane ( $C_8H_{18}$ )? **MISSED THIS?** *Read Section 14.2*
- $CH_3OH$
  - $CBr_4$
  - $H_2O$
  - $NH_3$
- Q2.** An aqueous solution is saturated in both potassium chloride and carbon dioxide gas at room temperature. What happens when the solution is warmed to  $85^\circ C$ ?
- MISSED THIS?** *Read Section 14.4; Watch KCV 14.4*
- Potassium chloride precipitates out of solution.
  - Carbon dioxide bubbles out of solution.
  - Potassium chloride precipitates out of solution and carbon dioxide bubbles out of solution.
  - 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  $1.3 \times 10^{-3} M/atm$ .)
- MISSED THIS?** *Read Section 14.4; Watch IWE 14.2*
- 15.7 g
  - $6.5 \times 10^{-3}$  g
  - 0.041 g
  - 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?
- MISSED THIS?** *Read Section 14.5; Watch IWE 14.3*
- 2.78 g
  - 2.70 g
  - 4.88 g
  - 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.) **MISSED THIS?** *Read Section 14.5; Watch KCV 14.5; Watch IWE 14.4*
- 0.238 m
  - 44.8 m
  - 0.249 m
  - 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. **MISSED THIS?** *Read Section 14.5; Watch KCV 14.5; Watch IWE 14.5*
- 1.44 M
  - 12.8 M
  - 6.67 M
  - 1.50 M
- Q7.** Determine the vapor pressure at  $25^\circ C$  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. **MISSED THIS?** *Read Section 14.6; Watch KCV 14.6; Watch IWE 14.6*
- 3.52 torr
  - 22.7 torr
  - 1.14 torr
  - 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?
- MISSED THIS?** *Read Section 14.6*
- 110 mmHg
  - 209 mmHg
  - 99.3 mmHg
  - 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  $-4.2^\circ C$ ? **MISSED THIS?** *Read Section 14.6; Watch KCV 14.6; Watch IWE 14.9*
- 0.023 kg
  - 4.1 kg
  - 0.41 kg
  - 14.1 kg
- Q10.** Which of these aqueous solutions has the highest boiling point? **MISSED THIS?** *Read Section 14.6; Watch KCV 14.6*
- 1.25 M  $C_6H_{12}O_6$
  - 1.25 M  $KNO_3$
  - 1.25 M  $Ca(NO_3)_2$
  - 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.
- MISSED THIS?** *Read Section 14.6*
- 246 g/mol
  - 3.85 g/mol
  - $2.93 \times 10^3$  g/mol
  - 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? **MISSED THIS?** *Read Section 14.3*
- $|\Delta H_{\text{solute}}| > |\Delta H_{\text{hydration}}|$
  - $|\Delta H_{\text{solute}}| < |\Delta H_{\text{hydration}}|$
  - $|\Delta H_{\text{solute}}| = |\Delta H_{\text{hydration}}|$
  - 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.
- MISSED THIS?** *Read Section 14.7*
- 2.8
  - 83
  - 0.73
  - 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)?
- MISSED THIS?** *Read Section 14.6*
- The intermolecular forces between particles A and B are *weaker* than those between particles of A and those between particles of B.
  - The intermolecular forces between particles A and B are *stronger* than those between particles of A and those between particles of B.
  - The intermolecular forces between particles A and B are *the same as* those between particles of A and those between particles of B.
  - Nothing can be concluded about the relative strengths of intermolecular forces from this observation.

—Continued on the next page

Continued—

- Q15.** An aqueous solution at 25 °C 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.

