Solutions

Spreading a soluble salt such as calcium chloride on icy roadways or sidewalks forms a solution with a lower freezing point than pure water, causing the ice or snow to melt at a lower temperature.

OBJECTIVES

After you have studied this chapter, you should be able to

- *Describe the factors that favor the dissolution process*

- *Describe the dissolution of solids in liquids, liquids in liquids, and gases in liquids*

- *Describe how temperature and pressure affect solubility*

- *Express concentrations of solutions in terms of molality and mole fractions*

- *Describe the four colligative properties of solutions and some of their applications*

- *Carry out calculations involving the four colligative properties of solutions: lowering of vapor pressure (Raoult's Law), boiling point elevation, freezing point depression and osmotic pressure*

- *Use colligative properties to determine molecular weights of compounds*

- *Describe dissociation and ionization of compounds, and the associated effects on colligative properties*

- *Recognize and describe colloids: the Tyndall effect, the adsorption phenomenon, hydrophilic and hydrophobic colloids*

A solution is defined as a *homogeneous mixture* of substances in which no settling occurs. A solution consists of a solvent and one or more solutes, whose proportions vary from one solution to another. By contrast, a pure substance has fixed composition. The *solvent* is the medium in which the *solutes* are dissolved. The fundamental units of solutes are usually ions or molecules.

Solutions include different combinations in which a solid, liquid, or gas acts as either solvent or solute. Usually the solvent is a liquid. For instance, sea water is an aqueous solution of many salts and some gases such as carbon dioxide and oxygen. Carbonated water is a saturated solution of carbon dioxide in water. Solutions are common in nature and are extremely important in all life processes, in all scientific areas, and in many industrial processes. The body fluids of all forms of life are solutions. Variations in concentrations of our bodily fluids, especially those of blood and urine, give physicians valuable clues about a person's health. Solutions in which the solvent is not a liquid are also common. Air is a solution of gases with variable composition. Dental fillings are solid amalgams, or solutions of liquid mercury dissolved in solid metals. Alloys are solid solutions of solids dissolved in a metal.

> Many naturally occurring fluids contain particulate matter suspended in a solution. For example, blood contains a solution (plasma) with suspended blood cells. Sea water contains dissolved substances as well as suspended solids.

It is usually obvious which of the components of a solution is the solvent and which is (are) the solute(s): The solvent is usually the most abundant species present. In a cup of instant coffee, the coffee and any added sugar are considered solutes, and the hot water is the solvent. If we mix 10 grams of alcohol with 90 grams of water, alcohol is the solute. If we mix 10 grams of water with 90 grams of alcohol, water is the solute. But which is the solute and which is the solvent in a solution of 50 grams of water and 50 grams of alcohol? In such cases, the terminology is arbitrary and, in fact, unimportant.

THE DISSOLUTION PROCESS

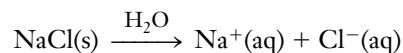## 14-1 SPONTANEITY OF THE DISSOLUTION PROCESS

In Section 4-2, part 5, we listed the solubility guidelines for aqueous solutions. Now we investigate the major factors that influence solubility.

A substance may dissolve with or without reaction with the solvent. For example, when metallic sodium reacts with water, there is the evolution of bubbles of hydrogen and a great deal of heat. A chemical change occurs in which H_2 and soluble ionic sodium hydroxide, NaOH, are produced.

$$2Na(s) + 2H_2O \longrightarrow 2Na^+(aq) + 2OH^-(aq) + H_2(g)$$
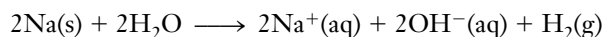
If the resulting solution is evaporated to dryness, solid sodium hydroxide, NaOH, is obtained rather than metallic sodium. This, along with the production of bubbles of hydrogen, is evidence of a reaction with the solvent. Reactions that involve oxidation state changes are usually considered as chemical reactions and not as dissolution.

Solid sodium chloride, NaCl, on the other hand, dissolves in water with no evidence of chemical reaction.

> Ionic solutes that do not react with the solvent undergo solvation. This is a kind of reaction in which molecules of solvent are attached in oriented clusters to the solute particles.

$$NaCl(s) \xrightarrow{H_2O} Na^+(aq) + Cl^-(aq)$$

Evaporation of the water from the sodium chloride solution yields the original NaCl. In this chapter we focus on dissolution processes of this type, in which no irreversible reaction occurs between components.

The ease of dissolution of a solute depends on two factors: (1) the change in energy and (2) the change in disorder (called entropy change) that accompanies the process. In the next chapter we will study both of these factors in detail for many kinds of physical and chemical changes. For now, we point out that a process is *favored* by (1) a *decrease in the energy* of the system, which corresponds to an *exothermic process*, and (2) an *increase in the disorder*, or randomness, of the system.
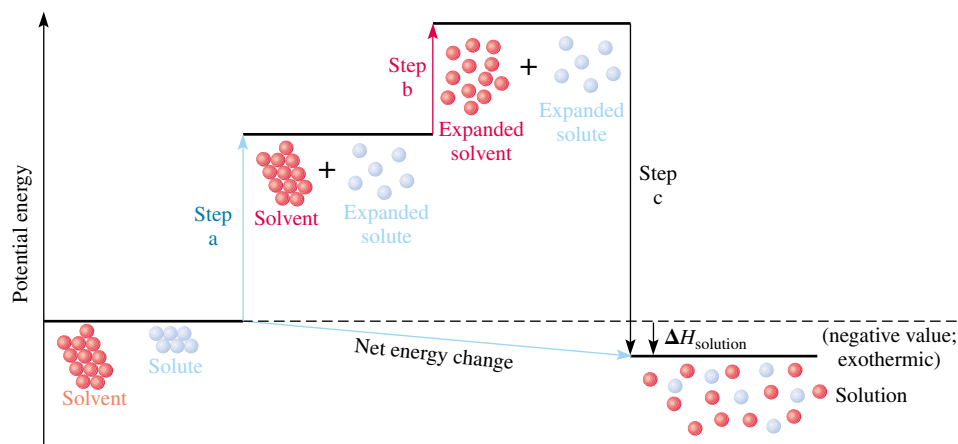
Let us look at the first of these factors. If a solution gets hotter as a substance dissolves, energy is being released in the form of heat. The energy change that accompanies a dissolution process is called the **heat of solution, $\Delta H_{solution}$.** It depends mainly on how strongly solute and solvent particles interact. A negative value of $\Delta H_{solution}$ designates the release of heat. More negative (less positive) values of $\Delta H_{solution}$ favor the dissolution process.

In a pure liquid all the intermolecular forces are between like molecules; when the liquid and a solute are mixed, each molecule then interacts with molecules (or ions) unlike it as well as with like molecules. The relative strengths of these interactions help to determine the extent of solubility of a solute in a solvent. The main interactions that affect the dissolution of a solute in a solvent follow.

> **a.** Weak solute–solute attractions favor solubility.
>
> **b.** Weak solvent–solvent attractions favor solubility.
>
> **c.** Strong solvent–solute attractions favor solubility.

See the Saunders Interactive General Chemistry CD-ROM, Screen 14.3, The Solution Process.

Figure 14-1 illustrates the interplay of these factors. The intermolecular or interionic attractions among solute particles in the pure solute must be overcome (step a) to dissolve the solute. This part of the process requires an *input* of energy (endothermic). Separating the solvent molecules from one another (step b) to "make room" for the solute particles also requires the *input* of energy (endothermic). Energy is *released*, however, as the solute particles and solvent molecules interact in the solution (step c, exothermic). The overall dissolution process is exothermic (and favored) if the amount of heat absorbed in hypothetical steps a and b is less than the amount of energy released in step c. The process is endothermic (and disfavored) if the amount of energy absorbed in steps a and b is greater than the amount of heat released in step c.

We can consider the energy changes separately, even though the actual process cannot be carried out in these separate steps.

Many solids do dissolve in liquids by *endothermic* processes, however. The reason such processes can occur is that the endothermicity can be outweighed by a large increase in disorder of the solute during the dissolution process. The solute particles are highly ordered in a solid crystal, but are free to move about randomly in liquid solutions. Likewise, the degree of disorder in the solvent increases as the solution is formed, because solvent molecules are then in a more random environment. They are surrounded by a mixture of solvent and solute particles.

Figure 14-1 A diagram representing the changes in energy content associated with the hypothetical three-step sequence in a dissolution process—in this case, for a solid solute dissolving in a liquid solvent. (Similar considerations would apply to other combinations.) An *exothermic* process is depicted here. The amount of energy absorbed in steps a and b is *less* than the amount of energy released in step c, so the energy of the solution is favorable. In an *endothermic* process (not shown), the heat content of the solution would be *higher* than that of the original solvent plus solute. Thus, the amount of energy absorbed in steps a and b would be *greater* than the amount of heat released in step c, so energy (heat of solution) would be unfavorable.

Most dissolving processes are accompanied by an overall increase in disorder. Thus, the disorder factor is usually *favorable* to solubility. The determining factor, then, is whether the heat of solution (energy) also favors dissolution or, if it does not, whether it is small enough to be outweighed by the favorable effects of the increasing disorder. In gases, for instance, the molecules are so far apart that intermolecular forces are quite weak. Thus, when gases are mixed, changes in the intermolecular forces are very slight. So the very favorable increase in disorder that accompanies mixing is always more important than possible changes in intermolecular attractions (energy). Hence, gases that do not react with one another can always be mixed in any proportion.

The most common types of solutions are those in which the solvent is a liquid. In the next several sections we consider liquid solutions in more detail.

One of the few exceptions is the dissolution of NaF. The water molecules become more ordered around the small F^- ions. This is due to the strong hydrogen bonding between H_2O molecules and F^- ions.

$$O-H\text{-}\text{-}\text{-}F^-\text{-}\text{-}\text{-}H-O$$
$$|\phantom{O-H\text{-}\text{-}\text{-}F^-\text{-}\text{-}\text{-}}|$$
$$H\phantom{O-H\text{-}\text{-}\text{-}F^-\text{-}\text{-}\text{-}}H$$
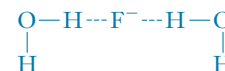
The amount of heat released on mixing, however, outweighs the disadvantage of this ordering.

DISSOLUTION OF SOLIDS IN LIQUIDS

The ability of a solid to go into solution depends most strongly on its crystal lattice energy, or the strength of attractions among the particles making up the solid. The **crystal lattice energy** is defined as the energy change accompanying the formation of one mole of formula units in the crystalline state from constituent particles in the gaseous state. This process is always exothermic; that is, crystal lattice energies are always *negative*. For an ionic solid, the process is written as

$$M^+(g) + X^-(g) \longrightarrow MX(s) + \text{energy}$$
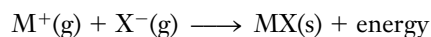
The amount of energy involved in this process depends on the attraction between ions in the solid. When these attractions are strong, a large amount of energy is released as the solid forms, and so the solid is very stable.
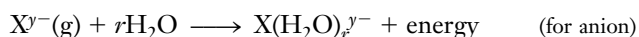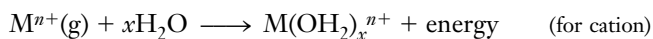
The reverse of the crystal formation reaction is the separation of the crystal into ions.

$$MX(s) + \text{energy} \longrightarrow M^+(g) + X^-(g)$$
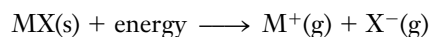
This process can be considered the hypothetical first step (step a in Figure 14-1) in forming a solution of a solid in a liquid. It is always endothermic. The smaller the magnitude of the crystal lattice energy (a measure of the solute–solute interactions), the more readily dissolution occurs. Less energy must be supplied to start the dissolution process.

If the solvent is water, the energy that must be supplied to expand the solvent (step b in Figure 14-1) includes that required to break up some of the hydrogen bonding between water molecules.

The third major factor contributing to the heat of solution is the extent to which solvent molecules interact with particles of the solid. The process in which solvent molecules surround and interact with solute ions or molecules is called **solvation.** When the solvent is water, the more specific term is **hydration. Hydration energy** (equal to the sum of steps b and c in Figure 14-1) is defined as the energy change involved in the (exothermic) hydration of one mole of gaseous ions.

$$M^{n+}(g) + xH_2O \longrightarrow M(OH_2)_x^{n+} + \text{energy} \qquad \text{(for cation)}$$
$$X^{y-}(g) + rH_2O \longrightarrow X(H_2O)_r^{y-} + \text{energy} \qquad \text{(for anion)}$$

Hydration is usually highly exothermic for ionic or polar covalent compounds, because the polar water molecules interact very strongly with ions and polar molecules. In fact, the only solutes that are appreciably soluble in water either undergo dissociation or ionization or are able to form hydrogen bonds with water.

A very negative crystal lattice energy indicates very strong attractions within the solid.

Hydration energy is also referred to as the **heat of hydration.**
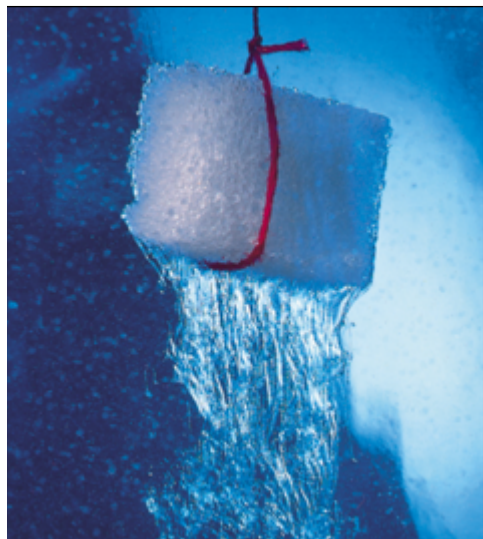
A cube of sugar is slowly lifted through a solution.

The overall heat of solution for a solid dissolving in a liquid is equal to the heat of solvation minus the crystal lattic energy.

$$\Delta H_{\text{solution}} = (\text{heat of solvation}) - (\text{crystal lattice energy})$$

Remember that both terms on the right are always negative.

Nonpolar solids such as naphthalene, $C_{10}H_8$, do not dissolve appreciably in polar solvents such as water because the two substances do not attract each other significantly. This is true despite the fact that crystal lattice energies of solids consisting of nonpolar molecules are much less negative (smaller in magnitude) than those of ionic solids. Naphthalene dissolves readily in nonpolar solvents such as benzene because there are no strong attractive forces between solute molecules or between solvent molecules. In such cases, the increase in disorder controls the process. These facts help explain the observation that "*like dissolves like.*"

> The statement "like dissolves like" means that polar solvents dissolve ionic and polar molecular solutes, and nonpolar solvents dissolve nonpolar molecular liquids.

Consider what happens when a piece of sodium chloride, a typical ionic solid, is placed in water. The $\delta+$ ends of water molecules attract the negative chloride ions on the surface of the solid NaCl, as shown in Figure 14-2. Likewise, the $\delta-$ ends of H_2O molecules (O atoms) orient themselves toward the Na^+ ions and solvate them. These attractions help to overcome the forces holding the ions in the crystal, and NaCl dissolves in the H_2O.

$$\text{NaCl(s)} \xrightarrow{\text{H}_2\text{O}} \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$$
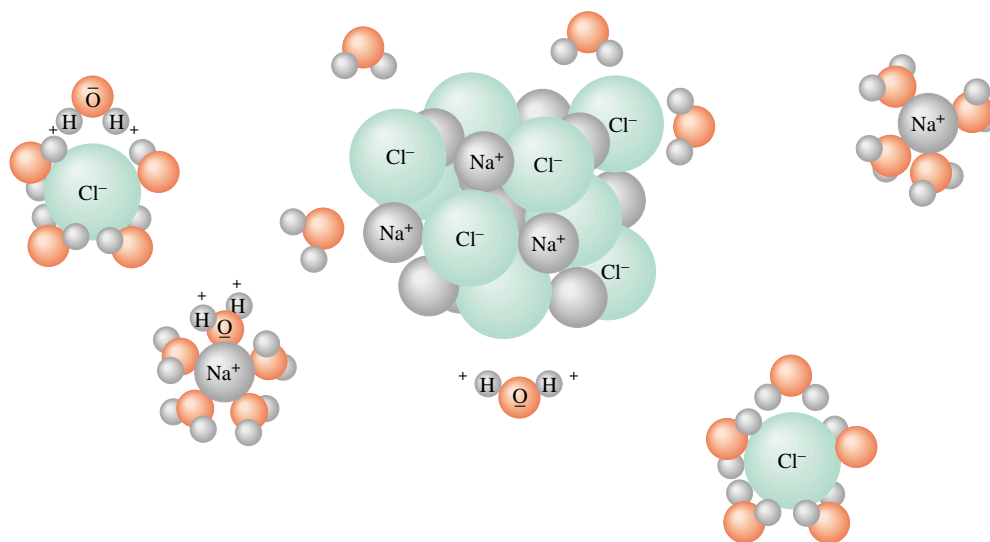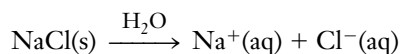

Figure 14-2 The role of electrostatic attractions in the dissolution of NaCl in water. The $\delta+$ H of the polar H_2O molecule helps to attract Cl^- away from the crystal. Likewise, Na^+ is attracted by the $\delta-$ O. Once they are separated from the crystal, both kinds of ions are surrounded by water molecules, to complete the hydration process.

When we write Na^+(aq) and Cl^-(aq), we refer to hydrated ions. The number of H_2O molecules attached to an ion differs with different ions. Sodium ions are thought to be hexahydrated; that is, Na^+(aq) probably represents $[Na(OH_2)_6]^+$. Most cations in aqueous solution are surrounded by four to nine H_2O molecules, with six being the most common. Generally, larger cations can accommodate more H_2O molecules than smaller cations.

Many solids that are appreciably soluble in water are ionic compounds. Magnitudes of crystal lattice energies generally increase with increasing charge and decreasing size of ions. That is, the size of the lattice energy increases as the ionic charge densities increase and, therefore, as the strength of electrostatic attractions within the crystal increases. Hydration energies vary in the same order (Table 14-1). As we indicated earlier, crystal lattice energies and hydration energies are generally much smaller in magnitude for molecular solids than for ionic solids.

Hydration and the effects of attractions in a crystal oppose each other in the dissolution process. Hydration energies and lattice energies are usually of about the same magnitude for low-charge species, so they often nearly cancel each other. As a result, the dissolution process is slightly endothermic for many ionic substances. Ammonium nitrate, NH_4NO_3, is an example of a salt that dissolves endothermically. This property is used in the "instant cold packs" used to treat sprains and other minor injuries. Ammonium nitrate and water are packaged in a plastic bag in which they are kept separate by a partition that is easily broken when squeezed. As the NH_4NO_3 dissolves in the H_2O, the mixture absorbs heat from its surroundings and the bag becomes cold to the touch.

Some ionic solids dissolve with the release of heat. Examples are anhydrous sodium sulfate, Na_2SO_4; calcium acetate, $Ca(CH_3COO)_2$; calcium chloride, $CaCl_2$; and lithium sulfate hydrate, $Li_2SO_4 \cdot H_2O$.

As the charge-to-size ratio (charge density) increases for ions in ionic solids, the magnitude of the crystal lattice energy usually increases more than the hydration energy. This makes dissolution of solids that contain highly charged ions—such as aluminum fluoride, AlF_3; magnesium oxide, MgO; and chromium(III) oxide, Cr_2O_3—very endothermic. As a result, these compounds are not very soluble in water.

For simplicity, we often omit the (aq) designations from dissolved ions. Remember that all ions are hydrated in aqueous solution, whether this is indicated or not.

Review the sizes of ions in Figure 6-1 carefully.

The charge/radius ratio is the ionic charge divided by the ionic radius in angstroms. This is a measure of the charge density around the ion. A negative value for heat of hydration indicates that heat is released during hydration.

Solid ammonium nitrate, NH_4NO_3, dissolves in water in a very endothermic process, absorbing heat from its surroundings. It is used in instant cold packs for early treatment of injuries, such as sprains and bruises, to minimize swelling.

TABLE 14-1	Ionic Radii, Charge/Radius Ratios, and Hydration Energies for Some Cations		
Ion	Ionic Radius (Å)	Charge/Radius Ratio	Hydration Energy (kJ/mol)
K^+	1.52	0.66	-351
Na^+	1.16	0.86	-435
Li^+	0.90	1.11	-544
Ca^{2+}	1.14	1.75	-1650
Fe^{2+}	0.76	2.63	-1980
Zn^{2+}	0.74	2.70	-2100
Cu^{2+}	0.72	2.78	-2160
Fe^{3+}	0.64	4.69	-4340
Cr^{3+}	0.62	4.84	-4370
Al^{3+}	0.68	4.41	-4750

14-3 DISSOLUTION OF LIQUIDS IN LIQUIDS (MISCIBILITY)

In science, **miscibility** is used to describe the ability of one liquid to dissolve in another. The three kinds of attractive interactions (solute–solute, solvent–solvent, and solvent–solute) must be considered for liquid–liquid solutions just as they were for solid–liquid solutions. Because solute–solute attractions are usually much weaker for liquid solutes than for solids, this factor is less important and so the mixing process is often exothermic for miscible liquids. Polar liquids tend to interact strongly with and dissolve readily in other polar liquids. Methanol, CH_3OH; ethanol, CH_3CH_2OH; acetonitrile, CH_3CN; and sulfuric acid, H_2SO_4, are all polar liquids that are soluble in most polar solvents (such as water). The hydrogen bonding between methanol and water molecules and the dipolar interaction between acetonitrile and water molecules are depicted in Figure 14-3.

