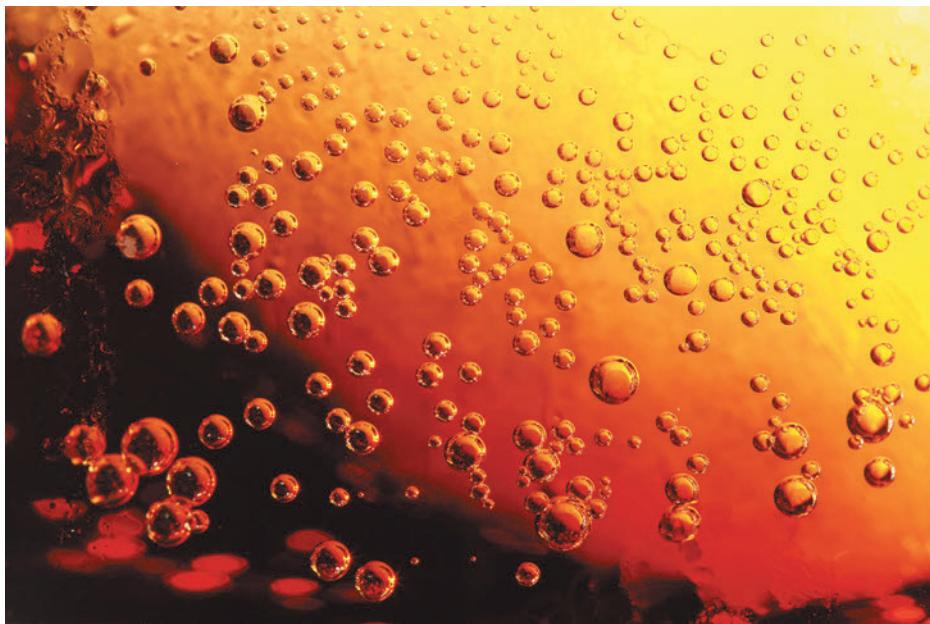


# 13

## PROPERTIES OF SOLUTIONS

### 13.1 | The Solution Process



In Chapters 10, 11, and 12, we explored the properties of pure gases, liquids, and solids. However, the examples of matter that we encounter in our daily lives, such as carbonated drinks, air, and glass, are frequently mixtures. In this chapter, we examine homogeneous mixtures.

### WHAT'S AHEAD

- 13.1 ► The Solution Process
- 13.2 ► Saturated Solutions and Solubility
- 13.3 ► Factors Affecting Solubility
- 13.4 ► Expressing Solution Concentration
- 13.5 ► Colligative Properties
- 13.6 ► Colloids

As we noted in the earlier chapters, homogeneous mixtures are called *solutions*. (Sections 1.2 and 4.1) When we think of solutions, we usually think of liquids. Solutions, however, can also be solids or gases. For example, sterling silver is a homogeneous mixture of about 7% copper in silver and so is a solid solution. The air we breathe is a homogeneous mixture of several gases, making air a gaseous solution. However, because liquid solutions are the most common, we focus our attention on them in this chapter. We will be particularly concerned with aqueous solutions, which contain water as the solvent and either a gas, liquid, or solid as a solute.

By the end of this section, you should be able to

- Describe how enthalpy and entropy changes affect solution formation.

Each substance in a solution is a *component* of the solution. As we saw in Chapter 4, the *solvent* is normally the component present in the greatest amount, and all the other components are called *solutes*. A *solution is formed when one component disperses uniformly throughout another*. The ability of substances to form solutions depends on two factors: (1) the natural tendency of substances to mix and spread into larger volumes when not restrained in some way and (2) the types of intermolecular interactions involved in the solution process.

### The Natural Tendency toward Mixing

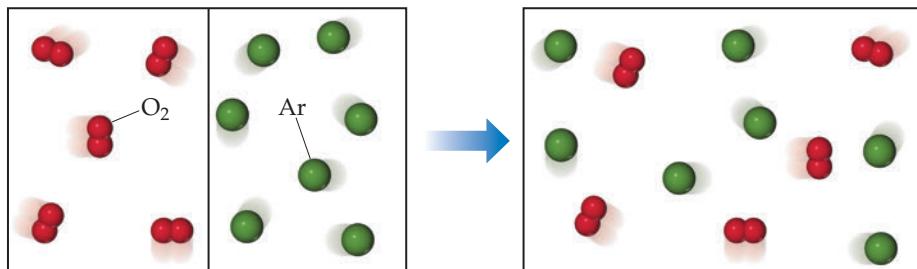
Suppose we have  $O_2(g)$  and  $Ar(g)$  separated by a barrier, as in [Figure 13.1](#). If the barrier is removed, the gases mix to form a solution. The molecules experience very little intermolecular interactions and behave like ideal gas particles. As a result, their molecular motion causes them to spread through the larger volume, and a gaseous solution is formed.

The mixing of gases is a *spontaneous* process, meaning it occurs of its own accord without any input of energy from outside the system. When the molecules mix and become more randomly distributed, there is an increase in a thermodynamic quantity called *entropy*. Entropy will be defined more rigorously in Chapter 19; but for now, we can consider that the entropy of a system increases if its degree of disorder increases, or if its energy becomes dispersed over a greater number of particles. Therefore, the mixing of gases we just described increases the entropy of the system. The enthalpy of the system, however, changes little upon gas mixing because there are few intermolecular interactions between the gas particles. All of the intermolecular forces (dispersion forces, dipole-dipole interactions, hydrogen bonding) and their corresponding energies are part of the enthalpy of the system. Decreasing the enthalpy of the system would correspond to increasing favorable intermolecular interactions between gas particles. Furthermore, the balance between increasing the entropy and decreasing the enthalpy of a system is what determines whether a process is spontaneous. Thus, the *formation of solutions is favored by the increase in entropy that accompanies mixing*.

When molecules of different types are brought together, mixing occurs spontaneously unless the molecules are restrained either by sufficiently strong intermolecular

#### Go Figure

What aspect of the kinetic theory of gases tells us that the gases will mix?



[▲ Figure 13.1](#) Spontaneous mixing of two gases to form a homogeneous mixture (a solution).

forces or by physical barriers. Thus, gases spontaneously mix unless restrained by their containers because with gases intermolecular forces are too weak to restrain the molecules. However, when the solvent or solute is a solid or liquid, intermolecular forces become important in determining whether a solution forms. For example, although ionic bonds hold sodium and chloride ions together in solid sodium chloride, the solid dissolves in water because of the compensating strength of the attractive forces between the ions and water molecules. Sodium chloride does not dissolve in petrol, however, because the intermolecular forces between the ions and the petrol molecules are too weak.

### The Effect of Intermolecular Forces on Solution Formation

Any of the intermolecular forces discussed in Chapter 11 can operate between solute and solvent particles in a solution. These forces are summarized in **Figure 13.2**. Dispersion forces, for example, dominate when one nonpolar substance, such as  $C_7H_{16}$ , dissolves in another, such as  $C_5H_{12}$ , and ion–dipole forces dominate in solutions of ionic substances in water.

Three kinds of intermolecular interactions are involved in solution formation:

1. *Solute–solute* interactions between solute particles must be overcome to disperse the solute particles through the solvent.
2. *Solvent–solvent* interactions between solvent particles must be overcome to make room for the solute particles in the solvent.
3. *Solvent–solute* interactions between the solvent and solute particles occur as the particles mix.

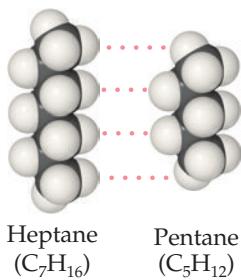
The extent to which one substance is able to dissolve in another depends on the relative magnitudes of these three types of interactions. Solutions form when the magnitudes of the solvent–solute interactions are either comparable to or greater than the solute–solute and solvent–solvent interactions. For example, heptane ( $C_7H_{16}$ ) and pentane ( $C_5H_{12}$ ) dissolve in each other in all proportions. For this discussion, we can arbitrarily call heptane the solvent and pentane the solute. Both substances are nonpolar, and the magnitudes of the solvent–solute interactions (attractive dispersion forces) are comparable to the solute–solute and the solvent–solvent interactions. Thus, no forces impede mixing, and the tendency to mix (increase entropy) causes the solution to form spontaneously.

An everyday example of solution formation occurs when you dissolve salt in water. Solid NaCl dissolves readily in water because the attractive solvent–solute interactions between the polar  $H_2O$  molecules and the ions are strong enough to overcome the attractive solute–solute interactions between ions in the NaCl(s) and the attractive solvent–solvent interactions between  $H_2O$  molecules. When NaCl is added to water

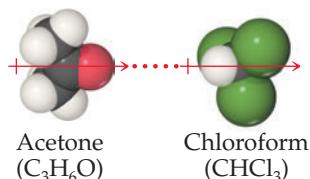
#### Go Figure

Which atom in water points toward  $Na^+$  in the ion–dipole interaction? Why?

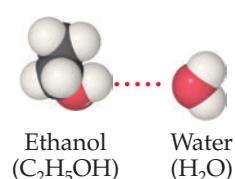
##### Dispersion



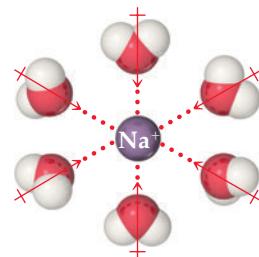
##### Dipole–dipole



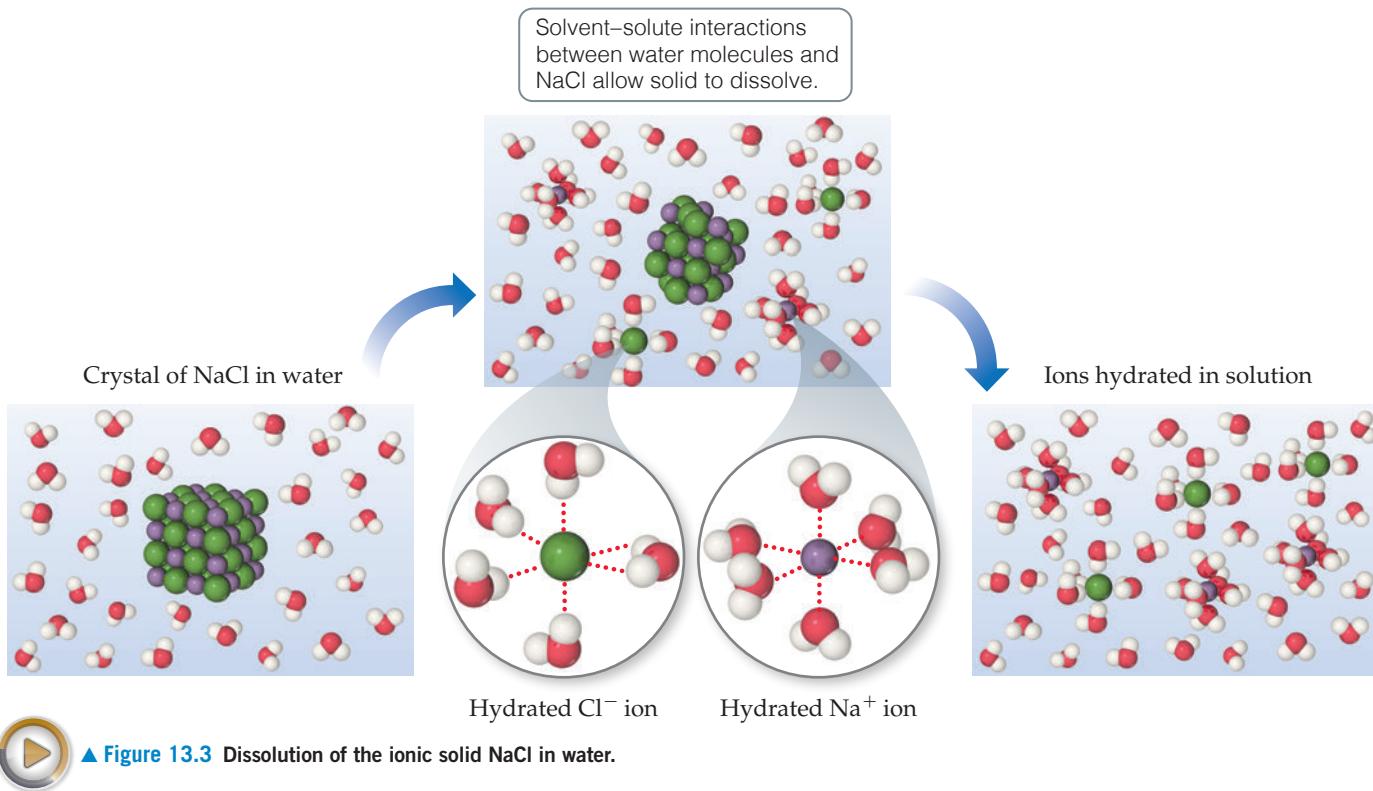
##### Hydrogen bond



##### Ion–dipole



**▲ Figure 13.2** Intermolecular interactions involved in solutions.



▲ **Figure 13.3** Dissolution of the ionic solid NaCl in water.

(Figure 13.3), the water molecules orient themselves on the surface of the NaCl crystals with the positive end of the water dipole oriented toward  $\text{Cl}^-$  ions and the negative end oriented toward  $\text{Na}^+$  ions. These ion–dipole attractions are strong enough to pull the surface ions away from the solid, thus overcoming the solute–solute interactions. For the solid to dissolve, some solvent–solvent interactions must also be overcome to create room for the ions to “fit” among all the water molecules.

Once separated from the solid, the  $\text{Na}^+$  and  $\text{Cl}^-$  ions are surrounded by water molecules. Interactions such as this between solute and solvent molecules are known as **solvation**. When the solvent is water, the interactions are referred to as **hydration**.

### Energetics of Solution Formation

Solution processes are typically accompanied by changes in enthalpy. For example, when NaCl dissolves in water, the process is slightly endothermic,  $\Delta H_{\text{soln}} = 3.9 \text{ kJ/mol}$ . We can use Hess’s law to analyze how the solute–solute, solvent–solvent, and solute–solvent interactions influence the enthalpy of solution.

We can imagine the solution process as having three components, each with an associated enthalpy change: A cluster of  $n$  solute particles must separate from one another ( $\Delta H_{\text{solute}}$ ), a cluster of  $m$  solvent particles separate from one another ( $\Delta H_{\text{solvent}}$ ), and these solute and solvent particles mix ( $\Delta H_{\text{mix}}$ ).

1.  $(\text{solute})_n \rightleftharpoons n \text{ solute}$   $\Delta H_{\text{solute}}$
  2.  $(\text{solvent})_m \rightleftharpoons m \text{ solvent}$   $\Delta H_{\text{solvent}}$
  3.  $n \text{ solute} + m \text{ solvent} \rightleftharpoons \text{solution}$   $\Delta H_{\text{mix}}$
- 
4.  $(\text{solute})_n + (\text{solvent})_m \rightleftharpoons \text{solution}$   $\Delta H_{\text{soln}} = \Delta H_{\text{solute}} + \Delta H_{\text{solvent}} + \Delta H_{\text{mix}}$

As seen earlier, the overall enthalpy change,  $\Delta H_{\text{soln}}$ , is the sum of the three steps:

$$\Delta H_{\text{soln}} = \Delta H_{\text{solute}} + \Delta H_{\text{solvent}} + \Delta H_{\text{mix}} \quad [13.1]$$

Separation of the solute particles from one another always requires an input of energy to overcome their attractive interactions. The process is therefore endothermic ( $\Delta H_{\text{solute}} > 0$ ). Likewise, separation of solvent molecules to accommodate the solute always requires energy ( $\Delta H_{\text{solvent}} > 0$ ). The third component, which arises from the

attractive interactions between solute particles and solvent particles, is always exothermic ( $\Delta H_{\text{mix}} < 0$ ).

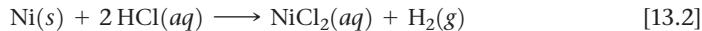
The three enthalpy terms in Equation 13.1 can be added together to give either a negative or a positive sum, depending on the actual numbers for the system being considered (Figure 13.4). Thus, the formation of a solution can be either exothermic or endothermic. For example, when magnesium sulfate ( $\text{MgSO}_4$ ) is added to water, the solution process is exothermic:  $\Delta H_{\text{soln}} = -91.2 \text{ kJ/mol}$ . In contrast, the dissolution of ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) is endothermic:  $\Delta H_{\text{soln}} = 26.4 \text{ kJ/mol}$ . These particular salts are the main components in the instant heat packs and ice packs used to treat athletic injuries.

The enthalpy change for a process can provide insight into the extent to which the process occurs. Exothermic processes tend to proceed spontaneously. On the other hand, if  $\Delta H_{\text{soln}}$  is too endothermic, the solute might not dissolve to any significant extent in the chosen solvent. Thus, for solutions to form, the solvent-solute interaction must be strong enough to make  $\Delta H_{\text{mix}}$  comparable in magnitude to  $\Delta H_{\text{solute}} + \Delta H_{\text{solvent}}$ . This fact further explains why ionic solutes do not dissolve in nonpolar solvents. The nonpolar solvent molecules experience only weak attractive interactions with the ions, and these interactions do not compensate for the energies required to separate the ions from one another.

By similar reasoning, a polar liquid solute, such as water, does not dissolve in a nonpolar liquid solvent, such as octane ( $\text{C}_8\text{H}_{18}$ ). The water molecules experience strong hydrogen-bonding interactions with one another—attractive forces that must be overcome if the water molecules are to be dispersed throughout the octane solvent. The energy required to separate the  $\text{H}_2\text{O}$  molecules from one another is not recovered in the form of attractive interactions between the  $\text{H}_2\text{O}$  and  $\text{C}_8\text{H}_{18}$  molecules.

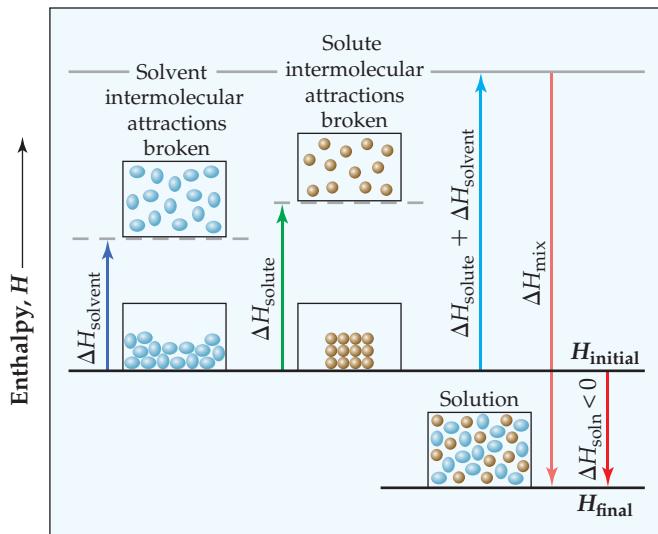
## Solution Formation and Chemical Reactions

In discussing solutions, we must be careful to distinguish the physical process of solution formation from chemical reactions that lead to a solution. For example, nickel metal dissolves on contact with an aqueous hydrochloric acid solution because the following reaction occurs:

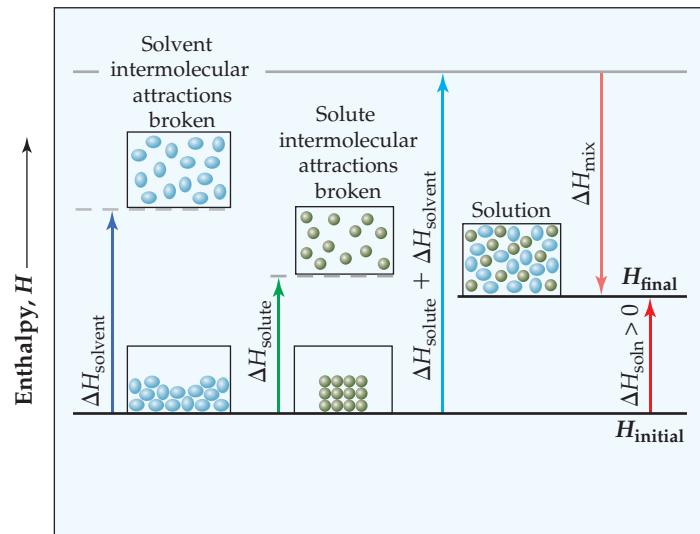


### Go Figure

How does the magnitude of  $\Delta H_{\text{mix}}$  compare with the magnitude of  $\Delta H_{\text{solvent}} + \Delta H_{\text{solute}}$  for exothermic solution processes?

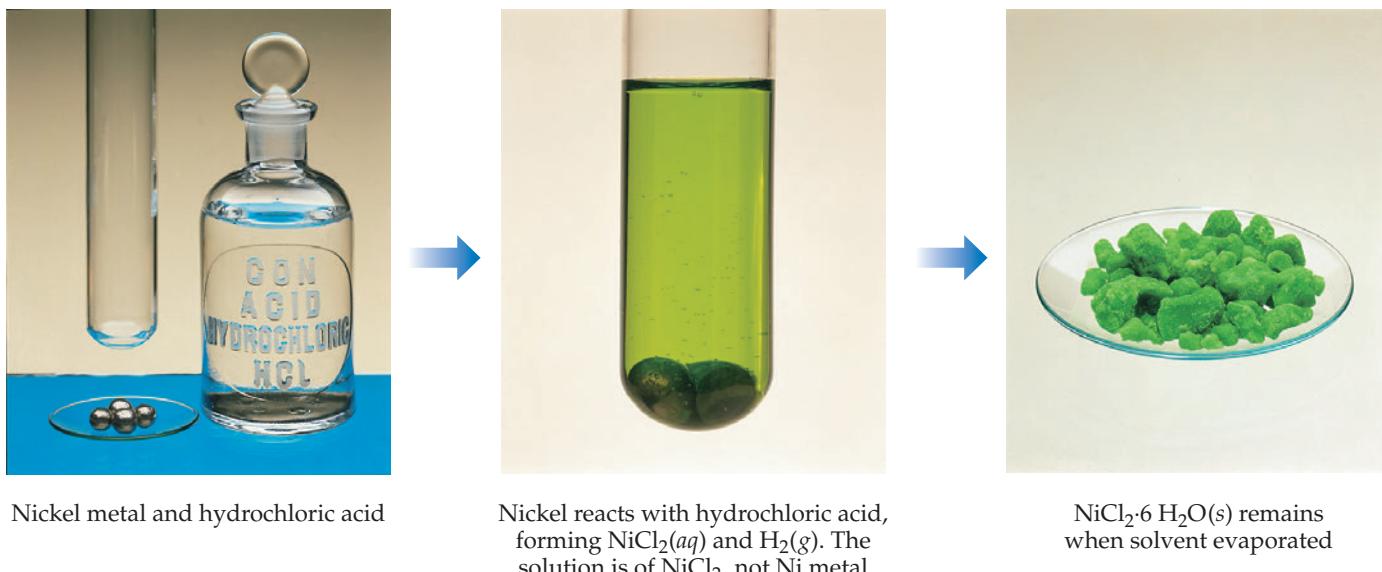


Exothermic solution process



Endothermic solution process

▲ Figure 13.4 Enthalpy changes accompanying the solution process.



▲ **Figure 13.5** The reaction between nickel metal and hydrochloric acid is *not* a simple dissolution. The product is  $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}(s)$ , nickel(II) chloride hexahydrate, which has exactly 6 waters of hydration in the crystal lattice for every nickel ion.

In this instance, one of the resulting solutes is not Ni metal but rather its salt  $\text{NiCl}_2$ . If the solution is evaporated to dryness,  $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}(s)$  is recovered (Figure 13.5). Compounds such as  $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}(s)$  that have a defined number of water molecules in the crystal lattice are known as *hydrates*. When  $\text{NaCl}(s)$  is dissolved in water, on the other hand, no chemical reaction occurs. If the solution is evaporated to dryness,  $\text{NaCl}$  is recovered. Our focus throughout this chapter is on solutions from which the solute can be recovered unchanged from the solution.

## Self-Assessment Exercise

- 13.1** What do you predict to be the enthalpy change when samples of  $\text{HCl}(g)$  and  $\text{CO}_2(g)$  are mixed?

- (a)  $\Delta H < 0$   
 (b)  $\Delta H > 0$   
 (c)  $\Delta H \approx 0$

## Exercises

- 13.2** Indicate whether each statement is true or false: (a)  $\text{NaCl}$  dissolves in water but not in benzene ( $\text{C}_6\text{H}_6$ ) because benzene is denser than water. (b)  $\text{NaCl}$  dissolves in water but not in benzene because water has a large dipole moment and benzene has zero dipole moment. (c)  $\text{NaCl}$  dissolves in water but not in benzene because the water-ion interactions are stronger than benzene-ion interactions.
- 13.3** Indicate the principal type of solute-solvent interaction in each of the following solutions and rank the solutions from weakest to strongest solute-solvent interaction: (a)  $\text{KCl}$  in water, (b)  $\text{CH}_2\text{Cl}_2$  in benzene ( $\text{C}_6\text{H}_6$ ), (c) methanol ( $\text{CH}_3\text{OH}$ ) in water.
- 13.4** An ionic compound has a very negative  $\Delta H_{\text{soln}}$  in water. (a) Would you expect it to be very soluble or nearly insoluble in water? (b) Which term would you expect to be the largest negative number:  $\Delta H_{\text{solvent}}$ ,  $\Delta H_{\text{solute}}$ , or  $\Delta H_{\text{mix}}$ ?