**MISSED THIS?** Read Section 14.4

- a)  $[O_2] > [N_2] > [He]$       b)  $[He] > [N_2] > [O_2]$   
 c)  $[N_2] > [He] > [O_2]$       d)  $[N_2] > [O_2] > [He]$

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

## CHAPTER 14 IN REVIEW

### TERMS

#### Section 14.1

- solution (580)  
 solvent (580)  
 solute (580)

#### Section 14.2

- aqueous solution (581)  
 solubility (581)  
 entropy (582)  
 miscible (583)

#### Section 14.3

- enthalpy of solution  
 $(\Delta H_{soln})$  (587)

#### heat of hydration

$(\Delta H_{hydration})$  (588)

#### Section 14.4

- dynamic equilibrium (590)  
 saturated solution (590)  
 unsaturated solution (590)  
 supersaturated solution (590)  
 recrystallization (591)  
 Henry's law (593)

#### Section 14.5

- dilute solution (594)  
 concentrated solution (595)  
 molarity (M) (595)

#### molality (*m*)

(596)

#### parts by mass (596)

#### percent by mass (596)

#### parts per million (ppm) (597)

#### parts per billion (ppb) (597)

#### parts by volume (597)

#### mole fraction ( $\chi_{solute}$ ) (598)

#### mole percent (mol %) (598)

#### freezing point

depression (608)

#### boiling point elevation (608)

#### osmosis (611)

#### semipermeable

membrane (611)

#### osmotic pressure (612)

#### Section 14.6

#### colligative property (601)

#### Raoult's law (603)

#### vapor pressure lowering

$(\Delta P)$  (603)

#### ideal solution (605)

#### van't Hoff factor (*i*) (613)

#### Section 14.8

- colloidal dispersion  
 (colloid) (616)  
 Tyndall effect (618)

### CONCEPTS

#### Solutions (14.1, 14.2)

- A solution is a homogeneous mixture of two or more substances. In a solution, the majority component is the solvent, and the minority component is the solute.
- The tendency toward greater entropy (or greater energy dispersal) is the driving force for solution formation.
- In aqueous solutions, water is a solvent, and a solid, liquid, or gas is the solute.

#### Solubility and Energetics of Solution Formation (14.2, 14.3)

- The solubility of a substance is the amount of the substance that dissolves in a given amount of solvent. The solubility of one substance in another depends on the types of intermolecular forces that exist *between* the substances as well as *within* each substance.
- We can determine the overall enthalpy change upon solution formation by adding the enthalpy changes for the three steps of solution formation: (1) separation of the solute particles, (2) separation of the solvent particles, and (3) mixing of the solute and solvent particles. The first two steps are both endothermic, whereas the last is exothermic.

- In aqueous solutions of an ionic compound, the combined change in enthalpy for steps 2 and 3 is the heat of hydration ( $\Delta H_{hydration}$ ), which is always negative.

#### Solution Equilibrium (14.4)

- Dynamic equilibrium in a solution occurs when the rates of dissolution and recrystallization in a solution are equal. A solution in this state is saturated. Solutions containing less than or more than the equilibrium amount of solute are unsaturated or supersaturated, respectively.
- The solubility of most solids in water increases with increasing temperature.
- The solubility of gases in water generally decreases with increasing temperature, but it increases with increasing pressure.

#### Concentration Units (14.5)

- Common units to express solution concentration include molarity (M), molality (*m*), mole fraction ( $\chi$ ), mole percent (mol %), percent (%) by mass or volume, parts per million (ppm) by mass or volume, and parts per billion (ppb) by mass or volume. Table 14.5 summarizes these units.

## Vapor Pressure Lowering, Freezing Point Depression, Boiling Point Elevation, and Osmosis (14.6, 14.7)

- The presence of a nonvolatile solute in a liquid results in a lower vapor pressure of the solution relative to the vapor pressure of the pure liquid. Raoult's law for an ideal solution predicts this lower vapor pressure.
- If the solute–solvent interactions are particularly strong, the actual vapor pressure is lower than that predicted by Raoult's law.
- If the solute–solvent interactions are particularly weak, the actual vapor pressure is higher than that predicted by Raoult's law.
- The addition of a nonvolatile solute to a liquid results in a solution with a lower freezing point and a higher boiling point than those of the pure solvent.
- The flow of solvent from a solution of lower concentration to a solution of higher concentration is osmosis.