Because hydrogen bonding is so strong between sulfuric acid, H_2SO_4, and water, a large amount of heat is released when concentrated H_2SO_4 is diluted with water (Figure 14-4). This can cause the solution to boil and spatter. If the major component of the mixture is water, this heat can be absorbed with less increase in temperature because of the unusually high specific heat of H_2O. For this reason, *sulfuric acid (as well as other mineral acids) is always diluted by adding the acid slowly and carefully to water. Water should never be added to the acid.* If spattering does occur when the acid is added to water, it is mainly water that spatters, not the corrosive concentrated acid.

Nonpolar liquids that do not react with the solvent generally are not very soluble in polar liquids because of the mismatch of forces of interaction. Nonpolar liquids are, however, usually quite soluble in other nonpolar liquids. Between nonpolar molecules (whether alike or different) there are only dispersion forces, which are weak and easily overcome. As a result, when two nonpolar liquids are mixed, their molecules just "slide between" one another.

Hydrogen bonding and dipolar interactions were discussed in Section 13-2.

When water is added to concentrated acid, the danger is due more to the spattering of the acid itself than to the steam from boiling water.

The nonpolar molecules in oil do not attract polar water molecules, so oil and water are immiscible. The polar water molecules attract one another strongly—they "squeeze out" the nonpolar molecules in the oil. Oil is less dense than water, so it floats on water.
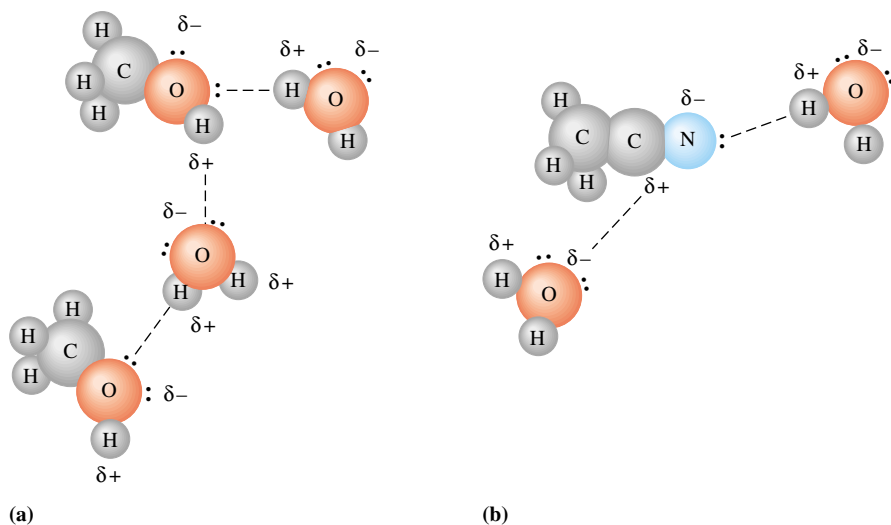
Figure 14-3 (a) Hydrogen bonding in methanol–water solution. (b) Dipolar interaction in acetonitrile–water solution. Each polar molecule is labeled with regions of highest negative charge ($\delta-$) and regions of highest positive charge ($\delta+$). Attractive forces are shown. Molecules tend to arrange themselves to maximize attractions by bringing regions of opposite charge together while minimizing repulsions by separating regions of like charge.
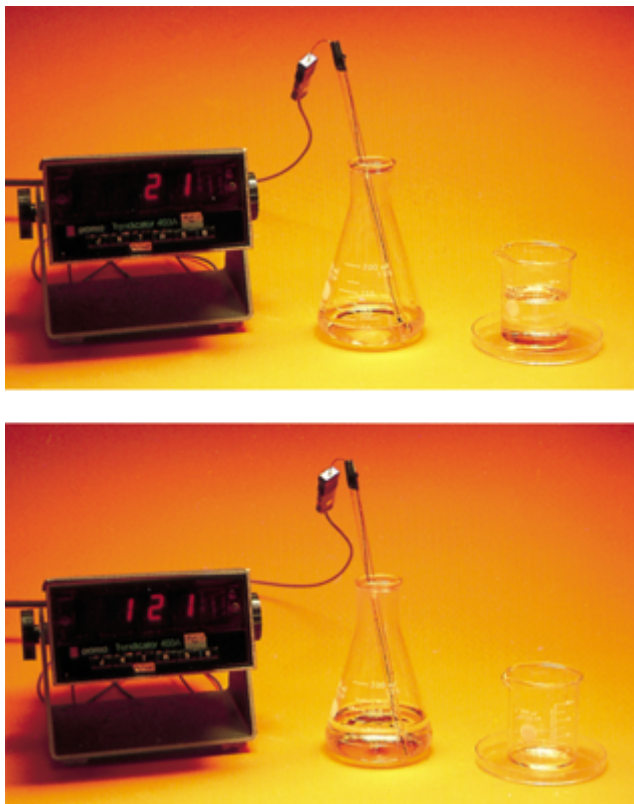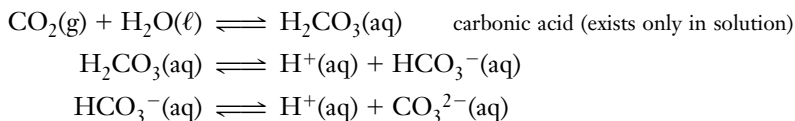
Figure 14-4   The heat released by pouring 50 mL of sulfuric acid, H_2SO_4, into 50 mL of water increases the temperature by 100°C (from 21°C to 121°C)!

14-4   DISSOLUTION OF GASES IN LIQUIDS

Based on Section 13-2 and the foregoing discussion, we expect that polar gases are most soluble in polar solvents and nonpolar gases are most soluble in nonpolar liquids. Although carbon dioxide and oxygen are nonpolar gases, they do dissolve slightly in water. CO_2 is somewhat more soluble because it reacts with water to some extent to form carbonic acid, H_2CO_3. This in turn ionizes slightly in two steps to give hydrogen ions, bicarbonate ions, and carbonate ions.

$$CO_2(g) + H_2O(\ell) \rightleftharpoons H_2CO_3(aq) \qquad \text{carbonic acid (exists only in solution)}$$
$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$
$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$$

Approximately 1.45 grams of CO_2 (0.0329 mole) dissolves in a liter of water at 25°C and one atmosphere pressure.

Oxygen, O_2, is less soluble in water than CO_2, but it does dissolve to a noticeable extent due to dispersion forces (induced dipoles, Section 13-2). Only about 0.041 gram of O_2 (1.3×10^{-3} mole) dissolves in a liter of water at 25°C and 1 atm pressure. This is sufficient to support aquatic life.

The hydrogen halides, HF, HCl, HBr, and HI, are all polar covalent gases. In the gas phase the interactions among the widely separated molecules are not very strong, so solute–solute attractions are minimal, and the dissolution processes in water are exothermic. The

Carbon dioxide is called an acid anhydride, that is, an "acid without water." As noted in Section 6-8, part 2, many other oxides of nonmetals, such as N_2O_5, SO_3, and P_4O_{10}, are also acid anhydrides.

Aqueous HCl, HBr, and HI are strong acids (Sections 4-2, part 2, and Section 10-7). Aqueous HF is a weak acid.

Oxygen gas is sufficiently soluble in water to support a wide variety of aquatic life.
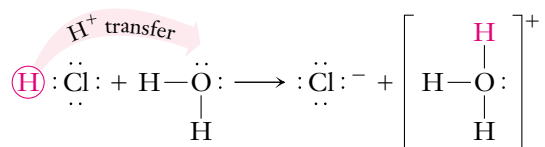
resulting solutions, called hydrohalic acids, contain predominantly ionized HX (X = Cl, Br, I). The ionization involves *protonation* of a water molecule by HX to form a hydrated hydrogen ion and halide ion X⁻ (also hydrated). HCl is used as an example.

$$\text{H⁺ transfer}$$

$$(H):\ddot{C}l: + H-\ddot{O}: \longrightarrow :\ddot{C}l:^- + \left[H-\overset{H}{\underset{H}{O}}: \right]^+$$

HF is only slightly ionized in aqueous solution because of the strong covalent bond. In addition, the polar bond between H and the small F atoms in HF causes very strong hydrogen bonding between H_2O and the largely intact HF molecules.

$$\overset{\delta+\quad\delta-\quad\delta+\quad\delta-}{H-\ddot{O}:\text{---}H-\ddot{F}:} \quad \text{as well as} \quad \overset{\delta+\quad\delta-\quad\delta+\quad\delta-}{H-\ddot{F}:\text{---}H-\ddot{O}:}$$

The only gases that dissolve appreciably in water are those that are capable of hydrogen bonding (such as HF), those that ionize (such as HCl, HBr, and HI), and those that react with water (such as CO_2).

A mortar and pestle are used for grinding solids.

14-5 RATES OF DISSOLUTION AND SATURATION

At a given temperature, the rate of dissolution of a solid increases if large crystals are ground to a powder. Grinding increases the surface area, which in turn increases the number of solute ions or molecules in contact with the solvent. When a solid is placed in water, some of its particles solvate and dissolve. The rate of this process slows as time passes because the surface area of the crystals gets smaller and smaller. At the same time, the number of solute particles in solution increases, so they collide with the solid more
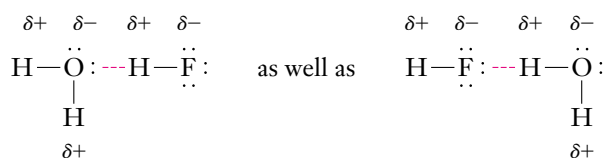
A saturated solution of copper(II) sulfate, $CuSO_4$, in water. As H_2O evaporates, blue $CuSO_4 \cdot 5H_2O$ crystals form. They are in dynamic equilibrium with the saturated solution.

A solution that contains less than the amount of solute necessary for saturation is said to be unsaturated.

(at constant *T*, *P*)

Supersaturated

Saturated

Unsaturated

Concentration of solute

0
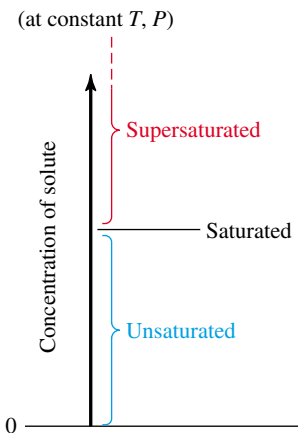
frequently. Some of these collisions result in recrystallization. The rates of the two opposing processes become equal after some time. The solid and dissolved ions are then in equilibrium with each other.

$$\text{solid} \underset{\text{crystallization}}{\overset{\text{dissolution}}{\rightleftharpoons}} \text{dissolved particles}$$
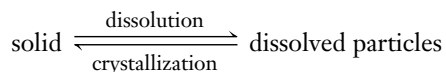
Such a solution is said to be **saturated.** Saturation occurs at very low concentrations of dissolved species for slightly soluble substances and at high concentrations for very soluble substances. When imperfect crystals are placed in saturated solutions of their ions, surface defects on the crystals are slowly "patched" with no net increase in mass of the solid. Often, after some time has passed, we see fewer but larger crystals. These observations provide evidence of the dynamic nature of the solubility equilibrium. After equilibrium is established, no more solid dissolves without the simultaneous crystallization of an equal mass of dissolved ions.

The solubilities of many solids increase at higher temperatures. **Supersaturated solutions** contain higher-than-saturated concentrations of solute. They can sometimes be prepared by saturating a solution at a high temperature. The saturated solution is cooled slowly, without agitation, to a temperature at which the solute is less soluble. At this point, the resulting supersaturated solution is *metastable* (temporarily stable). This may be thought of as a state of pseudoequilibrium in which the system is at a higher energy than in its most stable state. In such a case, the solute has not yet become sufficiently organized for crystallization to begin. A supersaturated solution produces crystals rapidly if it is slightly disturbed or if it is "seeded" with a dust particle or a tiny crystal. Under such conditions enough solid crystallizes to leave a saturated solution (Figure 14-5).

See the *Saunders Interactive General Chemistry CD-ROM,* Screen 14.2, Solubility.

Dynamic equilibria occur in all saturated solutions; for instance, there is a continuous exchange of oxygen molecules across the surface of water in an open container. This is fortunate for fish, which "breathe" dissolved oxygen.

A tiny crystal of sodium acetate, $NaCH_3COO$, was added to a clear, colorless, supersaturated solution of $NaCH_3COO$. This photo shows solid $NaCH_3COO$ just beginning to crystallize in a very rapid process.
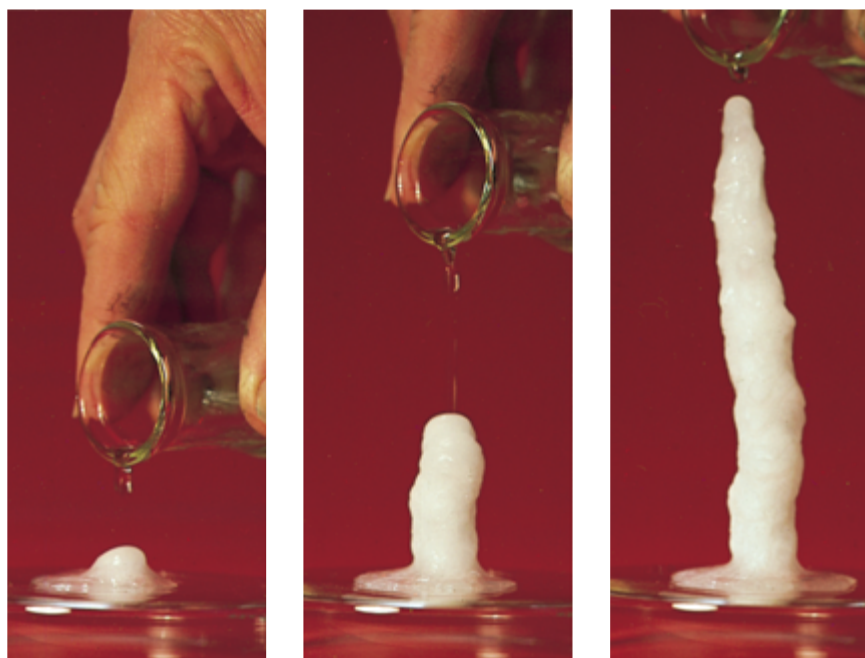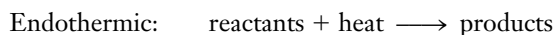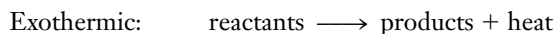

Figure 14-5 Another method of seeding a supersaturated solution is by pouring it very slowly onto a seed crystal. A supersaturated sodium acetate solution was used in these photographs.

Solid iodine, I_2, dissolves to a limited extent in water to give an orange solution. This aqueous solution does not mix with nonpolar carbon tetrachloride, CCl_4 (*left*). Iodine is much more soluble in the nonpolar carbon tetrachloride. After the funnel is shaken and the liquids are allowed to separate (*right*), the upper aqueous phase is lighter orange and the lower CCl_4 layer is much more highly colored. This is because iodine is much more soluble in the nonpolar carbon tetrachloride than in water; much of the iodine dissolves preferentially in the lower (CCl_4) phase. The design of the separatory funnel allows the lower (denser) layer to be drained off. Fresh CCl_4 could be added and the process repeated. This method of separation is called *extraction*. It takes advantage of the different solubilities of a solute in two immiscible liquids.

14-6 EFFECT OF TEMPERATURE ON SOLUBILITY

In Section 13-6 we introduced LeChatelier's Principle, which states that *when a stress is applied to a system at equilibrium, the system responds in a way that best relieves the stress.* Recall that exothermic processes release heat and endothermic processes absorb heat.

$$\text{Exothermic:} \qquad \text{reactants} \longrightarrow \text{products} + \text{heat}$$

$$\text{Endothermic:} \qquad \text{reactants} + \text{heat} \longrightarrow \text{products}$$

Many ionic solids dissolve by endothermic processes. Their solubilities in water usually *increase* as heat is added and the temperature increases. For example, KCl dissolves endothermically.

$$KCl(s) + 17.2 \text{ kJ} \xrightarrow{\text{H}_2\text{O}} K^+(aq) + Cl^-(aq)$$
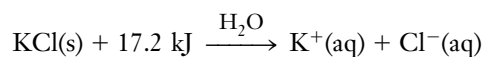
Figure 14-6 shows that the solubility of KCl increases as the temperature increases because more heat is available to increase the dissolving process. Raising the temperature (adding *heat*) causes a stress on the solubility equilibrium. This stress favors the process that *consumes* heat. In this case, more KCl dissolves.
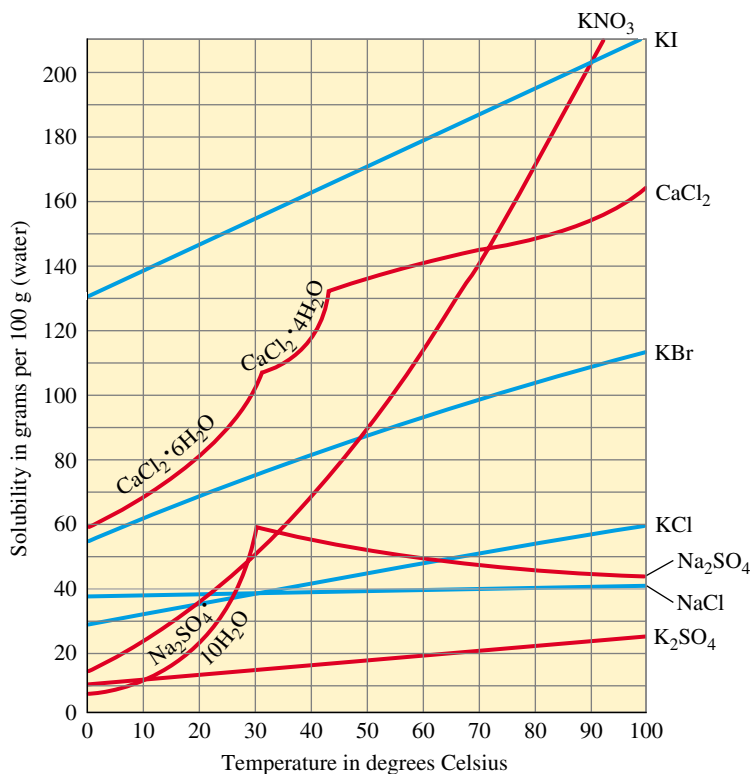
Figure 14-6 A graph that illustrates the effect of temperature on the solubilities of some salts. Some compounds exist either as nonhydrated crystalline substances or as hydrated crystals. Hydrated and nonhydrated crystal forms of the same compounds often have different solubilities because of the different total forces of attraction in the solids. The discontinuities in the solubility curves for $CaCl_2$ and Na_2SO_4 are due to transitions between hydrated and nonhydrated crystal forms.

See the *Saunders Interactive General Chemistry CD-ROM*, Screen 14.6, Factors Affecting Solubility (2): Temperature and LeChatelier's Principle.

Calcium acetate, $Ca(CH_3COO)_2$, is more soluble in cold water than in hot water. When a cold, concentrated solution of calcium acetate is heated, solid calcium acetate precipitates.

Some solids, such as anhydrous Na_2SO_4, and many liquids and gases dissolve by exothermic processes. Their solubilities usually decrease as temperature increases. The solubility of O_2 in water decreases (by 34%) from 0.041 gram per liter of water at 25°C to 0.027 gram per liter at 50°C. Raising the temperature of rivers and lakes by dumping heated waste water from industrial plants and nuclear power plants is called **thermal pollution.** A slight increase in the temperature of the water causes a small but significant decrease in the concentration of dissolved oxygen. As a result, the water can no longer support the marine life it ordinarily could.

*S*ee the *Saunders Interactive General Chemistry CD-ROM,* Screen 14.5, Factors Affecting Solubility (1): Henry's Law and Gas Pressure.
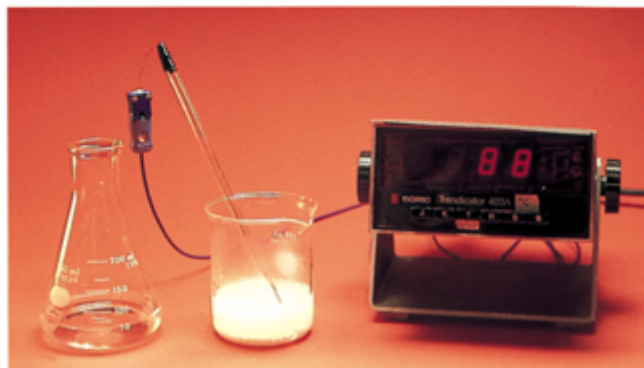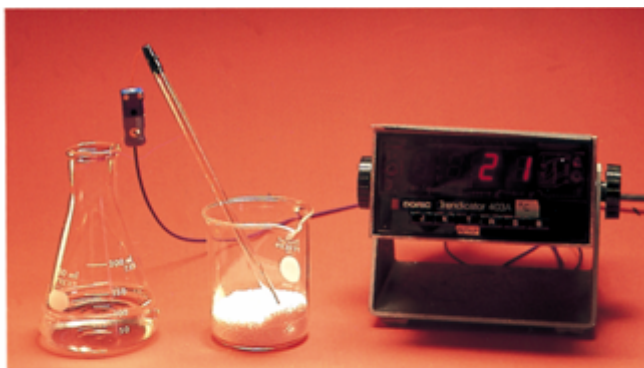
The dissolution of anhydrous calcium chloride, $CaCl_2$, in water is quite exothermic. This dissolution process is utilized in commercial instant hot packs for quick treatment of injuries requiring heat.

