Physical Properties of Solutions

A sugar cube dissolving in water. The properties of a solution are markedly different from those of its solvent. The solubility of sugar molecules in water is mainly due to hydrogen bond formation between the solute and the solvent. The models show glucose and water molecules.
A Look Ahead

- We begin by examining different types of solutions that can be formed from the three states of matter: solid, liquid, and gas. We also characterize a solution by the amount of solute present as unsaturated, saturated, and supersaturated. (12.1)
- Next we study the formation of solutions at the molecular level and see how intermolecular forces affect the energetics of the solution process and solubility. (12.2)
- We study the four major types of concentration units—percent by mass, mole fraction, molarity, and molality—and their interconversions. (12.3)
- Temperature in general has a marked effect on the solubility of gases as well as liquids and solids. (12.4)
- We see that pressure has no influence on the solubility of liquids and solids, but greatly affects the solubility of gases. The quantitative relationship between gas solubility and pressure is given by Henry’s law. (12.5)
- We learn that physical properties such as the vapor pressure, melting point, boiling point, and osmotic pressure of a solution depend only on the concentration and not the identity of the solute present. We first study these colligative properties and their applications for nonelectrolyte solutions. (12.6)
- We then extend our study of colligative properties to electrolyte solutions and learn about the influence of ion pair formation on these properties. (12.7)
- The chapter ends with a brief examination of colloids, which are particles larger than individual molecules that are dispersed in another medium. (12.8)

Most chemical reactions take place, not between pure solids, liquids, or gases, but among ions and molecules dissolved in water or other solvents. In Chapters 5 and 11 we looked at the properties of gases, liquids, and solids. In this chapter we examine the properties of solutions, concentrating mainly on the role of intermolecular forces in solubility and other physical properties of solution.
12.1 Types of Solutions

In Section 4.1 we noted that a solution is a homogeneous mixture of two or more substances. Because this definition places no restriction on the nature of the substances involved, we can distinguish six types of solutions, depending on the original states (solid, liquid, or gas) of the solution components. Table 12.1 gives examples of each type.

Our focus in this chapter will be on solutions involving at least one liquid component—that is, gas-liquid, liquid-liquid, and solid-liquid solutions. And, perhaps not too surprisingly, the liquid solvent in most of the solutions we will study is water.

Chemists also characterize solutions by their capacity to dissolve a solute. A **saturated solution** contains the maximum amount of a solute that will dissolve in a given solvent at a specific temperature. An **unsaturated solution** contains less solute than it has the capacity to dissolve. A third type, a **supersaturated solution**, contains more solute than is present in a saturated solution. Supersaturated solutions are not very stable. In time, some of the solute will come out of a supersaturated solution as crystals. **Crystallization** is the process in which dissolved solute comes out of solution and forms crystals (Figure 12.1). Note that both precipitation and crystallization describe the separation of excess solid substance from a supersaturated solution. However, solids formed by the two processes differ in appearance. We normally think of precipitates as being made up of small particles, whereas crystals may be large and well formed.

### Table 12.1 Types of Solutions

<table>
<thead>
<tr>
<th>Component 1</th>
<th>Component 2</th>
<th>State of Resulting Solution</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>Gas</td>
<td>Gas</td>
<td>Air</td>
</tr>
<tr>
<td>Gas</td>
<td>Liquid</td>
<td>Liquid</td>
<td>Soda water (CO₂ in water)</td>
</tr>
<tr>
<td>Gas</td>
<td>Solid</td>
<td>Solid</td>
<td>H₂ gas in palladium</td>
</tr>
<tr>
<td>Liquid</td>
<td>Liquid</td>
<td>Liquid</td>
<td>Ethanol in water</td>
</tr>
<tr>
<td>Solid</td>
<td>Liquid</td>
<td>Liquid</td>
<td>NaCl in water</td>
</tr>
<tr>
<td>Solid</td>
<td>Solid</td>
<td>Solid</td>
<td>Brass (Cu/Zn), solder (Sn/Pb)</td>
</tr>
</tbody>
</table>

**Figure 12.1** In a supersaturated sodium acetate solution (left), sodium acetate crystals rapidly form when a small seed crystal is added.
A Molecular View of the Solution Process

The intermolecular attractions that hold molecules together in liquids and solids also play a central role in the formation of solutions. When one substance (the solute) dissolves in another (the solvent), particles of the solute disperse throughout the solvent. The solute particles occupy positions that are normally taken by solvent molecules. The ease with which a solute particle replaces a solvent molecule depends on the relative strengths of three types of interactions:
- solvent-solvent interaction
- solute-solute interaction
- solvent-solute interaction

For simplicity, we can imagine the solution process taking place in three distinct steps (Figure 12.2). Step 1 is the separation of solvent molecules, and step 2 entails the separation of solute molecules. These steps require energy input to break attractive intermolecular forces; therefore, they are endothermic. In step 3 the solvent and solute molecules mix. This process can be exothermic or endothermic. The heat of solution $\Delta H_{\text{soln}}$ is given by

$$\Delta H_{\text{soln}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

If the solute-solvent attraction is stronger than the solvent-solvent attraction and solute-solute attraction, the solution process is favorable, or exothermic ($\Delta H_{\text{soln}} < 0$). If the solute-solvent interaction is weaker than the solvent-solvent and solute-solute interactions, then the solution process is endothermic ($\Delta H_{\text{soln}} > 0$).

You may wonder why a solute dissolves in a solvent at all if the attraction for its own molecules is stronger than the solute-solvent attraction. The solution process, like all physical and chemical processes, is governed by two factors. One is energy, which determines whether a solution process is exothermic or endothermic. The second factor is an inherent tendency toward disorder in all natural events. In much the same way that a deck of new playing cards becomes mixed up after it has been shuffled a few times, when solute and solvent molecules mix to form a solution, there is an increase in randomness, or disorder. In the pure state, the solvent and solute possess a fair degree of order, characterized by the more or less regular arrangement of atoms, molecules, or ions in three-dimensional space. Much of this order is destroyed when the solute dissolves in the solvent (see Figure 12.2). Therefore, the

Figure 12.2 A molecular view of the solution process portrayed as taking place in three steps: First the solvent and solute molecules are separated (steps 1 and 2). Then the solvent and solute molecules mix (step 3).
solution process is accompanied by an increase in disorder. It is the increase in disorder of the system that favors the solubility of any substance, even if the solution process is endothermic.

Solubility is a measure of how much solute will dissolve in a solvent at a specific temperature. The saying “like dissolves like” is helpful in predicting the solubility of a substance in a given solvent. What this expression means is that two substances with intermolecular forces of similar type and magnitude are likely to be soluble in each other. For example, both carbon tetrachloride (CCl₄) and benzene (C₆H₆) are nonpolar liquids. The only intermolecular forces present in these substances are dispersion forces (see Section 11.2). When these two liquids are mixed, they readily dissolve in each other, because the attraction between CCl₄ and C₆H₆ molecules is comparable in magnitude to the forces between CCl₄ molecules and between C₆H₆ molecules. Two liquids are said to be miscible if they are completely soluble in each other in all proportions. Alcohols such as methanol, ethanol, and 1,2-ethylene glycol are miscible with water because they can form hydrogen bonds with water molecules:

When sodium chloride dissolves in water, the ions are stabilized in solution by hydration, which involves ion-dipole interaction. In general, we predict that ionic compounds should be much more soluble in polar solvents, such as water, liquid ammonia, and liquid hydrogen fluoride, than in nonpolar solvents, such as benzene and carbon tetrachloride. Because the molecules of nonpolar solvents lack a dipole moment, they cannot effectively solvate the Na⁺ and Cl⁻ ions. (Solvation is the process in which an ion or a molecule is surrounded by solvent molecules arranged in a specific manner. The process is called hydration when the solvent is water.) The predominant intermolecular interaction between ions and nonpolar compounds is ion-induced dipole interaction, which is much weaker than ion-dipole interaction. Consequently, ionic compounds usually have extremely low solubility in nonpolar solvents.

Example 12.1 illustrates how to predict solubility based on a knowledge of the intermolecular forces in the solute and the solvent.

**EXAMPLE 12.1**

Predict the relative solubilities in the following cases: (a) Bromine (Br₂) in benzene (C₆H₆, μ = 0 D) and in water (μ = 1.87 D), (b) KCl in carbon tetrachloride (CCl₄, μ = 0 D) and in liquid ammonia (NH₃, μ = 1.46 D), (c) formaldehyde (CH₂O) in carbon disulfide (CS₂, μ = 0 D) and in water.