- 13.5** For the dissolution of  $\text{NaCl}$  in water,  $\Delta H_{\text{soln}} = +3 \text{ kJ/mol}$ . Which term would you expect to be the largest negative number:  $\Delta H_{\text{solute}}$ ,  $\Delta H_{\text{solvent}}$ , or  $\Delta H_{\text{mix}}$ ?
- 13.6** Two nonpolar organic liquids, benzene ( $\text{C}_6\text{H}_6$ ) and toluene ( $\text{C}_7\text{H}_8$ ), are mixed. (a) Do you expect  $\Delta H_{\text{soln}}$  to be a large positive number, a large negative number, or close to zero? Explain. (b) Benzene and toluene are miscible with each other in all proportions. In making a solution of them, is the entropy of the system increased, decreased, or close to zero, compared to the separate pure liquids?

13.1 (c)



## 13.2 | Saturated Solutions and Solubility



Sodium chloride, salt, is an essential part of our diet. One commercial way to obtain salt is to harvest it from the ocean. Sea water is allowed to evaporate in shallow ponds and as it does the solution becomes more and more concentrated in the dissolved salts. A point comes when the solution is saturated and further evaporation results in the precipitation of salt, which may be harvested.

By the end of this section, you should be able to

- Describe the role of equilibrium in the solution process and its relationship to the solubility of a solute.

As a solid solute begins to dissolve in a solvent, the concentration of solute particles in solution increases, increasing the chances that some solute particles will collide with the surface of the solid and reattach. This process, which is the opposite of the solution process, is called **crystallization**. Thus, two opposing processes occur in a solution in contact with undissolved solute. This situation is represented in this chemical equation:



When the rates of these opposing processes become equal, a *dynamic equilibrium* is established, and there is no further increase in the amount of solute in solution.

A solution that is in equilibrium with undissolved solute is **saturated**. Additional solute will not dissolve if added to a saturated solution. The amount of solute needed to form a saturated solution in a given quantity of solvent is known as the **solubility** of that solute. That is,

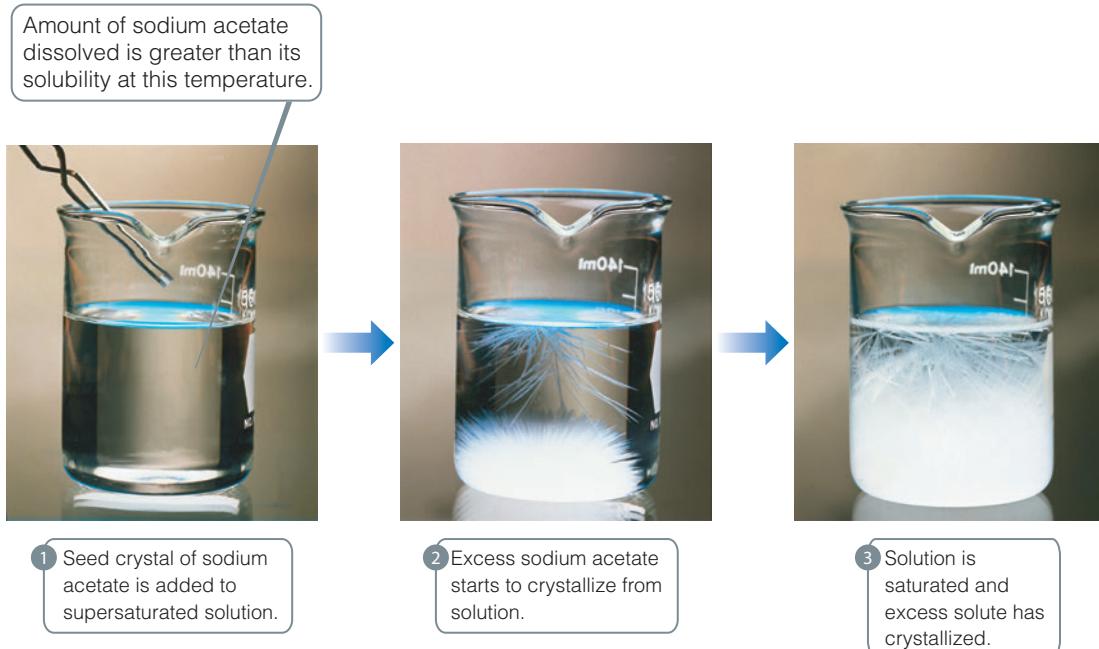
*the solubility of a particular solute in a particular solvent is the maximum amount of the solute that can dissolve in a given amount of the solvent at a specified temperature, assuming that excess solute is present.*

For example, the solubility of NaCl in water at 0 °C is 35.7 g per 100 mL of water. This is the maximum amount of NaCl that can be dissolved in water to give a stable equilibrium solution at that temperature.

If we dissolve less solute than the amount needed to form a saturated solution, the solution is **unsaturated**. Thus, a solution containing 10.0 g of NaCl per 100 mL of water at 0 °C is unsaturated because it has the capacity to dissolve more solute.

**Go Figure**

How many grams of sodium acetate are in solution in the third beaker?



**▲ Figure 13.6 Precipitation from a supersaturated sodium acetate solution.** The solution on the left was formed by dissolving about 170 g of the salt in 100 mL of water at 100 °C and then slowly cooling it to 20 °C. Because the solubility of sodium acetate in water at 20 °C is 46 g per 100 mL of water, the solution is supersaturated. Addition of a sodium acetate crystal causes the excess solute to crystallize from solution.

Under suitable conditions, it is possible to form solutions that contain a greater amount of solute than needed to form a saturated solution. Such solutions are **supersaturated**. For example, when a saturated solution of sodium acetate is made at a high temperature and then slowly cooled, all of the solute may remain dissolved even though its solubility decreases as the temperature decreases. Because the solute in a supersaturated solution is present in a concentration higher than the equilibrium concentration, supersaturated solutions are unstable with respect to crystallization of the solute. For crystallization to occur, however, the solute particles must arrange themselves properly to form crystals. The addition of a small crystal of the solute (a seed crystal) provides a template for crystallization of the excess solute, leading to a saturated solution in contact with excess solid (Figure 13.6).

## Self-Assessment Exercise

- 13.7 If a magnesium chloride is added to a saturated solution of magnesium chloride, will it dissolve?

(a) No

(b) Yes

## Exercises

- 13.8 The solubility of copper (II) sulfate pentahydrate ( $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ ) in water at 30 °C is 50 g per 100 mL of water.  
 (a) Is a 1.30 M solution of  $\text{CuSO}_4 \cdot 12 \text{H}_2\text{O}$  in water at 30 °C

saturated, supersaturated, or unsaturated? (b) Given a solution of  $\text{CuSO}_4 \cdot 12 \text{H}_2\text{O}$  of unknown concentration, what experiment could you perform to determine whether the new solution is saturated, supersaturated, or unsaturated?

13.7 (a)

Answers to Self-Assessment Exercises



## 13.3 | Factors Affecting Solubility



Have you noticed how ice cubes you make at home usually have bubbles in their center? This results from the solubility of air in water decreasing as the temperature drops. The water in your ice tray usually freezes from the outer edges. This concentrates the dissolved gases towards the center, the water becomes saturated, and further freezing results in the air bubbling out of the water and becoming trapped by the surrounding ice. So, how do you make clear ice cubes? If you boil the water before freezing it, the heat drives out most of the dissolved gases and results in clear ice.

By the end of this section, you should be able to

- Understand what factors affect solubility

The extent to which one substance dissolves in another depends on the nature of both substances. It also depends on temperature and, at least for gases, on pressure.

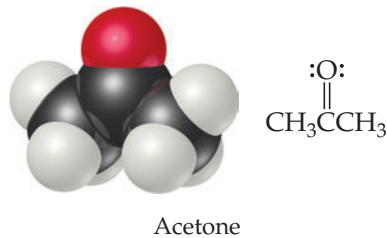
### Solute–Solvent Interactions

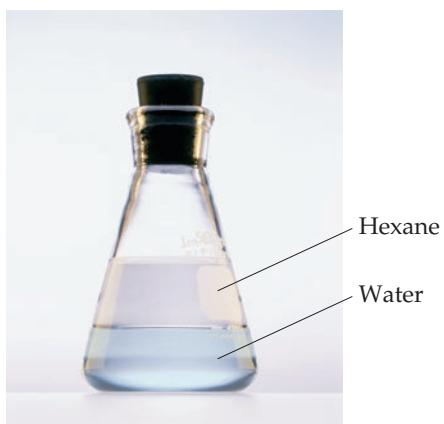
The natural tendency of substances to mix and the various interactions among solute and solvent particles are all involved in determining solubilities. Nevertheless, insight into variations in solubility can often be gained by focusing on the interaction between the solute and solvent. The data in **Table 13.1** show that the solubilities of various gases in water increase with increasing molar mass. The attractive forces between the gas molecules and solvent molecules are mainly dispersion forces, which increase with increasing size and molar mass. Thus, the data indicate that the solubilities of gases in water increase as the attraction between solute (gas) and solvent (water) increases. In general, when other factors are comparable, *the stronger the attractions between solute and solvent molecules, the greater the solubility of the solute in that solvent*.

Because of favorable dipole–dipole attractions between polar solvent molecules and polar solute molecules, *polar liquids tend to dissolve in polar solvents*. Water is both polar and able to form hydrogen bonds. Thus, polar molecules, especially those that can form hydrogen bonds with water molecules, tend to be soluble in water. For example, acetone, a polar molecule with the structural formula shown here, mixes in all proportions with water. Acetone has a strongly polar C=O bond and pairs of nonbonding electrons on the O atom that can form hydrogen bonds with water.

**TABLE 13.1 Solubilities of Gases in Water at 20 °C, at 101.3 kPa Gas Pressure**

Gas	Molar Mass (g/mol)	Solubility (M)
N <sub>2</sub>	28.0	$0.69 \times 10^{-3}$
O <sub>2</sub>	32.0	$1.38 \times 10^{-3}$
Ar	39.9	$1.50 \times 10^{-3}$
Kr	83.8	$2.79 \times 10^{-3}$





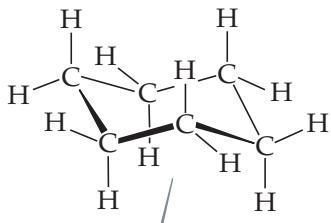
▲ **Figure 13.7** Hexane, a hydrocarbon, is immiscible with water. Hexane is the top layer because it is less dense than water.

Liquids that mix in all proportions, such as acetone and water, are **miscible**, whereas those that do not dissolve in one another are **immiscible**. Petrol, which is a mixture of hydrocarbons, is immiscible with water. Hydrocarbons are nonpolar substances because of several factors: The C—C bonds are nonpolar, the C—H bonds are nearly nonpolar, and the molecules are symmetrical enough to cancel much of the weak C—H bond dipoles. The attraction between the polar water molecules and the nonpolar hydrocarbon molecules is not sufficiently strong to allow the formation of a solution. *Nonpolar liquids tend to be insoluble in polar liquids*, as Figure 13.7 shows for hexane ( $C_6H_{14}$ ) and water.

Many organic compounds have polar groups attached to a nonpolar framework of carbon and hydrogen atoms. For example, the series of organic compounds in Table 13.2 all contain the polar OH group. Organic compounds with this molecular feature are called *alcohols*. The O—H bond is able to form hydrogen bonds. For example, ethanol ( $CH_3CH_2OH$ ) molecules can form hydrogen bonds with water molecules as well as with each other (Figure 13.8). As a result, the solute–solute, solvent–solvent, and solute–solvent forces are not greatly different in a mixture of  $CH_3CH_2OH$  and  $H_2O$ . No major change occurs in the environments of the molecules as they are mixed. Therefore, the increased entropy when the components mix plays a significant role in solution formation, and ethanol is completely miscible with water.

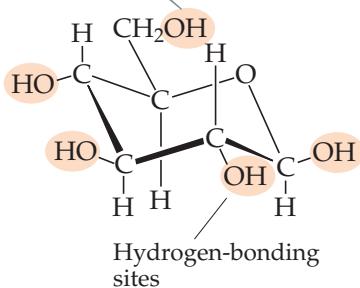
Notice in Table 13.2 that the number of carbon atoms in an alcohol affects its solubility in water. As this number increases, the polar OH group becomes an even smaller part of the molecule, and the molecule behaves more like a hydrocarbon. The solubility of the alcohol in water decreases correspondingly. On the other hand, the solubility of alcohols in a nonpolar solvent like hexane ( $C_6H_{14}$ ) increases as the nonpolar hydrocarbon chain lengthens.

One way to enhance the solubility of a substance in water is to increase the number of polar groups the substance contains. For example, increasing the number of OH groups in a solute increases the extent of hydrogen bonding between that solute and water, thereby increasing solubility. Glucose ( $C_6H_{12}O_6$ , Figure 13.9) has five OH groups on a six-carbon framework, which makes the molecule very soluble in



Cyclohexane,  $C_6H_{12}$ , which has no polar OH groups, is essentially insoluble in water.

In glucose, the OH groups enhance the aqueous solubility because of their ability to hydrogen-bond with  $H_2O$ .

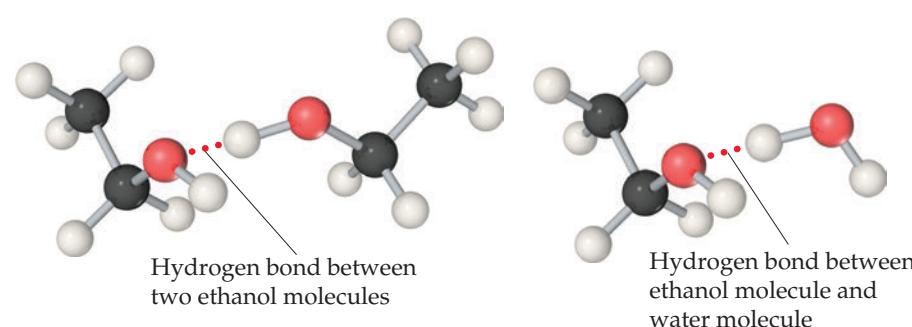


▲ **Figure 13.9** The correlation of molecular structure with solubility.

**TABLE 13.2 Solubilities of Some Alcohols in Water and in Hexane\***

Alcohol	Solubility in $H_2O$	Solubility in $C_6H_{14}$
$CH_3OH$ (methanol)	∞	0.12
$CH_3CH_2OH$ (ethanol)	∞	∞
$CH_3CH_2CH_2OH$ (propanol)	∞	∞
$CH_3CH_2CH_2CH_2OH$ (butanol)	0.11	∞
$CH_3CH_2CH_2CH_2CH_2OH$ (pentanol)	0.030	∞
$CH_3CH_2CH_2CH_2CH_2CH_2OH$ (hexanol)	0.0058	∞

\*Expressed in mol alcohol/100 g solvent at 20 °C. The infinity symbol (∞) indicates that the alcohol is completely miscible with the solvent.



▲ **Figure 13.8** Hydrogen bonding involving OH groups.

water: 830 g dissolves in 1.00 L of water at 17.5 °C. In contrast, cyclohexane ( $C_6H_{12}$ ), which has a similar structure to glucose but with all of the OH groups replaced by H, is essentially insoluble in water (only 55 mg of cyclohexane can dissolve in 1.00 L of water at 25 °C).

Over years of study, examination of different solvent–solute combinations has led to an important generalization:

*Substances with similar intermolecular attractive forces tend to be soluble in one another.*

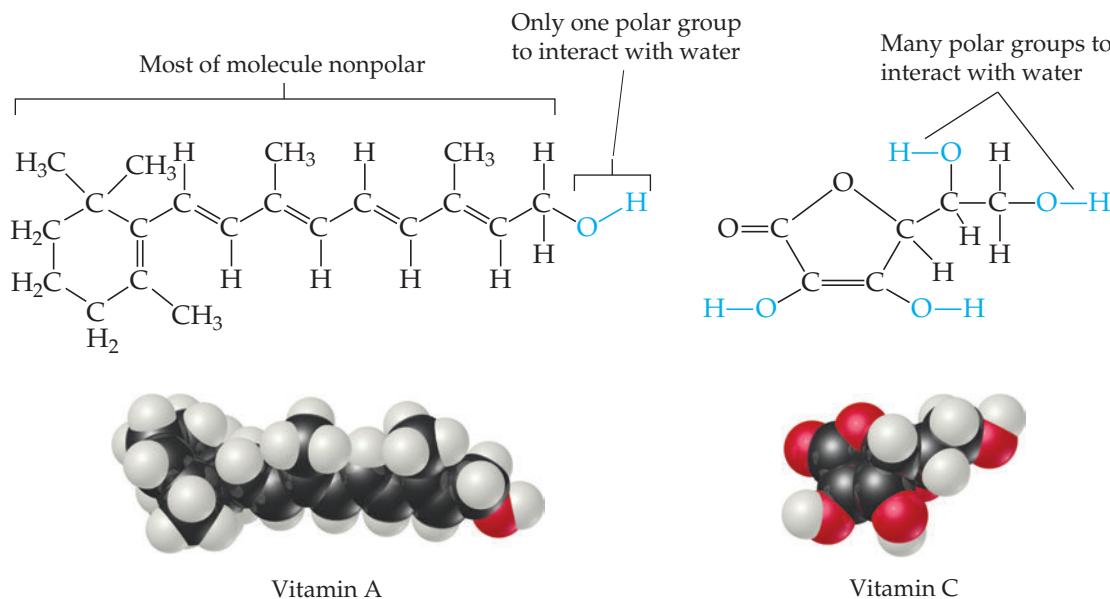
This generalization is often simply stated as “*like dissolves like*.” Nonpolar substances are more likely to be soluble in nonpolar solvents; ionic and polar solutes are more likely to be soluble in polar solvents. Network solids such as diamond and quartz are not soluble in either polar or nonpolar solvents because of the strong bonding within the solid.

## CHEMISTRY AND LIFE Fat-Soluble and Water-Soluble Vitamins

Vitamins have unique chemical structures that affect their solubilities in different parts of the human body. Vitamin C and the B vitamins are soluble in water, for example, whereas vitamins A, D, E, and K are soluble in nonpolar solvents and in fatty tissue (which is nonpolar). Because of their water solubility, vitamins B and C are not stored to any appreciable extent in the body, and so foods containing these vitamins should be included in the daily diet. In contrast, the fat-soluble vitamins are stored in sufficient quantities to keep vitamin-deficiency diseases from appearing even after a person has subsisted for a long period on a vitamin-deficient diet.

That some vitamins are soluble in water and others are not can be explained in terms of their structures. Notice in Figure 13.10 that vitamin A (retinol) is an alcohol with a very long carbon chain. Because the OH group is such a small part of the molecule, the molecule resembles the long-chain alcohols listed in Table 13.2. This vitamin is nearly nonpolar. In contrast, the vitamin C molecule is smaller and has several OH groups that can form hydrogen bonds with water, somewhat like glucose.

**Related Exercises: 13.22, 13.46**



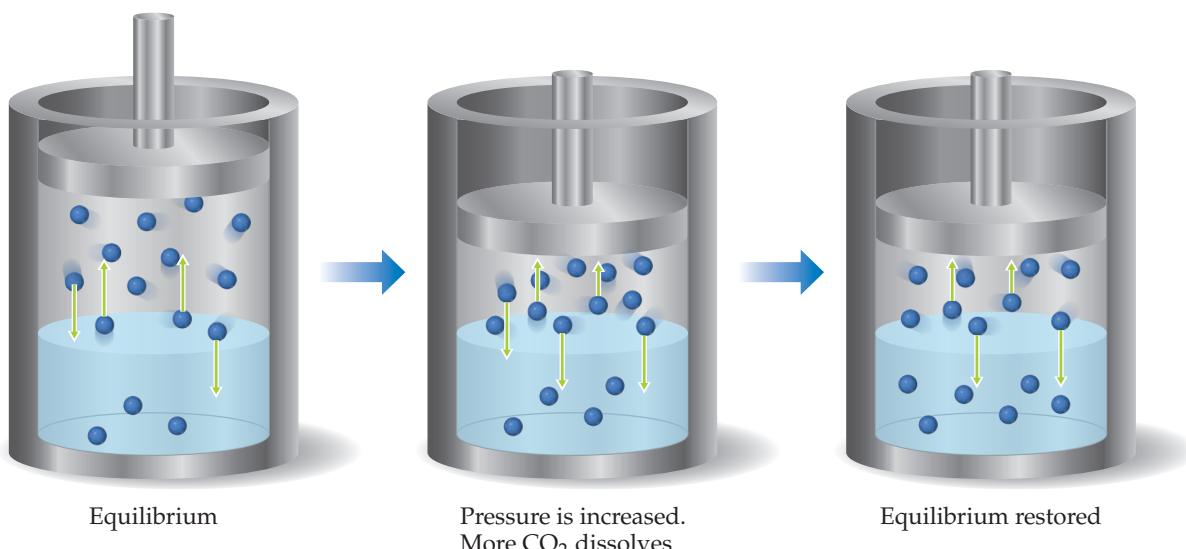
▲ Figure 13.10 The molecular structures of vitamins A and C.

## Pressure Effects

The solubilities of solids and liquids are not appreciably affected by pressure, whereas *the solubility of a gas in any solvent is increased as the partial pressure of the gas above the solvent increases*. We can understand the effect of pressure on gas solubility by considering Figure 13.11, which shows carbon dioxide gas distributed between the gas and solution phases. When equilibrium is established, the rate at which gas molecules enter the solution equals the rate at which solute molecules escape from the solution to enter the gas phase. The equal number of up and down arrows in the left container in Figure 13.11 represent these opposing processes.

**Go Figure**

If the partial pressure of a gas over a solution is doubled, how has the concentration of gas in the solution changed after equilibrium is restored?



▲ Figure 13.11 Effect of pressure on gas solubility.

**Sample Exercise 13.1****Predicting Solubility Patterns**

Predict whether each of the following substances is more likely to dissolve in the nonpolar solvent tetrachloromethane (CCl<sub>4</sub>) or in water: C<sub>7</sub>H<sub>16</sub>, Na<sub>2</sub>SO<sub>4</sub>, HCl, and I<sub>2</sub>.

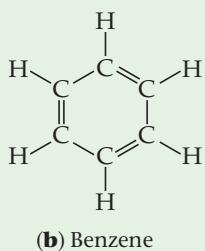
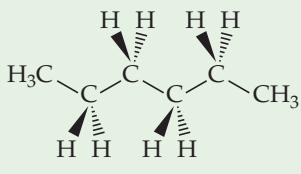
**SOLUTION**

**Analyze** We are given two solvents, one that is nonpolar (CCl<sub>4</sub>) and the other that is polar (H<sub>2</sub>O), and asked to determine which will be the better solvent for each solute listed.

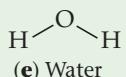
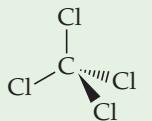
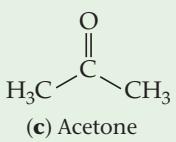
**Plan** By examining the formulas of the solutes, we can predict whether they are ionic or molecular. For those that are molecular, we can predict whether they are polar or nonpolar. We can then apply the idea that the nonpolar solvent will be better for the nonpolar solutes, whereas the polar solvent will be better for the ionic and polar solutes.

**Practice Exercise**

Which of the following solvents will best dissolve wax, which is a complex mixture of compounds that mostly are CH<sub>3</sub>—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—?



**Solve** C<sub>7</sub>H<sub>16</sub> is a hydrocarbon, so it is molecular and nonpolar. Na<sub>2</sub>SO<sub>4</sub>, a compound containing a metal and nonmetals, is ionic. HCl, a diatomic molecule containing two nonmetals that differ in electronegativity, is polar. I<sub>2</sub>, a diatomic molecule with atoms of equal electronegativity, is nonpolar. We would therefore predict that C<sub>7</sub>H<sub>16</sub> and I<sub>2</sub> (the nonpolar solutes) would be more soluble in the nonpolar CCl<sub>4</sub> than in polar H<sub>2</sub>O, whereas water would be the better solvent for Na<sub>2</sub>SO<sub>4</sub> and HCl (the ionic and polar covalent solutes).



Now suppose we exert greater pressure on the piston and compress the gas above the solution, as shown in the middle container in Figure 13.11. If we reduce the gas volume to half its original value, the pressure of the gas increases to about twice its original value. As a result of this pressure increase, the rate at which gas molecules strike the liquid surface and enter the solution phase increases. Thus, the solubility of the gas in the solution increases until equilibrium is again established; that is, solubility increases until the rate at which gas molecules enter the solution equals the rate at which they escape from the solution. Thus, *the solubility of a gas in a liquid solvent increases in direct proportion to the partial pressure of the gas above the solution* ([Figure 13.12](#)).