## EQUATIONS AND RELATIONSHIPS

Henry's Law: Solubility of Gases with Increasing Pressure (14.4)

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

Molarity (M) of a Solution (14.5)

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

Molality (m) of a Solution (14.5)

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

Concentration of a Solution in Parts by Mass and Parts by Volume (14.5)

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

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

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

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

Concentration of a Solution in Mole Fraction ( $\chi$ ) and Mole Percent (14.5)

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

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

- All of these phenomena (vapor pressure lowering, freezing point depression, boiling point elevation, and osmosis) are colligative properties and depend only on the number of solute particles added, not the type of solute particles.
- Electrolyte solutes have a greater effect on these properties than the corresponding amount of a nonelectrolyte solute as specified by the van't Hoff factor.

## Colloids (14.8)

- A colloid is a mixture in which a substance is finely divided in a dispersing medium.
- Colloidal mixtures occur when the dispersed substance ranges in size from 1 nm to 1000 nm.
- One way to identify colloidal mixtures is by their tendency to scatter light, known as the Tyndall effect.

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 ( $P_{\text{solvent}}^{\circ}$ ) (14.6)

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

The Vapor Pressure of a Solution Containing Two Volatile Components (14.6)

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

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

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

Relationship between Freezing Point Depression ( $\Delta T_f$ ), Molality ( $m$ ), and Freezing Point Depression Constant ( $K_f$ ) (14.6)

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

Relationship between Boiling Point Elevation ( $\Delta T_b$ ), Molality ( $m$ ), and Boiling Point Elevation Constant ( $K_b$ ) (14.6)

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

Relationship between Osmotic Pressure ( $\Pi$ ), Molarity (M), the Ideal Gas Constant ( $R$ ), and Temperature ( $T$ , in K) (14.6)

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

van't Hoff Factor ( $i$ ): Ratio of Moles of Particles in Solution to Moles of Formula Units Dissolved (14.7)

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

## LEARNING OUTCOMES

Chapter Objectives	Assessment
Determine the solubility of a solute (14.2)	Example 14.1 For Practice 14.1 Exercises 31–34
Analyze energy transfer for the formation of a solution (14.3)	Exercises 35–40
Evaluate the solubility of solids and gases with changing temperature and pressure (14.4)	Example 14.2 For Practice 14.2 Exercises 41–50

Perform calculations using varying concentration units ( <b>14.5</b> )	Examples 14.3, 14.4, 14.5   For Practice 14.3, 14.4, 14.5 For More Practice 14.3, 14.5   Exercises 51–68
Determine colligative properties of solutions containing a nonelectrolyte ( <b>14.6</b> )	Examples 14.6, 14.7, 14.8, 14.9, 14.10   For Practice 14.6, 14.7, 14.8, 14.9, 14.10   For More Practice 14.6   Exercises 69–86
Calculate colligative properties of solutions containing an ionic solute ( <b>14.7</b> )	Example 14.11   For Practice 14.11, 14.12   Exercises 87–98

## EXERCISES

**Mastering Chemistry** provides end-of-chapter exercises, feedback-enriched tutorial problems, animations, and interactive activities to encourage problem-solving practice and deeper understanding of key concepts and topics.

## 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 the 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

- 29.** Pick an appropriate solvent from Table 14.3 to dissolve each substance. State the kind of intermolecular forces that would occur between the solute and solvent in each case.

**MISSED THIS? Read Section 14.2**

- motor oil (nonpolar)
- ethanol (polar, contains an OH group)
- lard (nonpolar)
- potassium chloride (ionic)

- 30.** Pick an appropriate solvent from Table 14.3 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)

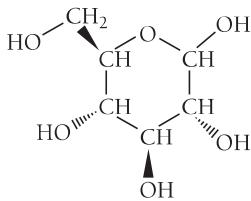
- 31.** Which molecule would you expect to be more soluble in water:  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$  or  $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{OH}$ ?

**MISSED THIS? Read Section 14.2**

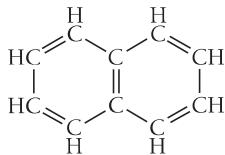
- 32.** Which molecule would you expect to be more soluble in water:  $\text{CCl}_4$  or  $\text{CH}_2\text{Cl}_2$ ?