**Strategy** In predicting solubility, remember the saying: Like dissolves like. A nonpolar solute will dissolve in a nonpolar solvent; ionic compounds will generally dissolve in polar solvents due to favorable ion-dipole interaction; solutes that can form hydrogen bonds with the solvent will have high solubility in the solvent.

**Solution** (a) Br₂ is a nonpolar molecule and therefore should be more soluble in C₆H₆, which is also nonpolar, than in water. The only intermolecular forces between Br₂ and C₆H₆ are dispersion forces.
(b) KCl is an ionic compound. For it to dissolve, the individual K\(^+\) and Cl\(^-\) ions must be stabilized by ion-dipole interaction. Because CCl\(_4\) has no dipole moment, KCl should be more soluble in liquid NH\(_3\), a polar molecule with a large dipole moment.

(c) Because CH\(_2\)O is a polar molecule and CS\(_2\) (a linear molecule) is nonpolar, 
\[
\begin{align*}
\text{H} & \quad \text{C} & \quad \text{O} \\
\text{H} & \quad \mu > 0 & \\
\text{S} & \quad \text{C} & \quad \text{S} \\
& \quad \mu = 0
\end{align*}
\]

the forces between molecules of CH\(_2\)O and CS\(_2\) are dipole-induced dipole and dispersion. On the other hand, CH\(_2\)O can form hydrogen bonds with water, so it should be more soluble in that solvent.

**Practice Exercise** Is iodine (I\(_2\)) more soluble in water or in carbon disulfide (CS\(_2\))?  

### 12.3 Concentration Units

Quantitative study of a solution requires knowing its concentration, that is, the amount of solute present in a given amount of solution. Chemists use several different concentration units, each of which has advantages as well as limitations. Let us examine the four most common units of concentration: percent by mass, mole fraction, molarity, and molality.

#### Types of Concentration Units

**Percent by Mass**

The percent by mass (also called percent by weight or weight percent) is the ratio of the mass of a solute to the mass of the solution, multiplied by 100 percent:

\[
\text{percent by mass} = \frac{\text{mass of solute}}{\text{mass of solute} + \text{mass of solvent}} \times 100\%
\]

or

\[
\text{percent by mass} = \frac{\text{mass of solute}}{\text{mass of soln}} \times 100\%
\]

The percent by mass is a unitless number because it is a ratio of two similar quantities.

**EXAMPLE 12.2**

A sample of 0.892 g of potassium chloride (KCl) is dissolved in 54.6 g of water. What is the percent by mass of KCl in the solution?

**Strategy** We are given the mass of a solute dissolved in a certain amount of solvent. Therefore, we can calculate the mass percent of KCl using Equation (12.1).
Physical Properties of Solutions

Similar problem: 12.15.

Solution We write

\[ \text{percent by mass of KCl} = \frac{\text{mass of solute}}{\text{mass of soln}} \times 100\% \]

\[ = \frac{0.892 \text{ g}}{0.892 \text{ g} + 54.6 \text{ g}} \times 100\% \]

\[ = 1.61\% \]

Practice Exercise A sample of 6.44 g of naphthalene (C_{10}H_{8}) is dissolved in 80.1 g of benzene (C_{6}H_{6}). Calculate the percent by mass of naphthalene in this solution.

Mole Fraction (X)
The mole fraction was introduced in Section 5.6. The mole fraction of a component of a solution, say, component A, is written \( X_A \) and is defined as

\[ \text{mole fraction of component A} = X_A = \frac{\text{moles of A}}{\text{sum of moles of all components}} \]

The mole fraction is also unitless, because it too is a ratio of two similar quantities.

Molarity (M)
In Section 4.5 molarity was defined as the number of moles of solute in 1 L of solution; that is,

\[ \text{molarity} = \frac{\text{moles of solute}}{\text{liters of soln}} \]

Thus, the units of molarity are mol/L.

Molality (m)
Molality is the number of moles of solute dissolved in 1 kg (1000 g) of solvent—that is,

\[ \text{molality} = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}} \] (12.2)

For example, to prepare a 1 molal, or 1 m, sodium sulfate (Na_{2}SO_{4}) aqueous solution, we need to dissolve 1 mole (142.0 g) of the substance in 1000 g (1 kg) of water. Depending on the nature of the solute-solvent interaction, the final volume of the solution will be either greater or less than 1000 mL. It is also possible, though very unlikely, that the final volume could be equal to 1000 mL.

Example 12.3 shows how to calculate the molality of a solution.

EXAMPLE 12.3

Calculate the molality of a sulfuric acid solution containing 24.4 g of sulfuric acid in 198 g of water. The molar mass of sulfuric acid is 98.09 g.

Strategy To calculate the molality of a solution, we need to know the number of moles of solute and the mass of the solvent in kilograms.
Comparison of Concentration Units

The choice of a concentration unit is based on the purpose of the experiment. For instance, the mole fraction is not used to express the concentrations of solutions for titrations and gravimetric analyses, but it is appropriate for calculating partial pressures of gases (see Section 5.6) and for dealing with vapor pressures of solutions (to be discussed later in this chapter).

The advantage of molarity is that it is generally easier to measure the volume of a solution, using precisely calibrated volumetric flasks, than to weigh the solvent, as we saw in Section 4.5. For this reason, molarity is often preferred over molality. On the other hand, molality is independent of temperature, because the concentration is expressed in number of moles of solute and mass of solvent. The volume of a solution typically increases with increasing temperature, so that a solution that is 1.0 M at 25°C may become 0.97 M at 45°C because of the increase in volume on warming. This concentration dependence on temperature can significantly affect the accuracy of an experiment. Therefore, it is sometimes preferable to use molality instead of molarity.

Percent by mass is similar to molality in that it is independent of temperature. Furthermore, because it is defined in terms of ratio of mass of solute to mass of solution, we do not need to know the molar mass of the solute in order to calculate the percent by mass.

Sometimes it is desirable to convert one concentration unit of a solution to another; for example, the same solution may be employed for different experiments that require different concentration units for calculations. Suppose we want to express the concentration of a 0.396 \( m \) glucose (\( \text{C}_6\text{H}_12\text{O}_6 \)) solution in molarity. We know there is 0.396 mole of glucose in 1000 g of the solvent and we need to determine the volume of this solution to calculate molarity. First, we calculate the mass of the solution from the molar mass of glucose:

\[
\text{mass of solution} = 0.396 \text{ mol} \times 180.2 \text{ g/mol} + 1000 \text{ g} = 1071 \text{ g}
\]

**Solution** The definition of molality (\( m \)) is

\[
m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}}
\]

First, we find the number of moles of sulfuric acid in 24.4 g of the acid, using its molar mass as the conversion factor.

\[
\text{moles of H}_2\text{SO}_4 = \frac{24.4 \text{ g H}_2\text{SO}_4}{98.09 \text{ g H}_2\text{SO}_4} = 0.249 \text{ mol H}_2\text{SO}_4
\]

The mass of water is 198 g, or 0.198 kg. Therefore,

\[
m = \frac{0.249 \text{ mol H}_2\text{SO}_4}{0.198 \text{ kg H}_2\text{O}} = 1.26 \text{ m}
\]

**Practice Exercise** What is the molality of a solution containing 7.78 g of urea \([\text{NH}_2\text{CO}]\) in 203 g of water?

**Solution** The definition of molality (\( m \)) is

\[
m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}}
\]

First, we find the number of moles of sulfuric acid in 24.4 g of the acid, using its molar mass as the conversion factor.

\[
\text{moles of H}_2\text{SO}_4 = \frac{24.4 \text{ g H}_2\text{SO}_4}{98.09 \text{ g H}_2\text{SO}_4} = 0.249 \text{ mol H}_2\text{SO}_4
\]

The mass of water is 198 g, or 0.198 kg. Therefore,

\[
m = \frac{0.249 \text{ mol H}_2\text{SO}_4}{0.198 \text{ kg H}_2\text{O}} = 1.26 \text{ m}
\]
The next step is to experimentally determine the density of the solution, which is found to be 1.16 g/mL. We can now calculate the volume of the solution in liters by writing

\[
\text{volume} = \frac{\text{mass}}{\text{density}} = \frac{1071 \text{ g}}{1.16 \text{ g/mL}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.923 \text{ L}
\]

Finally, the molarity of the solution is given by

\[
\text{molarity} = \frac{\text{moles of solute}}{\text{liters of soln}} = \frac{0.396 \text{ mol}}{0.923 \text{ L}} = 0.429 \text{ mol/L} = 0.429 \text{ M}
\]

As you can see, the density of the solution serves as a conversion factor between molality and molarity.