The relationship between pressure and gas solubility is expressed by **Henry's law**:

$$S_g = kP_g \quad [13.4]$$

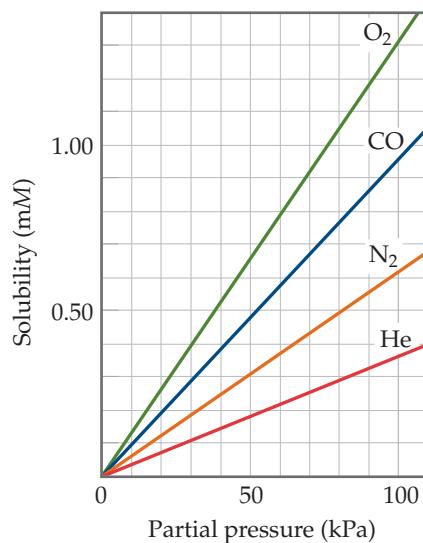
Here,  $S_g$  is the solubility of the gas in the solvent (usually expressed as molarity),  $P_g$  is the partial pressure of the gas over the solution, and  $k$  is a proportionality constant known as the *Henry's law constant*. The value of this constant depends on the solute, solvent, and temperature. As an example, the solubility of  $N_2$  gas in water at  $25^\circ\text{C}$  and 79.03 kPa pressure is  $4.75 \times 10^{-4} \text{ M}$ . The Henry's law constant for  $N_2$  in  $25^\circ\text{C}$  water is thus  $(4.75 \times 10^{-4} \text{ mol/L})/79.03 \text{ kPa} = 6.1 \times 10^{-6} \text{ mol/m}^3 \text{ Pa}$ . If the partial pressure of  $N_2$  is doubled, Henry's law predicts that the solubility in water at  $25^\circ\text{C}$  also doubles to  $9.50 \times 10^{-4} \text{ M}$ .

Bottlers use the effect of pressure on solubility in producing carbonated beverages, which are bottled under a carbon dioxide pressure greater than 101.3 kPa. When the bottles are opened to the air, the partial pressure of  $\text{CO}_2$  above the solution decreases. Hence, the solubility of  $\text{CO}_2$  decreases, and  $\text{CO}_2(g)$  escapes from the solution as bubbles ([Figure 13.13](#)).



### Go Figure

Does the gas with the largest molar mass have the highest or lowest solubility in water?



▲ **Figure 13.12** The solubility of a gas in water is directly proportional to the partial pressure of the gas. The solubilities are in millimoles of gas per liter of solution.



▲ **Figure 13.13** Gas solubility decreases as pressure decreases.  $\text{CO}_2$  bubbles out of solution when a carbonated beverage is opened because the  $\text{CO}_2$  partial pressure above the solution is reduced.



## Sample Exercise 13.2

### A Henry's Law Calculation

Calculate the concentration of CO<sub>2</sub> in a soft drink that is bottled with a partial pressure of CO<sub>2</sub> of 0.41 MPa over the liquid at 25 °C. The Henry's law constant for CO<sub>2</sub> in water at this temperature is  $3.4 \times 10^{-4}$  mol/m<sup>3</sup> Pa.

#### SOLUTION

**Analyze** We are given the partial pressure of CO<sub>2</sub>,  $P_{\text{CO}_2}$ , and the Henry's law constant,  $k$ , and asked to calculate the concentration of CO<sub>2</sub> in the solution.

**Plan** With the information given, we can use Henry's law, Equation 13.4, to calculate the solubility,  $S_{\text{CO}_2}$ .

$$\begin{aligned}\text{Solve } S_{\text{CO}_2} &= kP_{\text{CO}_2} = (3.4 \times 10^{-4} \text{ mol/m}^3 \text{ Pa})(0.41 \text{ MPa}) \\ &= 0.14 \text{ mol/L} = 0.14 \text{ M}\end{aligned}$$

**Check** The units are correct for solubility, and the answer has two significant figures consistent with both the partial pressure of CO<sub>2</sub> and the value of the Henry's law constant.

#### ► Practice Exercise

You double the partial pressure of a gas over a liquid at constant temperature. Which of these statements is then true?

- (a) The Henry's law constant is doubled.
- (b) The Henry's law constant is decreased by half.
- (c) There are half as many gas molecules in the liquid.
- (d) There are twice as many gas molecules in the liquid.
- (e) There is no change in the number of gas molecules in the liquid.

## Temperature Effects

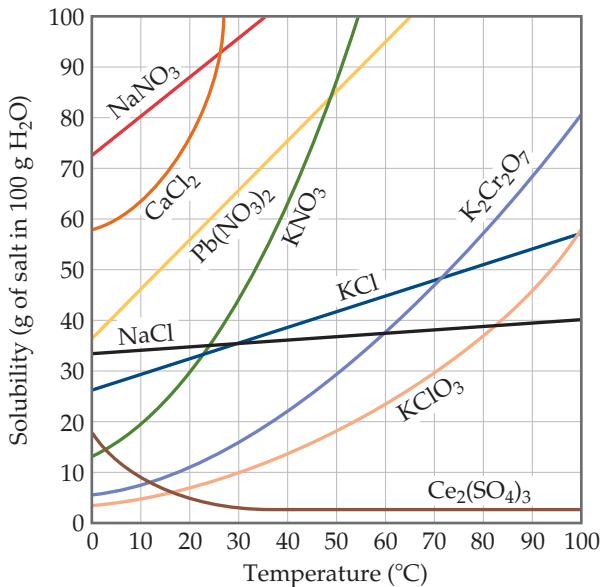
The solubility of most solid solutes in water increases as the solution temperature increases, as Figure 13.14 shows. There are exceptions to this rule, however, as seen for Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, whose solubility curve slopes downward with increasing temperature.

In contrast to solid solutes, the solubility of gases in water decreases with increasing temperature (Figure 13.15). If a glass of cold tap water is warmed, you can see bubbles on the inside of the glass because some of the dissolved air comes out of solution.



### Go Figure

How does the solubility of KCl at 80 °C compare with that of NaCl at the same temperature?

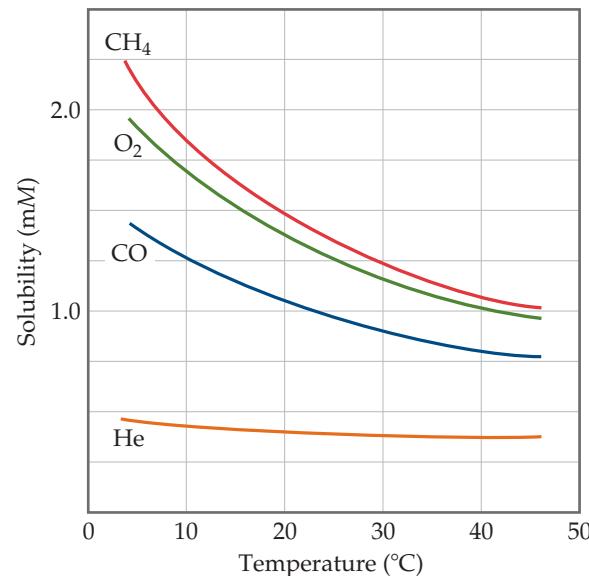


▲ Figure 13.14 Solubilities of some ionic compounds in water as a function of temperature.



### Go Figure

Between which two gases would you expect N<sub>2</sub> to fit on this graph?



▲ Figure 13.15 Solubilities of four gases in water as a function of temperature. The solubilities are in millimoles per liter of solution, for a constant total pressure of 1 atm in the gas phase.

Similarly, as carbonated beverages are allowed to warm, the solubility of CO<sub>2</sub> decreases, and CO<sub>2</sub>(g) escapes from the solution.

If you think about it, you can rationalize why the solubilities of gases and ionic solids in water respond differently to temperature. As you heat an aqueous solution that contains a gas, you give enough energy to the gas particles for them to escape from the solution and go into the gas phase. Thus, increasing temperature reduces the solubility of the gas. On the other hand, if you heat up a mixture of water and an ionic solid, you give energy to the solid so it can break into its constituent ions that are then hydrated by water. Thus, increasing temperature increases the solubility of the ionic solid.

## CHEMISTRY AND LIFE Blood Gases and Deep-Sea Diving

Because gas solubility increases with increasing pressure, divers who breathe compressed air (Figure 13.16) must be concerned about the solubility of gases in their blood. Although the gases are not very soluble at sea level, their solubilities can be appreciable at deep levels where their partial pressures are greater. Thus, divers must ascend slowly to prevent dissolved gases from being released rapidly from solution and forming bubbles in the blood and other fluids in the body. These bubbles affect nerve impulses and cause decompression sickness, or “the bends,” which is a painful and potentially fatal condition. Nitrogen is the main problem because it is the most abundant gas in air and because it can be removed from the body only through the respiratory system. Oxygen, in contrast, is consumed in metabolism.

Deep-sea divers sometimes substitute helium for nitrogen in the air they breathe because helium has a much lower solubility in biological fluids than N<sub>2</sub>. For example, divers working at a depth of 30 m experience a pressure of about 405.3 kPa. At this pressure, a mixture of 95% helium and 5% oxygen gives an oxygen partial pressure of about 20.3 kPa, which is the partial pressure of oxygen in normal air at



**▲ Figure 13.16** Gas solubility increases as pressure increases. Divers who use compressed gases must be concerned about the solubility of the gases in their blood.

101.3 kPa. If the oxygen partial pressure becomes too great, the urge to breathe is reduced, CO<sub>2</sub> is not removed from the body, and CO<sub>2</sub> poisoning occurs. At excessive concentrations in the body, carbon dioxide acts as a neurotoxin, interfering with nerve conduction and transmission.

**Related Exercises:** 13.25, 13.77, 13.112

## Self-Assessment Exercise

- 13.9** Is there likely to be more gases dissolved in a mountain lake or a pond at sea level?

- (a)** Mountain lake  
**(b)** Pond at sea level

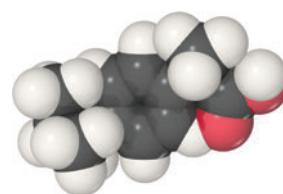
## Exercises

- 13.10** By referring to Figure 13.14, determine the mass of each of the following salts required to form a saturated solution in 250 g of water at 20 °C: **(a)** NaCl, **(b)** CaCl<sub>2</sub>, **(c)** KNO<sub>3</sub>.

- 13.11** Oil and water are immiscible. Which is the most likely reason? **(a)** Oil molecules are denser than water. **(b)** Oil molecules are composed mostly of carbon and hydrogen. **(c)** Oil molecules have higher molar masses than water. **(d)** Oil molecules have higher vapor pressures than water. **(e)** Oil molecules have higher boiling points than water.

- 13.12** Common laboratory solvents include acetone (CH<sub>3</sub>COCH<sub>3</sub>), methanol (CH<sub>3</sub>OH), toluene (C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>), and water. Which of these is the best solvent for nonpolar solutes?

- 13.13** Ibuprofen, widely used as a pain reliever, has a limited solubility in water, less than 1 mg/mL. Which part of the molecule's structure (gray, white, red) contributes to its water solubility? Which part of the molecule (gray, white, red) contributes to its water insolubility?



Ibuprofen

- 13.14** Which of the following in each pair is likely to be more soluble in water: **(a)** cyclohexane (C<sub>6</sub>H<sub>12</sub>) or glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>), **(b)** propanoic acid (CH<sub>3</sub>CH<sub>2</sub>COOH) or sodium propanoate (CH<sub>3</sub>CH<sub>2</sub>COONa), **(c)** HCl or ethyl chloride (CH<sub>3</sub>CH<sub>2</sub>Cl)? Explain in each case.

- 13.15** Indicate whether each statement is true or false:

- (a)** If you compare the solubility of a gas in water at two different temperatures, you find the gas is more soluble at the lower temperature.

- (b) The solubility of most ionic solids in water decreases as the temperature of the solution increases.
- (c) The solubility of most gases in water decreases as the temperature increases because water is breaking its hydrogen bonding to the gas molecules as the temperature is raised.
- (d) Some ionic solids become less soluble in water as the temperature is raised.

**13.16** The Henry's law constant for hydrogen gas ( $H_2$ ) in water at  $25^\circ C$  is  $7.7 \times 10^{-6} M/kPa$  and the constant for argon (Ar) at  $25^\circ C$  is  $1.4 \times 10^{-5} M/kPa$ . If the two gases are each present at 253 kPa pressure, calculate the solubility of each gas.

13.9 (b)

 **Answers to Self-Assessment Exercises**

## 13.4 | Expressing Solution Concentration



The concentration of a solution can be expressed either qualitatively or quantitatively. The terms *dilute* and *concentrated* are used to describe a solution qualitatively. A solution with a relatively small concentration of solute is said to be dilute; one with a large concentration is said to be concentrated. Chemists use various ways to express concentration quantitatively, and we examine several of these next.

By the end of this section, you should be able to convert between different concentration units.

### Mass Percentage, ppm, and ppb

One of the simplest quantitative expressions of concentration is the **mass percentage** of a component in a solution, given by

$$\text{Mass \% of component} = \frac{\text{mass of component in solution}}{\text{total mass of solution}} \times 100 \quad [13.5]$$

Because *percent* means “per hundred,” a solution of hydrochloric acid that is 36% HCl by mass contains 36 g of HCl for each 100 g of solution.

We often express the concentration of very dilute solutions in **parts per million (ppm)** or **parts per billion (ppb)**. These quantities are similar to mass percentage but use  $10^6$  (a million) or  $10^9$  (a billion), respectively, in place of 100, as a multiplier for the ratio of the mass of solute to the mass of solution. Thus, parts per million is defined as

$$\text{ppm of component} = \frac{\text{mass of component in solution}}{\text{total mass of solution}} \times 10^6 \quad [13.6]$$

A solution whose solute concentration is 1 ppm contains 1 g of solute for each million ( $10^6$ ) grams of solution or, equivalently, 1 mg of solute per kilogram of solution. Because the density of water is 1 g/mL, 1 kg of a dilute aqueous solution has a volume very close to 1 L. Thus, 1 ppm also corresponds to 1 mg of solute per liter of aqueous solution.

The acceptable maximum concentrations of toxic or carcinogenic substances in the environment are often expressed in ppm or ppb. For example, the World Health Organisation recommended maximum allowable concentration of arsenic in drinking water is 0.010 ppm; that is, 0.010 mg of arsenic per liter of water. This concentration corresponds to 10 ppb.

## Mole Fraction, Molarity, and Molality

Concentration expressions are often based on the number of moles of one or more components of the solution. Recall from Section 10.5 that the *mole fraction* of a component of a solution is given by

$$\text{Mole fraction of component} = \frac{\text{moles of component}}{\text{total moles of all components}} \quad [13.7]$$

### Sample Exercise 13.3

#### Calculation of Mass-Related Concentrations

- (a) A solution is made by dissolving 13.5 g of glucose ( $C_6H_{12}O_6$ ) in 0.100 kg of water. What is the mass percentage of solute in this solution?
- (b) A 2.5 g sample of groundwater was found to contain 5.4  $\mu\text{g}$  of  $Zn^{2+}$ . What is the concentration of  $Zn^{2+}$  in parts per million?

#### SOLUTION

**(a) Analyze** We are given the number of grams of solute (13.5 g) and the number of grams of solvent (0.100 kg = 100 g). From this, we must calculate the mass percentage of solute.

**Plan** We can calculate the mass percentage by using Equation 13.5. The mass of the solution is the sum of the mass of solute (glucose) and the mass of solvent (water).

$$\begin{aligned} \text{Solve Mass \% of glucose} &= \frac{\text{mass glucose}}{\text{mass solution}} \times 100 \\ &= \frac{13.5 \text{ g}}{(13.5 + 100) \text{ g}} \times 100 = 11.9\% \end{aligned}$$

**Comment** The mass percentage of water in this solution is  $(100 - 11.9)\% = 88.1\%$ .

**(b) Analyze** In this case we are given the number of micrograms of solute. Because 1  $\mu\text{g}$  is  $1 \times 10^{-6}$  g,  $5.4 \mu\text{g} = 5.4 \times 10^{-6}$  g.

**Plan** We calculate the parts per million using Equation 13.6.

$$\begin{aligned} \text{Solve ppm} &= \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6 \\ &= \frac{5.4 \times 10^{-6} \text{ g}}{2.5 \text{ g}} \times 10^6 = 2.2 \text{ ppm} \end{aligned}$$

#### ► Practice Exercise

Calculate the mass percentage of NaCl in a solution containing 1.50 g of NaCl in 50.0 g of water.

- (a) 0.0291% (b) 0.0300% (c) 0.0513% (d) 2.91% (e) 3.00%

The symbol  $X$  is commonly used for mole fraction, with a subscript to indicate the component of interest. For example, the mole fraction of HCl in a hydrochloric acid solution is represented as  $X_{\text{HCl}}$ . Thus, if a solution contains 1.00 mol of HCl (36.5 g) and 8.00 mol of water (144 g), the mole fraction of HCl is  $X_{\text{HCl}} = (1.00 \text{ mol}) / (1.00 \text{ mol} + 8.00 \text{ mol}) = 0.111$ . Mole fractions have no units because the units in the numerator and the denominator cancel. The sum of the mole fractions of all components of a solution must equal 1. Thus, in the aqueous HCl solution,  $X_{\text{H}_2\text{O}} = 1.000 - 0.111 = 0.889$ . Mole fractions are very useful when dealing with gases, as we saw in Section 10.5, but have limited use when dealing with liquid solutions.

Recall from Section 4.5 that the *molarity* ( $M$ ) of a solute in a solution is defined as

$$\text{Molarity} = \frac{\text{moles of solute}}{\text{liters of solution}} \quad [13.8]$$

For example, if you dissolve 0.500 mol of  $\text{Na}_2\text{CO}_3$  in enough water to form 0.250 L of solution, the molarity of  $\text{Na}_2\text{CO}_3$  in the solution is  $(0.500 \text{ mol})/(0.250 \text{ L}) = 2.00 \text{ M}$ . Molarity is especially useful for relating the volume of a solution to the quantity of solute contained in that volume, as we saw in our discussions of titrations.

The **molality** of a solution, denoted  $m$ , is a concentration unit that is also based on moles of solute. Molality equals the number of moles of solute per kilogram of solvent:

$$\text{Molality} = \frac{\text{moles of solute}}{\text{kilograms of solvent}} \quad [13.9]$$

Thus, if you form a solution by mixing 0.200 mol of  $\text{NaOH}$  (8.00 g) and 0.500 kg of water (500 g), the concentration of the solution is  $(0.200 \text{ mol})/(0.500 \text{ kg}) = 0.400 \text{ m}$  (that is, 0.400 molal) in  $\text{NaOH}$ .

The definitions of molarity and molality are similar enough that they can be easily confused.

- Molarity depends on the *volume of solution*.
- Molality depends on the *mass of solvent*.

When water is the solvent, the molality and molarity of dilute solutions are numerically about the same because 1 kg of solvent is nearly the same as 1 kg of solution, and 1 kg of the solution has a volume of about 1 L.

The molality of a given solution does not vary with temperature because masses do not vary with temperature. The molarity of the solution does change with temperature, however, because the volume of the solution expands or contracts with temperature. Thus, molality is often the concentration unit of choice when a solution is to be used over a range of temperatures.

## Sample Exercise 13.4

### Calculation of Molality

A solution is made by dissolving 4.35 g of glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) in 25.0 mL of water at 25 °C. Calculate the molality of glucose in the solution. Water has a density of 1.00 g/mL.

### SOLUTION

**Analyze** We are asked to calculate a solution concentration in units of molality. To do this, we must determine the number of moles of solute (glucose) and the number of kilograms of solvent (water).

### Solve

Use the molar mass of glucose, 180.2 g/mol, to convert grams to moles:

$$\text{Mol C}_6\text{H}_{12}\text{O}_6 = (4.35 \text{ g C}_6\text{H}_{12}\text{O}_6) \left( \frac{1 \text{ mol C}_6\text{H}_{12}\text{O}_6}{180.2 \text{ g C}_6\text{H}_{12}\text{O}_6} \right) = 0.0241 \text{ mol C}_6\text{H}_{12}\text{O}_6$$

Because water has a density of 1.00 g/mL, the mass of the solvent is:

$$(25.0 \text{ mL})(1.00 \text{ g/mL}) = 25.0 \text{ g} = 0.0250 \text{ kg}$$

Finally, use Equation 13.9 to obtain the molality:

$$\text{Molality of C}_6\text{H}_{12}\text{O}_6 = \frac{0.0241 \text{ mol C}_6\text{H}_{12}\text{O}_6}{0.0250 \text{ kg H}_2\text{O}} = 0.964 \text{ m}$$

**Plan** We use the molar mass of  $\text{C}_6\text{H}_{12}\text{O}_6$  to convert grams of glucose to moles. We use the density of water to convert milliliters of water to kilograms. The molality equals the number of moles of solute (glucose) divided by the number of kilograms of solvent (water).

### ► Practice Exercise

Suppose you take a solution and add more solvent, so that the original mass of solvent is doubled. You take this new solution and add more solute, so that the original mass of the solute is doubled. What happens to the molality of the final solution, compared to the original molality?

- (a) It is doubled.
- (b) It is decreased by half.
- (c) It is unchanged.
- (d) It will increase or decrease depending on the molar mass of the solute.
- (e) There is no way to tell without knowing the molar mass of the solute.

## Converting Concentration Units

If you follow the dimensional analysis techniques you learned in Chapter 1, you can convert between concentration units, as shown in Sample Exercise 13.5. To convert between molality and molarity, the density of the solution will be needed, as in Sample Exercise 13.6.

### Sample Exercise 13.5

#### Calculation of Mole Fraction and Molality

An aqueous solution of hydrochloric acid contains 36% HCl by mass. (a) Calculate the mole fraction of HCl in the solution. (b) Calculate the molality of HCl in the solution.

#### SOLUTION

**Analyze** We are asked to calculate the concentration of the solute, HCl, in two related concentration units, given only the percentage by mass of the solute in the solution.

**Plan** In converting concentration units based on the mass or moles of solute and solvent (mass percentage, mole fraction, and molality), it is useful to assume a certain total mass of

solution. Let's assume that there is exactly 100 g of solution. Because the solution is 36% HCl, it contains 36 g of HCl and  $(100 - 36)$  g = 64 g of H<sub>2</sub>O. We must convert grams of solute (HCl) to moles to calculate either mole fraction or molality. We must convert grams of solvent (H<sub>2</sub>O) to moles to calculate mole fractions and to kilograms to calculate molality.

#### Solve

- (a) To calculate the mole fraction of HCl, we convert the masses of HCl and H<sub>2</sub>O to moles and then use Equation 13.7:

$$\text{Moles HCl} = (36 \text{ g HCl}) \left( \frac{1 \text{ mol HCl}}{36.5 \text{ g HCl}} \right) = 0.99 \text{ mol HCl}$$

$$\text{Moles H}_2\text{O} = (64 \text{ g H}_2\text{O}) \left( \frac{1 \text{ mol H}_2\text{O}}{18 \text{ g H}_2\text{O}} \right) = 3.6 \text{ mol H}_2\text{O}$$

$$X_{\text{HCl}} = \frac{\text{moles HCl}}{\text{moles H}_2\text{O} + \text{moles HCl}} = \frac{0.99}{3.6 + 0.99} = \frac{0.99}{4.6} = 0.22$$

- (b) To calculate the molality of HCl in the solution, we use Equation 13.9. We calculated the number of moles of HCl in part (a), and the mass of solvent is 64 g = 0.064 kg:

Notice that we can't readily calculate the molarity of the solution because we don't know the volume of the 100 g of solution.

$$\text{Molality of HCl} = \frac{0.99 \text{ mol HCl}}{0.064 \text{ kg H}_2\text{O}} = 15 \text{ m}$$

#### ► Practice Exercise

The solubility of oxygen gas in water at 40 °C is 1.0 mmol per liter of solution. What is this concentration in units of mole fraction?

- (a)  $1.00 \times 10^{-6}$  (b)  $1.80 \times 10^{-5}$  (c)  $1.00 \times 10^{-2}$   
 (d)  $1.80 \times 10^{-2}$  (e)  $5.55 \times 10^{-2}$

### Sample Exercise 13.6

#### Calculation of Molarity Using the Density of the Solution

A solution with a density of 0.876 g/mL contains 5.0 g of toluene (C<sub>7</sub>H<sub>8</sub>) and 225 g of benzene. Calculate the molarity of the solution.

#### SOLUTION

**Analyze** Our goal is to calculate the molarity of a solution, given the masses of solute (5.0 g) and solvent (225 g) and the density of the solution (0.876 g/mL).

**Plan** The molarity of a solution is the number of moles of solute divided by the number of liters of solution (Equation 13.8). The number of moles of solute (C<sub>7</sub>H<sub>8</sub>) is calculated from the number of grams of solute and its molar mass. The volume of the solution is obtained from the mass of the solution (mass of solution = mass of solute + mass of solvent = 5.0 g + 225 g = 230 g) and its density.