- 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. **MISSED THIS? Read Section 14.2**

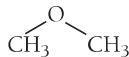
- a. glucose



- b. naphthalene

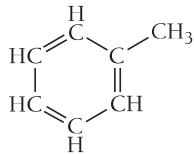


- c. dimethyl ether

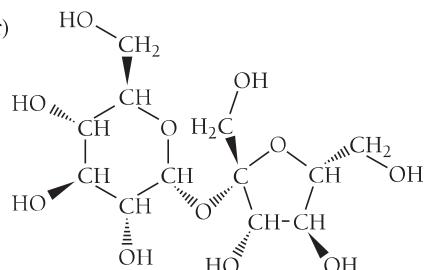


- 34.** For each compound, would you expect greater solubility in water or in hexane? Indicate the kinds of intermolecular forces that would occur between the solute and the solvent in which the molecule is most soluble.

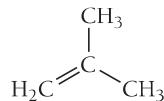
- a. toluene



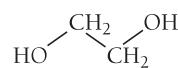
- b. sucrose (table sugar)



- 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. **MISSED THIS? Read Section 14.3**

- 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 14.7 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 14.7 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. **MISSED THIS? Read Section 14.3**

- 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. **MISSED THIS? Read Section 14.3**

- 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 NaCl per 100.0 g of water at 25 °C. Is the solution unsaturated, saturated, or supersaturated? (Use Figure 14.11.) **MISSED THIS? Read Section 14.4; Watch KCV 14.4**
- 42.** A solution contains 32 g of KNO<sub>3</sub> per 100.0 g of water at 25 °C. Is the solution unsaturated, saturated, or supersaturated? (Use Figure 14.11.)
- 43.** A KNO<sub>3</sub> solution containing 45 g of KNO<sub>3</sub> per 100.0 g of water is cooled from 40 °C to 0 °C. What happens during cooling? (Use Figure 14.11.) **MISSED THIS? Read Section 14.4; Watch KCV 14.4**
- 44.** A KCl solution containing 42 g of KCl per 100.0 g of water is cooled from 60 °C to 0 °C. What happens during cooling? (Use Figure 14.11.)
- 45.** Some laboratory procedures involving oxygen-sensitive reactants or products call for using water that has been boiled (and then cooled). Explain.  
**MISSED THIS? Read Section 14.4; Watch KCV 14.4**
- 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?  
**MISSED THIS? Read Section 14.4; Watch KCV 14.4**
- 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.  
**MISSED THIS? Read Section 14.4; Watch KCV 14.4, IWE 14.2**
- 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.)  
**MISSED THIS? Read Section 14.5; Watch KCV 14.5, IWE 14.4**
- 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?  
**MISSED THIS? Read Section 14.5; Watch KCV 14.5**
- 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.  
**MISSED THIS? Read Section 14.5; Watch KCV 14.5, IWE 14.3**
- 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 adults between 19 and 24 years old.)  
**MISSED THIS? Read Section 14.5; Watch KCV 14.5, IWE 14.3**
- 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.  
**MISSED THIS? Read Section 14.5; Watch KCV 14.5, IWE 14.3**
- 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. **MISSED THIS? Read Section 14.5; Watch KCV 14.5**
- a.  $1.00 \times 10^2$  mL of 0.500 M KCl
  - b.  $1.00 \times 10^2$  g of 0.500 *m* KCl
  - c.  $1.00 \times 10^2$  g of 5.0% KCl solution by mass
- 62.** Describe how to prepare each solution from the dry solute and the solvent.
- a. 125 mL of 0.100 M NaNO<sub>3</sub>
  - b. 125 g of 0.100 *m* NaNO<sub>3</sub>
  - c. 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.  
**MISSED THIS? Read Section 14.5; Watch KCV 14.5, IWE 14.4**
- a. molarity
  - b. molality
  - c. percent by mass
  - d. mole fraction
  - e. 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.
- a. molarity
  - b. molality
  - c. percent by mass
  - d. mole fraction
  - e. 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.)  
**MISSED THIS? Read Section 14.5; Watch KCV 14.5, IWE 14.5**
- 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.  
**MISSED THIS? Read Section 14.5; Watch KCV 14.5, IWE 14.5**
- 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? **MISSED THIS?** *Read Section 14.6; Watch KCV 14.6*
- 70.** Which solution has the highest vapor pressure?
- 20.0 g of glucose ( $C_6H_{12}O_6$ ) in 100.0 mL of water
  - 20.0 g of sucrose ( $C_{12}H_{22}O_{11}$ ) in 100.0 mL of water
  - 10.0 g of potassium acetate  $KC_2H_3O_2$  in 100.0 mL of water
- 71.** Calculate the vapor pressure of a solution containing 24.5 g of glycerin ( $C_3H_8O_3$ ) 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.  
**MISSED THIS?** *Read Section 14.6; Watch KCV 14.6, IWE 14.6*
- 72.** A solution contains naphthalene ( $C_{10}H_8$ ) dissolved in hexane ( $C_6H_{14}$ ) 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 ( $C_7H_{16}$ ) and 50.0 g of octane ( $C_8H_{18}$ ) 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:  
**MISSED THIS?** *Read Section 14.6; Watch KCV 14.6*
- 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 ( $CHCl_3$ ) and 9.29 g of acetone ( $CH_3COCH_3$ ). 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 is 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?  
**MISSED THIS?** *Read Section 14.6; Watch KCV 14.6, IWE 14.6*
- 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?