Examples 12.4 and 12.5 show concentration unit conversions.

**EXAMPLE 12.4**

The density of a 2.45 \text{ M} aqueous solution of methanol (CH\textsubscript{3}OH) is 0.976 g/mL. What is the molality of the solution? The molar mass of methanol is 32.04 g.

**Strategy** To calculate the molality, we need to know the number of moles of methanol and the mass of solvent in kilograms. We assume 1 L of solution, so the number of moles of methanol is 2.45 mol.

\[
m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}}
\]

**Solution** Our first step is to calculate the mass of water in one liter of the solution, using density as a conversion factor. The total mass of 1 L of a 2.45 \text{ M} solution of methanol is

\[
1 \text{ L-soln} \times \frac{1000 \text{ mL-soln}}{1 \text{ L-soln}} \times \frac{0.976 \text{ g}}{1 \text{ mL-soln}} = 976 \text{ g}
\]

Because this solution contains 2.45 moles of methanol, the amount of water (solvent) in the solution is

\[
\text{mass of H}_2\text{O} = \text{mass of soln} - \text{mass of solute} = 976 \text{ g} - \left(2.45 \text{ mol CH}_3\text{OH} \times \frac{32.04 \text{ g CH}_3\text{OH}}{1 \text{ mol CH}_3\text{OH}}\right) = 898 \text{ g}
\]

(Continued)
The molality of the solution can be calculated by converting 898 g to 0.898 kg:

\[
\text{molality} = \frac{2.45 \text{ mol CH}_3\text{OH}}{0.898 \text{ kg H}_2\text{O}} = 2.73 \text{ m}
\]

**Practice Exercise** Calculate the molality of a 5.86 M ethanol (C\textsubscript{2}H\textsubscript{5}OH) solution whose density is 0.927 g/mL.

---

**EXAMPLE 12.5**

Calculate the molality of a 35.4 percent (by mass) aqueous solution of phosphoric acid (H\textsubscript{3}PO\textsubscript{4}). The molar mass of phosphoric acid is 97.99 g.

**Strategy** In solving this type of problem, it is convenient to assume that we start with a 100.0 g of the solution. If the mass of phosphoric acid is 35.4 percent, or 35.4 g, the percent by mass and mass of water must be 100.0% \(\times\) 35.4% = 64.6% and 64.6 g.

**Solution** From the known molar mass of phosphoric acid, we can calculate the molality in two steps, as shown in Example 12.3. First we calculate the number of moles of phosphoric acid in 35.4 g of the acid

\[
\text{moles of H}_3\text{PO}_4 = \frac{35.4 \text{ g H}_3\text{PO}_4}{97.99 \text{ g H}_3\text{PO}_4} \times 1 \text{ mol H}_3\text{PO}_4 = 0.361 \text{ mol H}_3\text{PO}_4
\]

The mass of water is 64.6 g, or 0.0646 kg. Therefore, the molality is given by

\[
\text{molality} = \frac{0.361 \text{ mol H}_3\text{PO}_4}{0.0646 \text{ kg H}_2\text{O}} = 5.59 \text{ m}
\]

**Practice Exercise** Calculate the molality of a 44.6 percent (by mass) aqueous solution of sodium chloride.

---

**Review of Concepts**

A solution is prepared at 20°C and its concentration is expressed in three different units: percent by mass, molality, and molarity. The solution is then heated to 88°C. Which of the concentration units will change (increase or decrease)?

---

**12.4 The Effect of Temperature on Solubility**

Recall that solubility is defined as the maximum amount of a solute that will dissolve in a given quantity of solvent at a specific temperature. Temperature affects the solubility of most substances. In this section we will consider the effects of temperature on the solubility of solids and gases.
Solid Solubility and Temperature

Figure 12.3 shows the temperature dependence of the solubility of some ionic compounds in water. In most but certainly not all cases, the solubility of a solid substance increases with temperature. However, there is no clear correlation between the sign of $\Delta H_{\text{soln}}$ and the variation of solubility with temperature. For example, the solution process of CaCl$_2$ is exothermic, and that of NH$_4$NO$_3$ is endothermic. But the solubility of both compounds increases with increasing temperature. In general, the effect of temperature on solubility is best determined experimentally.

Fractional Crystallization

The dependence of the solubility of a solid on temperature varies considerably, as Figure 12.3 shows. The solubility of NaNO$_3$, for example, increases sharply with temperature, while that of NaCl changes very little. This wide variation provides a means of obtaining pure substances from mixtures. **Fractional crystallization** is the separation of a mixture of substances into pure components on the basis of their differing solubilities.

Suppose we have a sample of 90 g of KNO$_3$ that is contaminated with 10 g of NaCl. To purify the KNO$_3$ sample, we dissolve the mixture in 100 mL of water at 60°C and then gradually cool the solution to 0°C. At this temperature, the solubilities of KNO$_3$ and NaCl are 12.1 g/100 g H$_2$O and 34.2 g/100 g H$_2$O, respectively. Thus, (90 – 12) g, or 78 g, of KNO$_3$ will crystallize out of the solution, but all of the NaCl will remain dissolved (Figure 12.4). In this manner, we can obtain about 90 percent of the original amount of KNO$_3$ in pure form. The KNO$_3$ crystals can be separated from the solution by filtration.

Many of the solid inorganic and organic compounds that are used in the laboratory were purified by fractional crystallization. Generally, the method works best if the compound to be purified has a steep solubility curve, that is, if it is considerably more soluble at high temperatures than at low temperatures. Otherwise, much of it will remain dissolved as the solution is cooled. Fractional crystallization also works well if the amount of impurity in the solution is relatively small.
Gas Solubility and Temperature

The solubility of gases in water usually decreases with increasing temperature (Figure 12.5). When water is heated in a beaker, you can see bubbles of air forming on the side of the glass before the water boils. As the temperature rises, the dissolved air molecules begin to “boil out” of the solution long before the water itself boils.

The reduced solubility of molecular oxygen in hot water has a direct bearing on thermal pollution—that is, the heating of the environment (usually waterways) to temperatures that are harmful to its living inhabitants. It is estimated that every year in the United States some 100,000 billion gallons of water are used for industrial cooling, mostly in electric power and nuclear power production. This process heats the water, which is then returned to the rivers and lakes from which it was taken. Ecologists have become increasingly concerned about the effect of thermal pollution on aquatic life. Fish, like all other cold-blooded animals, have much more difficulty coping with rapid temperature fluctuation in the environment than humans do. An increase in water temperature accelerates their rate of metabolism, which generally doubles with each 10°C rise. The speedup of metabolism increases the fish’s need for oxygen at the same time that the supply of oxygen decreases because of its lower solubility in heated water. Effective ways to cool power plants while doing only minimal damage to the biological environment are being sought.

On the lighter side, a knowledge of the variation of gas solubility with temperature can improve one’s performance in a popular recreational sport—fishing. On a hot summer day, an experienced fisherman usually picks a deep spot in the river or lake to cast the bait. Because the oxygen content is greater in the deeper, cooler region, most fish will be found there.
12.5 The Effect of Pressure on the Solubility of Gases

For all practical purposes, external pressure has no influence on the solubilities of liquids and solids, but it does greatly affect the solubility of gases. The quantitative relationship between gas solubility and pressure is given by Henry’s law, which states that the solubility of a gas in a liquid is proportional to the pressure of the gas over the solution:

$$c \propto P$$

$$c = kP$$

(12.3)

Here $c$ is the molar concentration (mol/L) of the dissolved gas; $P$ is the pressure (in atm) of the gas over the solution at equilibrium; and, for a given gas, $k$ is a constant that depends only on temperature. The constant $k$ has the units mol/L · atm. You can see that when the pressure of the gas is 1 atm, $c$ is numerically equal to $k$. If several gases are present, $P$ is the partial pressure.