Figure 14-7 An illustration of Henry's Law. The solubility of a gas (that does not react completely with the solvent) increases with increasing pressure of the gas above the solution.
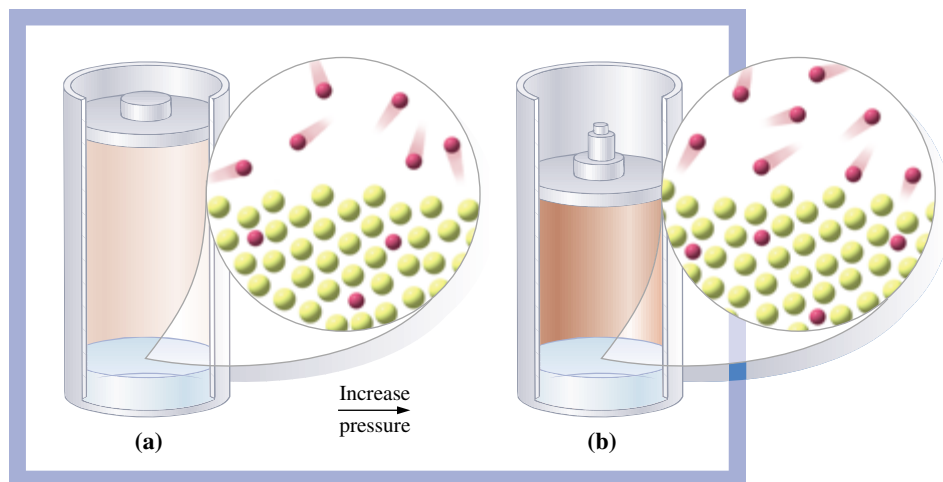
Carbonated beverages can be used to illustrate Henry's Law. When the bottle is opened, the equilibrium is disturbed and bubbles of CO_2 form within the liquid and rise to the surface. After some time, an equilibrium between dissolved CO_2 and atmospheric CO_2 is reached.

14-7 EFFECT OF PRESSURE ON SOLUBILITY

Changing the pressure has no appreciable effect on the solubilities of either solids or liquids in liquids. The solubilities of gases in all solvents increase, however, as the partial pressures of the gases increase (Figure 14-7). Carbonated water is a saturated solution of carbon dioxide in water under pressure. When a can or bottle of a carbonated beverage is opened, the pressure on the surface of the beverage is reduced to atmospheric pressure, and much of the CO_2 bubbles out of solution. If the container is left open, the beverage becomes "flat" because the released CO_2 escapes.

Henry's Law applies to gases that do not react with the solvent in which they dissolve (or, in some cases, gases that react incompletely). It is usually stated as follows.

> The pressure of a gas above the surface of a solution is proportional to the concentration of the gas in the solution. Henry's Law can be represented symbolically as
>
> $$P_{gas} = kC_{gas}$$

P_{gas} is the pressure of the gas above the solution, and k is a constant for a particular gas and solvent at a particular temperature. C_{gas} represents the concentration of dissolved gas; it is usually expressed either as molarity (Section 3-6) or as mole fraction (Section 14-8). The relationship is valid at low concentrations and low pressures.

14-8 MOLALITY AND MOLE FRACTION

We saw in Section 3-6 that concentrations of solutions are often expressed as percent by mass of solute or as molarity. Discussion of many physical properties of solutions is often made easier by expressing concentrations either in molality units or as mole fractions (Sections 14-9 to 14-14).

Molality

> The **molality,** *m*, of a solute in solution is the number of moles of solute *per kilogram of solvent*.
>
> $$\text{molality} = \frac{\text{number of moles solute}}{\text{number of kilograms solvent}}$$

Molality is based on the amount of solvent not solution.

EXAMPLE 14-1 *Molality*

What is the molality of a solution that contains 128 g of CH_3OH in 108 g of water?

Plan

We convert the amount of solute (CH_3OH) to moles, express the amount of solvent (water) in kilograms, and apply the definition of molality.

g CH_3OH $\longrightarrow$ mol CH_3OH

kg H_2O

g H_2O $\longrightarrow$ kg H_2O
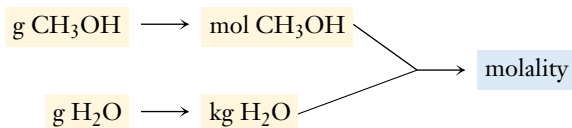
molality

Solution

$$\frac{\underline{?}\ \text{mol } CH_3OH}{\text{kg } H_2O} = \frac{128\ \text{g } CH_3OH}{0.108\ \text{kg } H_2O} \times \frac{1\ \text{mol } CH_3OH}{32.0\ \text{g } CH_3OH} = \frac{37.0\ \text{mol } CH_3OH}{\text{kg } H_2O}$$

$$= \boxed{37.0\ m\ CH_3OH}$$

You should now work Exercise 28.

Each beaker holds the amount of a crystalline ionic compound that will dissolve in 100. grams of water at 100°C. The compounds are *(top row, left to right)* 39 grams of sodium chloride (NaCl, *white*), 102 grams of potassium dichromate ($K_2Cr_2O_7$, *red-orange*), 341 grams of nickel sulfate hexahydrate ($NiSO_4 \cdot 6H_2O$, *green*); *(bottom row, left to right)* 79 grams of potassium chromate (K_2CrO_4, *yellow*), 191 grams of cobalt(II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$, *dark red*), and 203 grams of copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$, *blue*).

EXAMPLE 14-2 *Molality*

How many grams of H_2O must be used to dissolve 50.0 grams of sucrose to prepare a 1.25 *m* solution of sucrose, $C_{12}H_{22}O_{11}$?

Plan

We convert the amount of solute ($C_{12}H_{22}O_{11}$) to moles, solve the molality expression for kilograms of solvent (water), and then express the result in grams.

Solution

$$\underline{?}\ \text{mol } C_{12}H_{22}O_{11} = 50.0\ \text{g } C_{12}H_{22}O_{11} \times \frac{1\ \text{mol } C_{12}H_{22}O_{11}}{342\ \text{g } C_{12}H_{22}O_{11}} = 0.146\ \text{mol } C_{12}H_{22}O_{11}$$

$$\text{molality of solution} = \frac{\text{mol } C_{12}H_{22}O_{11}}{\text{kg } H_2O}$$

Rearranging gives

$$\text{kg } H_2O = \frac{\text{mol } C_{12}H_{22}O_{11}}{\text{molality of solution}} = \frac{0.146\ \text{mol } C_{12}H_{22}O_{11}}{1.25\ \text{mol } C_{12}H_{22}O_{11}/\text{kg } H_2O}$$

$$= 0.117\ \text{kg } H_2O = \boxed{117\ \text{g } H_2O}$$

In other examples later in this chapter we will calculate several properties of the solution in Example 14-2.

Mole Fraction

Recall that in Chapter 12 the **mole fractions,** X_A and X_B, of each component in a mixture containing components A and B were defined as

$$X_A = \frac{\text{no. mol A}}{\text{no. mol A} + \text{no. mol. B}} \quad \text{and} \quad X_B = \frac{\text{no. mol B}}{\text{no. mol A} + \text{no. mol B}}$$

Mole fraction is a dimensionless quantity, that is, it has no units.

EXAMPLE 14-3   *Mole Fraction*

What are the mole fractions of CH_3OH and H_2O in the solution described in Example 14-1? It contains 128 grams of CH_3OH and 108 grams of H_2O.

Plan

We express the amount of both components in moles, and then apply the definition of mole fraction.

Solution

$$\underline{?}\ \text{mol CH}_3\text{OH} = 128\ \text{g CH}_3\text{OH} \times \frac{1\ \text{mol CH}_3\text{OH}}{32.0\ \text{g CH}_3\text{OH}} = 4.00\ \text{mol CH}_3\text{OH}$$

$$\underline{?}\ \text{mol H}_2\text{O} = 108\ \text{g H}_2\text{O} \times \frac{1\ \text{mol H}_2\text{O}}{18.0\ \text{g H}_2\text{O}} = 6.00\ \text{mol H}_2\text{O}$$

Now we calculate the mole fraction of each component.

$$X_{CH_3OH} = \frac{\text{no. mol CH}_3\text{OH}}{\text{no. mol CH}_3\text{OH} + \text{no. mol H}_2\text{O}} = \frac{4.00\ \text{mol}}{(4.00 + 6.00)\ \text{mol}} = \boxed{0.400}$$

$$X_{H_2O} = \frac{\text{no. mol H}_2\text{O}}{\text{no. mol CH}_3\text{OH} + \text{no. mol H}_2\text{O}} = \frac{6.00\ \text{mol}}{(4.00 + 6.00)\ \text{mol}} = \boxed{0.600}$$

In any mixture the sum of the mole fractions must be 1:

$$0.400 + 0.600 = 1$$

You should now work Exercise 30.

COLLIGATIVE PROPERTIES OF SOLUTIONS

Colligative means "tied together."

Physical properties of solutions that depend on the *number*, but not the *kind*, of solute particles in a given amount of solvent are called **colligative properties.** There are four important colligative properties of a solution that are directly proportional to the number of solute particles present. They are (1) vapor pressure lowering, (2) boiling point elevation, (3) freezing point depression, and (4) osmotic pressure. These properties of a solution depend on the *total concentration of all solute particles*, regardless of their ionic or molecular nature, charge, or size. For most of this chapter, we will consider *nonelectrolyte* solutes (Section 4-2, part 1); these substances dissolve to give one mole of dissolved particles for each mole of solute. In Section 14-14 we will learn to modify our predictions of colligative properties to account for ion formation in electrolyte solutions.

14-9 LOWERING OF VAPOR PRESSURE AND RAOULT'S LAW

Many experiments have shown that a solution containing a *nonvolatile* liquid or a solid as a solute always has a lower vapor pressure than the pure solvent (Figure 14-8). The vapor pressure of a liquid depends on the ease with which the molecules are able to escape from the surface of the liquid. When a solute is dissolved in a liquid, some of the total volume of the solution is occupied by solute molecules, and so there are fewer solvent molecules *per unit area* at the surface. As a result, solvent molecules vaporize at a slower rate than if no solute were present. The increase in disorder that accompanies evaporation is also a significant factor. Because a solution is already more disordered ("mixed up") than a pure solvent, the evaporation of the pure solvent involves a larger increase in disorder, and is thus more favorable. Hence, the pure solvent exhibits a higher vapor pressure than does the solution. The lowering of the vapor pressure of the solution is a colligative property. It is a function of the number, and not the kind, of solute particles in solution. We emphasize that solutions of gases or low-boiling (volatile) liquid solutes can have *higher* total vapor pressures than the pure solvents, so this discussion does not apply to them.

A *vapor* is a gas formed by the boiling or evaporation of a liquid or sublimation of a solid. The *vapor pressure* of a liquid is the pressure (partial pressure) exerted by a vapor in equilibrium with its liquid (see Section 13-7).

The lowering of the vapor pressure of a solvent due to the presence of *nonvolatile*, *nonionizing* solutes is summarized by **Raoult's Law.**
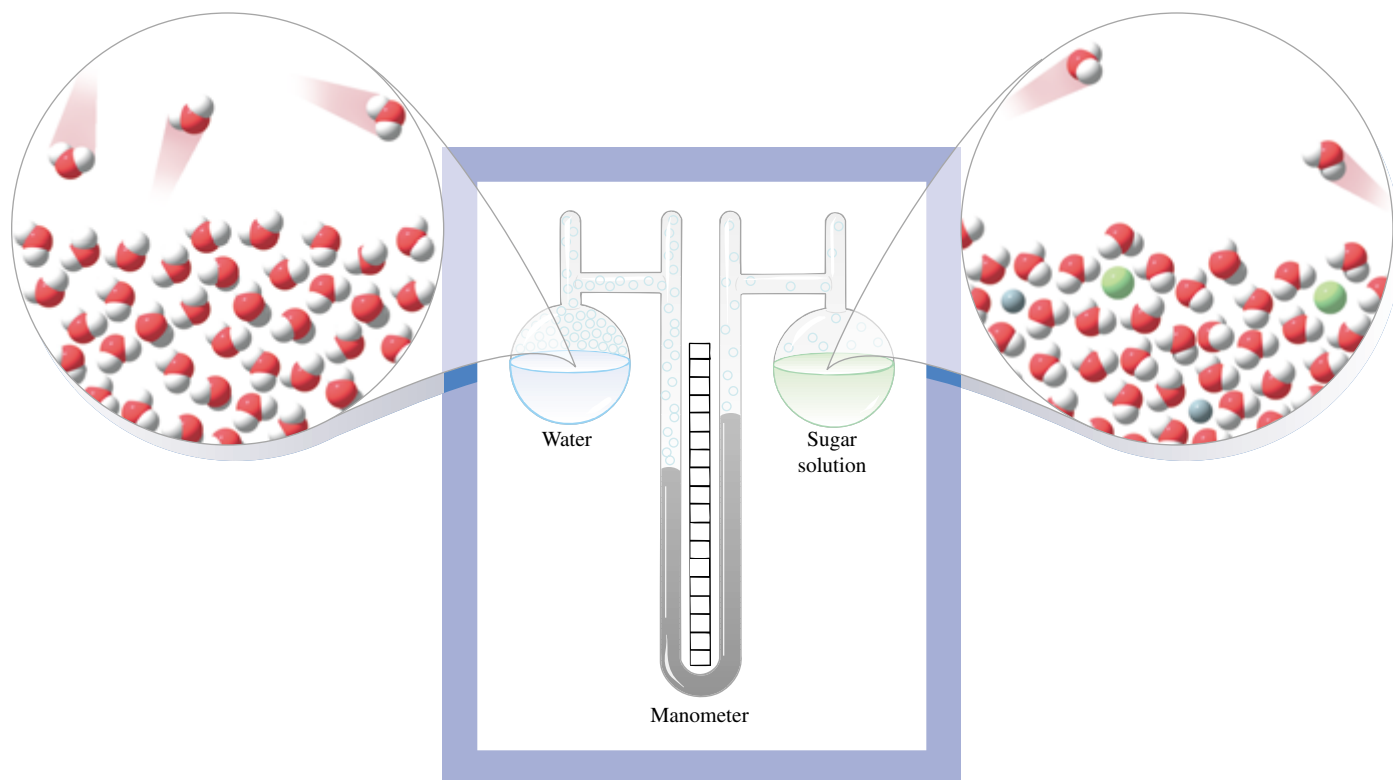

Figure 14-8 Lowering of vapor pressure. If no air is present in the apparatus, the pressure above each liquid is due to water vapor. This pressure is less over the solution of sugar and water.
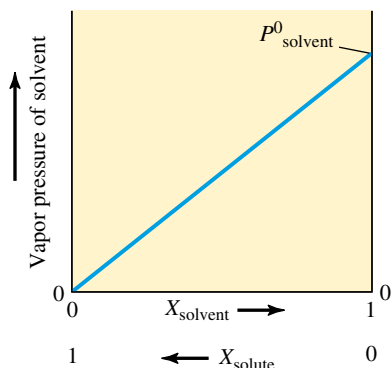
Figure 14-9 Raoult's Law for an ideal solution of a solute in a volatile liquid. The vapor pressure exerted by the liquid is proportional to its mole fraction in the solution.

> The vapor pressure of a solvent in an ideal solution is directly proportional to the mole fraction of the solvent in the solution.

The relationship can be expressed mathematically as

$$P_{solvent} = X_{solvent}P^0_{solvent}$$

where $X_{solvent}$ represents the mole fraction of the solvent in a solution, $P^0_{solvent}$ is the vapor pressure of the *pure* solvent, and $P_{solvent}$ is the vapor pressure of the solvent *in the solution* (see Figure 14-9). If the solute is nonvolatile, the vapor pressure of the solution is entirely due to the vapor pressure of the solvent, $P_{solution} = P_{solvent}$.

The *lowering* of the vapor pressure, $\Delta P_{solvent}$, is defined as

$$\Delta P_{solvent} = P^0_{solvent} - P_{solvent}$$

Thus,

$$\Delta P_{solvent} = P^0_{solvent} - (X_{solvent}P^0_{solvent}) = (1 - X_{solvent})P^0_{solvent}$$

Now $X_{solvent} + X_{solute} = 1$, so $1 - X_{solvent} = X_{solute}$. We can express the *lowering* of the vapor pressure in terms of the mole fraction of solute.

$$\Delta P_{solvent} = X_{solute}P^0_{solvent}$$

Solutions that obey this relationship exactly are called **ideal solutions.** The vapor pressures of many solutions, however, do not behave ideally.

EXAMPLE 14-4   *Vapor Pressure of a Solution of Nonvolatile Solute*

Sucrose is a nonvolatile, nonionizing solute in water. Determine the vapor pressure lowering, at 25°C, of the 1.25 *m* sucrose solution in Example 14-2. Assume that the solution behaves ideally. The vapor pressure of pure water at 25°C is 23.8 torr (Appendix E).

Plan

The solution in Example 14-2 was made by dissolving 50.0 grams of sucrose (0.146 mol) in 117 grams of water (6.50 mol). We calculate the mole fraction of solute in the solution. Then we apply Raoult's Law to find the vapor pressure lowering, $\Delta P_{solvent}$.

Solution

$$X_{sucrose} = \frac{0.146 \text{ mol}}{0.146 \text{ mol} + 6.50 \text{ mol}} = 0.0220$$

Applying Raoult's Law in terms of the vapor pressure lowering,

$$\Delta P_{solvent} = (X_{solute})(P^0_{solvent}) = (0.0220)(23.8 \text{ torr}) = \boxed{0.524 \text{ torr}}$$

You should now work Exercise 38.

See the *Saunders Interactive General Chemistry CD-ROM,* Screen 14.7, Colligative Properties (1): Vapor Pressure and Raoult's Law.

The vapor pressure of water in the solution is (23.8 − 0.524) torr = 23.3 torr. We could calculate this vapor pressure directly from the mole fraction of the solvent (water) in the solution, using the relationship

$$P_{solvent} = X_{solvent}P^0_{solvent}.$$

When a solution consists of two components that are very similar, each component behaves essentially as it would if it were pure. For example, the two liquids heptane, C_7H_{16}, and octane, C_8H_{18}, are so similar that each heptane molecule experiences nearly the same intermolecular forces whether it is near another heptane molecule or near an octane mole-

cule, and similarly for each octane molecule. The properties of such a solution can be predicted from a knowledge of its composition and the properties of each component. Such a solution is very nearly ideal.

Consider an ideal solution of two volatile components, A and B. The vapor pressure of each component above the solution is proportional to its mole fraction in the solution.

$$P_A = X_A P^0_A \quad \text{and} \quad P_B = X_B P^0_B$$

The total vapor pressure of the solution is, by Dalton's Law of Partial Pressures (Section 12-11), equal to the sum of the vapor pressures of the two components.

$$P_{total} = P_A + P_B \quad \text{or} \quad P_{total} = X_A P^0_A + X_B P^0_B$$

This is shown graphically in Figure 14-10. We can use these relationships to predict the vapor pressures of an ideal solution, as Example 14-5 illustrates.

> If component B were nonvolatile, then P^0_B would be zero, and this description would be the same as that given earlier for a solution of a nonvolatile, nonionizing solute in a volatile solvent, $P_{total} = P_{solvent}$.

EXAMPLE 14-5   *Vapor Pressure of a Solution of Volatile Components*

At 40°C, the vapor pressure of pure heptane is 92.0 torr and the vapor pressure of pure octane is 31.0 torr. Consider a solution that contains 1.00 mole of heptane and 4.00 moles of octane. Calculate the vapor pressure of each component and the total vapor pressure above the solution.

Plan

We first calculate the mole fraction of each component in the liquid solution. Then we apply Raoult's Law to each of the two volatile components. The total vapor pressure is the sum of the vapor pressures of the components.

Solution

We first calculate the mole fraction of each component in the liquid solution.

$$X_{heptane} = \frac{1.00 \text{ mol heptane}}{(1.00 \text{ mol heptane}) + (4.00 \text{ mol octane})} = 0.200$$

$$X_{octane} = 1 - X_{heptane} = 0.800$$

Then, applying Raoult's Law for volatile components,

$$P_{heptane} = X_{heptane} P^0_{heptane} = (0.200)(92.0 \text{ torr}) = \boxed{18.4 \text{ torr}}$$

$$P_{octane} = X_{octane} P^0_{octane} = (0.800)(31.0 \text{ torr}) = \boxed{24.8 \text{ torr}}$$

$$P_{total} = P_{heptane} + P_{octane} = 18.4 \text{ torr} + 24.8 \text{ torr} = \boxed{43.2 \text{ torr}}$$

You should now work Exercise 40.

Figure 14-10   Raoult's Law for an ideal solution of two volatile components. The left-hand side of the plot corresponds to pure B ($X_A = 0$, $X_B = 1$), and the right-hand side corresponds to pure A ($X_A = 1$, $X_B = 0$). Of these hypothetical liquids, B is more volatile than A ($P^0_B > P^0_A$).

The vapor in equilibrium with a liquid solution of two or more volatile components has a higher mole fraction of the more volatile component than does the liquid solution.

EXAMPLE 14-6   *Composition of Vapor*

Calculate the mole fractions of heptane and octane in the vapor that is in equilibrium with the solution in Example 14-5.