#### Solve

The number of moles of solute is:

$$\text{Moles C}_7\text{H}_8 = (5.0 \text{ g C}_7\text{H}_8) \left( \frac{1 \text{ mol C}_7\text{H}_8}{92 \text{ g C}_7\text{H}_8} \right) = 0.054 \text{ mol}$$

The density of the solution is used to convert the mass of the solution to its volume:

$$\text{Milliliters soln} = (230 \text{ g}) \left( \frac{1 \text{ mL}}{0.876 \text{ g}} \right) = 263 \text{ mL}$$

Molarity is moles of solute per liter of solution:

$$\text{Molarity} = \left( \frac{\text{moles C}_7\text{H}_8}{\text{liter soln}} \right) = \left( \frac{0.054 \text{ mol C}_7\text{H}_8}{263 \text{ mL soln}} \right) \left( \frac{1000 \text{ mL soln}}{1 \text{ L soln}} \right) = 0.21 \text{ M}$$

**Check** The magnitude of our answer is reasonable. Rounding moles to 0.05 and liters to 0.25 gives a molarity of  $(0.05 \text{ mol})/(0.25 \text{ L}) = 0.2 \text{ M}$ .

The units for our answer ( $\text{mol/L}$ ) are correct, and the answer, 0.21, has two significant figures, corresponding to the number of significant figures in the mass of solute (2).

**Comment** Because the mass of the solvent (0.225 kg) and the volume of the solution (0.263) are similar in magnitude,

the molarity and molality are also similar in magnitude:  $(0.054 \text{ mol C}_7\text{H}_8)/(0.225 \text{ kg solvent}) = 0.24 \text{ M}$ .

### ► Practice Exercise

A solution containing equal masses of glycerol ( $\text{C}_3\text{H}_8\text{O}_3$ ) and water has a density of 1.10 g/mL. Calculate (a) the molality of glycerol, (b) the mole fraction of glycerol, (c) the molarity of glycerol in the solution.

## Self-Assessment Exercise

- 13.17** Commercial concentrated aqueous ammonia is 28%  $\text{NH}_3$  by mass and has a density of 0.90 g/mL. What is the molarity of this solution?

- (a) 15 M
- (b) 16 M
- (c) 252 M

Assume 1.00 L of solution. Calculate mass of 1 L of solution using density.

$$1.00 \text{ L solution} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{0.90 \text{ g solution}}{1 \text{ mL solution}} = 9.0 \times 10^2 \text{ g solution/L}$$

Calculate mass of  $\text{NH}_3$  using mass %, then mol  $\text{NH}_3$  in 1.00 L.

$$\frac{900 \text{ g solution}}{1.00 \text{ L solution}} \times \frac{28 \text{ g NH}_3}{100 \text{ g solution}} \times \frac{1 \text{ mol NH}_3}{17.03 \text{ g NH}_3} = 14.80 = 15 \text{ mol NH}_3/\text{L solution} = 15 \text{ M NH}_3$$

## Exercises

- 13.18** (a) What is the mass percentage of iodine in a solution containing 0.035 mol  $\text{I}_2$  in 125 g of  $\text{CCl}_4$ ? (b) Seawater contains 0.0079 g of  $\text{Sr}^{2+}$  per kilogram of water. What is the concentration of  $\text{Sr}^{2+}$  in ppm?

- 13.19** A solution is made containing 20.8 g of phenol ( $\text{C}_6\text{H}_5\text{OH}$ ) in 425 g of ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ). Calculate (a) the mole fraction of phenol, (b) the mass percent of phenol, (c) the molality of phenol.

- 13.20** What is the molarity of each of the following solutions: (a) 15.0 g of  $\text{Al}_2(\text{SO}_4)_3$  in 0.250 mL solution, (b) 5.25 g of  $\text{Mn}(\text{NO}_3)_2 \cdot 2 \text{ H}_2\text{O}$  in 175 mL of solution, (c) 35.0 mL of 9.00 M  $\text{H}_2\text{SO}_4$  diluted to 0.500 L?

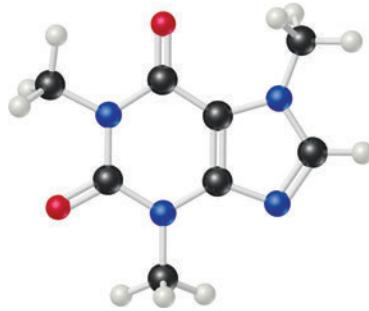
- 13.21** (a) What is the molality of a solution formed by dissolving 1.12 mol of  $\text{KCl}$  in 16.0 mol of water? (b) How many grams of sulfur ( $\text{S}_8$ ) must be dissolved in 100.0 g of naphthalene ( $\text{C}_{10}\text{H}_8$ ) to make a 0.12 m solution?

- 13.22** Ascorbic acid (vitamin C,  $\text{C}_6\text{H}_8\text{O}_6$ ) is a water-soluble vitamin. A solution containing 80.5 g of ascorbic acid dissolved in 210 g of water has a density of 1.22 g/mL at 55 °C. Calculate (a) the mass percentage, (b) the mole fraction, (c) the molality, (d) the molarity of ascorbic acid in this solution.

- 13.23** Calculate the number of moles of solute present in each of the following solutions: (a) 255 mL of 1.50 M  $\text{HNO}_3(aq)$ , (b) 50.0 mg of an aqueous solution that is 1.50 m  $\text{NaCl}$ ,

- (c) 75.0 g of an aqueous solution that is 1.50% sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) by mass.

- 13.24** Caffeine ( $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$ ) is a stimulant found in coffee and tea. If a solution of caffeine in the solvent chloroform ( $\text{CHCl}_3$ ) has a concentration of 0.0500 m, calculate (a) the percentage of caffeine by mass, (b) the mole fraction of caffeine in the solution.



Caffeine

- 13.25** Breathing air that contains 4.0 % by volume  $\text{CO}_2$  over time causes rapid breathing, throbbing headache, and nausea, among other symptoms. What is the concentration of  $\text{CO}_2$  in such air in terms of (a) mol percentage, (b) molarity, assuming 101.3 kPa pressure and a body temperature of 37 °C?

13.17 (a)



## 13.5 | Colligative Properties



If you scatter a small amount of icing sugar on a bowl of strawberries, they appear to become juicer. The sugar draws juice from inside the cells of the fruit to the outside. This is a process called osmosis and is one of four colligative properties that we study next. By the end of this section, you should be able to

- Identify the colligative property operating in a given situation
- Perform calculations involving colligative properties

Some physical properties of solutions differ in important ways from those of the pure solvent. For example, pure water freezes at 0 °C, but aqueous solutions freeze at lower temperatures. We apply this behavior when we add ethylene glycol antifreeze to a car's radiator to lower the freezing point of the solution. The added solute also raises the boiling point of the solution above that of pure water, making it possible to operate the engine at a higher temperature.

Lowering of the freezing point and raising of the boiling point are physical properties of solutions that depend on the *quantity* (concentration) but not on the *kind* or *identity* of the solute particles. Such properties are called **colligative properties**. (*Colligative* means “depending on the collection”; colligative properties depend on the collective effect of the number of solute particles.)

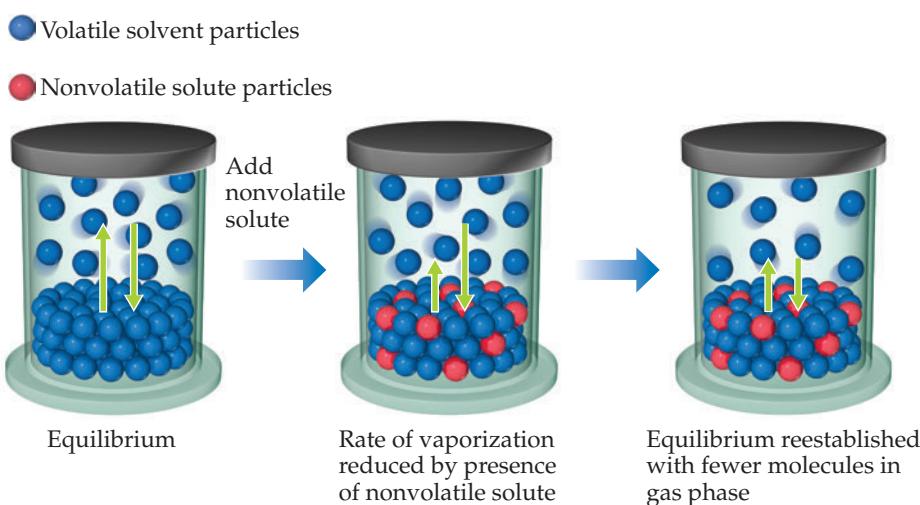
In addition to freezing-point lowering and boiling-point raising, two other important colligative properties are vapor-pressure lowering and osmotic pressure. As we examine each one, notice how solute concentration quantitatively affects the property.

### Vapor-Pressure Lowering

A liquid in a closed container establishes equilibrium with its vapor. The *vapor pressure* is the pressure exerted by the vapor when it is at equilibrium with the liquid (that is, when the rate of vaporization equals the rate of condensation). A substance that has no measurable vapor pressure is *nonvolatile*, whereas one that exhibits a vapor pressure is *volatile*.

A solution consisting of a *volatile* liquid solvent and a *nonvolatile* solute forms spontaneously because of the increase in entropy that accompanies their mixing. In effect, the solvent molecules are stabilized in their liquid state by this process and thus have a lower tendency to escape into the vapor state. Therefore, when a *nonvolatile* solute is present, the vapor pressure of the solvent is lower than the vapor pressure of the pure solvent, as illustrated in [Figure 13.17](#).

► **Figure 13.17 Vapor-pressure lowering.** The presence of nonvolatile solute particles in a liquid solvent results in a reduction of the vapor pressure above the liquid.



Ideally, the vapor pressure of a *volatile* solvent above a solution containing a *nonvolatile* solute is proportional to the solvent's concentration in the solution. This relationship is expressed quantitatively by **Raoult's law**, which states that the partial pressure exerted by solvent vapor above the solution,  $P_{\text{solution}}$ , equals the product of the mole fraction of the solvent,  $X_{\text{solvent}}$ , times the vapor pressure of the pure solvent,  $P_{\text{solvent}}^{\circ}$ :

$$P_{\text{solution}} = X_{\text{solvent}} P_{\text{solvent}}^{\circ} \quad [13.10]$$

For example, the vapor pressure of pure water at 20 °C is  $P_{\text{H}_2\text{O}}^{\circ} = 2.33 \text{ kPa}$ . Imagine holding the temperature constant while adding glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) to the water so that the mole fractions in the resulting solution are  $X_{\text{H}_2\text{O}} = 0.800$  and  $X_{\text{C}_6\text{H}_{12}\text{O}_6} = 0.200$ . According to Equation 13.10, the vapor pressure of the water above this solution is 80.0% of that of pure water:

$$P_{\text{solution}} = (0.800)(2.33 \text{ kPa}) = 1.87 \text{ kPa}$$

The presence of the *nonvolatile* solute lowers the vapor pressure of the *volatile* solvent by  $2.33 \text{ kPa} - 1.87 \text{ kPa} = 0.46 \text{ kPa}$ .

The vapor-pressure lowering,  $\Delta P$ , is directly proportional to the mole fraction of the solute,  $X_{\text{solute}}$ :

$$\Delta P = X_{\text{solute}} P_{\text{solvent}}^{\circ} \quad [13.11]$$

Thus, for the example of the solution of glucose in water, we have

$$\Delta P = X_{\text{C}_6\text{H}_{12}\text{O}_6} P_{\text{H}_2\text{O}}^{\circ} = (0.200)(2.33 \text{ kPa}) = 0.466 \text{ kPa}$$

The vapor-pressure lowering caused by adding a *nonvolatile* solute depends on the total concentration of solute particles, regardless of whether they are molecules or ions. Remember that vapor-pressure lowering is a colligative property, so its value for any solution depends on the concentration of solute particles and not on their kind or identity.

## Sample Exercise 13.7

### Calculation of Vapor Pressure of a Solution

Glycerin ( $\text{C}_3\text{H}_8\text{O}_3$ ) is a nonvolatile nonelectrolyte with a density of 1.26 g/mL at 25 °C. Calculate the vapor pressure at 25 °C of a solution made by adding 50.0 mL of glycerin to 500.0 mL of water. The vapor pressure of pure water at 25 °C is 3.17 kPa (Appendix B), and its density is 1.00 g/mL.

### SOLUTION

**Analyze** Our goal is to calculate the vapor pressure of a solution, given the volume of solute and solvent and the density of the solute.

**Plan** We can use Raoult's law (Equation 13.10) to calculate the vapor pressure of a solution. The mole fraction of the solvent in the solution,  $X_{\text{solvent}}$ , is the ratio of the number of moles of solvent ( $\text{H}_2\text{O}$ ) to total moles of solution (moles  $\text{C}_3\text{H}_8\text{O}_3$  + moles  $\text{H}_2\text{O}$ ).

**Solve**

To calculate the mole fraction of water in the solution, we must determine the number of moles of  $C_3H_8O_3$  and  $H_2O$ :

$$\text{Moles } C_3H_8O_3 = (50.0 \text{ mL } C_3H_8O_3) \left( \frac{1.26 \text{ g } C_3H_8O_3}{1 \text{ mL } C_3H_8O_3} \right) \left( \frac{1 \text{ mol } C_3H_8O_3}{92.1 \text{ g } C_3H_8O_3} \right) = 0.684 \text{ mol}$$

$$\text{Moles } H_2O = (500.0 \text{ mL } H_2O) \left( \frac{1.00 \text{ g } H_2O}{1 \text{ mL } H_2O} \right) \left( \frac{1 \text{ mol } H_2O}{18.0 \text{ g } H_2O} \right) = 27.8 \text{ mol}$$

$$X_{H_2O} = \frac{\text{mol } H_2O}{\text{mol } H_2O + \text{mol } C_3H_8O_3} = \frac{27.8}{27.8 + 0.684} = 0.976$$

We now use Raoult's law to calculate the vapor pressure of water for the solution:

$$P_{H_2O} = X_{H_2O} P_{H_2O}^\circ = (0.976)(3.17 \text{ kPa}) = 3.09 \text{ kPa}$$

**Comment** The vapor pressure of the solution has been lowered by  $3.17 \text{ kPa} - 3.09 \text{ kPa} = 0.08 \text{ kPa}$  relative to that of pure water. The vapor-pressure lowering can be calculated directly using Equation 13.11 together with the mole fraction of the solute,  $C_3H_8O_3$ :  $\Delta P = X_{C_3H_8O_3} P_{H_2O}^\circ = (0.024)(3.17 \text{ kPa}) = 0.076 \text{ kPa}$ . Notice that the use of Equation 13.11 gives one more significant figure than the number obtained by subtracting the vapor pressure of the solution from that of the pure solvent.

**► Practice Exercise**

The vapor pressure of pure water at  $110^\circ\text{C}$  is 142.7 kPa. A solution of ethylene glycol and water has a vapor pressure of 1.00 atm at  $110^\circ\text{C}$ . Assuming that Raoult's law is obeyed, what is the mole fraction of ethylene glycol in the solution?

**A CLOSER LOOK Ideal Solutions with Two or More Volatile Components**

Solutions sometimes have two or more volatile components. Petrol, for example, is a solution of several volatile liquids. To gain some understanding of such mixtures, consider an ideal solution of two volatile liquids, A and B. (For our purposes here, it does not matter which we call the solute and which the solvent.) The partial pressures above the solution are given by Raoult's law:

$$P_A = X_A P_A^\circ \quad \text{and} \quad P_B = X_B P_B^\circ$$

and the total vapor pressure above the solution is

$$P_{\text{total}} = P_A + P_B = X_A P_A^\circ + X_B P_B^\circ$$



▲ Figure 13.18 The volatile components of organic mixtures can be separated on an industrial scale in these distillation towers.

Consider a mixture of 1.0 mol of benzene ( $C_6H_6$ ) and 2.0 mol of toluene ( $C_7H_8$ ) ( $X_{\text{ben}} = 0.33$ ,  $X_{\text{tol}} = 0.67$ ). At  $20^\circ\text{C}$ , the vapor pressures of the pure substances are  $P_{\text{ben}}^\circ = 10 \text{ kPa}$  and  $P_{\text{tol}}^\circ = 2.9 \text{ kPa}$ . Thus, the partial pressures above the solution are

$$P_{\text{ben}} = (0.33)(10 \text{ kPa}) = 3.3 \text{ kPa}$$

$$P_{\text{tol}} = (0.67)(2.9 \text{ kPa}) = 1.9 \text{ kPa}$$

and the total vapor pressure above the liquid is

$$P_{\text{total}} = P_{\text{ben}} + P_{\text{tol}} = 3.3 \text{ kPa} + 1.9 \text{ kPa} = 5.2 \text{ kPa}$$

Note that the vapor is richer in benzene, the more volatile component.

The mole fraction of benzene in the vapor is given by the ratio of its vapor pressure to the total pressure (Equations 10.14 and 10.15):

$$X_{\text{ben}} \text{ in vapor} = \frac{P_{\text{ben}}}{P_{\text{total}}} = \frac{3.3 \text{ kPa}}{5.2 \text{ kPa}} = 0.63$$

Although benzene constitutes only 33% of the molecules in the solution, it makes up 63% of the molecules in the vapor.

When an ideal liquid solution containing two volatile components is in equilibrium with its vapor, the more volatile component will be relatively richer in the vapor. This fact forms the basis of *distillation*, a technique used to separate (or partially separate) mixtures containing volatile components. Distillation is a way of purifying liquids and is the procedure by which petrochemical plants achieve the separation of crude petroleum into gasoline, diesel fuel, lubricating oil, and other products (Figure 13.18). Distillation is also used routinely on a small scale in the laboratory.

**Related Exercises: 13.30, 13.82**

An ideal gas is defined as one that obeys the ideal-gas equation, and an **ideal solution** is defined as one that obeys Raoult's law. Whereas ideality for a gas arises from a complete lack of intermolecular interaction, ideality for a solution implies total uniformity of interaction. The molecules in an ideal solution all influence one

another in the same way—in other words, solute–solute, solvent–solvent, and solute–solvent interactions are indistinguishable from one another. Real solutions best approximate ideal behavior when the solute concentration is low and solute and solvent have similar molecular sizes and take part in similar types of intermolecular attractions.

Many solutions do not obey Raoult's law exactly and so are not ideal. If, for instance, the solvent–solute interactions in a solution are weaker than either the solvent–solvent or solute–solute interactions, the vapor pressure tends to be greater than that predicted by Raoult's law. When the solute–solvent interactions in a solution are exceptionally strong, as might be the case when hydrogen bonding exists, the vapor pressure is lower than that predicted by Raoult's law. Although you should be aware that these departures from ideality occur, we will ignore them for the remainder of this chapter.

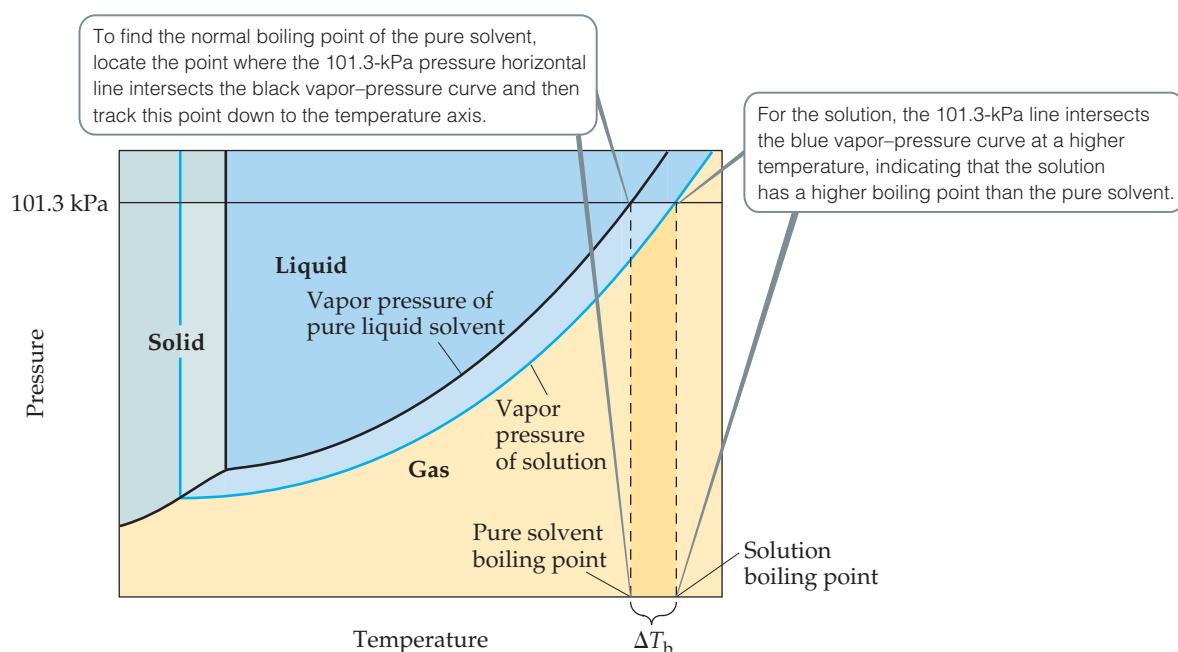
### Boiling-Point Elevation

In Sections 11.5 and 11.6, we examined the vapor pressures of pure substances and how to use them to construct phase diagrams. How does the phase diagram of a solution and, hence, its boiling and freezing points differ from that of the pure solvent? The addition of a nonvolatile solute lowers the vapor pressure of the solution. Thus, in **Figure 13.19** the vapor–pressure curve of the solution is shifted downward relative to the vapor–pressure curve of the pure solvent.

Recall from Section 11.5 that the normal boiling point of a liquid is the temperature at which its vapor pressure equals 101.3 kPa. Because the solution has a lower vapor pressure than the pure solvent, a higher temperature is required for the solution to achieve a vapor pressure of 101.3 kPa. As a result, *the boiling point of the solution is higher than that of the pure solvent*. This effect is seen in Figure 13.19.

The increase in the boiling point of a solution, relative to the pure solvent, depends on the molality of the solute. But it is important to remember that boiling-point elevation is proportional to the *total* concentration of solute particles, regardless of whether the particles are molecules or ions. When NaCl dissolves in water, 2 mol of solute particles (1 mol of  $\text{Na}^+$  and 1 mol of  $\text{Cl}^-$ ) are formed for each mole of NaCl that dissolves. We take this into account by defining *i*, the **van't Hoff factor**, as the number of fragments that a solute breaks up into for a particular solvent. The change in boiling point for a solution compared to the pure solvent is:

$$\Delta T_b = T_b(\text{solution}) - T_b(\text{solvent}) = iK_b m \quad [13.12]$$



**▲ Figure 13.19** Phase diagram illustrating boiling-point elevation. The black lines show the pure solvent's phase equilibria curves, and the blue lines show the solution's phase equilibria curves.

In this equation,  $T_b(\text{solution})$  is the boiling point of the solution,  $T_b(\text{solvent})$  is the boiling point of the pure solvent,  $m$  is the molality of the solute,  $K_b$  is the **molal boiling-point-elevation constant** for the solvent (which is a proportionality constant that is experimentally determined for each solvent), and  $i$  is the van't Hoff factor. For a non-electrolyte, we can always assume  $i = 1$ ; for an electrolyte,  $i$  will depend on how the substance ionizes in that solvent. For instance,  $i = 2$  for NaCl in water, assuming complete dissociation of ions. As a result, we expect the boiling-point elevation of a 1  $m$  aqueous solution of NaCl to be twice as large as the boiling-point elevation of a 1  $m$  solution of a nonelectrolyte such as sucrose. Thus, to properly predict the effect of a particular solute on boiling-point elevation (or any other colligative property), it is important to know whether the solute is an electrolyte or a nonelectrolyte.

## Freezing-Point Depression

The vapor-pressure curves for the liquid and solid phases meet at the triple point. In [Figure 13.20](#) we see that the triple-point temperature of the solution is lower than the triple-point temperature of pure liquid because the solution has a lower vapor pressure than the pure liquid.

The freezing point of a solution is the temperature at which the first crystals of pure solvent form in equilibrium with the solution. Recall from Section 11.6 that the line representing the solid–liquid equilibrium rises nearly vertically from the triple point. It is easy to see in [Figure 13.20](#) that the triple-point temperature of the solution is lower than that of the pure liquid, but it is also true for all points along the solid–liquid equilibrium curve: *the freezing point of the solution is lower than that of the pure liquid*.

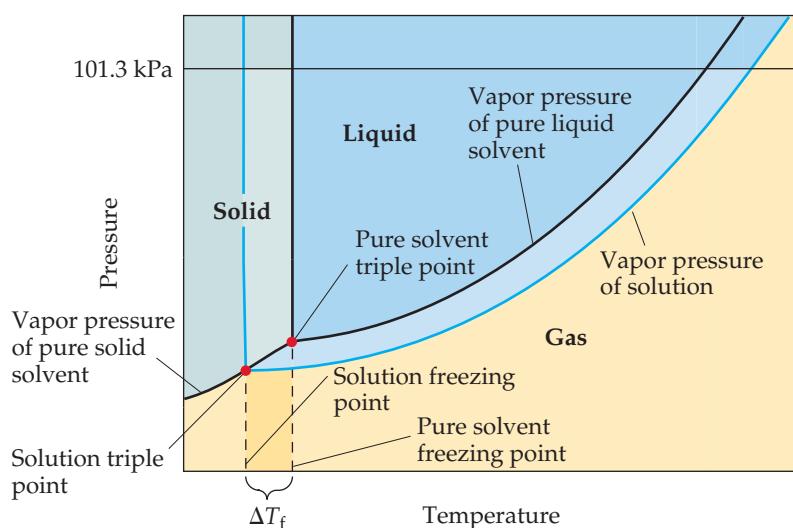
Like the boiling-point elevation, the change in freezing point  $\Delta T_f$  is directly proportional to solute molality, taking into account the van't Hoff factor  $i$ :

$$\Delta T_f = T_f(\text{solution}) - T_f(\text{solvent}) = -iK_f m \quad [13.13]$$

The proportionality constant  $K_f$  is the **molal freezing-point-depression constant**, analogous to  $K_b$  for boiling-point elevation. Note that because the solution freezes at a *lower* temperature than does the pure solvent, the value of  $\Delta T_f$  is *negative*.