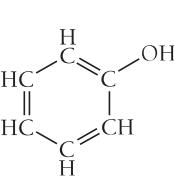
## Freezing Point Depression, Boiling Point Elevation, and Osmosis

- 77.** A glucose solution contains 55.8 g of glucose ( $C_6H_{12}O_6$ ) in 455 g of water. Determine the freezing point and boiling point of the solution.  
**MISSED THIS?** *Read Section 14.6; Watch KCV 14.6, IWE 14.9*

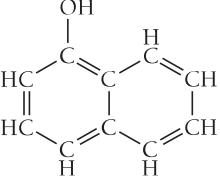
- 78.** An ethylene glycol solution contains 21.2 g of ethylene glycol ( $C_2H_6O_2$ ) in 85.4 mL of water. Determine the freezing point and boiling point of the solution. (Assume a density of 1.00 g/mL for water.)
- 79.** Calculate the freezing point and boiling point of a solution containing 10.0 g of naphthalene ( $C_{10}H_8$ ) in 100.0 mL of benzene. Benzene has a density of 0.877 g/cm<sup>3</sup>.  
**MISSED THIS?** *Read Section 14.6; Watch KCV 14.6, IWE 14.9*
- 80.** Calculate the freezing point and boiling point of a solution containing 7.55 g of ethylene glycol ( $C_2H_6O_2$ ) 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. **MISSED THIS?** *Read Section 14.6; Watch KCV 14.6*
- 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 ( $C_3H_8O_3$ ) in 250.0 mL of solution at 298 K.  
**MISSED THIS?** *Read Section 14.6; Watch KCV 14.6*
- 84.** What mass of sucrose ( $C_{12}H_{22}O_{11}$ ) 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?  
**MISSED THIS?** *Read Section 14.6; Watch KCV 14.6*
- 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.  
**MISSED THIS?** *Read Section 14.7*
- 0.100 m  $K_2S$
  - 21.5 g of  $CuCl_2$  in  $4.50 \times 10^2$  g water
  - 5.5%  $NaNO_3$  by mass (in water)
- 88.** Calculate the freezing point and boiling point in each solution, assuming complete dissociation of the solute.
- 10.5 g  $FeCl_3$  in  $1.50 \times 10^2$  g water
  - 3.5%  $KCl$  by mass (in water)
  - 0.150 m  $MgF_2$
- 89.** What mass of salt ( $NaCl$ ) 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  $NaCl$  and density of 1.00 g/mL for water. **MISSED THIS?** *Read Section 14.7*
- 90.** Determine the required concentration (in percent by mass) for an aqueous ethylene glycol ( $C_2H_6O_2$ ) solution to have a boiling point of 104.0 °C.
- 91.** Use the van't Hoff factors in Table 14.9 to calculate each colligative property: **MISSED THIS?** *Read Section 14.7*
- the melting point of a 0.100 m iron(III) chloride solution
  - the osmotic pressure of a 0.085 M potassium sulfate solution at 298 K
  - the boiling point of a 1.22% by mass magnesium chloride solution