Plan

We learned in Section 12-11 that the mole fraction of a component in a gaseous mixture equals the ratio of its partial pressure to the total pressure. In Example 14-5 we calculated the partial pressure of each component in the vapor and the total vapor pressure.

Solution

In the *vapor*

Heptane (pure vapor pressure = 92.0 torr at 40°C) is a more volatile liquid than octane (pure vapor pressure = 31.0 torr at 40°C). Its mole fraction in the vapor, 0.426, is higher than its mole fraction in the liquid, 0.200.

$$X_{heptane} = \frac{P_{heptane}}{P_{total}} = \frac{18.4 \text{ torr}}{43.2 \text{ torr}} = \boxed{0.426}$$

$$X_{octane} = \frac{P_{octane}}{P_{total}} = \frac{24.8 \text{ torr}}{43.2 \text{ torr}} = \boxed{0.574}$$

or

$$X_{octane} = 1.000 - 0.426 = \boxed{0.574}$$

You should now work Exercise 42.

Many dilute solutions behave ideally. Some solutions do not behave ideally over the entire concentration range. For some solutions, the observed vapor pressure is greater than that predicted by Raoult's Law (Figure 14-11a). This kind of deviation, known as a *positive deviation*, is due to differences in polarity of the two components. On the molecular level, the two substances do not mix entirely randomly, so there is self-association of each component with local regions enriched in one type of molecule or the other. In a region enriched in A molecules, substance A acts as though its mole fraction were greater than it is in the solution as a whole, and the vapor pressure due to A is greater than if the solution were ideal. A similar description applies to component B. The total vapor pressure is then greater than it would be if the solution were behaving ideally. A solution of acetone and carbon disulfide is an example of a solution that shows a positive deviation from Raoult's Law.
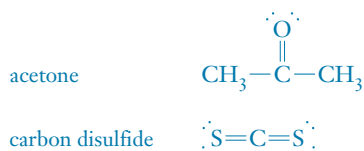
Another, more common type of deviation occurs when the total vapor pressure is less than that predicted (Figure 14-11b). This is called a *negative deviation*. Such an effect is due to unusually strong attractions (such as hydrogen bonding) between *unlike* molecules.

acetone

$$CH_3-\overset{\overset{\displaystyle ..O..}{\|}}{C}-CH_3$$

carbon disulfide $\overset{..}{S}=C=\overset{..}{S}$
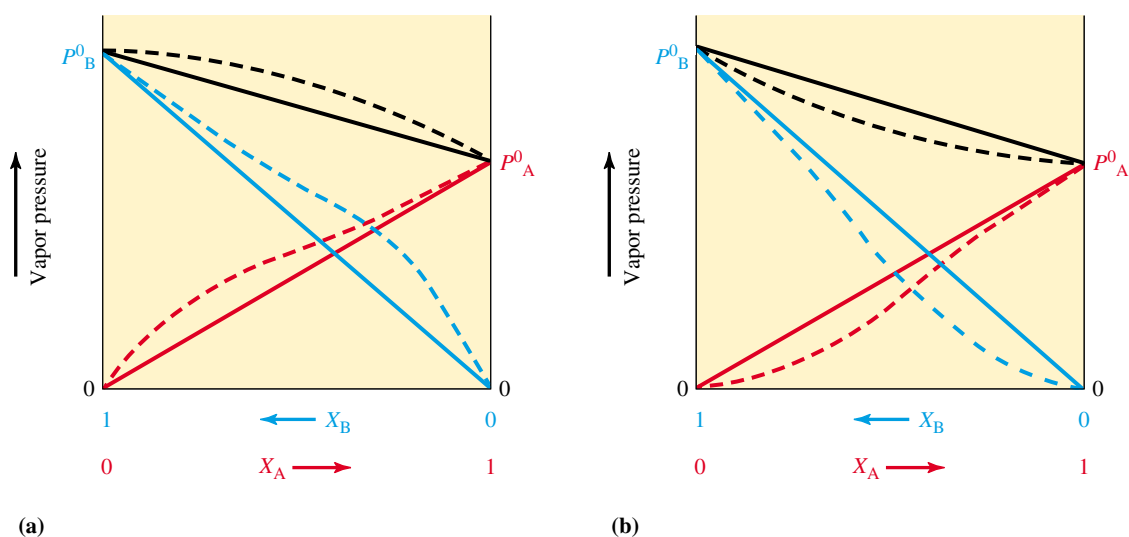
Figure 14-11   Deviations from Raoult's Law for two volatile components. (a) Positive deviation. (b) Negative deviation.

As a result, unlike species hold one another especially tightly in the liquid phase, so fewer molecules escape to the vapor phase. The observed vapor pressure of each component is thus less than ideally predicted. An acetone–chloroform solution and an ethanol–water solution are two examples that show negative deviations from Raoult's Law.

chloroform $CHCl_3$
ethanol CH_3CH_2OH

14-10 FRACTIONAL DISTILLATION

In Section 13-8 we described *simple* distillation as a process in which a liquid solution can be separated into volatile and nonvolatile components. But separation of volatile components is not very efficient by this method. Consider the simple distillation of a liquid solution consisting of two volatile components. If the temperature is slowly raised, the solution begins to boil when the sum of the vapor pressures of the components reaches the applied pressure on the surface of the solution. Both components exert vapor pressures, so both are carried away as a vapor. The resulting distillate is richer than the original liquid in the more volatile component (Example 14-6).

The applied pressure is usually atmospheric pressure.

As a mixture of volatile liquids is distilled, the compositions of both the liquid and the vapor, as well as the boiling point of the solution, change continuously. *At constant pressure*, we can represent these quantities in a **boiling point diagram,** Figure 14-12. In such a diagram the lower curve represents the boiling point of a liquid mixture with the indicated composition. The upper curve represents the composition of the *vapor* in equilibrium
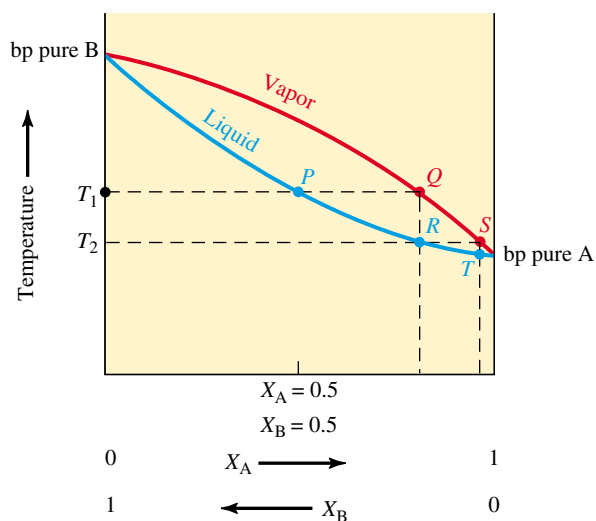
Figure 14-12   A boiling point diagram for a solution of two volatile liquids, A and B. The lower curve represents the boiling point of a liquid mixture with the indicated composition. The upper curve represents the composition of the *vapor* in equilibrium with the boiling liquid mixture at the indicated temperature. Pure liquid A boils at a lower temperature than pure liquid B; hence, A is the more volatile liquid in this illustration. Suppose we begin with an ideal equimolar mixture ($X_A = X_B = 0.5$) of liquids A and B. The point P represents the temperature at which this solution boils, T_1. The vapor that is present at this equilibrium is indicated by point Q ($X_A \approx 0.8$). Condensation of that vapor at temperature T_2 gives a liquid of the same composition (point R). At this point we have described one step of simple distillation. The boiling liquid at point R is in equilibrium with the vapor of composition indicated by point S ($X_A > 0.95$), and so on.

Distillation under vacuum lowers the applied pressure. This allows boiling at lower temperatures than under atmospheric pressure. This technique allows distillation of some substances that would decompose at higher temperatures.

Many fractions, such as gasoline, kerosene, fuel oil, paraffin, and asphalt, are separated from crude oil by fractional distillation.

with the boiling liquid mixture at the indicated temperature. The intercepts at the two vertical axes show the boiling points of the two pure liquids. The distillation of the two liquids is described in the legend to Figure 14-12.

From the boiling point diagram in Figure 14-12, we see that two or more volatile liquids cannot be completely separated from each other by a single distillation step. The vapor collected at any boiling temperature is always enriched in the more volatile component (A); however, at any temperature the vapor still contains both components. A *series* of simple distillations would provide distillates increasingly richer in the more volatile component, but the repeated distillations would be very tedious.

Repeated distillations may be avoided by using **fractional distillation.** A *fractionating column* is inserted above the solution and attached to the condenser, as shown in Figure 14-13. The column is constructed so that it has a large surface area or is packed with many small glass beads or another material with a large surface area. These provide surfaces on which condensation can occur. Contact between the vapor and the packing favors condensation of the less volatile component. The column is cooler at the top than at the bottom. By the time the vapor reaches the top of the column, practically all of the less volatile component has condensed and fallen back down the column. The more volatile component goes into the condenser, where it is liquefied and delivered as a highly enriched distillate into the collection flask. The longer the column or the greater the packing, the more efficient is the separation.

Figure 14-13 A fractional distillation apparatus. The vapor phase rising in the column is in equilibrium with the liquid phase that has condensed out and is flowing slowly back down the column.

Fractional distillation is used for separations in many industrial processes. In this Pennsylvania plant, atmospheric air is liquefied by cooling and compression and then is separated by distillation in towers. This plant produces more than 1000 tons daily of gases from air (nitrogen, oxygen, and argon).

14-11 BOILING POINT ELEVATION

Recall that the boiling point of a liquid is the temperature at which its vapor pressure equals the applied pressure on its surface (see Section 13-8). For liquids in open containers, this is atmospheric pressure. We have seen that the vapor pressure of a solvent at a given temperature is lowered by the presence in it of a *nonvolatile* solute. Such a solution must be heated to a higher temperature than the pure solvent to cause the vapor pressure of the solvent to equal atmospheric pressure (Figure 14-14). In accord with Raoult's Law, the elevation of the boiling point of a solvent caused by the presence of a nonvolatile, nonionized solute is proportional to the number of moles of solute dissolved in a given mass of solvent. Mathematically, this is expressed as

When the solute is nonvolatile, only the solvent distills from the solution.

$$\Delta T_b = K_b m$$

The term ΔT_b represents the elevation of the boiling point of the solvent, that is, the boiling point of the solution minus the boiling point of the pure solvent. The m is the molality of the solute, and K_b is a proportionality constant called the **molal boiling point elevation constant.** This constant is different for different solvents and does not depend on the solute (Table 14-2).

$\Delta T_b = T_{b(soln)} - T_{b(solvent)}$. The boiling points of solutions that contain nonvolatile solutes are always higher than the boiling points of the pure solvents. So ΔT_b is always positive.

K_b corresponds to the change in boiling point produced by a one-molal *ideal* solution of a nonvolatile nonelectrolyte. The units of K_b are °C/*m*.
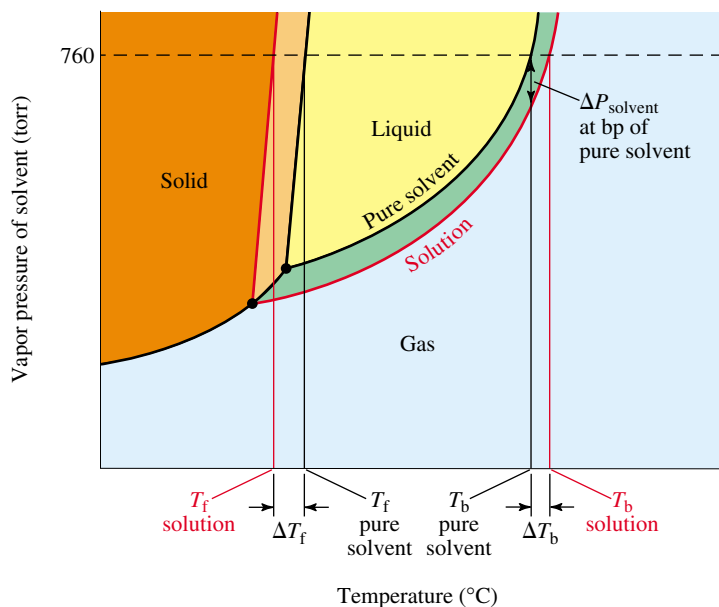
Figure 14-14 Because a *nonvolatile* solute lowers the vapor pressure of a solvent, the boiling point of a solution is higher and the freezing point lower than the corresponding points for the pure solvent. The magnitude of the boiling point elevation, ΔT_b, is less than the magnitude of the freezing point depression, ΔT_f.

TABLE 14-2	*Some Properties of Common Solvents*			
Solvent	bp (pure)	K_b (°C/m)	fp (pure)	K_f (°C/m)
water	100*	0.512	0*	1.86
benzene	80.1	2.53	5.48	5.12
acetic acid	118.1	3.07	16.6	3.90
nitrobenzene	210.88	5.24	5.7	7.00
phenol	182	3.56	43	7.40
camphor	207.42	5.61	178.40	40.0

Exact values.

Elevations of boiling points and depressions of freezing points, which will be discussed later, are usually quite small for solutions of typical concentrations. They can be measured, however, with specially constructed differential thermometers that measure small temperature changes accurately to the nearest 0.001°C.

EXAMPLE 14-7   *Boiling Point Elevation*

Predict the boiling point of the 1.25 *m* sucrose solution in Example 14-2.

Plan

We first find the *increase* in boiling point from the relationship $\Delta T_b = K_b m$. The boiling point is *higher* by this amount than the normal boiling point of pure water.

Solution

From Table 14-2, K_b for H_2O = 0.512°C/m, so

$$\Delta T_b = (0.512°C/m)(1.25\ m) = 0.640°C$$

The solution would boil at a temperature that is 0.640°C higher than pure water would boil. The normal boiling point of pure water is exactly 100°C, so at 1.00 atm this solution is predicted to boil at 100°C + 0.640°C = 100.640°C.

You should now work Exercise 46.

14-12   FREEZING POINT DEPRESSION

Molecules of liquids move more slowly and approach one another more closely as the temperature is lowered. The freezing point of a liquid is the temperature at which the forces of attraction among molecules are just great enough to overcome their kinetic energies and thus cause a phase change from the liquid to the solid state. Strictly speaking, the freezing (melting) point of a substance is the temperature at which the liquid and solid phases are in equilibrium. When a dilute solution freezes, it is the *solvent* that begins to solidify first, leaving the solute in a more concentrated solution. Solvent molecules in a solution are somewhat more separated from one another (because of solute particles) than they are in the pure solvent. Consequently, the temperature of a solution must be lowered below the freezing point of the pure solvent to freeze it.

When a solution freezes, the solvent solidifies as the pure substance. For this photo a dye has been added. As the solute freezes along the wall of the test tube, the dye concentration increases near the center.

The freezing point depressions of solutions of nonelectrolytes have been found to be equal to the molality of the solute times a proportionality constant called the **molal freezing point depression constant, K_f.**

$$\Delta T_f = K_f m$$

ΔT_f is the *depression* of freezing point. It is defined as

$$\Delta T_f = T_{f(solvent)} - T_{f(soln)}$$

so it is always *positive*.

The values of K_f for a few solvents are given in Table 14-2. Each is numerically equal to the freezing point depression of a one-molal *ideal* solution of a nonelectrolyte in that solvent.

EXAMPLE 14-8   *Freezing Point Depression*

When 15.0 grams of ethyl alcohol, C_2H_5OH, is dissolved in 750. grams of formic acid, the freezing point of the solution is 7.20°C. The freezing point of pure formic acid is 8.40°C. Evaluate K_f for formic acid.

See the *Saunders Interactive General Chemistry CD-ROM,* Screen 14.8, Colligative Properties (2): Boiling Point and Freezing Point.

Plan

The molality and the depression of the freezing point are calculated first. Then we solve the equation $\Delta T_f = K_f m$ for K_f and substitute values for m and ΔT_f.

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

Solution

$$\underset{?}{\frac{mol\ C_2H_5OH}{kg\ formic\ acid}} = \frac{15.0\ g\ C_2H_5OH}{0.750\ kg\ formic\ acid} \times \frac{1\ mol\ C_2H_5OH}{46.0\ g\ C_2H_5OH} = 0.435\ m$$

$$\Delta T_f = (T_{f[formic\ acid]}) - (T_{f[solution]}) = 8.40°C - 7.20°C = 1.20°C \qquad (depression)$$

Then $K_f = \dfrac{\Delta T_f}{m} = \dfrac{1.20°C}{0.435\ m} = \boxed{2.76°C/m}$ for formic acid.

You should now work Exercise 48.

EXAMPLE 14-9   *Freezing Point Depression*

Calculate the freezing point of the 1.25 *m* sucrose solution in Example 14-2.

Plan

We first find the *decrease* in freezing point from the relationship $\Delta T_f = K_f m$. The temperature at which the solution freezes is *lower* than the freezing point of pure water by this amount.

Solution

From Table 14-2, K_f for $H_2O = 1.86°C/m$, so

$$\Delta T_f = (1.86°C/m)(1.25\ m) = 2.32°C$$

The solution freezes at a temperature 2.32°C *below* the freezing point of pure water, or

$$T_{f(solution)} = 0.00°C - 2.32°C = \boxed{-2.32°C}$$

You should now work Exercise 56.

Lime, CaO, is added to molten iron ore during the manufacture of pig iron. It lowers the melting point of the mixture. The metallurgy of iron is discussed in more detail in Chapter 22.

The total concentration of all dissolved solute species determines the colligative properties. As we will emphasize in Section 14-14, we must take into account the extent of ion formation in solutions of ionic solutes.

You may be familiar with several examples of the effects we have studied. Sea water does not freeze on some days when fresh water does, because sea water contains higher concentrations of solutes, mostly ionic solutes. Spreading soluble salts such as sodium chloride, NaCl, or calcium chloride, $CaCl_2$, on an icy road lowers the freezing point of the ice, causing the ice to melt.

A familiar application is the addition of "permanent" antifreeze, mostly ethylene glycol, $HOCH_2CH_2OH$, to the water in an automobile radiator. Because the boiling point of the solution is elevated, addition of a solute as a winter antifreeze also helps protect against loss of the coolant by summer "boil-over." The amounts by which the freezing and boiling points change depend on the concentration of the ethylene glycol solution. The addition of too much ethylene glycol is counterproductive, however. The freezing point of pure ethylene glycol is about $-12°C$. A solution that is mostly ethylene glycol would have a somewhat lower freezing point due to the presence of water as a solute. Suppose you graph the freezing point depression of water below 0°C as ethylene glycol is added, and also graph the freezing point depression of ethylene glycol below $-12°C$ as water is added. These two curves would intersect at some temperature, indicating the limit of lowering that can occur. (At these high concentrations, the solutions do not behave ideally, so the temperatures could not be accurately predicted by the equations we have introduced in this chapter, but the main ideas still apply.) Most antifreeze labels recommend a 50:50 mixture by volume (fp $-34°F$, bp 265°F with a 15-psi pressure cap on the radiator), and cite the limit of possible protection with a 70:30 mixture by volume of antifreeze:water (fp $-84°F$, bp 276°F with a 15-psi pressure cap).

14-13 DETERMINATION OF MOLECULAR WEIGHT BY FREEZING POINT DEPRESSION OR BOILING POINT ELEVATION

The colligative properties of freezing point depression and, to a lesser extent, boiling point elevation are useful in the determination of molecular weights of solutes. The solutes *must* be nonvolatile in the temperature range of the investigation if boiling point elevations are to be determined. We will restrict our discussion of determination of molecular weight to nonelectrolytes.

EXAMPLE 14-10 *Molecular Weight from a Colligative Property*

A 1.20-gram sample of an unknown covalent compound is dissolved in 50.0 grams of benzene. The solution freezes at 4.92°C. Calculate the molecular weight of the compound.

Plan

To calculate the molecular weight of the unknown compound, we find the number of moles that is represented by the 1.20 grams of unknown compound. We first use the freezing point data to find the molality of the solution. The molality relates the number of moles of solute and the mass of solvent (known), so this allows us to calculate the number of moles of unknown.

Ethylene glycol, $HOCH_2CH_2OH$, is the major component of "permanent" antifreeze. It depresses the freezing point of water in an automobile radiator and also raises its boiling point. The solution remains in the liquid phase over a wider temperature range than does pure water. This protects against both freezing and boil-over.

Solution

From Table 14-2, the freezing point of pure benzene is 5.48°C and K_f is 5.12°C/m.

$$\Delta T_f = 5.48°C - 4.92°C = 0.56°C$$

$$m = \frac{\Delta T_f}{K_f} = \frac{0.56°C}{5.12°C/m} = 0.11\ m$$

The molality is the number of moles of solute per kilogram of benzene, so the number of moles of solute in 50.0 g (0.0500 kg) of benzene can be calculated.

$$0.11\ m = \frac{?\ \text{mol solute}}{0.0500\ \text{kg benzene}}$$

$$?\ \text{mol solute} = (0.11\ m)(0.0500\ \text{kg}) = 0.0055\ \text{mol solute}$$

$$\text{mass of 1.0 mol} = \frac{\text{no. of g solute}}{\text{no. of mol solute}} = \frac{1.20\ \text{g solute}}{0.0055\ \text{mol solute}} = 2.2 \times 10^2\ \text{g/mol}$$

$$\text{molecular weight} = \boxed{2.2 \times 10^2\ \text{amu}}$$

You should now work Exercise 61.