Some typical values of  $K_b$  and  $K_f$  for several common solvents are given in [Table 13.3](#). For water, the table shows  $K_b = 0.51 \text{ }^\circ\text{C}/m$ , which means that the boiling point of any aqueous solution that is 1  $m$  in nonvolatile solute particles is  $0.51 \text{ }^\circ\text{C}$  higher than the boiling point of pure water. Because solutions generally do not behave ideally, the constants listed in [Table 13.3](#) serve well only for solutions that are rather dilute.

For water,  $K_f$  is  $1.86 \text{ }^\circ\text{C}/m$ . Therefore, any aqueous solution that is 1  $m$  in nonvolatile solute particles (such as 1  $m$   $\text{C}_6\text{H}_{12}\text{O}_6$  or 0.5  $m$  NaCl) freezes at the temperature that is  $1.86 \text{ }^\circ\text{C}$  lower than the freezing point of pure water.



**◀ Figure 13.20** Phase diagram illustrating freezing-point depression. The black lines show the pure solvent's phase equilibria curves, and the blue lines show the solution's phase equilibria curves.

**TABLE 13.3 Molal Boiling-Point-Elevation and Freezing-Point-Depression Constants**

Solvent	Normal Boiling Point (°C)	$K_b$ (°C/m)	Normal Freezing Point (°C)	$K_f$ (°C/m)
Water, H <sub>2</sub> O	100.0	0.51	0.0	1.86
Benzene, C <sub>6</sub> H <sub>6</sub>	80.1	2.53	5.5	5.12
Ethanol, C <sub>2</sub> H <sub>5</sub> OH	78.4	1.22	-114.6	1.99
Tetrachloromethane, CCl <sub>4</sub>	76.8	5.02	-22.3	29.8
Trichloromethane, CHCl <sub>3</sub>	61.2	3.63	-63.5	4.68



### Sample Exercise 13.8

#### Calculation of Boiling-Point Elevation and Freezing-Point Depression

Automotive antifreeze contains ethylene glycol, CH<sub>2</sub>(OH)CH<sub>2</sub>(OH), a nonvolatile nonelectrolyte, in water. Calculate the boiling point and freezing point of a 25.0% by mass solution of ethylene glycol in water.

#### SOLUTION

**Analyze** We are given that a solution contains 25.0% by mass of a nonvolatile, nonelectrolyte solute and asked to calculate the boiling and freezing points of the solution. To do this, we need to calculate the boiling-point elevation and freezing-point depression.

**Plan** To calculate the boiling-point elevation and the freezing-point depression using Equations 13.12 and 13.13, we must express the concentration of the solution as molality. Let's assume for convenience that we have 1000 g of solution. Because the solution is 25.0% by mass ethylene glycol, the masses of ethylene glycol and water in the solution are 250 and 750 g, respectively. Using these quantities, we can calculate the molality of the solution, which we use with the molal boiling-point-elevation and freezing-point-depression constants (Table 13.3) to calculate  $\Delta T_b$  and  $\Delta T_f$ . We add  $\Delta T_b$  to the boiling point and  $\Delta T_f$  to the freezing point of the solvent to obtain the boiling point and freezing point of the solution.

#### Solve

The molality of the solution is calculated as follows:

$$\text{Molality} = \frac{\text{moles C}_2\text{H}_6\text{O}_2}{\text{kilograms H}_2\text{O}} \\ = \left( \frac{250 \text{ g C}_2\text{H}_6\text{O}_2}{750 \text{ g H}_2\text{O}} \right) \left( \frac{1 \text{ mol C}_2\text{H}_6\text{O}_2}{62.1 \text{ g C}_2\text{H}_6\text{O}_2} \right) \left( \frac{1000 \text{ g H}_2\text{O}}{1 \text{ kg H}_2\text{O}} \right) = 5.37 \text{ m}$$

We can now use Equations 13.12 and 13.13 to calculate the changes in the boiling and freezing points:

$$\Delta T_b = iK_b m = (1)(0.51 \text{ °C/m})(5.37 \text{ m}) = 2.7 \text{ °C} \\ \Delta T_f = -iK_f m = -(1)(1.86 \text{ °C/m})(5.37 \text{ m}) = -10.0 \text{ °C}$$

Hence, the boiling and freezing points of the solution are readily calculated:

$$\Delta T_b = T_b(\text{solution}) - T_b(\text{solvent}) \\ 2.7 \text{ °C} = T_b(\text{solution}) - 100.0 \text{ °C} \\ T_b(\text{solution}) = 102.7 \text{ °C} \\ \Delta T_f = T_f(\text{solution}) - T_f(\text{solvent}) \\ -10.0 \text{ °C} = T_f(\text{solution}) - 0.0 \text{ °C} \\ T_f(\text{solution}) = -10.0 \text{ °C}$$

**Comment** Notice that the solution is a liquid over a larger temperature range than the pure solvent.

#### ► Practice Exercise

Which aqueous solution will have the lowest freezing point?

- (a) 0.050 m CaCl<sub>2</sub>
- (b) 0.15 m NaCl
- (c) 0.10 m HCl
- (d) 0.050 m CH<sub>3</sub>COOH
- (e) 0.20 m C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>

The freezing-point depression caused by solutes has useful applications: it is why antifreeze works in car cooling systems and why calcium chloride ( $\text{CaCl}_2$ ) promotes the melting of ice on roads during winter.

## Osmosis

Certain materials, including many membranes in biological systems and synthetic substances such as cellophane, are *semipermeable*. When in contact with a solution, these materials allow only ions or small molecules—water molecules, for instance—to pass through their network of tiny pores.

Consider a situation in which only solvent molecules are able to pass through a semipermeable membrane placed between two solutions of different concentrations. The rate at which the solvent molecules pass from the less concentrated solution (lower solute concentration but higher solvent concentration) to the more concentrated solution (higher solute concentration but lower solvent concentration) is greater than the rate in the opposite direction. Thus, there is a net movement of solvent molecules from the solution with a lower solute concentration into the one with a higher solute concentration. In this process, called **osmosis**, *the net movement of solvent is always toward the solution with the lower solvent (higher solute) concentration*, as if the solutions were driven to attain equal concentrations.

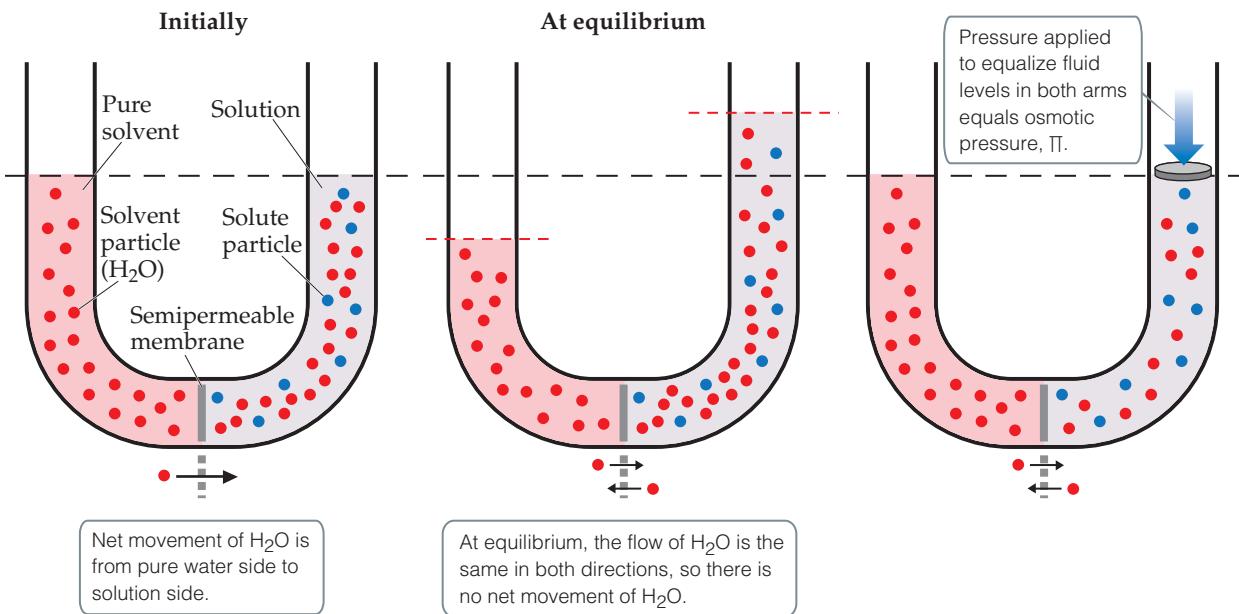
**Figure 13.21** shows the osmosis that occurs between an aqueous solution and pure water, separated by a semipermeable membrane. The U-tube contains water on the left and an aqueous solution on the right. Initially, there is a net movement of water through the membrane from left to right, leading to unequal liquid levels in the two arms of the U-tube. Eventually, at equilibrium (middle panel of Figure 13.21), the pressure difference resulting from the unequal liquid heights becomes so large that the net flow of water ceases. This pressure, which stops osmosis, is the **osmotic pressure**,  $\Pi$ , of the solution. If an external pressure equal to the osmotic pressure is applied to the solution, the liquid levels in the two arms can be equalized, as shown in the right panel of Figure 13.21.

The osmotic pressure obeys a law similar in form to the ideal gas law,  $\Pi V = i n R T$  where  $\Pi$  is the osmotic pressure,  $V$  is the volume of the solution,  $i$  is the van't Hoff factor,



### Go Figure

If the pure water in the left arm of the U-tube is replaced by a solution more concentrated than the one in the right arm, what will happen?



▲ **Figure 13.21** Osmosis is the process of a solvent moving from one compartment to another, across a semipermeable membrane, toward higher solute concentration. Osmotic pressure is generated at equilibrium due to the different heights of liquid on either side of the membrane and is equivalent to the pressure needed to equalize the fluid levels across the membrane.

$n$  is the number of moles of solute,  $R$  is the ideal-gas constant, and  $T$  is the absolute temperature. From this equation, we can write

$$\Pi = i \left( \frac{n}{V} \right) RT = iMRT \quad [13.14]$$

where  $M$  is the molarity of the solution. Because the osmotic pressure for any solution depends on the solution concentration, osmotic pressure is a colligative property.

If two solutions of identical osmotic pressure are separated by a semipermeable membrane, no osmosis will occur. The two solutions are *isotonic* with respect to each other. If one solution is of lower osmotic pressure, it is *hypotonic* with respect to the more concentrated solution. The more concentrated solution is *hypertonic* with respect to the dilute solution.

Osmosis plays an important role in living systems. The membranes of red blood cells, for example, are semipermeable. Placing a red blood cell in a solution that is *hypertonic* relative to the intracellular solution (the solution inside the cells) causes water to move out of the cell (Figure 13.22). This causes the cell to shrivel, a process called *crenation*. Placing the cell in a solution that is *hypotonic* relative to the intracellular fluid causes water to move into the cell, which may cause the cell to rupture, a process called *hemolysis*. People who need body fluids or nutrients replaced but cannot be fed orally are given solutions by intravenous (IV) infusion, which feeds nutrients directly into the veins. To prevent crenation or hemolysis of red blood cells, the IV solutions must be *isotonic* with the intracellular fluids of the blood cells.

There are many interesting biological examples of osmosis. A cucumber placed in concentrated brine loses water via osmosis and shrivels into a pickle. People who eat a lot of salty food retain water in tissue cells and intercellular space because of osmosis. The resultant swelling or puffiness is called *edema*. Water moves from soil into plant roots partly because of osmosis. Bacteria on salted meat or candied fruit lose water through osmosis, shrivel, and die—thus preserving the food.

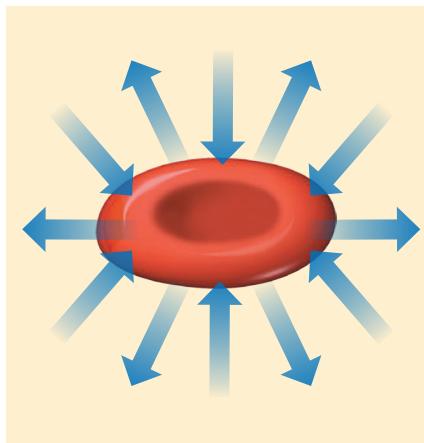
### Determination of Molar Mass from Colligative Properties

The colligative properties of solutions provide a useful means of determining the molar mass of solutes. Any of the four colligative properties can be used, as shown in Sample Exercises 13.10 and 13.11.

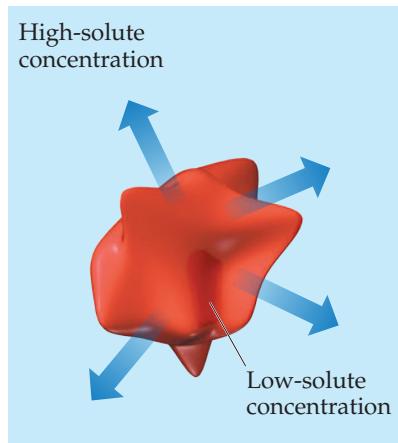
#### Go Figure

If the fluid surrounding a patient's red blood cells is depleted in electrolytes, is crenation or hemolysis more likely to occur?

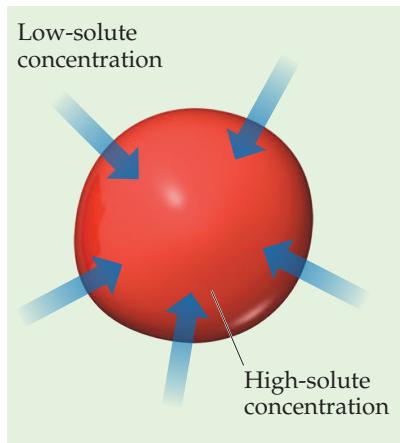
The arrows represent the net movement of water molecules.



Red blood cell in isotonic medium  
neither swells nor shrinks.



Crenation of red blood cell placed  
in hypertonic environment



Hemolysis of red blood cell placed  
in hypotonic environment

▲ **Figure 13.22 Osmosis through red blood cell walls.** If water moves out of the red blood cell, it shrivels (crenation); if water moves into the red blood cell, it will swell and may burst (hemolysis).



## Sample Exercise 13.9

### Osmotic Pressure Calculations

The average osmotic pressure of blood is 780 kPa at 25 °C. What molarity of glucose ( $C_6H_{12}O_6$ ) will be isotonic with blood?

#### SOLUTION

**Analyze** We are asked to calculate the concentration of glucose in water that would be isotonic with blood, given that the osmotic pressure of blood at 25 °C is 780 kPa.

**Plan** Because we are given the osmotic pressure and temperature, we can solve for the concentration, using Equation 13.14. Because glucose is a nonelectrolyte,  $i = 1$ .

#### Solve

$$\Pi = iMRT$$

$$M = \frac{\Pi}{iRT} = \frac{(780 \text{ kPa})}{(1)\left(8.314 \frac{\text{m}^3 \text{ Pa}}{\text{mol K}}\right)(298 \text{ K})} = 0.31 \text{ M}$$

**Comment** In clinical situations, the concentrations of solutions are generally expressed as mass percentages. The mass percentage of a 0.31 M solution of glucose is 5.3%. The concentration of NaCl that is isotonic with blood is 0.16 M, because  $i = 2$  for NaCl in water (a 0.155 M solution of NaCl is 0.310 M in particles). A 0.16 M solution of NaCl is 0.9% mass in NaCl. This kind of solution is known as a physiological saline solution.

#### ► Practice Exercise

Which of the following actions will raise the osmotic pressure of a solution? (a) decreasing the solute concentration (b) decreasing the temperature (c) adding more solvent (d) increasing the temperature (e) none of these



## Sample Exercise 13.10

### Molar Mass from Freezing-Point Depression or Boiling-Point Elevation

A solution of an unknown nonvolatile nonelectrolyte was prepared by dissolving 0.250 g of the substance in 40.0 g of  $CCl_4$ . The boiling point of the resulting solution was 0.357 °C higher than that of the pure solvent. Calculate the molar mass of the solute.

#### SOLUTION

**Analyze** Our goal is to calculate the molar mass of a solute based on knowledge of the boiling-point elevation of its solution in  $CCl_4$ ,  $\Delta T_b = 0.357 \text{ }^\circ\text{C}$ , and the masses of solute and solvent. Table 13.3 gives  $K_b$  for the solvent ( $CCl_4$ ),  $K_b = 5.02 \text{ }^\circ\text{C}/\text{m}$ .

**Plan** We can use Equation 13.12,  $\Delta T_b = iK_b m$ , to calculate the molality of the solution. Because the solute is a nonelectrolyte,  $i = 1$ . Then we can use molality and the quantity of solvent (40.0 g  $CCl_4$ ) to calculate the number of moles of solute. Finally, the molar mass of the solute equals the number of grams per mole, so we divide the number of grams of solute (0.250 g) by the number of moles we have just calculated.

#### Solve

From Equation 13.12, we have:

$$\text{Molality} = \frac{\Delta T_b}{iK_b} = \frac{0.357 \text{ }^\circ\text{C}}{(1)5.02 \text{ }^\circ\text{C}/\text{m}} = 0.0711 \text{ m}$$

Thus, the solution contains 0.0711 mol of solute per kilogram of solvent. The solution was prepared using 40.0 g = 0.0400 kg of solvent ( $CCl_4$ ). The number of moles of solute in the solution is therefore:

The molar mass of the solute is the number of grams per mole of the substance:

$$(0.0400 \text{ kg } CCl_4) \left( 0.0711 \frac{\text{mol solute}}{\text{kg } CCl_4} \right) = 2.84 \times 10^{-3} \text{ mol solute}$$

$$\text{Molar mass} = \frac{0.250 \text{ g}}{2.84 \times 10^{-3} \text{ mol}} = 88.0 \text{ g/mol}$$

#### ► Practice Exercise

A mysterious white powder could be powdered sugar ( $C_{12}H_{22}O_{11}$ ), cocaine ( $C_{17}H_{21}NO_4$ ), codeine ( $C_{18}H_{21}NO_3$ ), norfenefrine ( $C_8H_{11}NO_2$ ), or fructose ( $C_6H_{12}O_6$ ). When 80 mg of the powder is dissolved in 1.50 mL

of ethanol ( $d = 0.789 \text{ g/cm}^3$ , normal freezing point  $-114.6 \text{ }^\circ\text{C}$ ,  $K_f = 1.99 \text{ }^\circ\text{C}/\text{m}$ ), the freezing point is lowered to  $-115.5 \text{ }^\circ\text{C}$ . What is the identity of the white powder? (a) powdered sugar (b) cocaine (c) codeine (d) norfenefrine (e) fructose



## Sample Exercise 13.11

### Molar Mass from Osmotic Pressure

The osmotic pressure of an aqueous solution of a certain protein was measured to determine the protein's molar mass. The solution contained 3.50 mg of protein dissolved in sufficient water to form 5.00 mL of solution. The osmotic pressure of the solution at 25 °C was found to be 205 Pa. Treating the protein as a nonelectrolyte, calculate its molar mass.

#### SOLUTION

**Analyze** Our goal is to calculate the molar mass of a high-molecular-mass protein, based on the osmotic pressure and a knowledge of the mass of protein and solution volume. Since the protein will be considered as a nonelectrolyte,  $i = 1$ .

**Plan** The temperature ( $T = 25^\circ\text{C}$ ) and osmotic pressure ( $\Pi = 205 \text{ Pa}$ ) are given, and we know the value of  $R$  so we can

#### Solve

Solving Equation 13.14 for molarity gives:

Because the volume of the solution is  $5.00 \text{ mL} = 5.00 \times 10^{-3} \text{ L}$ , the number of moles of protein must be:

The molar mass is the number of grams per mole of the substance. Because we know the sample has a mass of  $3.50 \text{ mg} = 3.50 \times 10^{-3} \text{ g}$ , we can calculate the molar mass by dividing the number of grams in the sample by the number of moles we just calculated:

**Comment** Because small pressures can be measured easily and accurately, osmotic pressure measurements provide a useful way to determine the molar masses of large molecules.

use Equation 13.14 to calculate the molarity of the solution,  $M$ . In doing so, we must convert temperature from  $^\circ\text{C}$  to K. We then use the molarity and the volume of the solution (5.00 mL) to determine the number of moles of solute. Finally, we obtain the molar mass by dividing the mass of the solute (3.50 mg) by the number of moles of solute.

$$\text{Molarity} = \frac{\Pi}{iRT} = \frac{205 \text{ Pa}}{(1)\left(8.314 \frac{\text{m}^3 \text{Pa}}{\text{mol K}}\right)(298 \text{ K})} = 8.28 \times 10^{-5} \frac{\text{mol}}{\text{L}}$$

$$\text{Moles} = (8.28 \times 10^{-5} \text{ mol/L})(5.00 \times 10^{-3} \text{ L}) = 4.14 \times 10^{-7} \text{ mol}$$

$$\text{Molar mass} = \frac{\text{grams}}{\text{moles}} = \frac{3.50 \times 10^{-3} \text{ g}}{4.14 \times 10^{-7} \text{ mol}} = 8.45 \times 10^3 \text{ g/mol}$$

#### ► Practice Exercise

A sample of 2.05 g of polystyrene of uniform polymer chain length was dissolved in enough toluene to form 0.100 L of solution. The osmotic pressure of this solution was found to be 1.21 kPa at 25 °C. Calculate the molar mass of the polystyrene.

## A CLOSER LOOK The van't Hoff Factor

The colligative properties of solutions depend on the *total* concentration of solute particles, regardless of whether the particles are ions or molecules. Thus, we expect a 0.100  $m$  solution of NaCl to have a freezing-point depression of  $(2)(0.100 \text{ } m)(1.86 \text{ } ^\circ\text{C}/\text{m}) = 0.372 \text{ } ^\circ\text{C}$  because it is 0.100  $m$  in  $\text{Na}^+(\text{aq})$  and 0.100  $m$  in  $\text{Cl}^-(\text{aq})$ . The measured freezing-point depression is only 0.348 °C, however, and the situation is similar for other strong electrolytes. A 0.100  $m$  solution of KCl, for example, freezes at  $-0.344 \text{ } ^\circ\text{C}$ .

The difference between expected and observed colligative properties for strong electrolytes is due to electrostatic attractions between ions. As the ions move about in solution, ions of opposite charge collide and “stick together” for brief moments. While they are together, they behave as a single particle called an *ion pair* (Figure 13.23). The number of independent particles is thereby reduced, causing a

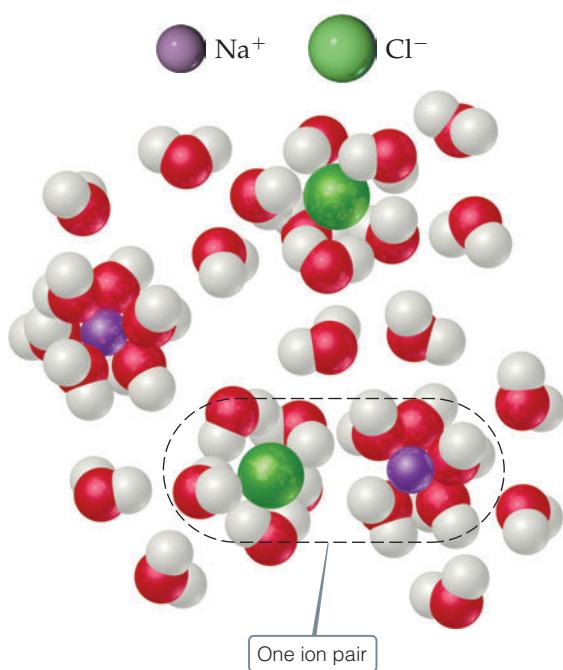
reduction in the freezing-point depression (as well as in boiling-point elevation, vapor-pressure reduction, and osmotic pressure).

We have been assuming that the van't Hoff factor,  $i$ , is equal to the number of ions per formula unit of the electrolyte. The true (measured) value of this factor, however, is given by the ratio of the measured value of a colligative property to the value calculated when the substance is assumed to be a nonelectrolyte. Using the freezing-point depression, for example, we have

$$i = \frac{\Delta T_f(\text{measured})}{\Delta T_f(\text{calculated for nonelectrolyte})} \quad [13.15]$$

The limiting value of  $i$  can be determined for a salt from the number of ions per formula unit. For NaCl, for example, the limiting van't Hoff factor is 2 because NaCl consists of one  $\text{Na}^+$  and one  $\text{Cl}^-$  per formula

*Continued*



**▲ Figure 13.23** Ion pairing and colligative properties. A solution of NaCl contains not only separated  $\text{Na}^+(aq)$  and  $\text{Cl}^-(aq)$  ions but ion pairs as well.