- 92.** Using the van't Hoff factors in Table 14.9, 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  $-1.0^\circ\text{C}$
  - $2.50 \times 10^2$  mL of a magnesium sulfate solution that has an osmotic pressure of 3.82 atm at  $298\text{ K}$
  - an iron(III) chloride solution containing  $2.50 \times 10^2$  g of water that has a boiling point of  $102^\circ\text{C}$
- 93.** A  $1.2\text{ m}$  aqueous solution of an ionic compound with the formula  $\text{MX}_2$  has a boiling point of  $101.4^\circ\text{C}$ . Calculate the van't Hoff factor ( $i$ ) for  $\text{MX}_2$  at this concentration.
- MISSED THIS? Read Section 14.7**
- 94.** A  $0.95\text{ m}$  aqueous solution of an ionic compound with the formula  $\text{MX}$  has a freezing point of  $-3.0^\circ\text{C}$ . 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  $8.3\text{ atm}$  at  $25^\circ\text{C}$ . Calculate the van't Hoff factor ( $i$ ) for this solution.
- MISSED THIS? Read Section 14.7**
- 96.** A solution contains  $8.92\text{ g}$  of  $\text{KBr}$  in  $500.0\text{ mL}$  of solution and has an osmotic pressure of  $6.97\text{ atm}$  at  $25^\circ\text{C}$ . Calculate the van't Hoff factor ( $i$ ) for  $\text{KBr}$  at this concentration.
- 97.** Calculate the vapor pressure at  $25^\circ\text{C}$  of an aqueous solution that is  $5.50\%$   $\text{NaCl}$  by mass. (Assume complete dissociation of the solute.)
- MISSED THIS? Read Section 14.7; Watch IWE 14.12**
- 98.** An aqueous  $\text{CaCl}_2$  solution has a vapor pressure of  $81.6\text{ mmHg}$  at  $50^\circ\text{C}$ . The vapor pressure of pure water at this temperature is  $92.6\text{ mmHg}$ . 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  $1.2\text{ g/L}$ . The solubility of chloroform ( $\text{CHCl}_3$ ) at the same temperature is  $10.1\text{ g/L}$ . 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  $87\text{ g/L}$ . The solubility of naphthol at the same temperature is only  $0.74\text{ g/L}$ . 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  $10.0\text{ g}$  of potassium perchlorate is dissolved with enough water to make  $100.0\text{ mL}$  of solution. (Assume a heat capacity of  $4.05\text{ J/g} \cdot {}^\circ\text{C}$  for the solution and a density of  $1.05\text{ g/mL}$ .)
- 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  $25.0\text{ g}$  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  $1.05\text{ g/mL}$ .)
- 103.** A saturated solution forms when  $0.0537\text{ L}$  of argon, at a pressure of  $1.0\text{ atm}$  and a temperature of  $25^\circ\text{C}$ , is dissolved in  $1.0\text{ L}$  of water. Calculate the Henry's law constant for argon.
- 104.** A gas has a Henry's law constant of  $0.112\text{ M/atm}$ . What total volume of solution is needed to completely dissolve  $1.65\text{ L}$  of the gas at a pressure of  $725\text{ torr}$  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  $0.0020\text{ ppm}$  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 ( $0.0040\text{ ppm}$ ). How much of this water would a person have to consume to ingest  $50.0\text{ mg}$  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  $2.4\text{ g}$  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  $1.0\text{ g/mL}$ .)
- 107.** An aqueous solution contains  $12.5\%$   $\text{NaCl}$  by mass. What mass of water (in grams) is contained in  $2.5\text{ L}$  of the vapor above this solution at  $55^\circ\text{C}$ ? The vapor pressure of pure water at  $55^\circ\text{C}$  is  $118\text{ torr}$ . (Assume complete dissociation of  $\text{NaCl}$ .)
- 108.** The vapor above an aqueous solution contains  $19.5\text{ mg}$  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  $20.5\text{ torr}$  at  $25^\circ\text{C}$ ? (Assume a nonvolatile solute.)
- 111.** An isotonic solution contains  $0.90\%$   $\text{NaCl}$  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.
 