EXAMPLE 14-11   *Molecular Weight from a Colligative Property*

Either camphor ($C_{10}H_{16}O$, molecular weight = 152 g/mol) or naphthalene ($C_{10}H_8$, molecular weight = 128 g/mol) can be used to make mothballs. A 5.2-gram sample of mothballs was dissolved in 100. grams of ethyl alcohol, and the resulting solution had a boiling point of 78.90°C. Were the mothballs made of camphor or naphthalene? Pure ethyl alcohol has a boiling point of 78.41°C; its K_b = 1.22°C/m.

Plan

We can distinguish between the two possibilities by determining the molecular weight of the unknown solute. We do this by the method shown in Example 14-10, except that now we use the observed boiling point data.

Solution

The observed boiling point elevation is

$$\Delta T_b = T_{b(\text{solution})} - T_{b(\text{solvent})} = (78.90 - 78.41)°C = 0.49°C$$

Using ΔT_b = 0.49°C and K_b = 1.22°C/m, we can find the molality of the solution.

$$\text{molality} = \frac{\Delta T_b}{K_b} = \frac{0.49°C}{1.22°C/m} = 0.40\ m$$

The number of moles of solute in the 100. g (0.1000 kg) of solvent used is

$$\left(0.40\ \frac{\text{mol solute}}{\text{kg solvent}}\right)(0.100\ \text{kg solvent}) = 0.040\ \text{mol solute}$$

The molecular weight of the solute is its mass divided by the number of moles.

$$\frac{?\ \text{g}}{\text{mol}} = \frac{5.2\ \text{g}}{0.040\ \text{mol}} = 130\ \text{g/mol}$$

The value 130 g/mol for the molecular weight indicates that naphthalene was used to make these mothballs.

You should now work Exercise 59.

14-14 COLLIGATIVE PROPERTIES AND DISSOCIATION OF ELECTROLYTES

$$\Delta T_f = K_f m = (1.86°C/m)(0.100\ m)$$
$$= 0.186°C$$

As we have emphasized, colligative properties depend on the *number* of solute particles in a given mass of solvent. A 0.100 molal *aqueous* solution of a covalent compound that does not ionize gives a freezing point depression of 0.186°C. If dissociation were complete, 0.100 m KBr would have an *effective* molality of 0.200 m (i.e., 0.100 m K$^+$ + 0.100 m Br$^-$). So we might predict that a 0.100 molal solution of this 1 : 1 strong electrolyte would have a freezing point depression of 2 × 0.186°C, or 0.372°C. In fact, the *observed* depression is only 0.349°C. This value for ΔT_f is about 6% less than we would expect for an effective molarity of 0.200 m.

In an ionic solution the solute particles are not randomly distributed. Rather, each positive ion has more negative than positive ions near it. The resulting electrical interactions cause the solution to behave nonideally. Some of the ions undergo **association** in solution (Figure 14-15). At any given instant, some K$^+$ and Br$^-$ ions collide and "stick together." During the brief time that they are in contact, they behave as a single particle. This tends to reduce the effective molality. The freezing point depression (ΔT_f) is therefore reduced (as well as the boiling point elevation (ΔT_b) and the lowering of vapor pressure).

Ionic solutions are elegantly described by the Debye–Hückel theory, which is beyond the scope of this text.

A (more concentrated) 1.00 m solution of KBr might be expected to have a freezing point depression of 2 × 1.86°C = 3.72°C, but the observed depression is only 3.29°C. This value for ΔT_f is about 11% less than we would expect. We see a greater deviation from the depression predicted (ignoring ionic association) in the more concentrated solution. This is because the ions are closer together and collide more often in the more concentrated solution. Consequently, the ionic association is greater.

One measure of the extent of dissociation (or ionization) of an electrolyte in water is the **van't Hoff factor, i,** for the solution. This is the ratio of the *actual* colligative property to the value that *would* be observed *if no dissociation occurred*.

Associated ions

Associated ions

$$i = \frac{\Delta T_{f(actual)}}{\Delta T_{f(if\ nonelectrolyte)}} = \frac{K_f m_{effective}}{K_f m_{stated}} = \frac{m_{effective}}{m_{stated}}$$
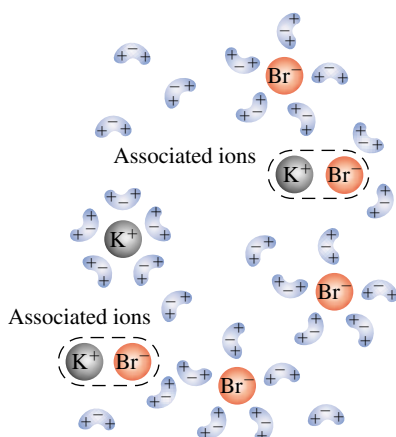
Figure 14-15 Diagrammatic representation of the various species thought to be present in a solution of KBr in water. This would explain unexpected values for its colligative properties, such as freezing point depression.

The ideal, or limiting, value of i for a solution of KBr would be 2, and the value for a 2 : 1 electrolyte such as Na$_2$SO$_4$ would be 3; these values would apply to infinitely dilute solutions in which no appreciable ion association occurs. For 0.10 m and 1.0 m solutions of KBr, i is *less than* 2.

$$\text{For 0.10 } m: \quad i = \frac{0.349°C}{0.186°C} = 1.88 \qquad \text{For 1.0 } m: \quad i = \frac{3.29°C}{1.86°C} = 1.77$$

Table 14-3 lists actual and ideal values of i for solutions of some strong electrolytes, based on measurements of freezing point depressions.

Many weak electrolytes are quite soluble in water, but they ionize only slightly. The percent ionization and i value for a weak electrolyte in solution can also be determined from freezing point depression data (Example 14-12).

Weak acids and weak bases (Section 4-2) are weak electrolytes.

	i for	i for
Compound	1.00 m Solution	0.100 m Solution

TABLE 14-3 *Actual and Ideal van't Hoff Factors, i, for Aqueous Solutions of Nonelectrolytes and Strong Electrolytes*

Compound	i for 1.00 m Solution	i for 0.100 m Solution
nonelectrolytes	1.00 (ideal)	1.00 (ideal)
sucrose, $C_{12}H_{22}O_{11}$	1.00	1.00
If 2 ions in solution/formula unit	2.00 (ideal)	2.00 (ideal)
KBr	1.77	1.88
NaCl	1.83	1.87
If 3 ions in solution/formula unit	3.00 (ideal)	3.00 (ideal)
K_2CO_3	2.39	2.45
K_2CrO_4	1.95	2.39
If 4 ions in solution/formula unit	4.00 (ideal)	4.00 (ideal)
$K_3[Fe(CN)_6]$	—	2.85

✓ **Problem-Solving Tip:** *Selection of a van't Hoff Factor*

Use an ideal value for the van't Hoff factor unless the question clearly indicates to do otherwise, as in the following example and in some of the end-of-chapter exercises. For a strong electrolyte dissolved in water, the ideal value for its van't Hoff factor is listed in Table 14-3. For nonelectrolytes dissolved in water or any solute dissolved in common nonaqueous solvents, the van't Hoff factor is considered to be 1. For weak electrolytes dissolved in water, the van't Hoff factor is a little greater than 1.

Enrichment

Percent Ionization and *i* Value from Freezing Point Depression Data

EXAMPLE 14-12 *Colligative Property and Weak Electrolytes*

Lactic acid, $C_2H_4(OH)COOH$, is found in sour milk. It is also formed in muscles during intense physical activity and is responsible for the pain felt during strenuous exercise. It is a weak monoprotic acid and therefore a weak electrolyte. The freezing point of a 0.0100 m aqueous solution of lactic acid is −0.0206°C. Calculate (a) the *i* value and (b) the percent ionization in the solution.

Plan for (a)

To evaluate the van't Hoff factor, *i*, we first calculate $m_{effective}$ from the observed freezing point depression and K_f for water; we then compare $m_{effective}$ and m_{stated} to find *i*.

Solution for (a)

$$m_{effective} = \frac{\Delta T_f}{K_f} = \frac{0.0206°C}{1.86°C/m} = 0.0111 \ m$$

$$i = \frac{m_{effective}}{m_{stated}} = \frac{0.0111 \ m}{0.0100 \ m} = \boxed{1.11}$$

(Enrichment, continued)

Plan for (b)

The percent ionization is given by

$$\% \text{ ionization} = \frac{m_{\text{ionized}}}{m_{\text{original}}} \times 100\% \qquad (\text{where } m_{\text{original}} = m_{\text{stated}} = 0.0100\ m)$$

The freezing point depression is caused by the $m_{\text{effective}}$, the total *concentration of all dissolved species*—in this case, the sum of the concentrations of HA, H^+, and A^-. We know the value of $m_{\text{effective}}$ from part (a). Thus, we need to construct an expression for the effective molality in terms of the amount of lactic acid that ionizes. We represent the molality of lactic acid that ionizes as an unknown, x, and write the concentrations of all species in terms of this unknown.

Solution for (b)

In many calculations, it is helpful to write down (1) the values, or symbols for the values, of initial concentrations; (2) changes in concentrations due to reaction; and (3) final concentrations, as shown here. The coefficients of the equation are all ones, so the reaction ratio must be 1:1:1.

To simplify the notation, we denote the weak acid as HA and its anion as A^-. The reaction summary used here to analyze the extent of reaction was introduced in Chapter 11.

Let x = molality of lactic acid that ionizes; then
$\quad x$ = molality of H^+ and lactate ions that have been formed

	HA	$\longrightarrow$	H^+	$+$	A^-
Start	0.0100 *m*		0		0
Change	$-x$ *m*		$+x$ *m*		$+x$ *m*
Final	$(0.0100 - \text{x})$ *m*		x *m*		x *m*

The $m_{\text{effective}}$ is equal to the sum of the molalities of all the solute particles.

$$m_{\text{effective}} = m_{\text{HA}} \qquad\qquad + m_{\text{H}^+} + m_{\text{A}^-}$$
$$= (0.0100 - x)\ m + x\ m\ + x\ m\ = (0.0100 + x)\ m$$

This must equal the value for $m_{\text{effective}}$ calculated earlier, 0.0111 *m*.

$$0.0111\ m = (0.0100 + x)\ m$$

$$x = 0.0011\ m = \text{molality of the acid that ionizes}$$

We can now calculate the percent ionization.

$$\% \text{ ionization} = \frac{m_{\text{ionized}}}{m_{\text{original}}} \times 100\% = \frac{0.0011\ m}{0.0100\ m} \times 100\% = \boxed{11\%}$$

This experiment shows that in 0.0100 *m* solutions, only 11% of the lactic acid has been converted into H^+ and $C_2H_4(OH)COO^-$ ions. The remainder, 89%, exists as nonionized molecules.

You should now work Exercises 78 and 80.

Osmosis is one of the main ways in which water molecules move into and out of living cells. The membranes and cell walls in living organisms allow solvent to pass through. Some of these also selectively permit passage of ions and other small solute particles.

14-15 OSMOTIC PRESSURE

Osmosis is the spontaneous process by which the solvent molecules pass through a semipermeable membrane from a solution of lower concentration of solute into a solution of higher concentration of solute. A **semipermeable membrane** (e.g., cellophane) separates

two solutions. Solvent molecules may pass through the membrane in either direction, but the rate at which they pass into the more concentrated solution is found to be greater than the rate in the opposite direction. The initial difference between the two rates is directly proportional to the difference in concentration between the two solutions. Solvent particles continue to pass through the membrane (Figure 14-16a). The column of liquid continues to rise until the hydrostatic pressure due to the weight of the solution in the column is sufficient to force solvent molecules back through the membrane at the same rate at which they enter from the dilute side. The pressure exerted under this condition is called the **osmotic pressure** of the solution.

See the *Saunders Interactive General Chemistry CD-ROM,* Screen 14.9, Colligative Properties (3): Osmosis.

(a)

(b)
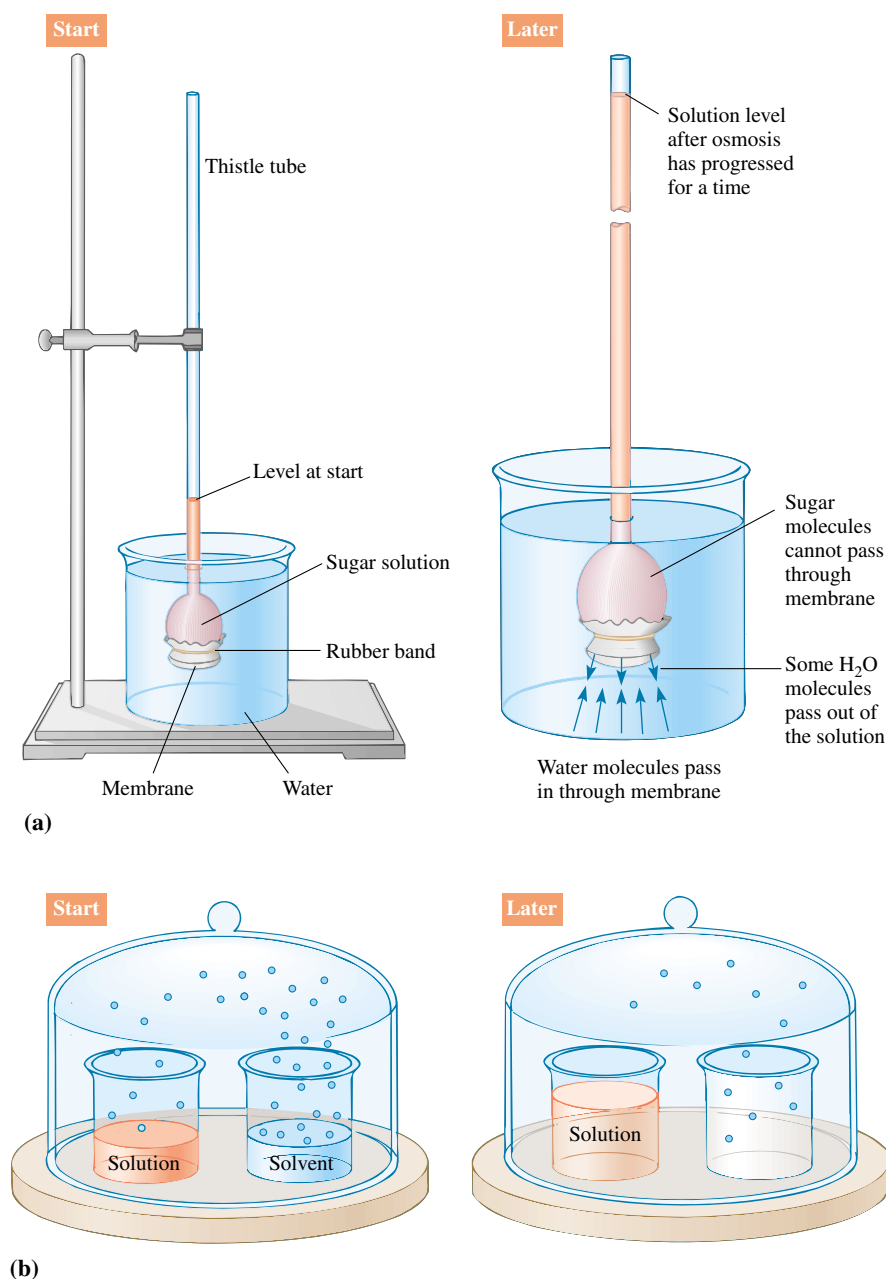
Figure 14-16 (a) Laboratory apparatus for demonstrating osmosis. The picture at the right gives some details of the process, which is analogous to the transfer of solvent into a solution through the space above them (b). In (a) the solute particles cannot pass through the semipermeable membrane. In (b) the solute particles cannot pass through the vapor phase because they are nonvolatile.

Osmotic pressure depends on the number, and not the kind, of solute particles in solution; it is therefore a colligative property.

The osmotic pressure of a given aqueous solution can be measured with an apparatus such as that depicted in Figure 14-16a. The solution of interest is placed inside an inverted glass (thistle) tube that has a membrane firmly fastened across the bottom. This part of the thistle tube and its membrane are then immersed in a container of pure water. As time passes, the height of the solution in the neck rises until the pressure it exerts just counterbalances the osmotic pressure.

Alternatively, we can view osmotic pressure as the external pressure exactly sufficient to prevent osmosis. The pressure required (Figure 14-17) is equal to the osmotic pressure of the solution.

Like molecules of an ideal gas, solute particles are widely separated in very dilute solutions and do not interact significantly with one another. For very dilute solutions, osmotic pressure, π, is found to follow the equation

$$\pi = \frac{nRT}{V}$$

In this equation n is the number of moles of solute in volume, V, (in liters) of the solution. The other quantities have the same meaning as in the ideal gas law. The term n/V is a concentration term. In terms of molarity, M,

$$\pi = MRT$$

Osmotic pressure increases with increasing temperature because T affects the number of solvent–membrane collisions per unit time. It also increases with increasing molarity because M affects the difference in the numbers of solvent molecules hitting the membrane from the two sides, and because a higher M leads to a stronger drive to equalize the concentration difference by dilution and to increase disorder in the solution. For *dilute aqueous solutions*, the molarity is approximately equal to the molality (because the density of the solution is nearly 1 kg/L), so

$$\pi = mRT \qquad \text{(dilute aqueous solutions)}$$

Osmotic pressures represent very significant forces. For example, a 1.00 molal solution of a nonelectrolyte in water at 0°C produces an equilibrium osmotic pressure of approximately 22.4 atmospheres ($\approx$330 psi).

EXAMPLE 14-13   *Osmotic Pressure Calculation*

What osmotic pressure would the 1.25 m sucrose solution in Example 14-2 exhibit at 25°C? The density of this solution is 1.34 g/mL.

Plan

We note that the approximation $M \approx m$ is not very good for this solution, because the density of this solution is quite different from 1 g/mL or kg/L. Thus, we must first find the molarity of sucrose, and then use the relationship $\pi = MRT$.

Solution

Recall from Example 14-2 that there is 50.0 g of sucrose (0.146 mol) in 117 g of H_2O which gives 167 g of solution. The volume of this solution is

$$\text{vol solution} = 167 \text{ g} \times \frac{1 \text{ mL}}{1.34 \text{ g}} = 125 \text{ mL, or } 0.125 \text{ L}$$

The greater the number of solute particles, the greater the height to which the column rises, and the greater the osmotic pressure.
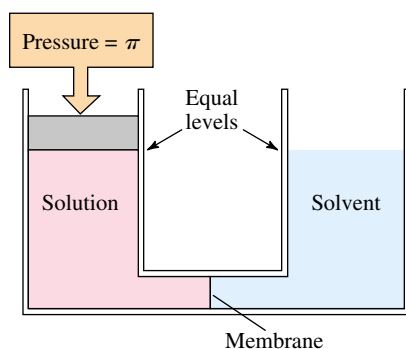

Figure 14-17 The pressure that is just sufficient to prevent solvent flow from the pure solvent side through the semipermeable membrane to the solution side is a measure of the osmotic pressure of the solution.

For a solution of an electrolyte, $\pi = m_{\text{effective}}RT$.

Thus, the molarity of sucrose in the solution is

$$M_{sucrose} = \frac{0.146 \text{ mol}}{0.125 \text{ L}} = 1.17 \text{ mol/L}$$

Now we can calculate the osmotic pressure.

$$\pi = MRT = (1.17 \text{ mol/L})\left(0.0821 \frac{\text{L·atm}}{\text{mol·K}}\right)(298 \text{ K}) = \boxed{28.6 \text{ atm}}$$

You should now work Exercise 84.

Let's compare the calculated values of the four colligative properties for the 1.25 *m* sucrose solution.

vapor pressure lowering	= 0.524 torr	(Example 14-4)
boiling point elevation	= 0.640°C	(Example 14-7)
freezing point depression	= 2.32°C	(Example 14-9)
osmotic pressure	= 28.6 atm	(Example 14-13)

The first of these is so small that it would be hard to measure precisely. Even this small lowering of the vapor pressure is sufficient to raise the boiling point by an amount that could be measured, although with difficulty. The freezing point depression is greater, but still could not be measured very precisely without a special apparatus. The osmotic pressure, on the other hand, is so large that it could be measured much more precisely. Thus, osmotic pressure is often the most easily measured of the four colligative properties, especially when very dilute solutions are used.

The use of measurements of osmotic pressure for the determination of molecular weights has several advantages. Even very dilute solutions give easily measurable osmotic pressures. This method therefore is useful in determination of the molecular weights of (1) very expensive substances, (2) substances that can be prepared only in very small amounts, and (3) substances of very high molecular weight that are not very soluble. Because high-molecular-weight materials are often difficult, and in some cases impossible, to obtain in a high state of purity, determinations of their molecular weights are not as accurate as we might like. Nonetheless, osmotic pressures provide a very useful method of estimating molecular weights.

An illustration of osmosis. When a carrot is soaked in a concentrated salt solution, water flows out of the plant cells by osmosis. A carrot soaked overnight in salt solution (*left*) has lost much water and become limp. A carrot soaked overnight in pure water (*right*) is little affected.

EXAMPLE 14-14   *Molecular Weight from Osmotic Pressure*

Pepsin is an enzyme present in the human digestive tract. A solution of a 0.500-gram sample of purified pepsin in 30.0 mL of aqueous solution exhibits an osmotic pressure of 8.92 torr at 27.0°C. Estimate the molecular weight of pepsin.

An enzyme is a protein that acts as a biological catalyst. Pepsin catalyzes the metabolic cleavage of amino acid chains (called peptide chains) in other proteins.