Henry’s law can be understood qualitatively in terms of the kinetic molecular theory. The amount of gas that will dissolve in a solvent depends on how frequently the gas molecules collide with the liquid surface and become trapped by the condensed phase. Suppose we have a gas in dynamic equilibrium with a solution [Figure 12.6(a)]. At every instant, the number of gas molecules entering the solution is equal to the number of dissolved molecules moving into the gas phase. If the partial pressure of the gas is increased [Figure 12.6(b)], more molecules dissolve in the liquid because more molecules are striking the surface of the liquid. This process continues until the concentration of the solution is again such that the number of molecules leaving the solution per second equals the number entering the solution. Because of the higher concentration of molecules in both the gas and solution phases, this number is greater in (b) than in (a), where the partial pressure is lower.

A practical demonstration of Henry’s law is the effervescence of a soft drink when the cap of the bottle is removed. Before the beverage bottle is sealed, it is pressurized with a mixture of air and CO$_2$ saturated with water vapor. Because of the high partial pressure of CO$_2$ in the pressurizing gas mixture, the amount dissolved in the soft drink is many times the amount that would dissolve under normal atmospheric conditions. When the cap is removed, the pressurized gases escape, eventually the pressure in the

---

Each gas has a different $k$ value at a given temperature.

William Henry (1775–1836). English chemist. Henry’s major contribution to science was his discovery of the law describing the solubility of gases, which now bears his name.

Figure 12.6 A molecular interpretation of Henry’s law. When the partial pressure of the gas over the solution increases from (a) to (b), the concentration of the dissolved gas also increases according to Equation (12.3).
The solubility of nitrogen gas at 25°C and 1 atm is \(6.8 \times 10^{-4}\) mol/L. What is the concentration (in molarity) of nitrogen dissolved in water under atmospheric conditions? The partial pressure of nitrogen gas in the atmosphere is 0.78 atm.

**Strategy** The given solubility enables us to calculate Henry’s law constant \((k)\), which can then be used to determine the concentration of the solution.

**Solution** The first step is to calculate the quantity \(k\) in Equation (12.3):

\[
c = kP
\]

\[
6.8 \times 10^{-4}\ \text{mol/L} = k \ (1\ \text{atm})
\]

\[
k = 6.8 \times 10^{-4}\ \text{mol/L} \cdot \text{atm}
\]

Therefore, the solubility of nitrogen gas in water is

\[
c = (6.8 \times 10^{-4}\ \text{mol/L} \cdot \text{atm})(0.78\ \text{atm})
\]

\[
= 5.3 \times 10^{-4}\ \text{mol/L}
\]

\[
= 5.3 \times 10^{-4}\ M
\]

The decrease in solubility is the result of lowering the pressure from 1 atm to 0.78 atm.

**Check** The ratio of the concentrations \([(5.3 \times 10^{-4}\ M/6.8 \times 10^{-4}\ M) = 0.78]\) should be equal to the ratio of the pressures \((0.78\ \text{atm}/1.0\ \text{atm} = 0.78)\).

**Practice Exercise** Calculate the molar concentration of oxygen in water at 25°C for a partial pressure of 0.22 atm. The Henry’s law constant for oxygen is \(1.3 \times 10^{-3}\ \text{mol/L} \cdot \text{atm}\).

Most gases obey Henry’s law, but there are some important exceptions. For example, if the dissolved gas reacts with water, higher solubilities can result. The solubility of ammonia is much higher than expected because of the reaction

\[
\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-
\]

Carbon dioxide also reacts with water, as follows:

\[
\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3
\]

Another interesting example is the dissolution of molecular oxygen in blood. Normally, oxygen gas is only sparingly soluble in water (see Practice Exercise in Example 12.6). However, its solubility in blood is dramatically greater because of the high content of hemoglobin (Hb) molecules. Each hemoglobin molecule can bind up to four oxygen molecules, which are eventually delivered to the tissues for use in metabolism:

\[
\text{Hb} + 4\text{O}_2 \rightleftharpoons \text{Hb(O}_2)_4
\]

It is this process that accounts for the high solubility of molecular oxygen in blood.

The Chemistry in Action essay on p. 526 explains a natural disaster with Henry’s law.
Review of Concepts

Which of the following gases has the greatest Henry’s law constant in water at 25°C: CH₄, Ne, HCl, H₂?

12.6 Colligative Properties of Nonelectrolyte Solutions

Colligative properties (or collective properties) are properties that depend only on the number of solute particles in solution and not on the nature of the solute particles. These properties are bound together by a common origin—they all depend on the number of solute particles present, regardless of whether they are atoms, ions, or molecules. The colligative properties are vapor-pressure lowering, boiling-point
elevation, freezing-point depression, and osmotic pressure. For our discussion of colligative properties of nonelectrolyte solutions it is important to keep in mind that we are talking about relatively dilute solutions, that is, solutions whose concentrations are \( \leq 0.2 \text{ M} \).

### Vapor-Pressure Lowering

If a solute is **nonvolatile** (that is, it does not have a measurable vapor pressure), the vapor pressure of its solution is always less than that of the pure solvent. Thus, the relationship between solution vapor pressure and solvent vapor pressure depends on the concentration of the solute in the solution. This relationship is expressed by **Raoult’s law**, which states that the vapor pressure of the pure solvent, \( P°_i \), times the mole fraction of the solvent in the solution, \( X_1 \):

\[
P_1 = X_1 P°_1
\]

In a solution containing only one solute, \( X_1 = 1 - X_2 \), where \( X_2 \) is the mole fraction of the solute. Equation (12.4) can therefore be rewritten as

\[
P_1 = (1 - X_2)P°_1
\]

or

\[
P_1 = P°_1 - X_2P°_1
\]

so that

\[
\Delta P = X_2 P°_1
\]

We see that the decrease in vapor pressure, \( \Delta P \), is directly proportional to the solute concentration (measured in mole fraction).

Example 12.7 illustrates the use of Raoult’s law [Equation (12.4)].

---

**EXAMPLE 12.7**

Calculate the vapor pressure of a solution made by dissolving 218 g of glucose (molar mass = 180.2 g/mol) in 460 mL of water at 30°C. What is the vapor-pressure lowering? The vapor pressure of pure water at 30°C is given in Table 5.3 (p. 200). Assume the density of the solution is 1.00 g/mL.

**Strategy** We need Raoult’s law [Equation (12.4)] to determine the vapor pressure of a solution. Note that glucose is a nonvolatile solute.

**Solution** The vapor pressure of a solution (\( P_1 \)) is

\[
P_1 = X_1 P°_1
\]

need to find
want to calculate
given

\[\text{(Continued)}\]

---

\(^{†}\)François Marie Raoult (1830–1901). French chemist. Raoult’s work was mainly in solution properties and electrochemistry.
Physical Properties of Solutions

Why is the vapor pressure of a solution less than that of the pure solvent? As was mentioned in Section 12.2, one driving force in physical and chemical processes is an increase in disorder—the greater the disorder, the more favorable the process. Vaporization increases the disorder of a system because molecules in a vapor have less order than those in a liquid. Because a solution is more disordered than a pure solvent, the difference in disorder between a solution and a vapor is less than that between a pure solvent and a vapor. Thus, solvent molecules have less of a tendency to leave a solution than to leave the pure solvent to become vapor, and the vapor pressure of a solution is less than that of the solvent.

If both components of a solution are volatile (that is, have measurable vapor pressure), the vapor pressure of the solution is the sum of the individual partial pressures. Raoult’s law holds equally well in this case:

\[ P_A = X_A P_A^0 \]
\[ P_B = X_B P_B^0 \]

where \( P_A \) and \( P_B \) are the partial pressures over the solution for components A and B; \( P_A^0 \) and \( P_B^0 \) are the vapor pressures of the pure substances; and \( X_A \) and \( X_B \) are their mole fractions. The total pressure is given by Dalton’s law of partial pressure (see Section 5.6):

\[ P_T = P_A + P_B \]

or

\[ P_T = X_A P_A^0 + X_B P_B^0 \]

First we calculate the number of moles of glucose and water in the solution:

\[ n_1 \text{(water)} = \frac{460 \text{ mL} \times 1.00 \text{ g}}{1 \text{ mL} \times 18.02 \text{ g}} = 25.5 \text{ mol} \]
\[ n_2 \text{(glucose)} = \frac{218 \text{ g} \times 1 \text{ mol}}{180.2 \text{ g}} = 1.21 \text{ mol} \]

The mole fraction of water, \( X_1 \), is given by

\[ X_1 = \frac{n_1}{n_1 + n_2} = \frac{25.5 \text{ mol}}{25.5 \text{ mol} + 1.21 \text{ mol}} = 0.955 \]

From Table 5.3, we find the vapor pressure of water at 30°C to be 31.82 mmHg. Therefore, the vapor pressure of the glucose solution is

\[ P_1 = 0.955 \times 31.82 \text{ mmHg} = 30.4 \text{ mmHg} \]

Finally, the vapor-pressure lowering is \((31.82 - 30.4) \text{ mmHg}\), or \(1.4 \text{ mmHg}\).