a. $\text{KCl}$	b. $\text{NaBr}$	c. 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  $28.5\text{ g}$  of magnesium citrate in  $235\text{ mL}$  of solution at  $37^\circ\text{C}$  (approximate body temperature). Assume complete dissociation of the ionic compound.
- 113.** A solution is prepared from  $4.5701\text{ g}$  of magnesium chloride and  $43.238\text{ g}$  of water. The vapor pressure of water above this solution is  $0.3624\text{ atm}$  at  $348.0\text{ K}$ . The vapor pressure of pure water at this temperature is  $0.3804\text{ atm}$ . 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  $-0.2929^\circ\text{C}$ . 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 will 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 °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%  $\text{NaCl}$  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  $\text{NaCl}$ .)
- 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  $m$  solution of sulfuric acid in water is  $272.76^\circ\text{K}$ . 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.

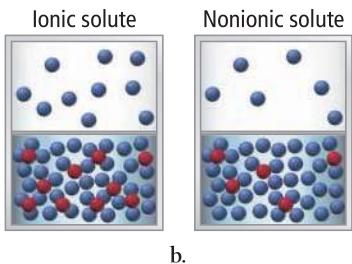
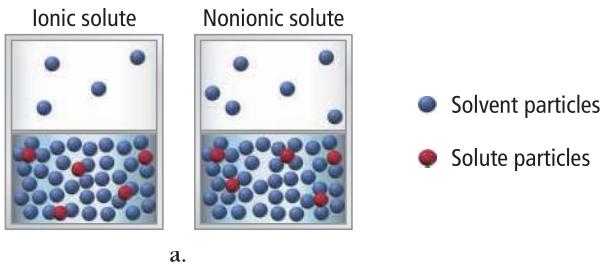
## CONCEPTUAL PROBLEMS

**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 substance 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?

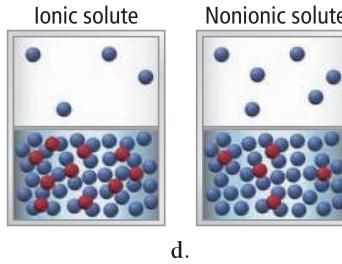
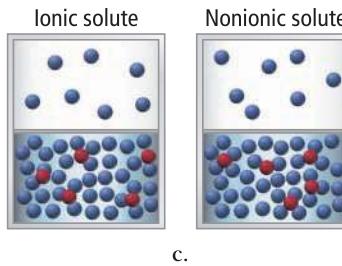
**136.** The vapor pressure of a 1 M ionic solution is different from the vapor pressure of a 1 M nonelectrolyte solution. In both cases, the solute is nonvolatile. Which set of diagrams best represents the differences between the two solutions and their vapors?



**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.



## QUESTIONS FOR GROUP WORK

Discuss these questions with the group and record your consensus answer.

**139.** Explain why 1-propanol ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ ) is miscible in both water ( $\text{H}_2\text{O}$ ) and hexane ( $\text{C}_6\text{H}_6$ ) when hexane and water are barely soluble in each other.

**140.** Have each group member make a flashcard with one of the following on the front:  $\Delta H_{\text{soln}}$ ,  $\Delta H_{\text{lattice}}$ ,  $\Delta H_{\text{solvent}}$ ,  $\Delta H_{\text{mix}}$ , and  $\Delta H_{\text{hydration}}$ . On the back of the card, each group member should describe (in words) the  $\Delta H$  process his or her card lists and how that  $\Delta H$  relates to other  $\Delta H$  values mathematically. Each member presents his or her  $\Delta H$  to the group. After everyone has presented, members should trade cards and quiz each other.