Plan

As we did in earlier molecular weight determinations (Section 14-13), we must first find *n*, the number of moles that 0.500 grams of pepsin represents. We start with the equation $\pi = MRT$. The molarity of pepsin is equal to the number of moles of pepsin per liter of solution, *n/V*. We substitute this for *M* and solve for *n*.
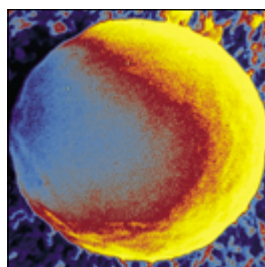
Solution

$$\pi = MRT = \left(\frac{n}{V}\right)RT \qquad \text{or} \qquad n = \frac{\pi V}{RT}$$

Cells expand in solution of lower solute concentration (a hypotonic solution)
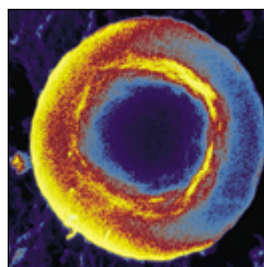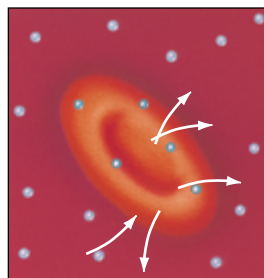
Normal cells in isotonic solution
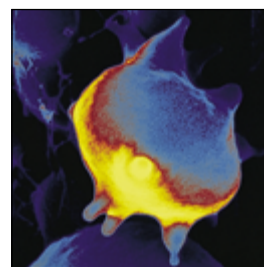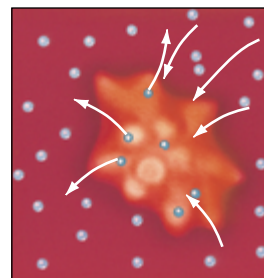
Cells shrink in solution of greater solute concentration (a hypertonic solution)

Living cells contain solutions. When living cells are put in contact with solutions having different total solute concentrations, the resulting osmotic pressure can cause solvent to flow into (*left*) or out of (*right*) the cells.

We convert 8.92 torr to atmospheres to be consistent with the units of R.

$$n = \frac{\pi V}{RT} = \frac{\left(8.92 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}}\right)(0.0300 \text{ L})}{\left(0.0821 \frac{\text{L·atm}}{\text{mol·K}}\right)(300 \text{ K})} = 1.43 \times 10^{-5} \text{ mol pepsin}$$

Thus, 0.500 g of pepsin is 1.43×10^{-5} mol. We now estimate its molecular weight.

$$\underline{?} \text{ g/mol} = \frac{0.500 \text{ g}}{1.43 \times 10^{-5} \text{ mol}} = \boxed{3.50 \times 10^4 \text{ g/mol}}$$

The molecular weight of pepsin is approximately 35,000 amu. This is typical for medium-sized proteins.

You should now work Exercise 90.

The freezing point depression of this very dilute solution would be only about 0.0009°C, which would be difficult to measure accurately. The osmotic pressure of 8.92 torr, on the other hand, is easily measured.

✓ **Problem-Solving Tip:** *Units in Osmotic Pressure Calculations*

Strictly speaking, the equation for osmotic pressure is presented in terms of molarity, $\pi = MRT$. Osmotic pressure, π, has the units of pressure (atmospheres); M (mol/L); and T (kelvins). Therefore, the appropriate value of R is $0.0821 \frac{\text{L·atm}}{\text{mol·K}}$. We can balance the units in this equation as follows.

$$\text{atm} = \left(\frac{\text{mol}}{\text{L}}\right)\left(\frac{\text{L·atm}}{\text{mol·K}}\right)(\text{K})$$

When we use the approximation that $M \approx m$, we might think that the units do not balance. For very dilute aqueous solutions, we can think of M as being *numerically* equal to m, but having the units mol/L, as shown above.

TABLE 14-4			*Types of Colloids*	
Dispersed (solute-like) Phase		**Dispersing (solvent-like) Medium**	**Common Name**	**Examples**
solid	in	solid	solid sol	Many alloys (e.g., steel and duralumin), some colored gems, reinforced rubber, porcelain, pigmented plastics
liquid	in	solid	solid emulsion	Cheese, butter, jellies
gas	in	solid	solid foam	Sponge, rubber, pumice, Styrofoam
solid	in	liquid	sols and gels	Milk of magnesia, paints, mud, puddings
liquid	in	liquid	emulsion	Milk, face cream, salad dressings, mayonnaise
gas	in	liquid	foam	Shaving cream, whipped cream, foam on beer
solid	in	gas	solid aerosol	Smoke, airborne viruses and particulate matter, auto exhaust
liquid	in	gas	liquid aerosol	Fog, mist, aerosol spray, clouds

Freshly made wines are often cloudy because of colloidal particles. Removing these colloidal particles clarifies the wine.

COLLOIDS

A solution is a homogeneous mixture in which no settling occurs and in which solute particles are at the molecular or ionic state of subdivision. This represents one extreme of mixtures. The other extreme is a suspension, a clearly heterogeneous mixture in which solute-like particles settle out after mixing with a solvent-like phase. Such a situation results when a handful of sand is stirred into water. **Colloids (colloidal dispersions)** represent an intermediate kind of mixture in which the solute-like particles, or **dispersed phase,** are suspended in the solvent-like phase, or **dispersing medium.** The particles of the dispersed phase are so small that settling is negligible. They are large enough, however, to make the mixture appear cloudy or even opaque, because light is scattered as it passes through the colloid.

Table 14-4 indicates that all combinations of solids, liquids, and gases can form colloids except mixtures of nonreacting gases (all of which are homogeneous and, therefore, true solutions). Whether a given mixture forms a solution, a colloidal dispersion, or a suspension depends on the size of the solute-like particles (Table 14-5), as well as solubility and miscibility.

See the *Saunders Interactive General Chemistry CD-ROM,* Screen 14.10, Colloids.

TABLE 14-5	*Approximate Sizes of Dispersed Particles*	
Mixture	**Example**	**Approximate Particle Size**
suspension	sand in water	larger than 10,000 Å
colloidal dispersion	starch in water	10–10,000 Å
solution	sugar in water	1–10 Å

CHEMISTRY IN USE

Our Daily Lives

Water Purification and Hemodialysis

Semipermeable membranes play important roles in the normal functioning of many living systems. In addition, they are used in a wide variety of industrial and medical applications. Membranes with different permeability characteristics have been developed for many different purposes. One of these is the purification of water by reverse osmosis.

Suppose we place a semipermeable membrane between a saline (salt) solution and pure water. If the saline solution is pressurized under a greater pressure than its osmotic pressure, the direction of flow can be reversed. That is, the net flow of water molecules will be from the saline solution through the membrane into the pure water. This process is called **reverse osmosis.** The membrane usually consists of cellulose acetate or hollow fibers of a material structurally similar to nylon. This method has been used for the purification of brackish (mildly saline) water. It has the economic advantages of low cost, ease of apparatus construction, and simplicity of operation. Because this method of water purification requires no heat, it has a great advantage over distillation.

The city of Sarasota, Florida, has built a large reverse osmosis plant to purify drinking water. It processes more than 4 million gallons of water per day from local wells. Total dissolved solids are reduced in concentration from 1744 parts per million (ppm) (0.1744% by mass) to 90 ppm. This water is mixed with additional well water purified by an ion exchange system. The final product is more than 10 million
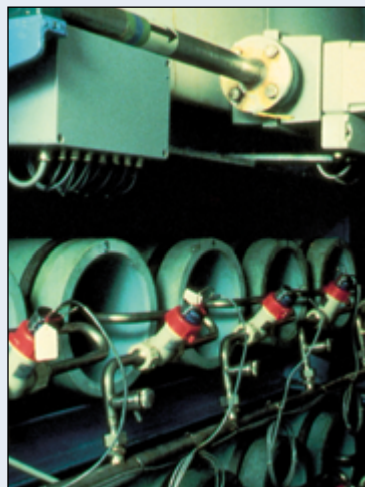
A reverse osmosis unit used to provide all the fresh water (82,500 gallons per day) for the steamship *Norway.*

gallons of water per day containing less than 500 ppm of total dissolved solids, the standard for drinking water set by the World Health Organization. The Kuwaiti and Saudi water purification plants that were of strategic concern in the Persian Gulf war use reverse osmosis in one of their primary stages.

Human kidneys carry out many important functions. One of the most crucial is the removal of metabolic waste prod-
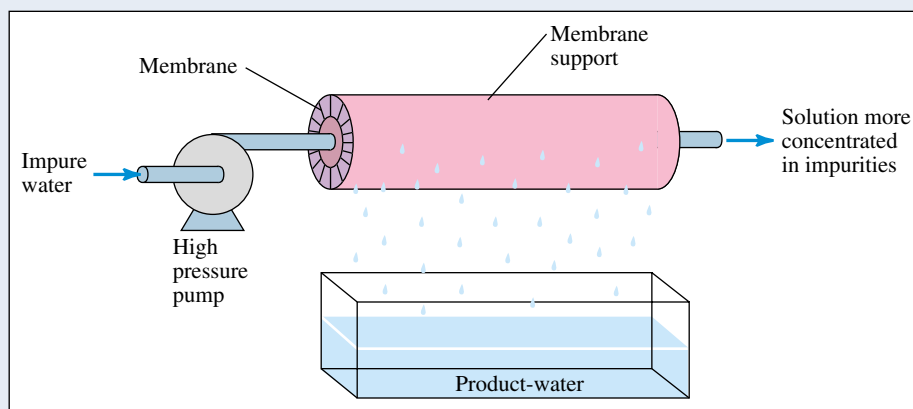
The reverse osmosis method of water purification.
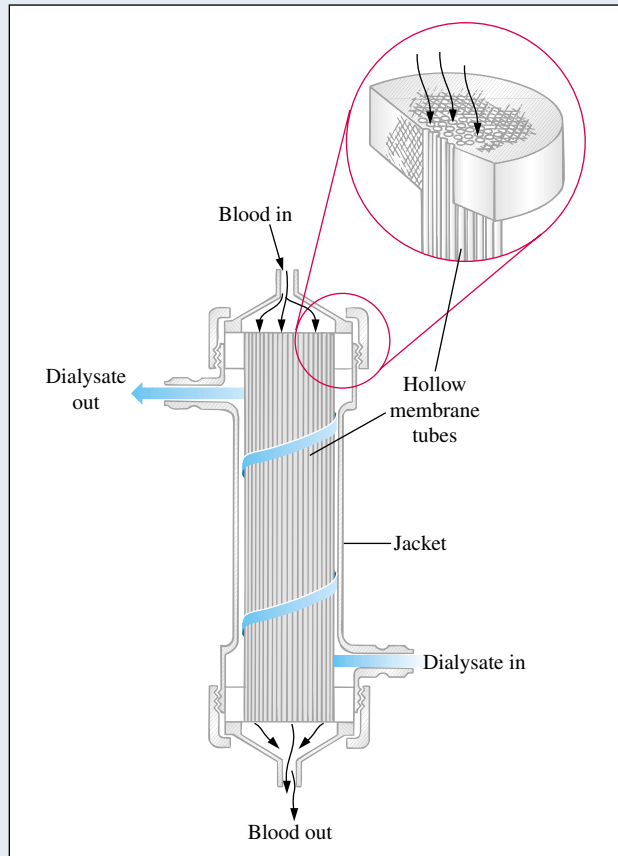
A schematic diagram of the hollow fiber (or capillary) dialyzer, the most commonly used artificial kidney. The blood flows through many small tubes constructed of semipermeable membrane; these tubes are bathed in the dialyzing solution.

ucts (e.g., creatinine, urea, and uric acid) from the blood without removal of substances needed by the body (e.g., glucose, electrolytes, and amino acids). The process by which this is accomplished in the kidney involves *dialysis*, a phenomenon in which the membrane allows transfer of both solvent molecules *and* certain solute molecules and ions, usually small ones. Many patients whose kidneys have failed can have this dialysis performed by an artificial kidney machine. In this

mechanical procedure, called *hemodialysis*, the blood is withdrawn from the body and passed in contact with a semipermeable membrane.

The membrane separates the blood from a dialyzing solution, or *dialysate*, that is similar to blood plasma in its concentration of needed substances (e.g., electrolytes and amino acids) but contains none of the waste products. Because the concentrations of undesirable substances are thus higher in the blood than in the dialysate, they flow preferentially out of the blood and are washed away. The concentrations of *needed* substances are the same on both sides of the membrane, so these substances are maintained at the proper concentrations in the blood. The small pore size of the membrane prevents passage of blood cells. However, Na^+ and Cl^- ions and some small molecules do pass through the membrane. A patient with total kidney failure may require up to four hemodialysis sessions per week, at 3 to 4 hours per session. To help hold down the cost of such treatment, the dialysate solution is later purified by a combination of filtration, distillation, and reverse osmosis and is then reused.

A portable dialysis unit.
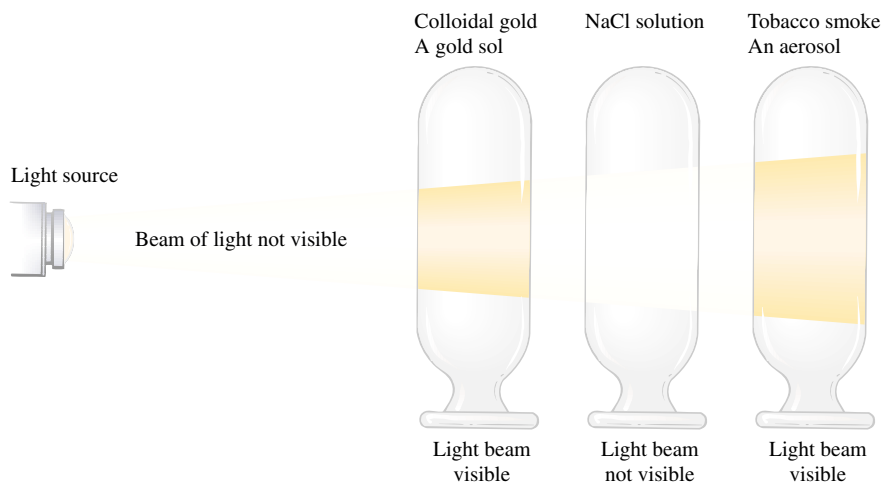
Figure 14-18   The dispersion of a beam of light by colloidal particles is called the Tyndall effect. The presence of colloidal particles is easily detected with the aid of a light beam.

14-16   THE TYNDALL EFFECT

The scattering of light by colloidal particles is called the **Tyndall effect** (Figure 14-18). Particles cannot scatter light if they are too small. Solute particles in solutions are below this limit. The maximum dimension of colloidal particles is about 10,000 Å.

   The scattering of light from automobile headlights by fogs and mists is an example of the Tyndall effect, as is the scattering of a light beam in a laser show by dust particles in the air in a darkened room.

14-17   THE ADSORPTION PHENOMENON

Much of the chemistry of everyday life is the chemistry of colloids, as one can tell from the examples in Table 14-4. Because colloidal particles are so finely divided, they have tremendously high total surface area in relation to their volume. It is not surprising, therefore, that an understanding of colloidal behavior requires an understanding of surface phenomena.

   Atoms on the surface of a colloidal particle are bonded only to other atoms of the particle on and below the surface. These atoms interact with whatever comes in contact with the surface. Colloidal particles often adsorb ions or other charged particles, as well as gases and liquids. The process of **adsorption** involves adhesion of any such species onto the surfaces of particles. For example, a bright red **sol** (solid dispersed in liquid) is formed by mixing hot water with a concentrated aqueous solution of iron(III) chloride (Figure 14-19).

$$2x[Fe^{3+}(aq) + 3Cl^-(aq)] + x(3 + y)H_2O \longrightarrow [Fe_2O_3{\cdot}yH_2O]_x(s) + 6x[H^+ + Cl^-]$$
<div style="text-align:center">yellow solution   bright red sol</div>
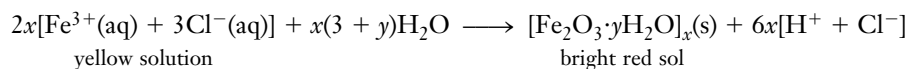
Each colloidal particle of this sol is a cluster of many formula units of hydrated Fe_2O_3. Each attracts positively charged Fe^{3+} ions to its surface. Because each particle is then surrounded by a shell of positively charged ions, the particles repel one another and cannot combine to the extent necessary to cause precipitation.
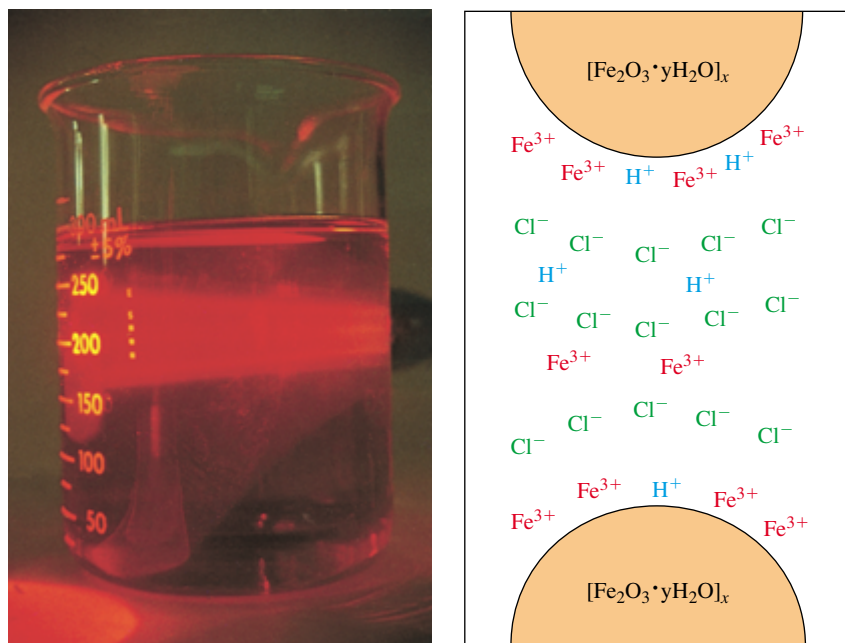
Figure 14-19 Stabilization of a colloid (Fe$_2$O$_3$ sol) by electrostatic forces. Each colloidal particle of this red sol is a cluster of many formula units of hydrated Fe$_2$O$_3$. Each attracts positively charged Fe^{3+} ions to its surface. (Fe^{3+} ions fit readily into the crystal structure, so they are preferentially adsorbed rather than the Cl$^-$ ions.) Each particle is then surrounded by a shell of positively charged ions, so the particles repel one another and cannot combine to the extent necessary to cause actual precipitation. The suspended particles scatter light, making the path of the light beam through the suspension visible.
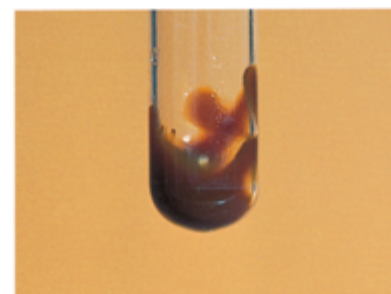
Fe(OH)$_3$ is a gelatinous precipitate (a gel).

14-18 HYDROPHILIC AND HYDROPHOBIC COLLOIDS

Colloids are classified as **hydrophilic** ("water loving") or **hydrophobic** ("water hating") based on the surface characteristics of the dispersed particles.

Hydrophilic Colloids

Proteins such as the oxygen-carrier hemoglobin form hydrophilic sols when they are suspended in saline aqueous body fluids such as blood plasma. Such proteins are macromolecules (giant molecules) that fold and twist in an aqueous environment so that polar groups are exposed to the fluid, whereas nonpolar groups are encased (Figure 14-20). Protoplasm and human cells are examples of **gels,** which are special types of sols in which the solid particles (in this case mainly proteins and carbohydrates) join together in a semirigid network structure that encloses the dispersing medium. Other examples of gels are gelatin, jellies, and gelatinous precipitates such as Al(OH)$_3$ and Fe(OH)$_3$.

Hydrophobic Colloids

Hydrophobic colloids cannot exist in polar solvents without the presence of **emulsifying agents,** or **emulsifiers.** These agents coat the particles of the dispersed phase to prevent their coagulation into a separate phase. Milk and mayonnaise are examples of hydrophobic

Figure 14-20 Examples of hydrophilic groups at the surface of a giant molecule (macromolecule) that help keep the macromolecule suspended in water.

Some edible colloids.

colloids (milk fat in milk, vegetable oil in mayonnaise) that stay suspended with the aid of emulsifying agents (casein in milk and egg yolk in mayonnaise).

Consider the mixture resulting from vigorous shaking of salad oil (nonpolar) and vinegar (polar). Droplets of hydrophobic oil are temporarily suspended in the water. In a short time, however, the very polar water molecules, which attract one another strongly, squeeze out the nonpolar oil molecules. The oil then coalesces and floats to the top. If we add an emulsifying agent, such as egg yolk, and shake or beat the mixture, a stable emulsion (mayonnaise) results.

Oil and grease are mostly long-chain hydrocarbons that are very nearly nonpolar. Our most common solvent is water, a polar substance that does not dissolve nonpolar substances. To use water to wash soiled fabrics, greasy dishes, or our bodies, we must enable the water to suspend and remove nonpolar substances. Soaps and detergents are emulsifying agents that accomplish this. Their function is controlled by the intermolecular interactions that result from their structures.