**Check** We can also calculate the vapor pressure lowering by using Equation (12.5). Because the mole fraction of glucose is \((1 - 0.955)\), or 0.045, the vapor pressure lowering is given by \((0.045)(31.82 \text{ mmHg})\) or 1.4 mmHg.

**Practice Exercise** Calculate the vapor pressure of a solution made by dissolving 82.4 g of urea (molar mass = 60.06 g/mol) in 212 mL of water at 35°C. What is the vapor-pressure lowering?

**Similar problems:** 12.49, 12.50.
For example, benzene and toluene are volatile components that have similar structures and therefore similar intermolecular forces:

\[
\text{benzene} \quad \text{toluene}
\]

\[
\text{CH}_3
\]

In a solution of benzene and toluene, the vapor pressure of each component obeys Raoult’s law. Figure 12.7 shows the dependence of the total vapor pressure \( (P_T) \) in a benzene-toluene solution on the composition of the solution. Note that we need only express the composition of the solution in terms of the mole fraction of one component. For every value of \( X_{\text{benzene}} \), the mole fraction of toluene, \( X_{\text{toluene}} \), is given by \( (1 - X_{\text{benzene}}) \). The benzene-toluene solution is one of the few examples of an ideal solution, which is any solution that obeys Raoult’s law. One characteristic of an ideal solution is that the heat of solution, \( \Delta H_{\text{soln}} \), is zero.

Most solutions do not behave ideally in this respect. Designating two volatile substances as A and B, we can consider the following two cases:

**Case 1:** If the intermolecular forces between A and B molecules are weaker than those between A molecules and between B molecules, then there is a greater tendency for these molecules to leave the solution than in the case of an ideal solution. Consequently, the vapor pressure of the solution is greater than the sum of the vapor pressures as predicted by Raoult’s law for the same concentration. This behavior gives rise to the positive deviation [Figure 12.8(a)]. In this case, the heat of solution is positive (that is, mixing is an endothermic process).

**Case 2:** If A molecules attract B molecules more strongly than they do their own kind, the vapor pressure of the solution is less than the sum of the vapor pressures as predicted by Raoult’s law. Here we have a negative deviation [Figure 12.8(b)]. In this case, the heat of solution is negative (that is, mixing is an exothermic process).

**Fractional Distillation**

Solution vapor pressure has a direct bearing on fractional distillation, a procedure for separating liquid components of a solution based on their different boiling points. Fractional distillation is somewhat analogous to fractional crystallization. Suppose we want to separate a binary system (a system with two components), say, benzene-toluene. Both

![Figure 12.7](image_url)  
**Figure 12.7** The dependence of the partial pressures of benzene and toluene on their mole fractions in a benzene-toluene solution \( (X_{\text{toluene}} = 1 - X_{\text{benzene}}) \) at 80°C. This solution is said to be ideal because the vapor pressures obey Raoult’s law.

![Figure 12.8](image_url)  
**Figure 12.8** Nonideal solutions. (a) Positive deviation occurs when \( P_T \) is greater than that predicted by Raoult’s law (the solid black line). (b) Negative deviation. Here, \( P_T \) is less than that predicted by Raoult’s law (the solid black line).
Physical Properties of Solutions

benzene and toluene are relatively volatile, yet their boiling points are appreciably different (80.1°C and 110.6°C, respectively). When we boil a solution containing these two substances, the vapor formed is somewhat richer in the more volatile component, benzene. If the vapor is condensed in a separate container and that liquid is boiled again, a still higher concentration of benzene will be obtained in the vapor phase. By repeating this process many times, it is possible to separate benzene completely from toluene.

In practice, chemists use an apparatus like that shown in Figure 12.9 to separate volatile liquids. The round-bottomed flask containing the benzene-toluene solution is fitted with a long column packed with small glass beads. When the solution boils, the vapor condenses on the beads in the lower portion of the column, and the liquid falls back into the distilling flask. As time goes on, the beads gradually heat up, allowing the vapor to move upward slowly. In essence, the packing material causes the benzene-toluene mixture to be subjected continuously to numerous vaporization-condensation steps. At each step the composition of the vapor in the column will be richer in the more volatile, or lower boiling-point, component (in this case, benzene). The vapor that rises to the top of the column is essentially pure benzene, which is then condensed and collected in a receiving flask.

Fractional distillation is as important in industry as it is in the laboratory. The petroleum industry employs fractional distillation on a large scale to separate the components of crude oil. More will be said of this process in Chapter 24.

**Boiling-Point Elevation**

The boiling point of a solution is the temperature at which its vapor pressure equals the external atmospheric pressure (see Section 11.8). Because the presence of a non-volatile solute lowers the vapor pressure of a solution, it must also affect the boiling point of the solution. Figure 12.10 shows the phase diagram of water and the changes
that occur in an aqueous solution. Because at any temperature the vapor pressure of
the solution is lower than that of the pure solvent regardless of temperature, the liquid-
vapor curve for the solution lies below that for the pure solvent. Consequently, the
dashed solution curve intersects the horizontal line that marks $P = 1$ atm at a *higher*
temperature than the normal boiling point of the pure solvent. This graphical analysis
shows that the boiling point of the solution is higher than that of water. The *boiling-
point elevation* ($\Delta T_b$) is defined as the boiling point of the solution ($T_b$) minus the
boiling point of the pure solvent ($T^o_b$):

$$\Delta T_b = T_b - T^o_b$$

Because $T_b > T^o_b$, $\Delta T_b$ is a positive quantity.

The value of $\Delta T_b$ is proportional to the vapor-pressure lowering, and so it is also
proportional to the concentration (molality) of the solution. That is,

$$\Delta T_b \propto m$$

$$\Delta T_b = K_b m$$

(12.6)

where $m$ is the molality of the solution and $K_b$ is the *molal boiling-point elevation constant*. The units of $K_b$ are $^\circ C/m$. It is important to understand the choice of concentration unit here. We are dealing with a system (the solution) whose temperature is *not* constant, so we cannot express the concentration units in molarity because molarity changes with temperature.

Table 12.2 lists values of $K_b$ for several common solvents. Using the boiling-point elevation constant for water and Equation (12.6), you can see that if the molality of an aqueous solution is 1.00 $m$, the boiling point will be 100.52$^\circ C$.

**Freezing-Point Depression**

A nonscientist may remain forever unaware of the boiling-point elevation phenomenon, but a careful observer living in a cold climate is familiar with freezing-point depression. Ice on frozen roads and sidewalks melts when sprinkled with salts such as NaCl or CaCl$_2$. This method of thawing succeeds because it depresses the freezing point of water.

![Figure 12.10](image-url)
Figure 12.10 shows that lowering the vapor pressure of the solution shifts the solid-liquid curve to the left. Consequently, this line intersects the horizontal line at a temperature lower than the freezing point of water. The freezing point depression ($\Delta T_f$) is defined as the freezing point of the pure solvent ($T_f^\circ$) minus the freezing point of the solution ($T_f$):

$$\Delta T_f = T_f^\circ - T_f$$

Because $T_f^\circ > T_f$, $\Delta T_f$ is a positive quantity. Again, $\Delta T_f$ is proportional to the concentration of the solution:

$$\Delta T_f \propto m$$

$$\Delta T_f = K_f m \quad (12.7)$$

where $m$ is the concentration of the solute in molality units, and $K_f$ is the molal freezing-point depression constant (see Table 12.2). Like $K_b$, $K_f$ has the units °C/m.

A qualitative explanation of the freezing-point depression phenomenon is as follows. Freezing involves a transition from the disordered state to the ordered state. For this to happen, energy must be removed from the system. Because a solution has greater disorder than the solvent, more energy needs to be removed from it to create order than in the case of a pure solvent. Therefore, the solution has a lower freezing point than its solvent. Note that when a solution freezes, the solid that separates is the pure solvent component.