**TABLE 13.4 Measured and Expected van't Hoff Factors for Several Substances at 25 °C**

Compound	Concentration			Expected Value
	0.100 m	0.0100 m	0.00100 m	
Sucrose	1.00	1.00	1.00	1.00
NaCl	1.87	1.94	1.97	2.00
$\text{K}_2\text{SO}_4$	2.32	2.70	2.84	3.00
$\text{MgSO}_4$	1.21	1.53	1.82	2.00

unit; for  $\text{K}_2\text{SO}_4$  it is 3 because  $\text{K}_2\text{SO}_4$  consists of two  $\text{K}^+$  and one  $\text{SO}_4^{2-}$  per formula unit. In the absence of any information about the actual value of  $i$  for a solution, we will use the limiting value in calculations.

Two trends are evident in Table 13.4, which gives measured van't Hoff factors for several substances at different dilutions. First, dilution affects the value of  $i$  for electrolytes; the more dilute the solution, the more closely  $i$  approaches the expected value based on the number of ions in the formula unit. Thus, we conclude that the extent of ion pairing in electrolyte solutions decreases upon dilution. Second, the lower the charges on the ions, the less  $i$  departs from the expected value because the extent of ion pairing decreases as the ionic charges decrease. Both trends are consistent with simple electrostatics: The force of interaction between charged particles decreases as their separation increases and as their charges decrease.

**Related Exercises:** 13.35, 13.93, 13.108, 13.110

## Self-Assessment Exercises

- 13.26** A desalination plant is able to produce pure water from saltwater by a process called reverse osmosis. Which statement is true?
- Water freely moves through a semi-permeable membrane from the saltwater to the freshwater side.
  - A pressure in excess of the osmotic pressure of the solution is placed on the saltwater side of the semi-permeable membrane to drive water through to the freshwater side of the membrane.
  - The semi-permeable membrane allows ions but not water molecules to pass through.

- 13.27** Is the osmotic pressure of a 0.15 M solution of  $\text{NaNO}_3$  greater than, less than, or equal to that of a 0.10 M solution of  $\text{Ca}(\text{NO}_3)_2$ ?

- Osmotic pressure of 0.15 M  $\text{NaNO}_3$  > Osmotic pressure of 0.10 M  $\text{Ca}(\text{NO}_3)_2$
- Osmotic pressure of 0.15 M  $\text{NaNO}_3$  < Osmotic pressure of 0.10 M  $\text{Ca}(\text{NO}_3)_2$
- Osmotic pressure of 0.15 M  $\text{NaNO}_3$  = Osmotic pressure of 0.10 M  $\text{Ca}(\text{NO}_3)_2$

## Exercises

- 13.28** You make a solution of a nonvolatile solute with a liquid solvent. Indicate if each of the following statements is true or false. (a) The freezing point of the solution is unchanged by addition of the solvent. (b) The solid that forms as the solution freezes is nearly pure solute. (c) The freezing point of the solution is independent of the concentration of the solute. (d) The boiling point of the solution increases in proportion to the concentration of the solute. (e) At any temperature, the vapor pressure of the solvent over the solution is lower than what it would be for the pure solvent.
- 13.29** (a) Calculate the vapor pressure of water above a solution prepared by dissolving 28.5 g of glycerin ( $\text{C}_3\text{H}_8\text{O}_3$ ) in 125 g of water at 343 K. (The vapor pressure of water is given in Appendix B.) (b) Calculate the mass of ethylene glycol ( $\text{C}_2\text{H}_6\text{O}_2$ ) that must be added to 1.00 kg of ethanol

( $\text{C}_2\text{H}_5\text{OH}$ ) to reduce its vapor pressure by 1.33 kPa at 35 °C. The vapor pressure of pure ethanol at 35 °C is 13.3 kPa.

- 13.30** At 63.5 °C, the vapor pressure of  $\text{H}_2\text{O}$  is 23.3 kPa, and that of ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) is 53.3 kPa. A solution is made by mixing equal masses of  $\text{H}_2\text{O}$  and  $\text{C}_2\text{H}_5\text{OH}$ . (a) What is the mole fraction of ethanol in the solution? (b) Assuming ideal-solution behavior, what is the vapor pressure of the solution at 63.5 °C? (c) What is the mole fraction of ethanol in the vapor above the solution?

- 13.31** List the following aqueous solutions in order of decreasing freezing point: 0.040 M glycerin ( $\text{C}_3\text{H}_8\text{O}_3$ ), 0.020 M KBr, 0.030 M phenol ( $\text{C}_6\text{H}_5\text{OH}$ ).

- 13.32** Using data from Table 13.3, calculate the freezing and boiling points of each of the following solutions: (a) 0.25 m

glucose in ethanol; (b) 20.0 g of decane,  $C_{10}H_{22}$ , in 50.0 g  $CHCl_3$ ; (c) 3.50 g NaOH in 175 g of water, (d) 0.45 mol ethylene glycol and 0.15 mol KBr in 150 g  $H_2O$ .

- 13.33** The Baltic Sea has a salinity of 1.0%, that is, its water contains 10 g of salt for every liter of solution. Assuming that the solute consists entirely of NaCl (in fact, over 90% of the salt is indeed NaCl), calculate the osmotic pressure of this seawater at 15 °C.

- 13.34** Lysozyme is an enzyme that breaks bacterial cell walls. A solution containing 0.150 g of this enzyme in 210 mL of solution has an osmotic pressure of 0.127 kPa at 25 °C. What is the molar mass of lysozyme?

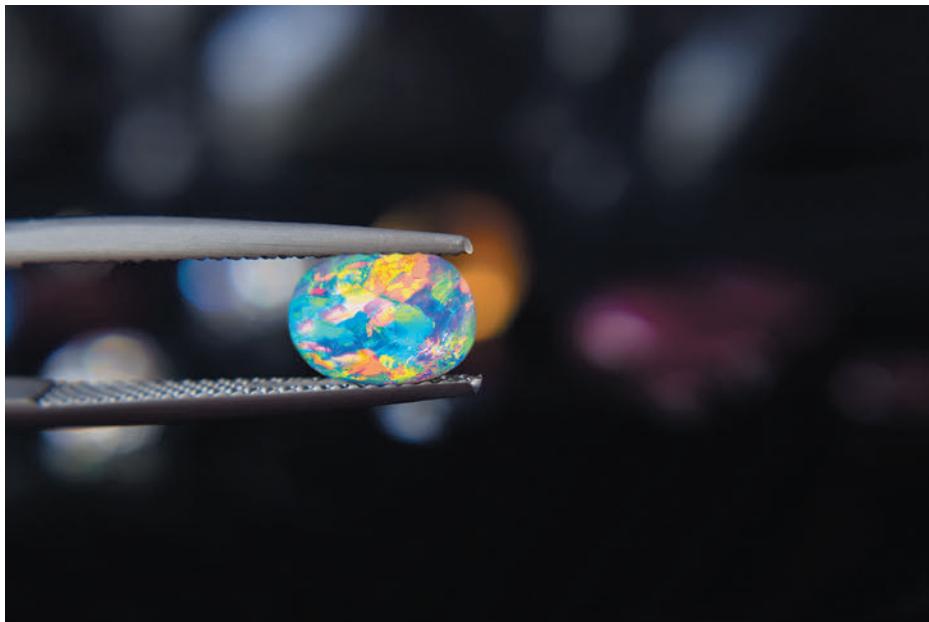
- 13.35** Based on the data given in Table 13.4, which solution would give the larger freezing-point lowering, a 0.030 *m* solution of NaCl or a 0.020 *m* solution of  $K_2SO_4$ ?

13.26 (b) 13.27 (c)

Answers to Self-Assessment Exercises



## 13.6 | Colloids



The beautiful play of colors of the precious opal result from amorphous particles of hydrated silica that are of a similar size to the wavelength of visible light and act as a diffraction grating splitting white light into its spectral colors.

By the end of this section, you should be able to

- Articulate some of the characteristics of a colloid

Some substances appear to initially dissolve in a solvent, but over time, the substance separates from the pure solvent. For example, finely divided clay particles dispersed in water eventually settle out because of gravity. Gravity affects the clay particles because they are much larger than most molecules, consisting of thousands or even millions of atoms. In contrast, the dispersed particles in a true solution (ions in a salt solution or glucose molecules in a sugar solution) are small. Between these extremes lie dispersed particles that are larger than typical molecules but not so large that the components of the mixture separate under the influence of gravity. These intermediate types of dispersions are called either **colloidal dispersions** or simply **colloids**. Colloids form the dividing line between solutions and heterogeneous mixtures. Like solutions, colloids can be gases, liquids, or solids. Examples of each are listed in **Table 13.5**.

Particle size can be used to classify a mixture as colloid or solution. Colloid particles range in diameter from 5 to 1000 nm; solute particles are smaller than 5 nm in diameter. The nanomaterials we saw in Chapter 12, when dispersed in a liquid, are colloids. A colloid particle may even consist of a single giant molecule. The hemoglobin molecule, for example, which carries oxygen in your blood, has molecular dimensions of  $6.5 \times 5.5 \times 5.0$  nm and a molar mass of 64,500 g/mol.

**TABLE 13.5 Types of Colloids**

Phase of Colloid	Dispersing (solvent-like) Substance	Dispersed (solute-like) Substance	Colloid Type	Example
Gas	Gas	Gas	—	None (all are solutions)
Gas	Gas	Liquid	Aerosol	Fog
Gas	Gas	Solid	Aerosol	Smoke
Liquid	Liquid	Gas	Foam	Whipped cream
Liquid	Liquid	Liquid	Emulsion	Milk
Liquid	Liquid	Solid	Sol	Paint
Solid	Solid	Gas	Solid foam	Marshmallow
Solid	Solid	Liquid	Solid emulsion	Butter
Solid	Solid	Solid	Solid sol	Ruby glass

Although colloid particles may be so small that the dispersion appears uniform even under a microscope, they are large enough to scatter light. Consequently, most colloids appear cloudy or opaque unless they are very dilute. (For example, homogenized milk is a colloid of fat and protein molecules dispersed in water.) Furthermore, because they scatter light, a light beam can be seen as it passes through a colloidal dispersion (Figure 13.24). This scattering of light by colloidal particles, known as the **Tyndall effect**, makes it possible to see the light beam of an automobile on a dusty dirt road, or the sunlight streaming through trees or clouds. Not all wavelengths are scattered to the same extent. Colors at the blue end of the visible spectrum are scattered more than those at the red end by the molecules and small dust particles in the atmosphere. As a result, our sky appears blue. At sunset, light from the sun travels through more of the atmosphere; blue light is scattered even more, allowing the reds and yellows to pass through and be seen.

### Hydrophilic and Hydrophobic Colloids

The most important colloids are those in which the dispersing medium is water. These colloids may be **hydrophilic** (“water loving”) or **hydrophobic** (“water fearing”). Hydrophilic colloids are most like the solutions that we have previously examined. In the human body, the extremely large protein molecules such as enzymes and antibodies are kept in suspension by interaction with surrounding water molecules. A hydrophilic molecule folds in such a way that its hydrophobic groups are away from the water molecules, on the inside of the folded molecule, while its hydrophilic, polar groups are on

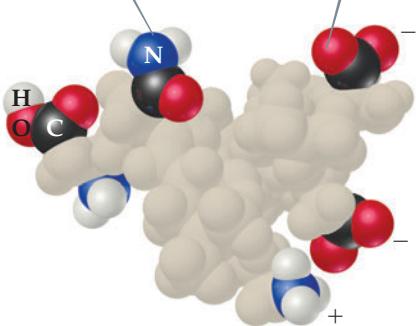


◀ **Figure 13.24** Tyndall effect in the laboratory. The glass on the right contains a colloidal dispersion; that on the left contains a solution.

### Go Figure

What is the chemical composition of the groups that carry a negative charge?

Hydrophilic polar and charged groups on a molecule's surface help the molecule remain dispersed in water and other polar solvents.



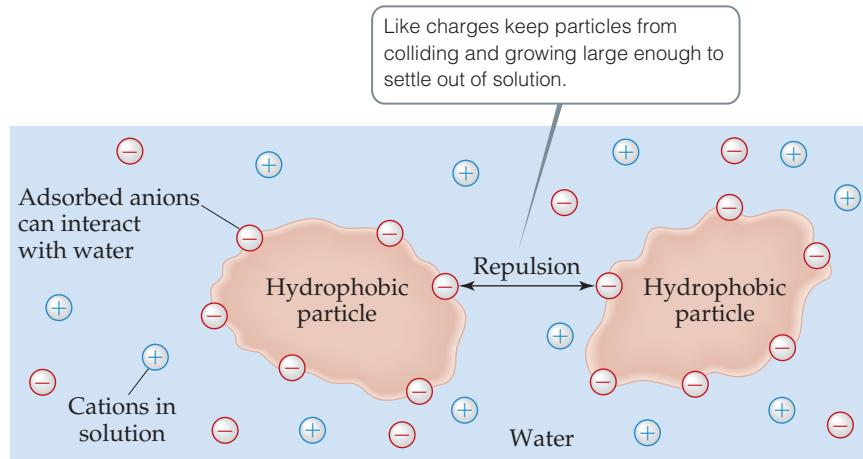
▲ Figure 13.25 Hydrophilic colloidal particle.

Examples of the hydrophilic groups that help to keep a giant molecule (macromolecule) suspended in water.

the surface, interacting with the water molecules. The hydrophilic groups generally contain oxygen or nitrogen and often carry a charge (Figure 13.25).

Hydrophobic colloids can be dispersed in water only if they are stabilized in some way. Otherwise, their natural lack of affinity for water causes them to separate from the water. One method of stabilization involves adsorbing ions on the surface of the hydrophobic particles (Figure 13.26). (*Adsorption* means to adhere to a surface. It differs from *absorption*, which means to pass into the interior, as when a sponge absorbs water.) The adsorbed ions can interact with water, thereby stabilizing the colloid. At the same time, the electrostatic repulsion between adsorbed ions on neighboring colloid particles keeps the particles from sticking together rather than dispersing in the water.

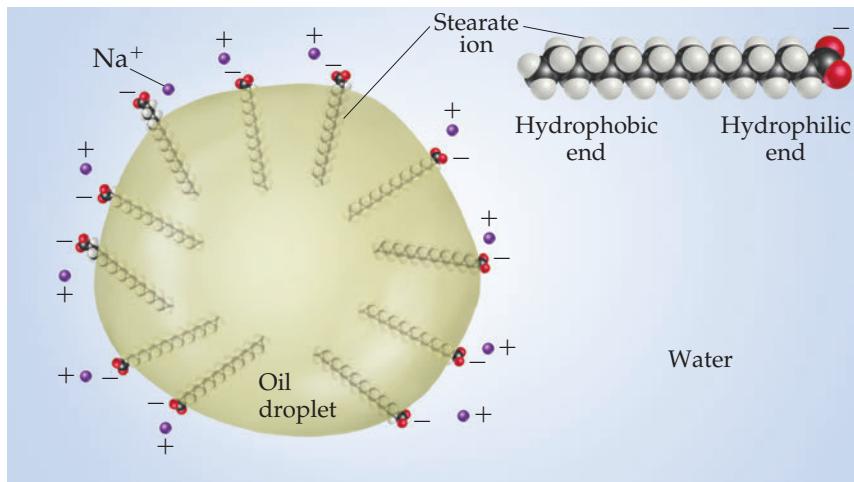
Hydrophobic colloids can also be stabilized by hydrophilic groups on their surfaces. Oil drops are hydrophobic, for example, and they do not remain suspended in water. Instead, they aggregate, forming an oil slick on the water surface. Sodium stearate (Figure 13.27), or any similar substance having one end that is hydrophilic (either polar or charged) and one end that is hydrophobic (nonpolar), will stabilize a suspension of oil in water. Stabilization results from the interaction of the hydrophobic ends of the stearate ions with the oil drops and the hydrophilic ends with the water.



▲ Figure 13.26 Hydrophobic colloids stabilized in water by adsorbed anions.

### Go Figure

Which kind of intermolecular force attracts the stearate ion to the oil drop?

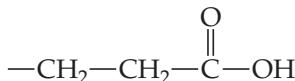


▲ Figure 13.27 Stabilization of an emulsion of oil in water by stearate ions.

## CHEMISTRY AND LIFE Sickle-Cell Anemia

Our blood contains the complex protein hemoglobin, which carries oxygen from the lungs to other parts of the body. In the genetic disease sickle-cell anemia, hemoglobin molecules are abnormal and have a lower solubility in water, especially in their unoxygenated form. Consequently, as much as 85% of the hemoglobin in red blood cells crystallizes out of solution.

The cause of the insolubility is a structural change in one part of an amino acid. Normal hemoglobin molecules contain an amino acid that has a  $-\text{CH}_2\text{CH}_2\text{COOH}$  group:

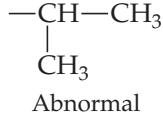


Normal

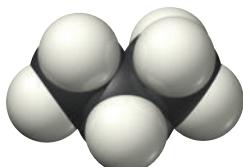


Normal

The polarity of the  $-\text{COOH}$  group contributes to the solubility of the hemoglobin molecule in water. In the hemoglobin molecules of sickle-cell anemia patients, the  $-\text{CH}_2\text{CH}_2\text{COOH}$  chain is absent and in its place is the nonpolar (hydrophobic)  $-\text{CH}(\text{CH}_3)_2$  group:



Abnormal



Abnormal

This change leads to the aggregation of the defective form of hemoglobin into particles too large to remain suspended in biological fluids. It also causes the cells to distort into the sickle shape shown in **Figure 13.28**. The sickled cells tend to clog capillaries, causing severe pain, weakness, and the gradual deterioration of vital organs. The disease is hereditary, and if both parents carry the defective genes, it is likely that their children will possess only abnormal hemoglobin.

You might wonder how it is that a life-threatening disease such as sickle-cell anemia has persisted in humans through evolutionary time. The answer in part is that people with the gene are far less susceptible to malaria. Thus, in tropical climates rife with malaria, those with sickle-cell genes have lower incidence of this debilitating disease.



**▲ Figure 13.28** A scanning electron micrograph of normal (round) and sickle (crescent-shaped) red blood cells. Normal red blood cells are about  $6 \times 10^{-3}$  mm in diameter.

Colloid stabilization has an interesting application in the human digestive system. When fats in our diet reach the small intestine, a hormone causes the gallbladder to excrete a fluid called bile. Among the components of bile are compounds that have chemical structures similar to sodium stearate; that is, they have a hydrophilic (polar) end and a hydrophobic (nonpolar) end. These compounds emulsify the fats in the intestine and thus permit digestion and absorption of fat-soluble vitamins through the intestinal wall. The term *emulsify* means “to form an emulsion,” a suspension of one liquid in another, with milk being one example (Table 13.5). A substance that aids in the formation of an emulsion is called an emulsifying agent. If you read the labels on foods and other materials, you will find that a variety of chemicals are used as emulsifying agents. These chemicals typically have a hydrophilic end and a hydrophobic end.

## Colloidal Motion in Liquids

We learned in Chapter 10 that gas molecules move at some average speed that depends inversely on their molar mass, in a straight line, until they collide with something. The *mean free path* is the average distance molecules travel between collisions. Recall also that the kinetic-molecular theory of gases assumes that gas molecules are in continuous, random motion.

Colloidal particles in a solution undergo random motion as a result of collisions with solvent molecules. Because the colloidal particles are massive in comparison with solvent molecules, their movements from any one collision are very tiny. However, there are many such collisions, and they cause a random motion of the entire colloidal particle, called **Brownian motion**. In 1905, Einstein developed an equation for the average square of the displacement of a colloidal particle, a historically very important development. As you might expect, the larger the colloidal particle, the shorter its mean

free path in a given liquid (Table 13.6). Today, the understanding of Brownian motion is applied to diverse problems in everything from cheese-making to medical imaging.

**TABLE 13.6 Calculated Mean Free Path, after One Hour, for Uncharged Colloidal Spheres in Water at 20 °C**

Radius of sphere, nm	Mean Free Path, mm
1	1.23
10	0.390
100	0.123
1000	0.039

## Self-Assessment Exercise

- 13.36** Potassium ions are transported into the cell through a protein channel in the cell membrane. Which type of groups would be facing the ions to help the ion transport?

- (a) Hydrophilic groups  
(b) Hydrophobic groups

## Exercises

- 13.37** Choose the best answer: A colloidal dispersion of one liquid in another is called (a) a gel, (b) an emulsion, (c) a foam, (d) an aerosol.
- 13.38** Aerosols are important components of the atmosphere. Does the presence of aerosols in the atmosphere increase or decrease the amount of sunlight that arrives at the Earth's surface, compared to an "aerosol-free" atmosphere? Explain your reasoning.
- 13.39** Soaps consist of compounds such as sodium stearate,  $\text{CH}_3(\text{CH}_2)_{16}\text{COO}^-\text{Na}^+$ , that have both hydrophobic and hydrophilic parts. Consider the hydrocarbon part of sodium stearate to be the "tail" and the charged part to be the "head."

- (a) Which part of sodium stearate, head or tail, is more likely to be solvated by water?  
(b) Grease is a complex mixture of (mostly) hydrophobic compounds. Which part of sodium stearate, head or tail, is most likely to bind to grease?  
(c) If you have large deposits of grease that you want to wash away with water, you can see that adding sodium stearate will help you produce an emulsion. What intermolecular interactions are responsible for this?

13.36 (a)

Answers to Self-Assessment Exercises



## Sample Integrative Exercise

### Putting Concepts Together

A 0.100 L solution is made by dissolving 0.441 g of  $\text{CaCl}_2(s)$  in water. (a) Calculate the osmotic pressure of this solution at 27 °C, assuming that it is completely dissociated into its component ions. (b) The measured osmotic pressure of this solution is 259.4 kPa at 27 °C. Explain why it is less than the value calculated in (a), and calculate the van't Hoff factor, *i*, for the solute in this solution. (c) The enthalpy of solution for  $\text{CaCl}_2$  is  $\Delta H = -81.3 \text{ kJ/mol}$ . If the final temperature of the solution is 27 °C, what was its initial temperature? (Assume that the density of the solution is 1.00 g/mL, that its specific heat is 4.18 J/g K, and that the solution loses no heat to its surroundings.)

### SOLUTION

- (a) The osmotic pressure is given by Equation 13.14,  $\Pi = iMRT$ . We know the temperature,  $T = 27^\circ\text{C} = 300 \text{ K}$ , and the gas constant,  $R = 8.314 \text{ m}^3 \text{ Pa/mol K}$ . We can calculate the molarity of the solution from the mass of  $\text{CaCl}_2$  and the volume of the solution:

$$\begin{aligned} \text{Molarity} &= \left( \frac{0.441 \text{ g CaCl}_2}{0.100 \text{ L}} \right) \left( \frac{1 \text{ mol CaCl}_2}{110 \text{ g CaCl}_2} \right) \\ &= 0.0397 \text{ mol CaCl}_2/\text{L} \end{aligned}$$

Soluble ionic compounds are strong electrolytes. Thus,  $\text{CaCl}_2$  consists of metal cations ( $\text{Ca}^{2+}$ ) and nonmetal anions ( $\text{Cl}^-$ ). When completely dissociated, each  $\text{CaCl}_2$  unit forms three ions (one  $\text{Ca}^{2+}$  and two  $\text{Cl}^-$ ). Hence, the calculated osmotic pressure is:

- (b) The actual values of colligative properties of electrolytes are less than those calculated because the electrostatic interactions between ions limit their independent movements. In this case, the van't Hoff factor, which measures the extent to which electrolytes actually dissociate into ions, is given by:

Thus, the solution behaves as if the  $\text{CaCl}_2$  has dissociated into 2.62 particles instead of the ideal 3.