Solid soaps are usually sodium salts of long-chain organic acids called fatty acids. They have a polar "head" and a nonpolar "hydrocarbon tail." Sodium stearate, a typical soap, is shown here.

> "Dry" cleaning, on the other hand, does not involve water. The solvents that are used in dry cleaning dissolve grease to form true solutions.

hydrocarbon tail (soluble in oil) polar head (soluble in H_2O)

sodium stearate (a soap)

> Sodium stearate is also a major component of some stick deodorants.

The stearate ion is typical of the anions in soaps. It has a polar carboxylate head, $-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{O}^-$, and a long nonpolar tail, $CH_3(CH_2)_{16}-$. The head of the stearate ion is compatible with ("soluble in") water, whereas the hydrocarbon tail is compatible with ("soluble in") oil and grease. Groups of such ions can be dispersed in water because they form **micelles** (Figure 14-21a). Their "water-insoluble" tails are in the interior of a micelle and their polar heads on the outside where they can interact with the polar water molecules. When sodium stearate is stirred into water, the result is not a true solution. Instead it contains negatively charged micelles of stearate ions, surrounded by the positively

> (Right) Powdered sulfur floats on pure water because of the high surface tension of water.
> (Left) When a drop of detergent solution is added to the water, its surface tension is lowered and sulfur sinks. This lowering of surface tension enhances the cleaning action of detergent solutions.

Oil droplet (dirt)
suspended in water

Water-soluble portion
of detergent, −COO⁻
or −SO₄⁻ (polar part)

Long-chain-hydrocarbon
portion of detergent
(oil-soluble)

(a)

(b)

Figure 14-21 (a) A representation of a micelle. The nonpolar tails "dissolve" in one another in the center of the cluster and the polar heads on the outside interact favorably with the polar water molecules. (b) Attachment of soap or detergent molecules to a droplet of oily dirt to suspend it in water.

charged Na^+ ions. The result is a suspension of micelles in water. These micelles are large enough to scatter light, so a soap–water mixture appears cloudy. Oil and grease "dissolve" in soapy water because the nonpolar oil and grease are taken into the nonpolar interior of micelles (Figure 14-21b). Micelles form a true emulsion in water, so the oil and grease can be washed away. Sodium stearate is called a **surfactant** (meaning "surface-active agent") or wetting agent because it has the ability to suspend and wash away oil and grease. Other soaps and detergents behave similarly.
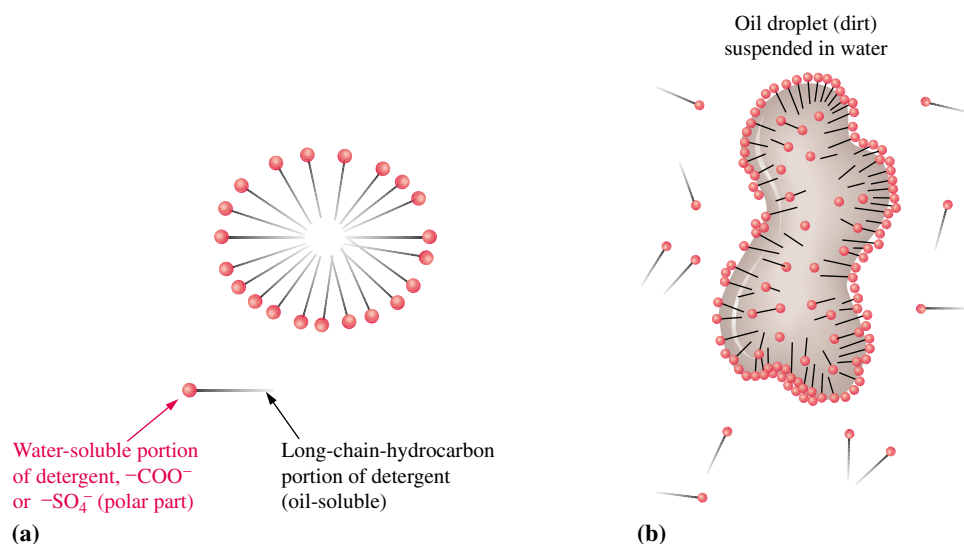
"Hard" water contains Fe^{3+}, Ca^{2+}, and/or Mg^{2+} ions, all of which displace Na^+ from soaps to form precipitates. This removes the soap from the water and puts an undesirable coating on the bathtub or on the fabric being laundered. **Synthetic detergents** are soaplike emulsifiers that contain sulfonate, $-SO_3{}^-$, or sulfate, $-OSO_3{}^-$, instead of carboxylate groups, $-COO^-$. They do not precipitate the ions of hard water, so they can be used in hard water as soap substitutes without forming undesirable scum.

Phosphates were added to commercial detergents for various purposes. They complexed the metal ions that contribute to water hardness and kept them dissolved, controlled acidity, and influenced micelle formation. The use of detergents containing phosphates is now discouraged because they cause **eutrophication** in rivers and streams that receive sewage.

See the *Saunders Interactive General Chemistry CD-ROM*, Screen 14.11, Surfactants.

Phosphates and nonbiodegradable detergents are responsible for the devastation of plant life in and along this river.

This is a condition (not related to colloids) in which an overgrowth of vegetation is caused by the high concentration of phosphorus, a plant nutrient. This overgrowth and the subsequent decay of the dead plants lead to decreased dissolved O_2 in the water, which causes the gradual elimination of marine life. There is also a foaming problem associated with branched alkylbenzenesulfonate (ABS) detergents in streams and in pipes, tanks, and pumps of sewage treatment plants. Such detergents are not **biodegradable;** that is, they cannot be broken down by bacteria.

$$\left[\begin{array}{c} \overset{CH_3}{|} \quad \overset{CH_3}{|} \quad \overset{CH_3}{|} \quad \overset{CH_3}{|} \\ CH_3CHCH_2CHCH_2CHCH_2CH - \bigcirc - SO_3 \end{array} \right]^{-} Na^{+}$$
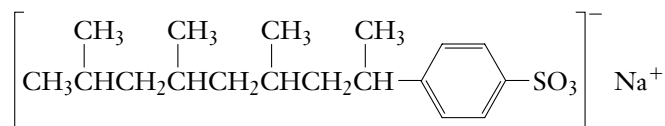
a sodium branched alkylbenzenesulfonate (ABS)—a nonbiodegradable detergent

The two detergents shown here each have a $C_{12}H_{25}$ tail but the branched one is not biodegradable.
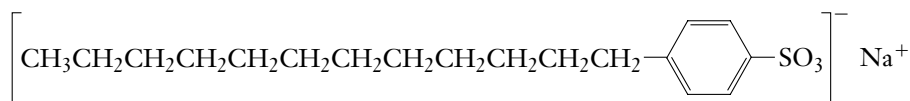
Currently used linear-chain alkylbenzenesulfonate (LAS) detergents are biodegradable and do not cause such foaming.

$$\left[CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2 - \bigcirc - SO_3 \right]^{-} Na^{+}$$

sodium lauryl benzenesulfonate
a linear alkylbenzenesulfonate (LAS)—a biodegradable detergent

CHEMISTRY IN USE   *Our Daily Lives*

Why Does Red Wine Go with Red Meat?

Choosing the appropriate wine to go with dinner is a problem for some diners. Experts, however, have offered a simple rule for generations, "serve red wine with red meat and white wine with fish and chicken." Are these cuisine choices just traditions, or are there fundamental reasons for them?

Red wine is usually served with red meat because of a desirable matching of the chemicals found in each. The most influential ingredient in red meat is fat; it gives red meats their desirable flavor. As you chew a piece of red meat, the fat from the meat coats your tongue and palate, which desensitizes your taste buds. As a result, your second bite of red meat is less tasty than the first. Your steak would taste better if you washed your mouth between mouthfuls; there is an easy way to wash away the fat deposits.

Red wine contains a surfactant that cleanses your mouth, removing fat deposits, re-exposing your taste buds, and allowing you to savor the next bite of red meat almost as well as the first bite. The tannic acid (also called tannin) in red wine provides a soap-like action. Like soap, tannic acid consists of both a nonpolar complex hydrocarbon part as well as a polar

one. The polar part of tannic acid dissolves in polar saliva, while the nonpolar part dissolves in the fat film that coats your palate. When you sip red wine, a suspension of micelles forms in the saliva. This micelle emulsion has the fat molecules in its interior; the fat is washed away by swallowing the red wine.

White wines go poorly with red meats because they lack the tannic acid needed to cleanse the palate. In fact, the presence or absence of tannic acid distinguishes red wines from white wines. Grapes fermented with their skins produce red wines; grapes fermented without their skins produce white wines.

Because fish and chicken have less fat than red meats, they can be enjoyed without surfactants to cleanse the palate. Also, tannic acid has a strong flavor that can overpower the delicate flavor of many fish. The absence of tannic acid in white wines gives them a lighter flavor than red wines, and many people prefer this lighter flavor with their fish or chicken dinners.

Ronald DeLorenzo
Middle Georgia College

Key Terms

The following terms were defined at the end of Chapter 3: **concentration, dilution, molarity, percent by mass, solute, solution,** and **solvent.** The following terms were defined at the end of Chapter 13: **condensation, condensed phases, evaporation, phase diagram,** and **vapor pressure.**

Adsorption   Adhesion of species onto surfaces of particles.

Associated ions   Short-lived species formed by the collision of dissolved ions of opposite charge.

Biodegradability   The ability of a substance to be broken down into simpler substances by bacteria.

Boiling point elevation   The increase in the boiling point of a solvent caused by dissolution of a nonvolatile solute.

Boiling point elevation constant, K_b   A constant that corresponds to the change (increase) in boiling point produced by a one-molal *ideal* solution of a nonvolatile nonelectrolyte.

Colligative properties   Physical properties of solutions that depend on the number but not the kind of solute particles present.

Colloid   A heterogeneous mixture in which solute-like particles do not settle out; also called *colloidal dispersion.*

Crystal lattice energy   The energy change when one mole of formula units of a crystalline solid is formed from its ions, atoms, or molecules in the gas phase; always negative.

Detergent   A soap-like emulsifier that contains a sulfonate, $-SO_3^-$, or sulfate, $-OSO_3^-$, group instead of a carboxylate, $-COO^-$, group.

Dispersed phase   The solute-like species in a colloid.

Dispersing medium   The solvent-like phase in a colloid.

Dispersion   See *Colloid.*

Distillation   The process in which components of a mixture are separated by boiling away the more volatile liquid.

Effective molality   The sum of the molalities of all solute particles in solution.

Emulsifier   See *Emulsifying agent.*

Emulsifying agent   A substance that coats the particles of a dispersed phase and prevents coagulation of colloidal particles; an emulsifier.

Emulsion   A colloidal dispersion of a liquid in a liquid.

Eutrophication   The undesirable overgrowth of vegetation caused by high concentrations of plant nutrients in bodies of water.

Foam   A colloidal dispersion of a gas in a liquid.

Fractional distillation   The process in which a fractionating column is used in a distillation apparatus to separate components of a liquid mixture that have different boiling points.

Freezing point depression   The decrease in the freezing point of a solvent caused by the presence of a solute.

Freezing point depression constant, K_f   A constant that corresponds to the change in freezing point produced by a one-molal *ideal* solution of a nonvolatile nonelectrolyte.

Gel   A colloidal dispersion of a solid in a liquid; a semirigid sol.

Hard water   Water containing Fe^{3+}, Ca^{2+}, or Mg^{2+} ions, which form precipitates with soaps.

Heat of solution (molar)   The amount of heat absorbed in the formation of a solution that contains one mole of solute; the value is positive if heat is absorbed (endothermic) and negative if heat is released (exothermic).

Henry's Law   The pressure of the gas above a solution is proportional to the concentration of the gas in the solution.

Hydration   The interaction (surrounding) of solute particles with water molecules.

Hydration energy (molar) of an ion   The energy change accompanying the hydration of a mole of gaseous ions.

Hydrophilic colloids   Colloidal particles that attract water molecules.

Hydrophobic colloids   Colloidal particles that repel water molecules.

Ideal solution   A solution that obeys Raoult's Law exactly.

Liquid aerosol   A colloidal dispersion of a liquid in a gas.

Micelle   A cluster of a large number of soap or detergent molecules or ions, assembled with their hydrophobic tails directed toward the center and their hydrophilic heads directed outward.

Miscibility   The ability of one liquid to mix with (dissolve in) another liquid.

Molality (*m*)   Concentration expressed as number of moles of solute per kilogram of solvent.

Mole fraction of a component in solution   The number of moles of the component divided by the total number of moles of all components.

Osmosis   The process by which solvent molecules pass through a semipermeable membrane from a dilute solution into a more concentrated solution.

Osmotic pressure   The hydrostatic pressure produced on the surface of a semipermeable membrane by osmosis.

Percent ionization of weak electrolytes   The percent of the weak electrolyte that ionizes in a solution of a given concentration.

Raoult's Law   The vapor pressure of a solvent in an ideal solution is directly proportional to the mole fraction of the solvent in the solution.

Reverse osmosis   The forced flow of solvent molecules through a semipermeable membrane from a concentrated solution into a dilute solution. This is accomplished by application of hydrostatic pressure on the concentrated side greater than the osmotic pressure that is opposing it.

Saturated solution   A solution in which no more solute will dissolve at a given temperature.

Semipermeable membrane   A thin partition between two solutions through which certain molecules can pass but others cannot.

Soap   An emulsifier that can disperse nonpolar substances in water; the sodium salt of a long-chain organic acid; consists of a long hydrocarbon chain attached to a carboxylate group, $-CO_2^-Na^+$.

Sol   A colloidal dispersion of a solid in a liquid.

Solid aerosol   A colloidal dispersion of a solid in a gas.

Solid emulsion A colloidal dispersion of a liquid in a solid.

Solid foam A colloidal dispersion of a gas in a solid.

Solid sol A colloidal dispersion of a solid in a solid.

Solvation The process by which solvent molecules surround and interact with solute ions or molecules.

Supersaturated solution A (metastable) solution that contains a higher-than-saturation concentration of solute; slight disturbance or seeding causes crystallization of excess solute.

Surfactant A "surface-active agent"; a substance that has the abil-ity to emulsify and wash away oil and grease in an aqueous sus-pension.

Thermal pollution Introduction of heated waste water into nat-ural waters.

Tyndall effect The scattering of light by colloidal particles.

van't Hoff factor, i A number that indicates the extent of dis-sociation or ionization of a solute; equal to the actual colligative property divided by the colligative property calculated assum-ing no ionization or dissociation.

Exercises

General Concepts: The Dissolving Process

1. Support or criticize the statement "Solutions and mix-tures are the same thing."

2. Give an example of a solution that contains each of the following: (a) a solid dissolved in a liquid; (b) a gas dis-solved in a gas; (c) a gas dissolved in a liquid; (d) a liquid dissolved in a liquid; (e) a solid dissolved in a solid. Iden-tify the solvent and the solute in each case.

3. There are no *true* solutions in which the solvent is gaseous and the solute is either liquid or solid. Why?

4. Explain why (a) solute–solute, (b) solvent–solvent, and (c) solute–solvent interactions are important in deter-mining the extent to which a solute dissolves in a solvent.

5. Define and distinguish between dissolution, solvation, and hydration.

6. The amount of heat released or absorbed in the dissolu-tion process is important in determining whether the dissolution process is spontaneous, meaning, whether it can occur. What is the other important factor? How does it influence solubility?

7. An old saying is that "oil and water don't mix." Explain, on a molecular basis, why this saying is true.

8. Two liquids, A and B, do not react chemically and are completely miscible. What would be observed as one is poured into the other? What would be observed in the case of two completely immiscible liquids and in the case of two partially miscible liquids?

9. Consider the following solutions. In each case, predict whether the solubility of the solute should be high or low. Justify your answers. (a) KCl in hexane, C_6H_{14}; (b) $CaCl_2$ in H_2O; (c) C_6H_{14} in H_2O; (d) CCl_4 in C_6H_{14}; (e) C_6H_{14} in CCl_4.

10. Consider the following solutions. In each case predict whether the solubility of the solute should be high or low. Justify your answers. (a) HCl in H_2O; (b) HF in H_2O; (c) Al_2O_3 in H_2O; (d) S_8 in H_2O; (e) $NaNO_3$ in hexane, C_6H_{14}.

11. For those solutions in Exercise 9 that can be prepared in "reasonable" concentrations, classify the solutes as non-electrolytes, weak electrolytes, or strong electrolytes.

12. For those solutions in Exercise 10 that can be prepared in "reasonable" concentrations, classify the solutes as non-electrolytes, weak electrolytes, or strong electrolytes.

13. Both methanol, CH_3OH, and ethanol, CH_3CH_2OH, are completely miscible with water at room tem-perature because of strong solvent–solute intermo-lecular attractions. Predict the trend in solubility in water for 1-propanol, $CH_3CH_2CH_2OH$; 1-butanol, $CH_3CH_2CH_2CH_2OH$; and 1-pentanol, $CH_3CH_2CH_2CH_2CH_2OH$.

14. (a) Does the solubility of a solid in a liquid exhibit an appreciable dependence on pressure? (b) Is the same true for the solubility of a liquid in a liquid? Why?

15. Describe a technique for determining whether or not a solution contains an electrolyte.

16. A reagent bottle in the storeroom is labeled as contain-ing a saturated sodium chloride solution. How can one determine whether or not the solution is saturated?

*17. A handbook lists the value of the Henry's Law constant as 3.02×10^4 atm for ethane, C_2H_6, dissolved in water at 25°C. The absence of concentration units on k means that the constant is meant to be used with concentration expressed as a mole fraction. Calculate the mole fraction of ethane in water at an ethane pressure of 0.15 atm.

*18. The mole fraction of methane, CH_4, dissolved in water can be calculated from the Henry's Law constants of 4.13×10^4 atm at 25°C and 5.77×10^4 atm at 50.°C. Calcu-late the solubility of methane at these temperatures for a methane pressure of 10. atm above the solution. Does the solubility increase or decrease with increasing tempera-ture? (See Exercise 17 for interpretation of units.)

19. Choose the ionic compound from each pair for which the crystal lattice energy should be the most negative. Justify your choice. (a) LiF or LiBr; (b) KF or CaF_2; (c) FeF_2 or FeF_3; (d) NaF or KF.

20. Choose the ion from each pair that should be more strongly hydrated in aqueous solution. Justify your choice. (a) Na^+ or Rb^+; (b) Cl^- or Br^-; (c) Fe^{3+} or Fe^{2+}; (d) Na^+ or Mg^{2+}.

*21. The crystal lattice energy for LiBr(s) is -818.6 kJ/mol at 25°C. The hydration energy of the ions of LiBr is -867.4 kJ/mol at 25°C (for infinite dilution). (a) What is the heat of solution of LiBr(s) at 25°C (for infinite

dilution)? (b) The hydration energy of $Li^+(g)$ is −544 kJ/mol at 25°C. What is the hydration energy for $Br^-(g)$ at 25°C?

22. Why is the dissolving of many ionic solids in water an endothermic process, whereas the mixing of most miscible liquids is an exothermic process?

Concentrations of Solutions

23. Under what conditions are the molarity and molality of a solution nearly the same? Which concentration unit is more useful when measuring volume with burets, pipets, and volumetric flasks in the laboratory? Why?

24. Many handbooks list solubilities in units of (g solute/ 100. g H_2O). How would you convert from this unit to mass percent?

25. A 60.0-mL sample of diethyl ether, $(C_2H_5)_2O$, is dissolved in enough methanol, CH_3OH, to make 300.0 mL of solution. The density of the ether is 0.714 g/mL. What is the molarity of this solution?

*26. Describe how to prepare 1.000 L of 0.215 m NaCl. The density of this solution is 1.01 g/mL.

*27. Urea, $(NH_2)_2CO$, is a product of metabolism of proteins. An aqueous solution is 32.0% urea by mass and has a density of 1.087 g/mL. Calculate the molality of urea in the solution.

28. Calculate the molality of a solution that contains 71.5 g of benzoic acid, C_6H_5COOH, in 325 mL of ethanol, C_2H_5OH. The density of ethanol is 0.789 g/mL.

29. Sodium fluoride has a solubility of 4.22 g in 100.0 g of water at 18°C. Express the solute concentration in terms of (a) mass percent, (b) mole fraction, and (c) molality.

30. What are the mole fractions of ethanol, C_2H_5OH, and water in a solution prepared by mixing 70.0 g of ethanol with 30.0 g of water?

31. What are the mole fractions of ethanol, C_2H_5OH, and water in a solution prepared by mixing 70.0 mL of ethanol with 30.0 mL of water at 25°C? The density of ethanol is 0.789 g/mL, and that of water is 1.00 g/mL.

32. The density of an aqueous solution containing 12.50 g K_2SO_4 in 100.00 g solution is 1.083 g/mL. Calculate the concentration of this solution in terms of molarity, molality, percent of K_2SO_4, and mole fraction of solvent.

*33. A piece of jewelry is marked "14 carat gold," meaning that on a mass basis the jewelry is 14/24 pure gold. What is the molality of this alloy—considering the other metal as the solvent?

*34. A solution that is 24.0% fructose, $C_6H_{12}O_6$, in water has a density of 1.10 g/mL at 20°C. (a) What is the molality of fructose in this solution? (b) At a higher temperature, the density is lower. Would the molality be less than, greater than, or the same as the molality at 20°C? Explain.

35. The density of a sulfuric acid solution taken from a car battery is 1.225 g/cm³. This corresponds to a 3.75 M solution. Express the concentration of this solution in terms

of molality, mole fraction of H_2SO_4, and percentage of water by mass.