In order for boiling-point elevation to occur, the solute must be nonvolatile, but no such restriction applies to freezing-point depression. For example, methanol ($\text{CH}_3\text{OH}$), a fairly volatile liquid that boils at only 65°C, has sometimes been used as an antifreeze in automobile radiators.

A practical application of the freezing-point depression is described in Example 12.8.

### Table 12.2 Molal Boiling-Point Elevation and Freezing-Point Depression Constants of Several Common Liquids

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Normal Freezing Point (°C)*</th>
<th>$K_f$ (°C/m)</th>
<th>Normal Boiling Point (°C)*</th>
<th>$K_b$ (°C/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0</td>
<td>1.86</td>
<td>100</td>
<td>0.52</td>
</tr>
<tr>
<td>Benzene</td>
<td>5.5</td>
<td>5.12</td>
<td>80.1</td>
<td>2.53</td>
</tr>
<tr>
<td>Ethanol</td>
<td>−117.3</td>
<td>1.99</td>
<td>78.4</td>
<td>1.22</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>16.6</td>
<td>3.90</td>
<td>117.9</td>
<td>2.93</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>6.6</td>
<td>20.0</td>
<td>80.7</td>
<td>2.79</td>
</tr>
</tbody>
</table>

*Measured at 1 atm.

In calculating the new freezing point, subtract $\Delta T_f$ from the normal freezing point of the solvent.

### Example 12.8

Ethylene glycol (EG), $\text{CH}_2(\text{OH})\text{CH}_2(\text{OH})$, is a common automobile antifreeze. It is water soluble and fairly nonvolatile (b.p. 197°C). Calculate the freezing point of a solution containing 651 g of this substance in 2505 g of water. Would you keep this substance in your car radiator during the summer? The molar mass of ethylene glycol is 62.01 g.

(Continued)
12.6 Colligative Properties of Nonelectrolyte Solutions

**Strategy** This question asks for the depression in freezing point of the solution.

\[
\Delta T_f = K_f m
\]

want to calculate

The information given enables us to calculate the molality of the solution and we refer to Table 12.2 for the \(K_f\) of water.

**Solution** To solve for the molality of the solution, we need to know the number of moles of EG and the mass of the solvent in kilograms. We find the molar mass of EG, and convert the mass of the solvent to 2.505 kg, and calculate the molality as follows:

\[
m = \frac{651 \text{ g EG}}{62.07 \text{ g EG/mol}} \times \frac{1 \text{ mol EG}}{10.5 \text{ mol EG}} = 10.5 \text{ mol EG}
\]

\[
m = \frac{10.5 \text{ mol EG}}{2.505 \text{ kg H}_2\text{O}} = 4.19 \text{ mol/kg H}_2\text{O}
\]

\[
m = 4.19 m
\]

From Equation (12.7) and Table 12.2 we write

\[
\Delta T_f = K_f m
\]

\[
= (1.86 ^\circ C/m)(4.19 m)
\]

\[
= 7.79 ^\circ C
\]

Because pure water freezes at 0°C, the solution will freeze at \((0 - 7.79) ^\circ C\) or \(-7.79 ^\circ C\). We can calculate boiling-point elevation in the same way as follows:

\[
\Delta T_b = K_b m
\]

\[
= (0.52 ^\circ C/m)(4.19 m)
\]

\[
= 2.2 ^\circ C
\]

Because the solution will boil at \((100 + 2.2) ^\circ C\), or 102.2°C, it would be preferable to leave the antifreeze in your car radiator in summer to prevent the solution from boiling.

**Practice Exercise** Calculate the boiling point and freezing point of a solution containing 478 g of ethylene glycol in 3202 g of water.

**Review of Concepts**

The diagram here shows the vapor pressure curves for pure benzene and a solution of a nonvolatile solute in benzene. Estimate the molality of the benzene solution.
Osmotic Pressure

Many chemical and biological processes depend on osmosis, the selective passage of solvent molecules through a porous membrane from a dilute solution to a more concentrated one. Figure 12.11 illustrates this phenomenon. The left compartment of the apparatus contains pure solvent; the right compartment contains a solution. The two compartments are separated by a semipermeable membrane, which allows the passage of solvent molecules but blocks the passage of solute molecules. At the start, the water levels in the two tubes are equal [see Figure 12.11(a)]. After some time, the level in the right tube begins to rise and continues to go up until equilibrium is reached, that is, until no further change can be observed. The osmotic pressure ($\pi$) of a solution is the pressure required to stop osmosis. As shown in Figure 12.11(b), this pressure can be measured directly from the difference in the final fluid levels.

What causes water to move spontaneously from left to right in this case? The situation depicted in Figure 12.12 helps us understand the driving force behind osmosis. Because the vapor pressure of pure water is higher than the vapor pressure of the solution, there is a net transfer of water from the left beaker to the right one. Given enough time, the transfer will continue until no more water remains in the left beaker. A similar driving force causes water to move from the pure solvent into the solution during osmosis.
The osmotic pressure of a solution is given by

\[ \pi = MRT \]  

(12.8)

where \( M \) is the molarity of solution, \( R \) is the gas constant (0.0821 L \cdot atm/K \cdot mol), and \( T \) is the absolute temperature. The osmotic pressure, \( \pi \), is expressed in atm. Because osmotic pressure measurements are carried out at constant temperature, we express the concentration in terms of the more convenient units of molarity rather than molality.

Like boiling-point elevation and freezing-point depression, osmotic pressure is directly proportional to the concentration of solution. This is what we would expect, because all colligative properties depend only on the number of solute particles in solution. If two solutions are of equal concentration and, hence, have the same osmotic pressure, they are said to be isotonic. If two solutions are of unequal osmotic pressures, the more concentrated solution is said to be hypertonic and the more dilute solution is described as hypotonic (Figure 12.13).

Although osmosis is a common and well-studied phenomenon, relatively little is known about how the semipermeable membrane stops some molecules yet allows others to pass. In some cases, it is simply a matter of size. A semipermeable membrane may have pores small enough to let only the solvent molecules through. In other cases, a different mechanism may be responsible for the membrane’s selectivity—for example, the solvent’s greater “solubility” in the membrane.

The osmotic pressure phenomenon manifests itself in many interesting applications. To study the contents of red blood cells, which are protected from the external environment by a semipermeable membrane, biochemists use a technique called hemolysis. The red blood cells are placed in a hypotonic solution. Because the hypotonic...
solution is less concentrated than the interior of the cell, water moves into the cells, as shown in the middle photo of Figure 12.13(d). The cells swell and eventually burst, releasing hemoglobin and other molecules.

Home preserving of jam and jelly provides another example of the use of osmotic pressure. A large quantity of sugar is actually essential to the preservation process because the sugar helps to kill bacteria that may cause botulism. As Figure 12.13(c) shows, when a bacterial cell is in a hypertonic (high-concentration) sugar solution, the intracellular water tends to move out of the bacterial cell to the more concentrated solution by osmosis. This process, known as crenation, causes the cell to shrink and, eventually, to cease functioning. The natural acidity of fruits also inhibits bacteria growth.

Osmotic pressure also is the major mechanism for transporting water upward in plants. Because leaves constantly lose water to the air, in a process called transpiration, the solute concentrations in leaf fluids increase. Water is pulled up through the trunk, branches, and stems of trees by osmotic pressure. Up to 10 to 15 atm pressure is necessary to transport water to the leaves at the tops of California’s redwoods, which reach about 120 m in height. (The capillary action discussed in Section 11.3 is responsible for the rise of water only up to a few centimeters.) Example 12.9 shows that an osmotic pressure measurement can be used to find the concentration of a solution.

**EXAMPLE 12.9**

The average osmotic pressure of seawater, measured in the kind of apparatus shown in Figure 12.11, is about 30.0 atm at 25°C. Calculate the molar concentration of an aqueous solution of sucrose \( \text{C}_{12}\text{H}_{22}\text{O}_{11} \) that is isotonic with seawater.

**Strategy** When we say the sucrose solution is isotonic with seawater, what can we conclude about the osmotic pressures of these two solutions?

**Solution** A solution of sucrose that is isotonic with seawater must have the same osmotic pressure, 30.0 atm. Using Equation (12.8).

\[
\pi = MRT
\]

\[
M = \frac{\pi}{RT} = \frac{30.0 \text{ atm}}{(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})}
\]

\[
= 1.23 \text{ mol/L}
\]

\[
= 1.23 \text{ M}
\]

**Practice Exercise** What is the osmotic pressure (in atm) of a 0.884 \( M \) urea solution at 16°C?

**Review of Concepts**

What does it mean when we say that the osmotic pressure of a sample of seawater is 25 atm at a certain temperature?