- (c) If the solution is 0.0397 M in  $\text{CaCl}_2$  and has a total volume of 0.100 L, the number of moles of solute is:

Hence, the quantity of heat generated in forming the solution is:

The solution absorbs this heat, causing its temperature to increase. The relationship between temperature change and heat is given by Equation 5.22:

The heat absorbed by the solution is

$q = +0.323 \text{ kJ} = 323 \text{ J}$ . The mass of the 0.100 L of solution is  $(100 \text{ mL})(1.00 \text{ g/mL}) = 100 \text{ g}$  (to three significant figures). Thus, the temperature change is:

A kelvin has the same size as a degree Celsius. Because the solution temperature increases by 0.773 °C, the initial temperature was:

$$\begin{aligned}\Pi &= iMRT = (3)(0.0397 \text{ mol/L})(8.314 \text{ m}^3 \text{ Pa/mol K})(300 \text{ K}) \\ &= 297 \text{ kPa}\end{aligned}$$

$$\begin{aligned}i &= \frac{\Pi(\text{measured})}{\Pi(\text{calculated for nonelectrolyte})} \\ &= \frac{259.4 \text{ kPa}}{(0.0397 \text{ mol/L})(8.314 \text{ m}^3 \text{ Pa/mol K})(300 \text{ K})} = 2.62\end{aligned}$$

$$(0.100 \text{ L})(0.0397 \text{ mol/L}) = 0.00397 \text{ mol}$$

$$(0.00397 \text{ mol})(-81.3 \text{ kJ/mol}) = -0.323 \text{ kJ}$$

$$q = (\text{specific heat})(\text{grams})(\Delta T)$$

$$\begin{aligned}\Delta T &= \frac{q}{(\text{specific heat of solution})(\text{grams of solution})} \\ &= \frac{323 \text{ J}}{(4.18 \text{ J/g K})(100 \text{ g})} = 0.773 \text{ K}\end{aligned}$$

$$27.0^\circ\text{C} - 0.773^\circ\text{C} = 26.2^\circ\text{C}$$

## Chapter Summary and Key Terms

**THE SOLUTION PROCESS (SECTION 13.1)** Solutions form when one substance disperses uniformly throughout another. The attractive interaction of solvent molecules with solute is called **solvation**. When the solvent is water, the interaction is called **hydration**. The dissolution of ionic substances in water is promoted by hydration of the separated ions by the polar water molecules. The overall enthalpy change upon solution formation may be either positive or negative. Solution formation is favored both by a positive entropy change, corresponding to an increased dispersal of the components of the solution, and by a negative enthalpy change, indicating an exothermic process.

**SATURATED SOLUTIONS AND SOLUBILITY (SECTION 13.2)** The equilibrium between a saturated solution and undissolved solute is dynamic; the process of solution and the reverse process, **crystallization**, occur simultaneously. In a solution in equilibrium with undissolved solute, the two processes occur at equal rates, giving a **saturated** solution. If there is less solute present than is needed to saturate the solution, the solution is **unsaturated**. When solute concentration is greater than the equilibrium concentration value, the solution is **supersaturated**. This is an unstable condition, and separation of some solute from the solution will occur if the process is initiated with a solute seed crystal. The amount of solute needed to form a saturated solution at any particular temperature is the **solubility** of that solute at that temperature.

**FACTORS AFFECTING SOLUBILITY (SECTION 13.3)** The solubility of one substance in another depends on the tendency of systems to become more random, by becoming more dispersed in space, and on the relative intermolecular solute-solute and solvent-solvent

energies compared with solute-solvent interactions. Polar and ionic solutes tend to dissolve in polar solvents, and nonpolar solutes tend to dissolve in nonpolar solvents (“like dissolves like”). Liquids that mix in all proportions are **miscible**; those that do not dissolve significantly in one another are **immiscible**. Hydrogen-bonding interactions between solute and solvent often play an important role in determining solubility; for example, ethanol and water, whose molecules form hydrogen bonds with each other, are miscible. The solubilities of gases in a liquid are generally proportional to the pressure of the gas over the solution, as expressed by **Henry's law**:  $S_g = kP_g$ . The solubilities of most solid solutes in water increase as the temperature of the solution increases. In contrast, the solubilities of gases in water generally decrease with increasing temperature.

**EXPRESSING SOLUTION CONCENTRATIONS (SECTION 13.4)** Concentrations of solutions can be expressed quantitatively by several different measures, including **mass percentage** [(mass solute/mass solution)  $\times 100$ ], **parts per million (ppm)**, **parts per billion (ppb)**, and **mole fraction**. Molarity,  $M$ , is defined as moles of solute per liter of solution; **molality**,  $m$ , is defined as moles of solute per kilogram of solvent. Molarity can be converted to these other concentration units if the density of the solution is known.

**COLLIGATIVE PROPERTIES (SECTION 13.5)** A physical property of a solution that depends on the concentration of solute particles present, regardless of the nature of the solute, is a **colligative property**. Colligative properties include vapor-pressure lowering, freezing-point lowering, boiling-point elevation, and osmotic pressure. **Raoult's law** expresses the lowering of vapor pressure. An **ideal solution**

obeys Raoult's law. Differences in solvent–solute as compared with solvent–solvent and solute–solute intermolecular forces cause many solutions to depart from ideal behavior.

A solution containing a nonvolatile solute possesses a higher boiling point than the pure solvent. The **molal boiling-point-elevation constant**,  $K_b$ , represents the increase in boiling point for a 1  $m$  solution of solute particles as compared with the pure solvent. Similarly, the **molal freezing-point-depression constant**,  $K_f$ , measures the lowering of the freezing point of a solution for a 1  $m$  solution of solute particles. The temperature changes are given by the equations  $\Delta T_b = iK_b m$  and  $\Delta T_f = -iK_f m$  where  $i$  is the **van't Hoff factor**, which represents how many particles the solute breaks up into in the solvent. When NaCl dissolves in water, two moles of solute particles are formed for each mole of dissolved salt. The boiling point or freezing point is thus elevated or depressed, respectively, approximately twice as much as that of a nonelectrolyte solution of the same concentration. Similar considerations apply to other strong electrolytes.

**Osmosis** is the movement of solvent molecules through a semipermeable membrane from a less concentrated to a more concentrated solution. This net movement of solvent generates an **osmotic pressure**,  $\Pi$ , which can be measured in units of gas pressure,

such as atm. The osmotic pressure of a solution is proportional to the solution molarity:  $\Pi = iMRT$ . Osmosis is a very important process in living systems, in which cell walls act as semipermeable membranes, permitting the passage of water but restricting the passage of ionic and macromolecular components.

**COLLOIDS (SECTION 13.6)** Particles that are large on the molecular scale but still small enough to remain suspended indefinitely in a solvent system form **colloids**, or **colloidal dispersions**. Colloids, which are intermediate between solutions and heterogeneous mixtures, have many practical applications. One useful physical property of colloids, the scattering of visible light, is referred to as the **Tyndall effect**. Aqueous colloids are classified as **hydrophilic** or **hydrophobic**. Hydrophilic colloids are common in living organisms, in which large molecular aggregates (enzymes, antibodies) remain suspended because they have many polar, or charged, atomic groups on their surfaces that interact with water. Hydrophobic colloids, such as small droplets of oil, may remain in suspension through adsorption of charged particles on their surfaces.

Colloids undergo **Brownian motion** in liquids, analogous to the random three-dimensional motion of gas molecules.

## Learning Outcomes After studying this chapter, you should be able to:

- Describe how enthalpy and entropy changes affect solution formation. (Section 13.1) *Related Exercises: 13.6, 13.40, 13.56*
- Describe the relationship between intermolecular forces and solubility, including use of the “like dissolves like” rule. (Sections 13.1 and 13.3) *Related Exercises: 13.3, 13.53*
- Describe the role of equilibrium in the solution process and its relationship to the solubility of a solute. (Section 13.2) *Related Exercises: 13.8, 13.57*
- Describe the effect of temperature on the solubility of solids and gases in liquids. (Section 13.3) *Related Exercises: 13.16, 13.63*
- Describe the relationship between the partial pressure of a gas and its solubility. (Section 13.3) *Related Exercises: 13.16*
- Calculate the concentration of a solution in terms of molarity, molality, mole fraction, percent composition, and parts per million and be able to interconvert between them. (Section 13.4) *Related Exercises: 13.22, 13.69*
- Describe what a colligative property is and explain the van't Hoff factor. (Section 13.5) *Related Exercises: 13.28, 13.78, 13.83, 13.84*
- Calculate the vapor pressure of a solvent over a solution. (Section 13.5) *Related Exercises: 13.79, 13.81*
- Calculate the boiling-point elevation and freezing-point depression of a solution. (Section 13.5) *Related Exercises: 13.32, 13.86*
- Calculate the osmotic pressure of a solution. (Section 13.5) *Related Exercises: 13.33, 13.89*
- Use colligative properties of solutions to calculate molar masses of solutes. (Section 13.5) *Related Exercises: 13.34, 13.90*
- Explain the difference between a solution and a colloid. (Section 13.6) *Related Exercises: 13.37, 13.94*
- Explain how hydrophilic and hydrophobic colloids can be stabilized in water. (Section 13.6) *Related Exercises: 13.39, 13.95*

## Key Equations

- $S_g = kP_g$
- Mass % of component =  $\frac{\text{mass of component in soln}}{\text{total mass of soln}} \times 100$
- ppm of component =  $\frac{\text{mass of component in soln}}{\text{total mass of soln}} \times 10^6$
- Mole fraction of component =  $\frac{\text{moles of component}}{\text{total moles of all components}}$
- Molarity =  $\frac{\text{moles of solute}}{\text{liters of soln}}$
- Molality =  $\frac{\text{moles of solute}}{\text{kilograms of solvent}}$
- $P_{\text{solution}} = X_{\text{solvent}} P_{\text{solvent}}^\circ$
- $\Delta T_b = iK_b m$

- |         |  |
|---------|--|
| [13.4]  | Henry's law, which relates gas solubility to partial pressure        |
| [13.5]  | Concentration in terms of mass percent                               |
| [13.6]  | Concentration in terms of parts per million (ppm)                    |
| [13.7]  | Concentration in terms of mole fraction                              |
| [13.8]  | Concentration in terms of molarity                                   |
| [13.9]  | Concentration in terms of molality                                   |
| [13.10] | Raoult's law, calculating vapor pressure of solvent above a solution |
| [13.12] | The boiling-point elevation of a solution                            |

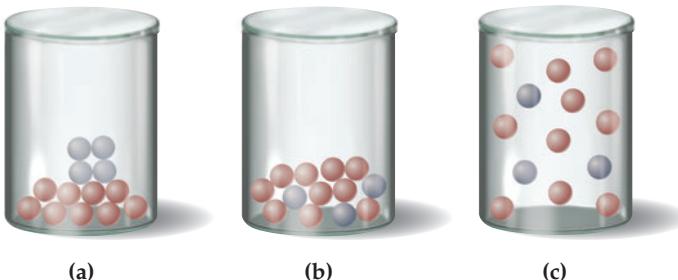
- $\Delta T_f = -iK_f m$
- $\Pi = i\left(\frac{n}{V}\right)RT = iMRT$

- [13.13] The freezing-point depression of a solution  
 [13.14] The osmotic pressure of a solution

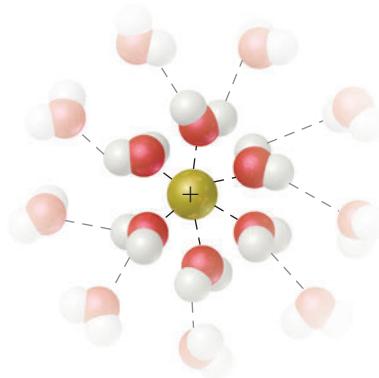
## Exercises

### Visualizing Concepts

**13.40** Rank the contents of the following containers in order of increasing entropy: [Section 13.1]



**13.41** This figure shows the interaction of a cation with surrounding water molecules.



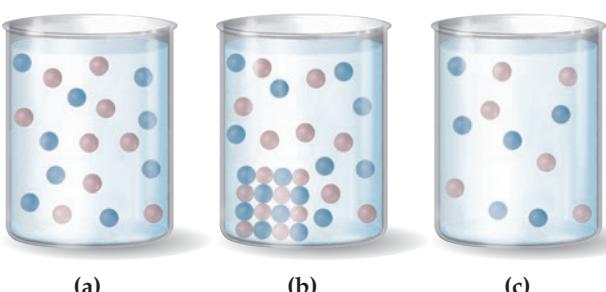
- (a) Which atom of water is associated with the cation? Explain.  
 (b) Which of the following explanations accounts for the fact that the ion-solvent interaction is greater for  $\text{Li}^+$  than for  $\text{K}^+$ ?
  - $\text{Li}^+$  is of lower mass than  $\text{K}^+$ .
  - The ionization energy of Li is higher than that for K.
  - $\text{Li}^+$  has a smaller ionic radius than  $\text{K}^+$ .
  - Li has a lower density than K.
  - Li reacts with water more slowly than K. [Section 13.1]

**13.42** Consider two ionic solids, both composed of singly charged ions, that have different lattice energies. (a) Will the solids have the same solubility in water? (b) If not, which solid will be more soluble in water, the one with the larger lattice energy or the one with the smaller lattice energy? Assume that solute-solvent interactions are the same for both solids. [Section 13.1]

- 13.43** Which *two* statements about gas mixtures are true? [Section 13.1]
  - Gases always mix with other gases because the gas particles are too far apart to feel significant intermolecular attractions or repulsions.
  - Just like water and oil don't mix in the liquid phase, two gases can be immiscible and not mix in the gas phase.

- (c) If you cool a gaseous mixture, you will liquefy all the gases at the same temperature.  
 (d) Gases mix in all proportions in part because the entropy of the system increases upon doing so.

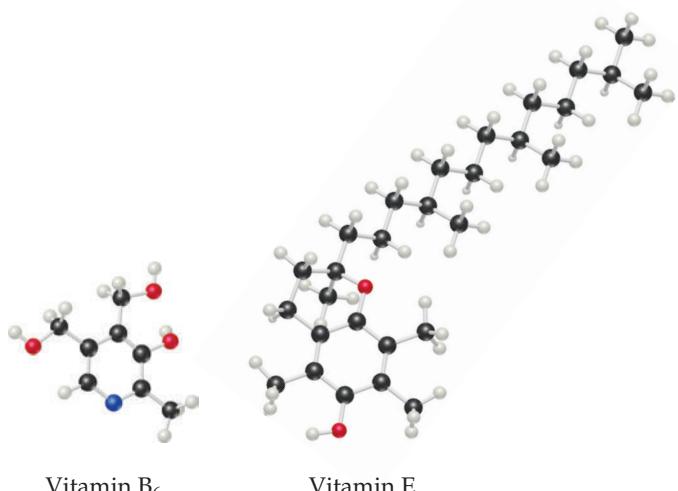
**13.44** Which of the following is the best representation of a saturated solution? Explain your reasoning. [Section 13.2]



**13.45** If you compare the solubilities of the noble gases in water, you find that solubility increases from smallest atomic weight to largest,  $\text{Ar} < \text{Kr} < \text{Xe}$ . Which of the following statements is the best explanation? [Section 13.3]

- The heavier the gas, the more it sinks to the bottom of the water and leaves room for more gas molecules at the top of the water.
- The heavier the gas, the more dispersion forces it has, and, therefore, the more attractive interactions it has with water molecules.
- The heavier the gas, the more likely it is to hydrogen-bond with water.
- The heavier the gas, the more likely it is to make a saturated solution in water.

**13.46** The structures of vitamins E and B<sub>6</sub> are shown here. Predict which is more water soluble and which is more fat soluble. [Section 13.3]



Vitamin B<sub>6</sub>

Vitamin E

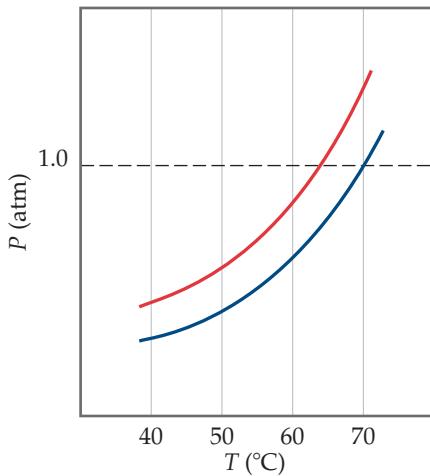
- 13.47** You take a sample of water that is at room temperature and in contact with air and put it under a vacuum. Right away, you see bubbles leave the water, but after a little while, the bubbles stop. As you keep applying the vacuum, more bubbles appear. A friend tells you that the first bubbles were water vapor, and the low pressure had reduced the boiling point of water, causing the water to boil. Another friend tells you that the first bubbles were gas molecules from the air (oxygen, nitrogen, and so forth) that were dissolved in the water. Which friend is mostly likely to be correct? What, then, is responsible for the second batch of bubbles? [Section 13.4]

- 13.48** The figure shows two identical volumetric flasks containing the same solution at two temperatures.

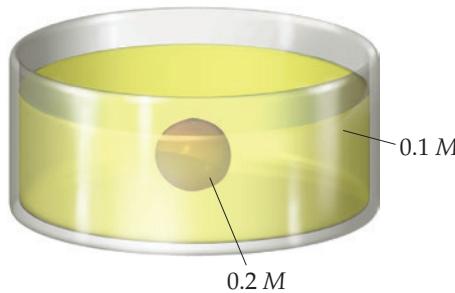
- (a) Does the molarity of the solution change with the change in temperature?  
 (b) Does the molality of the solution change with the change in temperature? [Section 13.4]



- 13.49** This portion of a phase diagram shows the vapor-pressure curves of a volatile solvent and of a solution containing a nonvolatile solute. (a) Which line represents the solution? (b) What are the normal boiling points of the solvent and the solution? [Section 13.5]

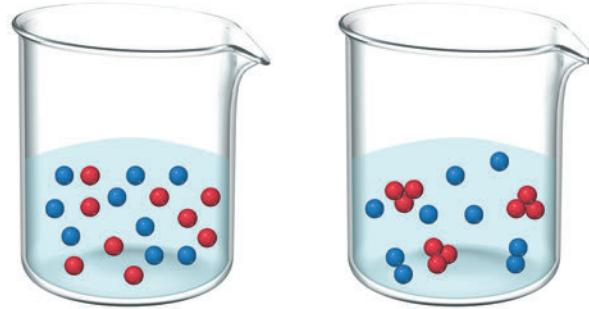


- 13.50** Suppose you had a balloon made of some highly flexible semipermeable membrane. The balloon is filled completely with a 0.2 M solution of some solute and is submerged in a 0.1 M solution of the same solute:

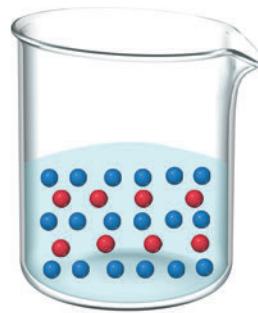


Initially, the volume of solution in the balloon is 0.25 L. Assuming the volume outside the semipermeable membrane is large, as the illustration shows, what would you expect for the solution volume inside the balloon once the system has come to equilibrium through osmosis? [Section 13.5]

- 13.51** Which diagram best represents a liquid–liquid emulsion such as milk? The colored balls represent different liquid molecules. [Section 13.6]



(a) (b)



(c)

### The Solution Process (Section 13.1)

- 13.52** Indicate whether each statement is true or false:

- (a) A solute will dissolve in a solvent if solute–solute interactions are stronger than solute–solvent interactions.  
 (b) In making a solution, the enthalpy of mixing is always a positive number.  
 (c) An increase in entropy favors mixing.

- 13.53** Indicate the type of solute–solvent interaction that should be most important in each of the following solutions:  
 (a) CCl<sub>4</sub> in benzene (C<sub>6</sub>H<sub>6</sub>), (b) methanol (CH<sub>3</sub>OH) in water, (c) KBr in water, (d) HCl in acetonitrile (CH<sub>3</sub>CN).

- 13.54** When ammonium chloride dissolves in water, the solution becomes colder. (a) Is the solution process exothermic or endothermic? (b) Why does the solution form?

- 13.55** (a) In Equation 13.1, which of the enthalpy terms for dissolving an ionic solid would correspond to the lattice energy? (b) Which energy term in this equation is always exothermic?

- 13.56** KBr is relatively soluble in water, yet its enthalpy of solution is +19.8 kJ/mol. Which of the following statements provides the best explanation for this behavior?

- (a) Potassium salts are always soluble in water.
- (b) The entropy of mixing must be unfavorable.
- (c) The enthalpy of mixing must be small compared to the enthalpies for breaking up water–water interactions and K–Br ionic interactions.
- (d) KBr has a high molar mass compared to other salts like NaCl.

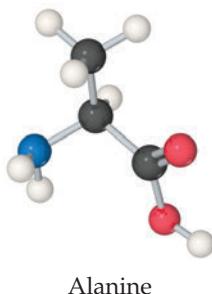
### Saturated Solutions; Factors Affecting Solubility (Sections 13.2 and 13.3)

- 13.57** The solubility of alum,  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , in water at is 44 g per 100 g of water at 50 °C. A solution of alum in water at 80 °C is formed by dissolving 130 g in 100 g of water. When this solution is slowly cooled to 50 °C, no precipitate forms. (a) Is the solution that has cooled down to 50 °C unsaturated, saturated, or supersaturated? (b) You take a metal spatula and scratch the side of the glass vessel that contains this cooled solution, and crystals start to appear. What has just happened? (c) At equilibrium, what mass of crystals do you expect to form?

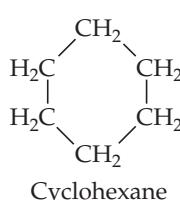
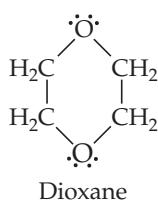
- 13.58** By referring to Figure 13.14, determine whether the addition of 50.0 g of each of the following ionic solids to 100 g of water at 20 °C will lead to a saturated solution: (a) NaCl, (b)  $\text{CaCl}_2$ , (c)  $\text{KNO}_3$ , (d)  $\text{NaNO}_3$ .

- 13.59** Consider water and glycerol,  $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{OH}$ . (a) Would you expect them to be miscible in all proportions? (b) List the intermolecular attractions that occur between a water molecule and a glycerol molecule.

- 13.60** Would you expect alanine (an amino acid) to be more soluble in water or in hexane?



- 13.61** (a) Would you expect stearic acid,  $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ , to be more soluble in water or in carbon tetrachloride? (b) Which would you expect to be more soluble in water, cyclohexane or dioxane?



- 13.62** Which of the following in each pair is likely to be more soluble in hexane,  $\text{C}_6\text{H}_{14}$ : (a)  $\text{CCl}_4$  or  $\text{CaCl}_2$ , (b) benzene ( $\text{C}_6\text{H}_6$ ) or glycerol,  $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{OH}$ , (c) octanoic

acid,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$ , or acetic acid,  $\text{CH}_3\text{COOH}$ ? Explain your answer in each case.

- 13.63** Indicate whether each statement is true or false:

- (a) The higher the temperature, the more soluble most gases are in water.
- (b) The higher the temperature, the more soluble most ionic solids are in water.
- (c) As you cool a saturated solution from high temperature to low temperature, solids start to crystallize out of solution if you achieve a supersaturated solution.
- (d) If you take a saturated solution and raise its temperature, you can (usually) add more solute and make the solution even more concentrated.

- 13.64** The mole fraction of  $\text{N}_2$  in air at sea level is 0.78. Using the data in Table 13.1, together with Henry's law, calculate the molar concentration of  $\text{N}_2$  in the surface water of a mountain lake saturated with air at 20 °C and an atmospheric pressure of 86.6 kPa.

### Concentrations of Solutions (Section 13.4)

- 13.65** (a) Calculate the mass percentage of  $\text{NaNO}_3$  in a solution containing 13.6 g of  $\text{NaNO}_3$  in 834 g of water. (b) An alloy contains 2.86 g of chromium per 100 kg of alloy. What is the concentration of chromium in ppm?

- 13.66** A solution is made containing 50.0 g of ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) in 1000 g of  $\text{H}_2\text{O}$ . Calculate (a) the mole fraction of  $\text{C}_2\text{H}_5\text{OH}$ , (b) the mass percent of  $\text{C}_2\text{H}_5\text{OH}$ , (c) the molality of  $\text{C}_2\text{H}_5\text{OH}$ .

- 13.67** Calculate the molarity of the following aqueous solutions: (a) 0.640 g of  $\text{Mg}(\text{NO}_3)_2$  in 500.0 mL of solution, (b) 50.0 g of  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$  in 250 mL of solution, (c) 125 mL of 3.00 M  $\text{HNO}_3$  diluted to 1.00 L.

- 13.68** Calculate the molality of each of the following solutions: (a) 10.0 g of benzene ( $\text{C}_6\text{H}_6$ ) dissolved in 50.0 g of carbon tetrachloride ( $\text{CCl}_4$ ), (b) 5.00 g of NaCl dissolved in 0.100 L of water.

- 13.69** A sulfuric acid solution containing 697.6 g of  $\text{H}_2\text{SO}_4$  per liter of solution has a density of 1.395 g/cm<sup>3</sup>. Calculate (a) the mass percentage, (b) the mole fraction, (c) the molality, (d) the molarity of  $\text{H}_2\text{SO}_4$  in this solution.

- 13.70** The density of acetonitrile ( $\text{CH}_3\text{CN}$ ) is 0.786 g/mL and the density of methanol ( $\text{CH}_3\text{OH}$ ) is 0.791 g/mL. A solution is made by dissolving 25.0 mL of  $\text{CH}_3\text{OH}$  in 100 mL of  $\text{CH}_3\text{CN}$ . (a) What is the mole fraction of methanol in the solution? (b) What is the molality of the solution? (c) Assuming that the volumes are additive, what is the molarity of  $\text{CH}_3\text{OH}$  in the solution?

- 13.71** The density of toluene ( $\text{C}_7\text{H}_8$ ) is 0.867 g/mL, and the density of thiophene ( $\text{C}_4\text{H}_4\text{S}$ ) is 1.065 g/mL. A solution is made by dissolving 8.10 g of thiophene in 250.0 mL of toluene. (a) Calculate the mole fraction of thiophene in the solution. (b) Calculate the molality of thiophene in the solution. (c) Assuming that the volumes of the solute and solvent are additive, what is the molarity of thiophene in the solution?