Raoult's Law and Vapor Pressure

36. In your own words, explain briefly *why* the vapor pressure of a solvent is lowered by dissolving a nonvolatile solute in it.

37. (a) Calculate the vapor pressure lowering associated with dissolving 35.5 g of table sugar, $C_{12}H_{22}O_{11}$, in 400. g of water at 25.0°C. (b) What is the vapor pressure of the solution? Assume that the solution is ideal. The vapor pressure of pure water at 25°C is 23.76 torr. (c) What is the vapor pressure of the solution at 100.°C?

38. Calculate (a) the lowering of the vapor pressure and (b) the vapor pressure of a solution prepared by dissolving 35.5 g of naphthalene, $C_{10}H_8$ (a nonvolatile nonelectrolyte), in 150.0 g of benzene, C_6H_6, at 20.°C. Assume that the solution is ideal. The vapor pressure of pure benzene is 74.6 torr at 20.°C.

39. At −100.°C ethane, CH_3CH_3, and propane, $CH_3CH_2CH_3$, are liquids. At that temperature, the vapor pressure of pure ethane is 394 torr and that of pure propane is 22 torr. What is the vapor pressure at −100.°C over a solution containing equal molar amounts of these substances?

40. Using Raoult's Law, predict the partial pressures in the vapor above a solution containing 0.250 mol acetone ($P^0 = 345$ torr) and 0.300 mol chloroform ($P^0 = 295$ torr).

41. What is the composition of the vapor above the solution described in Exercise 39?

42. What is the composition of the vapor above the solution described in Exercise 40?

43. Use the following vapor pressure diagram to estimate (a) the partial pressure of chloroform, (b) the partial pressure of acetone, and (c) the total vapor pressure of a solution in which the mole fraction of $CHCl_3$ is 0.30, assuming *ideal* behavior.
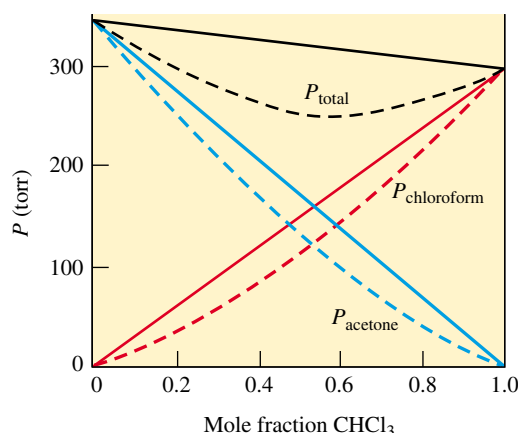
44. Answer Exercise 43 for the *real* solution of acetone and chloroform.

45. A solution is prepared by mixing 60.0 g of dichloromethane, CH_2Cl_2, and 30.0 g of dibromomethane, CH_2Br_2, at 0°C. The vapor pressure at 0°C of pure CH_2Cl_2 is 0.175 atm, and that of CH_2Br_2 is 0.0150 atm. (a) Assuming ideal behavior, calculate the total vapor pressure of the solution. (b) Calculate the mole fractions of CH_2Cl_2 and CH_2Br_2 in the *vapor* above the liquid. Assume that both the vapor and the solution behave ideally.

Boiling Point Elevation and Freezing Point Depression: Solutions of Nonelectrolytes

46. Calculate the boiling point of a 2.15 *m* aqueous solution of ethylene glycol, a nonvolatile nonelectrolyte.


Ethylene glycol solutions.

47. A solution is prepared by dissolving 6.41 g of ordinary sugar (sucrose, $C_{12}H_{22}O_{11}$, 342 g/mol) in 32.0 g of water. Calculate the boiling point of the solution. Sucrose is a nonvolatile nonelectrolyte.

48. What is the freezing point of the solution described in Exercise 46?

49. What is the freezing point of the solution described in Exercise 47?

50. Refer to Table 14-2. Suppose you had a 0.150 *m* solution of a nonvolatile nonelectrolyte in each of the solvents listed there. Which one should have (a) the greatest freezing point depression, (b) the lowest freezing point, (c) the greatest boiling point elevation, and (d) the highest boiling point?

51. A 5.00% solution of dextrose, $C_6H_{12}O_6$, in water is referred to as DW_5. This solution can be used as a source of nourishment when introduced by intravenous injection. Calculate the freezing point and the boiling point of a DW_5 solution.

52. Lemon juice is a complex solution that does not freeze in a home freezer at temperatures as low as −11°C. At what temperature will the lemon juice freeze if its effective molality is the equivalent of a 10.48 *m* glucose solution?

*53. The "proof" of an alcoholic beverage is twice the volume percent of ethyl alcohol, C_2H_5OH, in water. The density of ethyl alcohol is 0.789 g/mL and that of water is 1.00 g/mL. A bottle of 100-proof rum is left outside on a cold winter day. (a) Will the rum freeze if the temperature drops to −18°C? (b) Rum is used in cooking and baking. At what temperature does 100-proof rum boil?

54. A 3.0-g sample of a nonelectrolyte was isolated from beef fat. The molecular weight of the compound was determined to be 137 amu. The sample was dissolved in 250.0 mL of ethyl alcohol. At what temperature should the solution boil? For ethyl alcohol: boiling point = 78.41°C; K_b = 1.22°C/*m*, density = 0.789 g/mL.

55. The normal boiling point of benzene is 80.1°C. A 0.77-gram sample of a nonvolatile compound with the molar mass of 185 g/mol is dissolved in 2.75 g of benzene. What is the expected boiling point of this solution?

56. Pure copper melts at 1083°C. Its molal freezing point depression constant is 23°C/*m*. What will be the melting point of a brass made of 10% Zn and 90% Cu by mass?

57. How many grams of the nonelectrolyte sucrose, $C_{12}H_{22}O_{11}$, should be dissolved in 575 g of water to produce a solution that freezes at −1.75°C?

58. What mass of naphthalene, $C_{10}H_8$, should be dissolved in 375 g of nitrobenzene, $C_6H_5NO_2$, to produce a solution that boils at 214.20°C? See Table 14-2.

59. A solution was made by dissolving 3.75 g of a nonvolatile solute in 108.7 g of acetone. The solution boiled at 56.58°C. The boiling point of pure acetone is 55.95°C, and K_b = 1.71°C/*m*. Calculate the molecular weight of the solute.

60. The molecular weight of an organic compound was determined by measuring the freezing point depression of a benzene solution. A 0.500-g sample was dissolved in 50.0 g of benzene, and the resulting depression was 0.42°C. What is the approximate molecular weight? The compound gave the following elemental analysis: 40.0% C, 6.67% H, 53.3% O by mass. Determine the formula and exact molecular weight of the substance.

61. When 0.154 g of sulfur is finely ground and melted with 4.38 g of camphor, the freezing point of the camphor is lowered by 5.47°C. What is the molecular weight of sulfur? What is its molecular formula?

*62. (a) Suppose we dissolve a 6.00-g sample of a mixture of naphthalene, $C_{10}H_8$, and anthracene, $C_{14}H_{10}$, in 360. g of benzene. The solution is observed to freeze at 4.85°C. Find the percent composition (by mass) of the sample. (b) At what temperature should the solution boil? Assume that naphthalene and anthracene are nonvolatile nonelectrolytes.

Boiling Point Elevation and Freezing Point Depression: Solutions of Electrolytes

63. What is ion association in solution? Can you suggest why the term "ion pairing" is sometimes used to describe this phenomenon?

64. You have separate 0.10 M aqueous solutions of the following salts: $LiNO_3$, $Ca(NO_3)_2$, and $Al(NO_3)_3$. In which one would you expect to find the highest particle concentration? Which solution would you expect to conduct electricity most strongly? Explain your reasoning.

65. What is the significance of the van't Hoff factor, i?

66. What is the value of the van't Hoff factor, i, for the following strong electrolytes at infinite dilution? (a) Na_2SO_4; (b) KOH; (c) $Al_2(SO_4)_3$; (d) $SrSO_4$.

67. Compare the number of solute particles that are present in solutions of equal concentrations of strong electrolytes, weak electrolytes, and nonelectrolytes.

68. Four beakers contain 0.010 m aqueous solutions of CH_3OH, $KClO_3$, $CaCl_2$, and CH_3COOH, respectively. Without calculating the actual freezing points of each of these solutions, arrange them from lowest to highest freezing point.

*69. A 0.050 m aqueous solution of $K_3[Fe(CN)_6]$ has a freezing point of $-0.2800°C$. Calculate the total concentration of solute particles in this solution and interpret your results.

*70. A solution is made by dissolving 1.00 gram each of $NaCl$, $NaBr$, and NaI in 100. g of water. What is the vapor pressure above this solution at 100°C? Assume complete dissociation of the three salts.

71. The ice fish lives under the polar ice cap where the water temperature is $-4°C$. This fish does not freeze at that temperature due to the solutes in its blood. The solute concentration of the fish's blood can be related to a sodium chloride solution that would have the same freezing point. What is the minimum concentration of a sodium chloride solution that would not freeze at $-4°C$?

72. Which solution freezes at a lower temperature, 0.1 m sodium sulfate or 0.1 m calcium sulfate? Explain.

73. Solutions are produced by dissolving 25.0 grams of sodium sulfate in 0.500 kg of water and by dissolving 25.0 grams of calcium sulfate in 0.500 kg of water. Which solution will freeze at a lower temperature? Explain.

74. A series of 1.1 m aqueous solutions is produced. Predict which solution of each pair would boil at the higher temperature. (a) $NaCl$ or $LiCl$; (b) $LiCl$ or Li_2SO_4; (c) Li_2SO_4 or HCl; (d) HCl or $C_6H_{12}O_6$; (e) $C_6H_{12}O_6$ or CH_3OH; (f) CH_3OH or CH_3COOH; (g) CH_3COOH or $NaCl$.

75. Identify which of the following solutions, each prepared by dissolving 65.0 g of the solute in 150. mL of water, will display the highest boiling point and explain your choice. (a) $NaCl$ or $LiCl$; (b) $LiCl$ or Li_2SO_4; (c) Li_2SO_4 or HCl; (d) HCl or $C_6H_{12}O_6$; (e) $C_6H_{12}O_6$ or CH_3OH; (f) CH_3OH or CH_3COOH; (g) CH_3COOH or $NaCl$.

76. Synthetic ocean water can be produced by dissolving 36.0 g of table salt in 1000. mL of water. What is the boiling point of this solution? (Assume that the density of the water is 0.998 g/mL and that table salt is pure sodium chloride.)

77. Formic acid, HCOOH, ionizes slightly in water.

$$HCOOH(aq) \rightleftharpoons H^+(aq) + HCOO^-(aq)$$
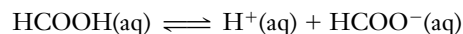
A 0.0100 m formic acid solution freezes at $-0.0209°C$. Calculate the percent ionization of HCOOH in this solution.

78. A 0.100 m acetic acid solution in water freezes at $-0.1884°C$. Calculate the percent ionization of CH_3COOH in this solution.

*79. In a home ice cream freezer, we lower the freezing point of the water bath surrounding the ice cream can by dissolving NaCl in water to make a brine solution. A 15.0% brine solution is observed to freeze at $-10.888°C$. What is the van't Hoff factor, i, for this solution?

80. CsCl dissolves in water according to

$$CsCl(s) \xrightarrow{H_2O} Cs^+(aq) + Cl^-(aq)$$
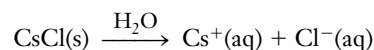
A 0.121 m solution of CsCl freezes at $-0.403°C$. Calculate i and the apparent percent dissociation of CsCl in this solution.

Osmotic Pressure

81. What are osmosis and osmotic pressure?

*82. Show numerically that the molality and molarity of 1.00×10^{-4} M aqueous sodium chloride are nearly equal. Why is this true? Would this be true if another solvent, say acetonitrile, CH_3CN, replaced water? Why or why not? The density of CH_3CN is 0.786 g/mL at 20.0°C.

83. Show how the expression $\pi = MRT$, where π is osmotic pressure, is similar to the ideal gas law. Rationalize qualitatively why this should be so.

84. What is the osmotic pressure associated with a 0.0111 M aqueous solution of a nonvolatile nonelectrolyte solute at 75°C?

85. The osmotic pressure of an aqueous solution of a nonvolatile nonelectrolyte solute is 1.17 atm at 0.0°C. What is the molarity of the solution?

86. Calculate the freezing point depression and boiling point elevation associated with the solution in Exercise 85.

87. Estimate the osmotic pressure associated with 24.5 g of an enzyme of molecular weight 4.21×10^6 dissolved in 1740. mL of ethyl acetate solution at 38.0°C.

88. Calculate the osmotic pressure at 25°C of 0.10 m K_2CrO_4 in water, taking ion association into account. Refer to Table 14-3.

89. Estimate the osmotic pressure at 25°C of 0.10 m K_2CrO_4 in water, assuming no ion association.

*90. Many biological compounds are isolated and purified in very small amounts. We dissolve 11.0 mg of a biological macromolecule with molecular weight of 2.00×10^4 in 10.0 g of water. (a) Calculate the freezing point of the solution. (b) Calculate the osmotic pressure of the solution at 25°C. (c) Suppose we are trying to use freezing point measurements to *determine* the molecular weight of this substance and that we make an error of only 0.001°C in the temperature measurement. What percent error would this cause in the calculated molecular weight? (d) Suppose we could measure the osmotic pressure with an error of only 0.1 torr (not a very difficult experiment). What percent error would this cause in the calculated molecular weight?

Colloids

91. How does a colloidal dispersion differ from a true solution?
92. Distinguish among (a) sol, (b) gel, (c) emulsion, (d) foam, (e) solid sol, (f) solid emulsion, (g) solid foam, (h) solid aerosol, and (i) liquid aerosol. Try to give an example of each that is not listed in Table 14-4.
93. What is the Tyndall effect, and how is it caused?
94. Distinguish between hydrophilic and hydrophobic colloids.
95. What is an emulsifier?
96. Distinguish between soaps and detergents. How do they interact with hard water? Write an equation to show the interaction between a soap and hard water that contains Ca^{2+} ions.
97. What is the disadvantage of branched alkylbenzenesulfonate (ABS) detergents compared with linear alkylbenzenesulfonate (LAS) detergents?

Mixed Exercises

*98. The heat of solution (for infinite dilution) of KF(s) is -17.7 kJ/mol at 25°C. The crystal lattice energy, ΔH_{xtal}, is -825.9 kJ/mol at 25°C. What is the hydration energy of KF for infinite dilution at 25°C? [Here we refer to the sum of the hydration energies of $K^+(g)$ and $F^-(g)$.]
99. Dry air contains 20.94% O_2 by volume. The solubility of O_2 in water at 25°C is 0.041 gram O_2 per liter of water. How many liters of water would dissolve the O_2 in one liter of dry air at 25°C and 1.00 atm?
100. (a) The freezing point of a 1.00% aqueous solution of acetic acid, CH_3COOH, is -0.310°C. What is the approximate formula weight of acetic acid in water? (b) A 1.00% solution of acetic acid in benzene has a freezing point depression of 0.441°C. What is the formula weight of acetic acid in this solvent? Explain the difference.
101. An aqueous ammonium chloride solution contains 6.50 mass % NH_4Cl. The density of the solution is 1.0201 g/mL.

Express the concentration of this solution in molarity, molality, and mole fraction of solute.
102. Starch contains C—C, C—H, C—O, and O—H bonds. Hydrocarbons contain only C—C and C—H bonds. Both starch and hydrocarbon oils can form colloidal dispersions in water. (a) Which dispersion is classified as hydrophobic? (b) Which is hydrophilic? (c) Which dispersion would be easier to make and maintain?
*103. Suppose we put some one-celled microorganisms in various aqueous NaCl solutions. We observe that the cells remain unperturbed in 0.7% NaCl, whereas they shrink in more concentrated solutions and expand in more dilute solutions. Assume that 0.7% NaCl behaves as an *ideal* 1:1 electrolyte. Calculate the osmotic pressure of the aqueous fluid within the cells at 25°C.
*104. A sample of a drug ($C_{21}H_{23}O_5N$, molecular weight = 369 g/mol) mixed with lactose (a sugar, $C_{12}H_{22}O_{11}$, molecular weight = 342 g/mol) was analyzed by osmotic pressure to determine the amount of sugar present. If 100. mL of solution containing 1.00 g of the drug–sugar mixture has an osmotic pressure of 527 torr at 25°C, what is the percent sugar present?
105. A solution containing 4.22 g of a nonelectrolyte polymer per liter of benzene solution has an osmotic pressure of 0.646 torr at 20.0°C. (a) Calculate the molecular weight of the polymer. (b) Assume that the density of the dilute solution is the same as that of benzene, 0.879 g/mL. What would be the freezing point depression for this solution? (c) Why are boiling point elevations and freezing point depressions difficult to use to measure molecular weights of polymers?
106. On what basis would you choose the components to prepare an ideal solution of a molecular solute? Which of the following combinations would you expect to act most nearly ideally? (a) $CH_4(\ell)$ and $CH_3OH(\ell)$; (b) $CH_3OH(\ell)$ and NaCl(s); (c) $CH_4(\ell)$ and $CH_3CH_3(\ell)$.
107. Physiological saline (normal saline) is a 0.90% NaCl solution. This solution is isotonic with human blood. Calculate the freezing point and boiling point of physiological saline.

CONCEPTUAL EXERCISES

108. In the first five sections of this chapter the term "dissolution" was used to describe the process by which a solute is dispersed by a solvent to form a solution. A popular dictionary defines dissolution as "decomposition into fragments or parts." Using either of the definitions, compare the following two uses of the term. "It was ruled that there must be dissolution of the estate." "The ease of dissolution of a solute depends on two factors. . . ."
109. Consider two nonelectrolytes A and B; A has a higher molecular weight than B, and both are soluble in solvent

C. A solution is made by dissolving x grams of A in 100 grams of C; another solution is made by dissolving the same number of grams, x, of B in 100 grams of C. Assume that the two solutions have the same density. (a) Which solution has the higher molality? (b) Which solution has the higher mole fraction? (c) Which solution has the higher percent by mass? (d) Which solution has the higher molarity?

110. Can the actual value for the van't Hoff factor, i, ever be larger than the ideal value? Could the actual value ever be less than 1?

111. When the van't Hoff factor, i, is included, the boiling point elevation equation becomes $\Delta T_b = i K_b m$. The van't Hoff factor can be inserted in a similar fashion in the freezing point depression equation and the osmotic pressure equation. The van't Hoff factor, however, cannot be inserted in the same way into the vapor pressure-lowering equation. Show that $\Delta P_{solvent} = i X_{solute} P^0_{solvent}$ is not equivalent to $\Delta P_{solvent} = \{(i\,x\,\text{moles}_{solute})/[(i\,x\,\text{moles}_{solute}) + (\text{moles}_{solvent})]\}P^0_{solvent}$. Which equation for $\Delta P_{solvent}$ is correct?

112. The two solutions shown were both prepared by dissolving 194 g of K_2CrO_4 (1.00 mol) in a 1.00-L volumetric flask. One was diluted to the 1-L mark on the neck of the flask, and the other was diluted by adding 1.00 L of water. Which solution, the one on the left or the one on the right, is: (a) more concentrated; (b) a 1.00 m solution; (c) a 1.00 M solution?

113. Would you expect lowering the freezing point or elevating the boiling point to be the better method to obtain the approximate molecular weight of an unknown? Explain your choice.

114. Rock candy consists of crystals of sugar on a string or stick. Propose a method of making rock candy, and explain each step.

115. Concentrations expressed in units of parts per million and parts per billion often have no meaning for people until they relate these small and large numbers to their own experiences. How many seconds are equal to 1 ppm of a year?

BUILDING YOUR KNOWLEDGE

116. DDT is a toxin still found in the fatty tissues of some animals. DDT was transported into our lakes and streams as runoff from agricultural operations where it was originally used several years ago as an insecticide. In the lakes and streams it did not dissolve to any great extent; it collected in the lake and stream bottoms. It entered the bodies of animals via fatty tissues in their diet; microorganisms collected the DDT, the fish ate the microorganisms, and so on. Fortunately, much of the once large quantities of DDT in lakes and streams has biodegraded. Based on this information, what can you conclude regarding the intermolecular forces present in DDT?

117. Draw Figure 14-1, but instead of using colored circles to represent the solvent and solute molecules, use Lewis formulas to represent water as the solvent and acetone, CH_3COCH_3, as the solute. Use dashed lines to show hydrogen bonds. Twelve water molecules and two acetone molecules should be sufficient to illustrate the interaction between these two kinds of molecules.

118. A sugar maple tree grows to a height of about 45 feet, and its roots are in contact with water in the soil. What must be the concentration of the sugar in its sap if osmotic pressure is responsible for forcing the sap to the top of the tree at 10°C? The density of mercury is 13.6 g/cm^3, and the density of the sap can be considered to be 1.10 g/cm^3.

119. Many metal ions become hydrated in solution by forming coordinate covalent bonds with the unshared pair of electrons from the water molecules to form "AB$_6$" ions. Because of their sizes, these hydrated ions are unable to pass through the semipermeable membrane described in Section 14-15, whereas water as a trimer, $(H_2O)_3$, or a tetramer, $(H_2O)_4$, can pass through. Anions tend to be less hydrated. Using the VSEPR theory, prepare three-dimensional drawings of $Cu(H_2O)_6^{2+}$ and a possible $(H_2O)_3$ that show their relative shapes and sizes.