**Using Colligative Properties to Determine Molar Mass**

The colligative properties of nonelectrolyte solutions provide a means of determining the molar mass of a solute. Theoretically, any of the four colligative properties
is suitable for this purpose. In practice, however, only freezing-point depression and osmotic pressure are used because they show the most pronounced changes. The procedure is as follows. From the experimentally determined freezing-point depression or osmotic pressure, we can calculate the molality or molarity of the solution. Knowing the mass of the solute, we can readily determine its molar mass, as Examples 12.10 and 12.11 demonstrate.

**EXAMPLE 12.10**

A 7.85-g sample of a compound with the empirical formula $\text{C}_5\text{H}_4$ is dissolved in 301 g of benzene. The freezing point of the solution is 1.05°C below that of pure benzene. What are the molar mass and molecular formula of this compound?

**Strategy** Solving this problem requires three steps. First, we calculate the molality of the solution from the depression in freezing point. Next, from the molality we determine the number of moles in 7.85 g of the compound and hence its molar mass. Finally, comparing the experimental molar mass with the empirical molar mass enables us to write the molecular formula.

**Solution** The sequence of conversions for calculating the molar mass of the compound is

\[
\text{freezing-point depression} \rightarrow \text{molality} \rightarrow \text{number of moles} \rightarrow \text{molar mass}
\]

Our first step is to calculate the molality of the solution. From Equation (12.7) and Table 12.2 we write

\[
\text{molality} = \frac{\Delta T_f}{K_f} = \frac{1.05^\circ \text{C}}{5.12^\circ \text{C/m}} = 0.205 \text{ m}
\]

Because there is 0.205 mole of the solute in 1 kg of solvent, the number of moles of solute in 301 g, or 0.301 kg, of solvent is

\[
0.301 \text{ kg} \times \frac{0.205 \text{ mol}}{1 \text{ kg}} = 0.0617 \text{ mol}
\]

Thus, the molar mass of the solute is

\[
\text{molar mass} = \frac{\text{grams of compound}}{\text{moles of compound}} = \frac{7.85 \text{ g}}{0.0617 \text{ mol}} = 127 \text{ g/mol}
\]

Now we can determine the ratio

\[
\frac{\text{molar mass}}{\text{empirical molar mass}} = \frac{127 \text{ g/mol}}{64 \text{ g/mol}} \approx 2
\]

Therefore, the molecular formula is $(\text{C}_5\text{H}_4)_2$ or $\text{C}_{10}\text{H}_8$ (naphthalene).

**Practice Exercise** A solution of 0.85 g of an organic compound in 100.0 g of benzene has a freezing point of 5.16°C. What are the molality of the solution and the molar mass of the solute?
EXAMPLE 12.11

A solution is prepared by dissolving 35.0 g of hemoglobin (Hb) in enough water to make up 1 L in volume. If the osmotic pressure of the solution is found to be 10.0 mmHg at 25°C, calculate the molar mass of hemoglobin.

**Strategy** We are asked to calculate the molar mass of Hb. The steps are similar to those outlined in Example 12.10. From the osmotic pressure of the solution, we calculate the molarity of the solution. Then, from the molarity, we determine the number of moles in 35.0 g of Hb and hence its molar mass. What units should we use for \( \pi \) and temperature?

**Solution** The sequence of conversions is as follows:

- osmotic pressure \( \rightarrow \) molarity \( \rightarrow \) number of moles \( \rightarrow \) molar mass

First we calculate the molarity using Equation (12.8)

\[
\pi = MRT \\
M = \frac{\pi}{RT} \\
10.0 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} \\
= \frac{1 \text{ atm}}{(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})} \\
= 5.38 \times 10^{-4} \text{ M}
\]

The volume of the solution is 1 L, so it must contain 5.38 \( \times \) 10\(^{-4} \) mol of Hb. We use this quantity to calculate the molar mass:

\[
\text{molecules of Hb} = \frac{\text{mass of Hb}}{\text{molar mass of Hb}} \\
\text{molar mass of Hb} = \frac{\text{mass of Hb}}{\text{molecules of Hb}} \\
= 35.0 \text{ g} \\
= 6.51 \times 10^4 \text{ g/mol}
\]

**Practice Exercise** A 202-mL benzene solution containing 2.47 g of an organic polymer has an osmotic pressure of 8.63 mmHg at 21°C. Calculate the molar mass of the polymer.

A pressure of 10.0 mmHg, as in Example 12.11, can be measured easily and accurately. For this reason, osmotic pressure measurements are very useful for determining the molar masses of large molecules, such as proteins. To see how much more practical the osmotic pressure technique is than freezing-point depression would be, let us estimate the change in freezing point of the same hemoglobin solution. If an aqueous solution is quite dilute, we can assume that molarity is roughly equal to molality. (Molarity would be equal to molality if the density of the aqueous solution were 1 g/mL.) Hence, from Equation (12.7) we write

\[
\Delta T_f = (1.86^\circ \text{C/m})(5.38 \times 10^{-4} \text{ m}) \\
= 1.00 \times 10^{-3}^\circ \text{C}
\]

The freezing-point depression of one-thousandth of a degree is too small a temperature change to measure accurately. For this reason, the freezing-point depression technique

---

The density of mercury is 13.6 g/mL. Therefore, 10 mmHg corresponds to a column of water 13.6 cm in height.
is more suitable for determining the molar mass of smaller and more soluble molecules, those having molar masses of 500 g or less, because the freezing-point depressions of their solutions are much greater.

12.7 Colligative Properties of Electrolyte Solutions

The study of colligative properties of electrolytes requires a slightly different approach than the one used for the colligative properties of nonelectrolytes. The reason is that electrolytes dissociate into ions in solution, and so one unit of an electrolyte compound separates into two or more particles when it dissolves. (Remember, it is the total number of solute particles that determines the colligative properties of a solution.) For example, each unit of NaCl dissociates into two ions—Na\(^+\) and Cl\(^-\). Thus, the colligative properties of a 0.1 m NaCl solution should be twice as great as those of a 0.1 m solution containing a nonelectrolyte, such as sucrose. Similarly, we would expect a 0.1 m CaCl\(_2\) solution to depress the freezing point by three times as much as a 0.1 m sucrose solution because each CaCl\(_2\) produces three ions. To account for this effect we define a quantity called the van’t Hoff factor, given by

\[
i = \frac{\text{actual number of particles in soln after dissociation}}{\text{number of formula units initially dissolved in soln}}
\]

Thus, \(i\) should be 1 for all nonelectrolytes. For strong electrolytes such as NaCl and KNO\(_3\), \(i\) should be 2, and for strong electrolytes such as Na\(_2\)SO\(_4\) and CaCl\(_2\), \(i\) should be 3. Consequently, the equations for colligative properties must be modified as

\[
\Delta T_b = iK_b m
\]

\[
\Delta T_i = iK_i m
\]

\[
\pi = iMRT
\]

In reality, the colligative properties of electrolyte solutions are usually smaller than anticipated because at higher concentrations, electrostatic forces come into play and bring about the formation of ion pairs. An **ion pair** is made up of **one or more cations and one or more anions held together by electrostatic forces**. The presence of an ion pair reduces the number of particles in solution, causing a reduction in the colligative properties (Figure 12.14). Electrolytes containing multicharged ions such as Mg\(^{2+}\), Al\(^{3+}\), SO\(_4^{2-}\), and PO\(_4^{3-}\) have a greater tendency to form ion pairs than electrolytes such as NaCl and KNO\(_3\), which are made up of singly charged ions.

Table 12.3 shows the experimentally measured values of \(i\) and those calculated assuming complete dissociation. As you can see, the agreement is close but not perfect, indicating that the extent of ion-pair formation in these solutions at that concentration is appreciable.