- 13.72** Calculate the number of moles of solute present in each of the following aqueous solutions: (a) 750 mL of 0.120 M  $\text{SrBr}_2$ , (b) 70.0 g of 0.200 M KCl, (c) 150.0 g of a solution that is 5.75% glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) by mass.

- 13.73** Describe how you would prepare each of the following aqueous solutions, starting with solid KBr: (a) 0.75 L of  $1.5 \times 10^{-2}$  M KBr, (b) 125 g of 0.180 M KBr, (c) 1.85 L of a solution that is 12.0% KBr by mass (the density of the solution is 1.10 g/mL), (d) a 0.150 M solution of KBr that contains just enough KBr to precipitate 16.0 g of  $\text{AgBr}$  from a solution containing 0.480 mol of  $\text{AgNO}_3$ .

**13.74** Describe how you would prepare each of the following aqueous solutions: (a) 1.50 L of 0.110 M  $(\text{NH}_4)_2\text{SO}_4$  solution, starting with solid  $(\text{NH}_4)_2\text{SO}_4$ ; (b) 225 g of a solution that is 0.65 m in  $\text{Na}_2\text{CO}_3$ , starting with the solid solute; (c) 1.20 L of a solution that is 15.0%  $\text{Pb}(\text{NO}_3)_2$  by mass (the density of the solution is 1.16 g/mL), starting with solid solute; (d) a 0.50 M solution of HCl that would just neutralize 5.5 g of  $\text{Ba}(\text{OH})_2$  starting with 6.0 M HCl.

**13.75** Commercial aqueous nitric acid has a density of 1.12 g/mL and is 3.7 M. Calculate the percent  $\text{HNO}_3$  by mass in the solution.

**13.76** Brass is a substitutional alloy consisting of a solution of copper and zinc. A particular sample of yellow brass consisting of 65.0% Cu and 35.0% Zn by mass has a density of 8470 kg/m<sup>3</sup>. (a) What is the molality of Zn in the solid solution? (b) What is the molarity of Zn in the solution?

**13.77** During a person's typical breathing cycle, the  $\text{CO}_2$  concentration in the expired air rises to a peak of 4.6% by volume. (a) Calculate the partial pressure of the  $\text{CO}_2$  in the expired air at its peak, assuming 101.3 kPa pressure and a body temperature of 37 °C. (b) What is the molarity of the  $\text{CO}_2$  in the expired air at its peak, assuming a body temperature of 37 °C?

### Colligative Properties (Section 13.5)

**13.78** You make two solutions of a nonvolatile solute with a liquid solvent, 0.01 M and 1.00 M. Indicate whether each of the following statements is true or false. (a) The vapor pressure of the concentrated solution is higher than that of the diluted solution. (b) The osmotic pressure of the concentrated solution is higher than that of the diluted solution. (c) The boiling point of the concentrated solution is higher than that of the diluted solution. (d) The freezing point of the concentrated solution is higher than that of the diluted solution.

**13.79** Consider two solutions, one formed by adding 150 g of glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) to 1 L of water and the other formed by adding 150 g of sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) to 1 L of water. Calculate the vapor pressure for each solution at 25 °C; the vapor pressure of pure water at this temperature is 3.17 kPa.

**13.80** The vapor pressure of pure water at 70 °C is 31.2 kPa. The vapor pressure of water over a solution at 70 °C containing equal numbers of moles of water and glycerol ( $\text{C}_3\text{H}_5(\text{OH})_3$ , a nonvolatile solute) is 13.3 kPa. Is the solution ideal according to Raoult's law?

**13.81** (a) Calculate the vapor pressure of water above a solution prepared by adding 22.5 g of lactose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) to 200.0 g of water at 338 K. (Vapor-pressure data for water are given in Appendix B.) (b) Calculate the mass of propene glycol ( $\text{C}_3\text{H}_8\text{O}_2$ ) that must be added to 0.340 kg of water to reduce the vapor pressure by 384 Pa at 40 °C.

**13.82** At 20 °C, the vapor pressure of benzene ( $\text{C}_6\text{H}_6$ ) is 10 kPa, and that of toluene ( $\text{C}_7\text{H}_8$ ) is 2.9 kPa. Assume that benzene and toluene form an ideal solution. (a) What is the composition in mole fraction of a solution that has a vapor pressure of 4.7 kPa at 20 °C? (b) What is the mole fraction of benzene in the vapor above the solution described in part (a)?

**13.83** (a) Does a 0.10 m aqueous solution of KCl have a higher freezing point, a lower freezing point, or the same freezing point as a 0.10 m aqueous solution of urea ( $\text{CO}(\text{NH}_2)_2$ )? (b) The experimental freezing point of the KCl solution is higher than that calculated assuming that KCl is completely dissociated in solution. Why is this the case?

**13.84** Arrange the following aqueous solutions, each 10% by mass in solute, in order of increasing boiling point: glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ), sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ), sodium nitrate ( $\text{NaNO}_3$ ).

**13.85** List the following aqueous solutions in order of increasing boiling point: 0.080 M KBr, 0.130 M urea ( $\text{CO}(\text{NH}_2)_2$ ), 0.080 M  $\text{Mg}(\text{NO}_3)_2$ .

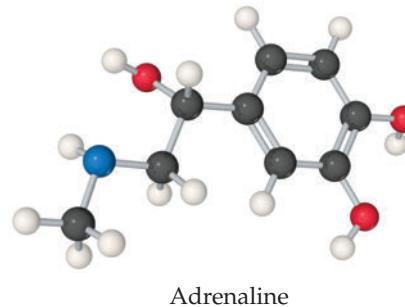
**13.86** Using data from Table 13.3, calculate the freezing and boiling points of each of the following solutions: (a) 0.22 m glycerol ( $\text{C}_3\text{H}_8\text{O}_3$ ) in ethanol, (b) 0.240 mol of naphthalene ( $\text{C}_{10}\text{H}_8$ ) in 2.45 mol of chloroform, (c) 1.50 g NaCl in 0.250 kg of water, (d) 2.04 g KBr and 4.82 g glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) in 188 g of water.

**13.87** How many grams of ethylene glycol ( $\text{C}_2\text{H}_6\text{O}_2$ ) must be added to 2.00 kg of water to produce a solution that freezes at -10.00 °C?

**13.88** What is the freezing point of an aqueous solution that boils at 105.0 °C?

**13.89** What is the osmotic pressure formed by dissolving 50.0 mg of acetylsalicylic acid ( $\text{C}_9\text{H}_8\text{O}_4$ ) in 0.100 L of water at 37 °C?

**13.90** Adrenaline is the hormone that triggers the release of extra glucose molecules in times of stress or emergency. A solution of 0.64 g of adrenaline in 36.0 g of  $\text{CCl}_4$  elevates the boiling point by 0.49 °C. Calculate the approximate molar mass of adrenaline from this data.



**13.91** Lauryl alcohol is obtained from coconut oil and is used to make detergents. A solution of 5.00 g of lauryl alcohol in 0.100 kg of benzene freezes at 4.1 °C. What is the molar mass of lauryl alcohol from this data?

**13.92** A dilute aqueous solution of fructose in water is formed by dissolving 1.25 g of the compound in water to form 0.150 L of solution. The resulting solution has an osmotic pressure of 112.8 kPa at 20 °C. Assuming that the organic compound is a nonelectrolyte, what is its molar mass?

**13.93** The osmotic pressure of a 0.010 M aqueous solution of  $\text{CaCl}_2$  is found to be 68.3 kPa at 25 °C. Calculate the van't Hoff factor, *i*, for the solution.

### Colloids (Section 13.6)

**13.94** (a) Do colloids made only of gases exist? Why or why not? (b) In the 1850s, Michael Faraday prepared ruby-red colloids of gold nanoparticles in water that are still stable today. These brightly colored colloids look like solutions. What experiment(s) could you do to determine whether a given colored preparation is a solution or colloid?

**13.95** An "emulsifying agent" is a compound that helps stabilize a hydrophobic colloid in a hydrophilic solvent (or a hydrophilic colloid in a hydrophobic solvent). Which of the following choices is the best emulsifying agent? (a)  $\text{CH}_3\text{COOH}$ , (b)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ , (c)  $\text{CH}_3(\text{CH}_2)_{11}\text{COOH}$ , (d)  $\text{CH}_3(\text{CH}_2)_{11}\text{COONa}$ .

**13.96** Proteins can be precipitated out of aqueous solution by the addition of an electrolyte; this process is called "salting out" the protein. (a) Do you think that all proteins would be precipitated out to the same extent by the same concentration of the same electrolyte? (b) If a protein has been salted out, are the protein-protein interactions stronger or weaker than they were before the electrolyte was added? (c) A friend of yours who is taking a biochemistry class says that salting out works because the waters of hydration that surround the protein prefer to surround the electrolyte as

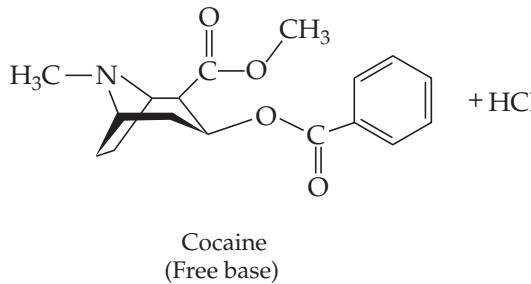
the electrolyte is added; therefore, the protein's hydration shell is stripped away, leading to protein precipitation. Another friend of yours in the same biochemistry class says that salting out works because the incoming ions adsorb tightly to the protein, making ion pairs on the protein

surface, which end up giving the protein a zero net charge in water and therefore leading to precipitation. Discuss these two hypotheses. What kind of measurements would you need to make to distinguish between these two hypotheses?

## Additional Exercises

**13.97** The “free-base” form of cocaine ( $C_{17}H_{21}NO_4$ ) and its protonated hydrochloride form ( $C_{17}H_{22}ClNO_4$ ) are shown here; the free-base form can be converted to the hydrochloride form with one equivalent of HCl. For clarity, not all the carbon and hydrogen atoms are shown; each vertex represents a carbon atom with the appropriate number of hydrogen atoms so that each carbon makes four bonds to other atoms.

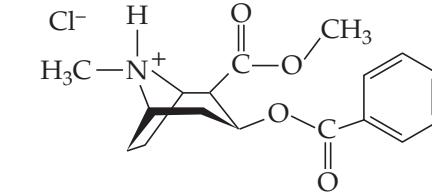
- (a) One of these forms of cocaine is relatively water-soluble: which form, the free base or the hydrochloride?
- (b) One of these forms of cocaine is relatively insoluble in water: which form, the free base or the hydrochloride?



(c) The free-base form of cocaine has a solubility of 1.00 g in 6.70 mL ethanol ( $CH_3CH_2OH$ ). Calculate the molarity of a saturated solution of the free-base form of cocaine in ethanol.

(d) The hydrochloride form of cocaine has a solubility of 1.00 g in 0.400 mL water. Calculate the molarity of a saturated solution of the hydrochloride form of cocaine in water.

(e) How many mL of a concentrated 18.0 M HCl aqueous solution would it take to convert 1.00 kilograms (a “kilo”) of the free-base form of cocaine into its hydrochloride form?



**13.98** A supersaturated solution of sucrose ( $C_{12}H_{22}O_{11}$ ) is made by dissolving sucrose in hot water and slowly letting the solution cool to room temperature. After a long time, the excess sucrose crystallizes out of the solution. Indicate whether each of the following statements is true or false:

- (a) After the excess sucrose has crystallized out, the remaining solution is saturated.
- (b) After the excess sucrose has crystallized out, the system is now unstable and is not in equilibrium.
- (c) After the excess sucrose has crystallized out, the rate of sucrose molecules leaving the surface of the crystals to be hydrated by water is equal to the rate of sucrose molecules in water attaching to the surface of the crystals.

**13.99** Some soft drinks contain up to 85 ppm oxygen. (a) What is this concentration in mol/L? (b) What partial pressure of  $O_2$  above water is needed to obtain 85 ppm  $O_2$  in water at 10 °C? (The Henry's law constant for  $O_2$  at this temperature is  $1.69 \times 10^{-5}$  mol/m<sup>3</sup> Pa.)

**13.100** The presence of the radioactive gas radon (Rn) in well water presents a possible health hazard in parts of the United States. (a) Assuming that the solubility of radon in water with 15.2 kPa pressure of the gas over the water at 30 °C is 0.109 M, what is the Henry's law constant for radon in water at this temperature? (b) A sample consisting of various gases contains 4.5-ppm radon (mole fraction). This gas at a total pressure of 5.07 MPa is shaken with water at 30 °C. Calculate the molar concentration of radon in the water.

**13.101** Glucose makes up about 0.10% by mass of human blood. Calculate this concentration in (a) ppm, (b) molality. (c) What further information would you need to determine the molarity of the solution?

**13.102** The maximum allowable concentration of lead in drinking water is 9.0 ppb. (a) Calculate the molarity of lead in a 9.0 ppb solution. (b) How many grams of lead are in a swimming pool containing 9.0 ppb lead in 60 m<sup>3</sup> of water?

**13.103** Acetonitrile ( $CH_3CN$ ) is a polar organic solvent that dissolves a wide range of solutes, including many salts. The density of a 1.80 M LiBr solution in acetonitrile is 0.826 g/cm<sup>3</sup>. Calculate the concentration of the solution in (a) molality, (b) mole fraction of LiBr, (c) mass percentage of  $CH_3CN$ .

**13.104** A “canned heat” product used to warm buffet dishes consists of a homogeneous mixture of ethanol ( $C_2H_5OH$ ) and paraffin, which has an average formula of  $C_{24}H_{50}$ . What mass of  $C_2H_5OH$  should be added to 620 kg of the paraffin to produce 1.07 kPa of ethanol vapor pressure at 35 °C? The vapor pressure of pure ethanol at 35 °C is 13.3 kPa.

**13.105** A solution contains 0.50 mol  $H_2O$  and an unknown number of moles of sodium chloride. The vapor pressure of the solution at 29 °C is 3.85 kPa. The vapor pressure of pure water at this temperature is 4.05 kPa. Calculate the number of grams of sodium chloride in the solution. (Hint: Remember that sodium chloride is a strong electrolyte.)

**13.106** Two beakers are placed in a sealed box at 25 °C. One beaker contains 50.0 mL of a 0.050 M aqueous solution of a NaCl. The other beaker contains 50.0 mL of a 0.040 M aqueous solution of  $CaCl_2$ . The water vapor pressure of the two solutions reaches equilibrium. (a) In which beaker does the solution level rise, and in which one does it fall? (b) What are the volumes in the two beakers when equilibrium is attained, assuming ideal behavior?

**13.107** The normal boiling point of ethanol,  $CH_3CH_2OH$ , is 78.4 °C. When 3.26 g of a soluble nonelectrolyte is dissolved in 100.0 g of ethanol at that temperature, the vapor pressure of the solution is 100 kPa. What is the molar mass of the solute?

**13.108** Calculate the freezing point of a 0.100 m aqueous solution of  $K_2SO_4$ , (a) ignoring interionic attractions, and (b) taking interionic attractions into consideration by using the van't Hoff factor (Table 13.4).

**13.109** Benzene ( $C_6H_6$ ) boils at 80.1 °C and has a density of 0.876 g/mL. (a) When 0.100 mol of a nondissociating

solute is dissolved in 500 mL of C<sub>6</sub>H<sub>6</sub>, the solution boils at 79.52 °C. What is the molal boiling-point-elevation constant for C<sub>6</sub>H<sub>6</sub>? (b) When 10.0 g of a nondissociating unknown is dissolved in 500 mL of C<sub>6</sub>H<sub>6</sub>, the solution boils at 79.23 °C. What is the molar mass of the unknown?

- 13.110** A lithium salt used in lubricating grease has the formula LiC<sub>n</sub>H<sub>2n+1</sub>O<sub>2</sub>. The salt is soluble in water to the extent of 0.036 g per 100 g of water at 25 °C. The osmotic pressure of this solution is found to be 7.61 kPa. Assuming that molality and molarity in such a dilute solution are the same and that the lithium salt is completely dissociated in the solution, determine an appropriate value of *n* in the formula for the salt.

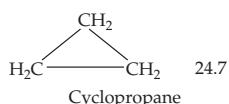
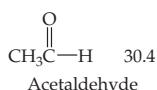
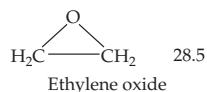
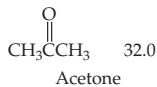
## Integrative Exercises

- 13.111** Fluorocarbons (compounds that contain both carbon and fluorine) were, until recently, used as refrigerants. The compounds listed in the following table are all gases at 25 °C, and their solubilities in water at 25 °C and 101.3 kPa fluorocarbon pressure are given as mass percentages. (a) For each fluorocarbon, calculate the molality of a saturated solution. (b) Which molecular property best predicts the solubility of these gases in water: molar mass, dipole moment, or ability to hydrogen-bond to water? (c) Infants born with severe respiratory problems are sometimes given *liquid ventilation*: They breathe a liquid that can dissolve more oxygen than air can hold. One of these liquids is a fluorinated compound, CF<sub>3</sub>(CF<sub>2</sub>)<sub>7</sub>Br. The solubility of oxygen in this liquid is 66 mL O<sub>2</sub> per 100 mL liquid. In contrast, air is 21% oxygen by volume. Calculate the moles of O<sub>2</sub> present in an infant's lungs (volume: 15 mL) if the infant takes a full breath of air compared to taking a full "breath" of a saturated solution of O<sub>2</sub> in the fluorinated liquid. Assume a pressure of 101.3 kPa in the lungs.

Fluorocarbon	Solubility (mass %)
CF <sub>4</sub>	0.0015
CClF <sub>3</sub>	0.009
CCl <sub>2</sub> F <sub>2</sub>	0.028
CHClF <sub>2</sub>	0.30

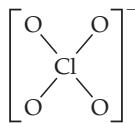
- 13.112** At ordinary body temperature (37 °C), the solubility of N<sub>2</sub> in water at ordinary atmospheric pressure is 0.015 g/L. Air is approximately 78 mol % N<sub>2</sub>. (a) Calculate the number of moles of N<sub>2</sub> dissolved per liter of blood, assuming blood is a simple aqueous solution. (b) At a depth of 30.5 m in water, the external pressure is 405 kPa. What is the solubility of N<sub>2</sub> from air in blood at this pressure? (c) If a scuba diver suddenly surfaces from this depth, how many milliliters of N<sub>2</sub> gas, in the form of tiny bubbles, are released into the bloodstream from each liter of blood?

- 13.113** Consider the following values for enthalpy of vaporization (kJ/mol) of several organic substances:

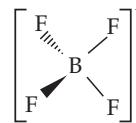


- (a) Account for the variations in heats of vaporization for these substances, considering their relative intermolecular forces. (b) How would you expect the solubilities of these substances to vary in hexane as solvent? In ethanol? Use intermolecular forces, including hydrogen-bonding interactions where applicable, to explain your responses.

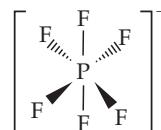
- 13.114** A series of anions is shown here:



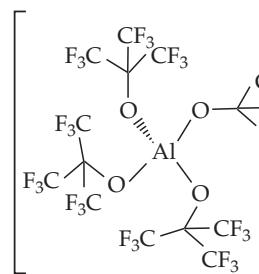
(i)



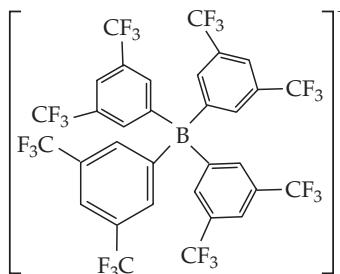
(ii)



(iii)



(iv)



(v)

The anion on the far right is called "BARF" by chemists, as its common abbreviation sounds similar to this word.

- (a) What is the central atom and the number of electron-pair domains around the central atom in each of these anions?  
 (b) What is the electron-domain geometry around the central B in BARF?  
 (c) Which, if any, of these anions has an expanded octet around its central atom?  
 (d) Tetrabutylammonium, (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>N<sup>+</sup> is a bulky cation. Which anion, when paired with the tetrabutylammonium cation, would lead to a salt that will be most soluble in nonpolar solvents?

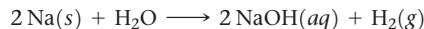
- 13.115** (a) A sample of hydrogen gas is generated in a closed container by reacting 1.750 g of zinc metal with 50.0 mL of 1.00 M hydrochloric acid. Write the balanced equation for the reaction, and calculate the number of moles of hydrogen formed, assuming that the reaction is complete.

**(b)** The volume over the solution in the container is 150 mL. Calculate the partial pressure of the hydrogen gas in this volume at 25 °C, ignoring any solubility of the gas in the solution. **(c)** The Henry's law constant for hydrogen in water at 25 °C is  $7.7 \times 10^{-6}$  mol/m<sup>3</sup> Pa. Estimate the number of moles of hydrogen gas that remain dissolved in the solution. What fraction of the gas molecules in the system is dissolved in the solution? Was it reasonable to ignore any dissolved hydrogen in part (b)?

- 13.116** The following table presents the solubilities of several gases in water at 25 °C under a total pressure of gas and water vapor of 101.3 kPa. **(a)** What volume of CH<sub>4</sub>(g) under standard conditions of temperature and pressure is contained in 4.0 L of a saturated solution at 25 °C? **(b)** The solubilities (in water) of the hydrocarbons are as follows: methane ethane ethene. Is this because ethene is the most polar molecule? **(c)** What intermolecular interactions can these hydrocarbons have with water? **(d)** Draw the Lewis dot structures for the three hydrocarbons. Which of these hydrocarbons possess  $\pi$  bonds? Based on their solubilities, would you say  $\pi$  bonds are more or less polarizable than  $\sigma$  bonds? **(e)** Explain why NO is more soluble in water than either N<sub>2</sub> or O<sub>2</sub>. **(f)** H<sub>2</sub>S is more water-soluble than almost all the other gases in table. What intermolecular forces is H<sub>2</sub>S likely to have with water? **(g)** SO<sub>2</sub> is by far the most water-soluble gas in table. What intermolecular forces is SO<sub>2</sub> likely to have with water?

Gas	Solubility (mM)
CH <sub>4</sub> (methane)	1.3
C <sub>2</sub> H <sub>6</sub> (ethane)	1.8
C <sub>2</sub> H <sub>4</sub> (ethene)	4.7
N <sub>2</sub>	0.6
O <sub>2</sub>	1.2
NO	1.9
H <sub>2</sub> S	99
SO <sub>2</sub>	1476

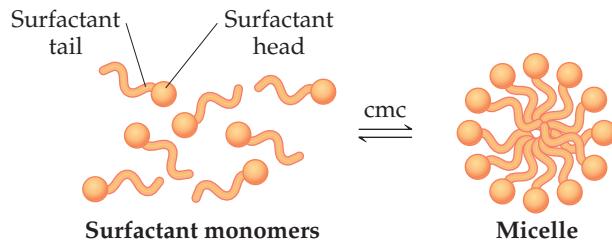
- 13.117** A small cube of sodium (density = 0.968 g/cm<sup>3</sup>) measuring 1.0 mm on each edge is added to 0.100 L of water. The following reaction occurs:



What is the freezing point of the resulting solution, assuming that the reaction goes to completion?

- 13.118** At 35 °C the vapor pressure of acetone, (CH<sub>3</sub>)<sub>2</sub>CO, is 47.9 kPa, and that of carbon disulfide, CS<sub>2</sub>, is 66.7 kPa. A solution composed of an equal number of moles of acetone and carbon disulfide has a vapor pressure of 86.7 kPa at 35 °C. **(a)** What would be the vapor pressure of the solution if it exhibited ideal behavior? **(b)** Based on the behavior of the solution, predict whether the mixing of acetone and carbon disulfide is an exothermic ( $\Delta H_{\text{soln}} < 0$ ) or endothermic ( $\Delta H_{\text{soln}} > 0$ ) process.

- 13.119** Compounds like sodium stearate, called "surfactants" in general, can form structures known as micelles in water, once the solution concentration reaches the value known as the critical micelle concentration (cmc). Micelles contain dozens to hundreds of molecules. The cmc depends on the substance, the solvent, and the temperature.



At and above the cmc, the properties of the solution vary drastically.

- (a)** The turbidity (the amount of light scattering) of solutions increases dramatically at the cmc. Suggest an explanation. **(b)** The ionic conductivity of the solution dramatically changes at the cmc. Suggest an explanation. **(c)** Chemists have developed fluorescent dyes that glow brightly only when the dye molecules are in a hydrophobic environment. Predict how the intensity of such fluorescence would relate to the concentration of sodium stearate as the sodium stearate concentration approaches and then increases past the cmc.

## Design an Experiment

Based on Figure 13.17, you might think that the reason volatile solvent molecules in a solution are less likely to escape to the gas phase, compared to the pure solvent, is because the solute molecules are physically blocking the solvent molecules from leaving

at the surface. This is a common misconception. Design an experiment to test the hypothesis that solute blocking of solvent vaporization is not the reason that solutions have lower vapor pressures than pure solvents.