**141.** Complete the following table by adding *increases*, *decreases*, or *no effect*:

	Increasing Temperature	Increasing Pressure
solubility of gas in water		
solubility of a solid in water		

### Active Classroom Learning

**142.** When 13.62 g (about one tablespoon) of table sugar (sucrose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) is dissolved in 241.5 mL of water (density 0.997 g/mL), the final volume is 250.0 mL (about one cup). Have each group member calculate one of the following for the solution and present his or her answer to the group:

- mass percent
- molarity
- molality

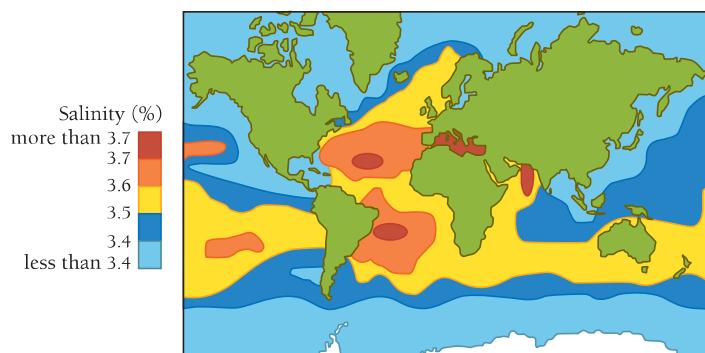
**143.** Calculate the expected boiling and freezing point for the solution in the previous problem. If you had to bring this syrup to the boiling point for a recipe, would you expect it to take much more time than it takes to boil the same amount of pure water? Why or why not? Would the syrup freeze in a typical freezer ( $-18^\circ\text{C}$ )? Why or why not?



## DATA INTERPRETATION AND ANALYSIS

### Freezing Point of Salt Water

- 14.4.** The salinity of seawater can vary in the world's oceans as shown in the map, which indicates salinity in units of percent by mass NaCl. Examine the image and answer the questions that follow.



Salinity of Seawater

- Which regions of the globe generally have higher salinity? Lower salinity? State your answer as a general trend in the salinity of seawater.
- Speculate on possible reasons for the trend you observed in part a.
- Calculate the freezing point of a sample of seawater taken from the middle of the Atlantic Ocean. Use a van't Hoff factor of 1.9 for your calculation.
- Make a graph of the freezing point of the seawater versus salinity for the range of salinities in the world's oceans.



## ANSWERS TO CONCEPTUAL CONNECTIONS

### Mixing of Ideal Gases

- 14.1** (d) When gases mix, the kinetic energy of each gas is spread out over more space, so entropy increases.

### Solution Formation

- 14.2** (a) When solvent–solute interactions in a mixture are comparable in strength to the solvent–solvent interactions and the solute–solute interactions, entropy drives the formation of a homogeneous mixture.

### Solubility

- 14.3** (c) 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

- 14.4** (b) 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

- 14.5** (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

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

### Molality

- 14.7** (b) The solution has a molality of 10.0 *m*. You combined 1.00 mol of solute with 0.100 kg of solvent, so the molality is  $1.00 \text{ mol}/0.100 \text{ kg} = 10.0 \text{ m}$ .

### Solution Vapor Pressure

- 14.8** (b) The vapor pressure of a solution is the mole fraction of the solvent times the vapor pressure of the pure solvent. Since the mole fraction of the solvent is 0.800, the vapor pressure of the solution is  $0.800 \times 100.0 \text{ torr}$ , which equals 80.0 torr.

### Raoult's Law

- 14.9** (a) 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

- 14.10** (b) Solution B because  $K_b$  for ethanol is greater than  $K_b$  for water.

### Colligative Properties

- 14.11** (c) The 0.50 M MgCl<sub>2</sub> solution has the highest boiling point because it has the highest concentration of particles. We expect 1 mol of MgCl<sub>2</sub> to form 3 mol of particles in solution (although it effectively forms slightly fewer).