---

\(^1\) Jacobus Hendricus van’t Hoff (1852–1911). Dutch chemist. One of the most prominent chemists of his time, van’t Hoff did significant work in thermodynamics, molecular structure and optical activity, and solution chemistry. In 1901 he received the first Nobel Prize in Chemistry.
### TABLE 12.3  The van’t Hoff Factor of 0.0500 M Electrolyte Solutions at 25°C

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>( i ) (Measured)</th>
<th>( i ) (Calculated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sucrose*</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>HCl</td>
<td>1.9</td>
<td>2.0</td>
</tr>
<tr>
<td>NaCl</td>
<td>1.9</td>
<td>2.0</td>
</tr>
<tr>
<td>MgSO(_4)</td>
<td>1.3</td>
<td>2.0</td>
</tr>
<tr>
<td>MgCl(_2)</td>
<td>2.7</td>
<td>3.0</td>
</tr>
<tr>
<td>FeCl(_3)</td>
<td>3.4</td>
<td>4.0</td>
</tr>
</tbody>
</table>

*Sucrose is a nonelectrolyte. It is listed here for comparison only.

### Review of Concepts

Indicate which compound in each of the following groups has a greater tendency to form ion pairs in water: (a) NaCl or Na\(_2\)SO\(_4\), (b) MgCl\(_2\) or MgSO\(_4\), (c) LiBr or KBr.

### EXAMPLE 12.12

The osmotic pressure of a 0.010 M potassium iodide (KI) solution at 25°C is 0.465 atm. Calculate the van’t Hoff factor for KI at this concentration.

**Strategy**  Note that KI is a strong electrolyte, so we expect it to dissociate completely in solution. If so, its osmotic pressure would be

\[
2(0.010 \text{ M})(0.0821 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(298 \text{ K}) = 0.489 \text{ atm}
\]

However, the measured osmotic pressure is only 0.465 atm. The smaller than predicted osmotic pressure means that there is ion-pair formation, which reduces the number of solute particles (K\(^+\) and I\(^-\) ions) in solution.

**Solution**  From Equation (12.12) we have

\[
i = \frac{\pi}{MRT} = \frac{0.465 \text{ atm}}{(0.010 \text{ M})(0.0821 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(298 \text{ K})} = 1.90
\]

**Practice Exercise**  The freezing-point depression of a 0.100 \( m \) MgSO\(_4\) solution is 0.225°C. Calculate the van’t Hoff factor of MgSO\(_4\) at this concentration.

### Review of Concepts

The osmotic pressure of blood is about 7.4 atm. What is the approximate concentration of a saline solution (NaCl solution) a physician should use for intravenous injection? Use 37°C for physiological temperature.

The Chemistry in Action essay on p. 541 describes three physical techniques for obtaining the pure solvent (water) from a solution (seawater).
### 12.8 Colloids

The solutions discussed so far are true homogeneous mixtures. Now consider what happens if we add fine sand to a beaker of water and stir. The sand particles are suspended at first but then gradually settle to the bottom. This is an example of a heterogeneous mixture. Between these two extremes is an intermediate state called a colloidal suspension, or simply, a colloid. A colloid is a dispersion of particles of one substance (the dispersed phase) throughout a dispersing medium made of another substance. Colloidal...
particles are much larger than the normal solute molecules; they range from $1 \times 10^3$ pm to $1 \times 10^6$ pm. Also, a colloidal suspension lacks the homogeneity of an ordinary solution. The dispersed phase and the dispersing medium can be gases, liquids, solids, or a combination of different phases, as shown in Table 12.4.

A number of colloids are familiar to us. An aerosol consists of liquid droplets or solid particles dispersed in a gas. Examples are fog and smoke. Mayonnaise, which is made by breaking oil into small droplets in water, is an example of emulsion, which consists of liquid droplets dispersed in another liquid. Milk of magnesia is an example of sol, a suspension of solid particles in a liquid.

Reverse Osmosis

Both distillation and freezing involve phase changes that require considerable energy. On the other hand, desalination by reverse osmosis does not involve a phase change and is economically more desirable. Reverse osmosis uses high pressure to force water from a more concentrated solution to a less concentrated one through a semipermeable membrane. The osmotic pressure of seawater is about 30 atm—this is the pressure that must be applied to the saline solution in order to stop the flow of water from left to right. If the pressure on the salt solution were increased beyond 30 atm, the osmotic flow would be reversed, and freshwater would actually pass from the solution through the membrane into the left compartment. Desalination by reverse osmosis is considerably cheaper than distillation and it avoids the technical difficulties associated with freezing. The main obstacle to this method is the development of a membrane that is permeable to water but not to other dissolved substances and that can be used on a large scale for prolonged periods under high-pressure conditions. Once this problem has been solved, and present signs are encouraging, reverse osmosis could become a major desalination technique.
One way to distinguish a solution from a colloid is by the Tyndall\textsuperscript{†} effect. When a beam of light passes through a colloid, it is scattered by the dispersed phase (Figure 12.15). No such scattering is observed with ordinary solutions because the solute molecules are too small to interact with visible light. Another demonstration of the Tyndall effect is the scattering of sunlight by dust or smoke in the air (Figure 12.16).

Hydrophilic and Hydrophobic Colloids

Among the most important colloids are those in which the dispersing medium is water. Such colloids are divided into two categories called hydrophilic, or water-loving, and hydrophobic, or water-fearing. Hydrophilic colloids are usually solutions containing extremely large molecules such as proteins. In the aqueous phase, a protein like hemoglobin folds in such a way that the hydrophilic parts of the molecule, the parts that can interact favorably with water molecules by ion-dipole forces or hydrogen-bond formation, are on the outside surface (Figure 12.17).

A hydrophobic colloid normally would not be stable in water, and the particles would clump together, like droplets of oil in water merging to form a film of oil at water’s surface. They can be stabilized, however, by adsorption of ions on their surface (Figure 12.18). (Adsorption refers to adherence onto a surface. It differs from absorption in that the latter means passage to the interior of the medium.) These adsorbed ions can

\[ \text{HO} \quad \text{NH}_3 \quad \text{O} \quad \text{C} \quad \text{O} \quad \text{NH}_4^+ \]

Protein

\[ \text{HO} \quad \text{C} \quad \text{O} \quad \text{NH}_2 \]

1John Tyndall (1820–1893). Irish physicist. Tyndall did important work in magnetism, and explained glacier motion.

\[ \text{Figure 12.15 Three beams of white light, passing through a colloid of sulfur particles in water, change to orange, pink, and bluish-green. The colors produced depend on the size of the particles and also on the position of the viewer. The smaller the dispersed particles, the shorter (and bluer) the wavelengths.} \]

\[ \text{Figure 12.16 Sunlight scattered by dust particles in the air.} \]

\[ \text{Figure 12.17 Hydrophilic groups on the surface of a large molecule such as protein stabilizes the molecule in water. Note that all these groups can form hydrogen bonds with water.} \]
Figure 12.18 Diagram showing the stabilization of hydrophobic colloids. Negative ions are adsorbed onto the surface and the repulsion between like charges prevents the clumping of the particles.

interact with water, thus stabilizing the colloid. At the same time, the electrostatic repulsion between the particles prevents them from clumping together. Soil particles in rivers and streams are hydrophobic particles stabilized in this way. When the freshwater enters the sea, the charges on the particles are neutralized by the high-salt medium, and the particles clump together to form the silt that is seen at the mouth of the river.

Another way hydrophobic colloids can be stabilized is by the presence of other hydrophilic groups on their surfaces. Consider sodium stearate, a soap molecule that has a polar head and a long hydrocarbon tail that is nonpolar (Figure 12.19). The cleansing action of soap is the result of the dual nature of the hydrophobic tail and the hydrophilic end group. The hydrocarbon tail is readily soluble in oily substances, which are also nonpolar, while the ionic \(-\text{COO}^-\) group remains outside the oily surface. When enough soap molecules have surrounded an oil droplet, as shown in Figure 12.20, the entire system becomes solubilized in water because the exterior portion is now largely hydrophilic. This is how greasy substances are removed by the action of soap.

Figure 12.19 (a) A sodium stearate molecule. (b) The simplified representation of the molecule that shows a hydrophilic head and a hydrophobic tail.

Figure 12.20 The cleansing action of soap. (a) Grease (oily substance) is not soluble in water. (b) When soap is added to water, the nonpolar tails of soap molecules dissolve in grease. (c) Finally, the grease is removed in the form of an emulsion. Note that each oily droplet now has an ionic exterior that is hydrophilic.
### Key Equations

\[
molality (m) = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}}
\]  
(12.2) Calculating the molality of a solution.

\[c = kP\]
(12.3) Henry’s law for calculating solubility of gases.

\[P_i = X_i P^o_i\]
(12.4) Raoult’s law relating the vapor pressure of a liquid to its vapor pressure in a solution.

\[
\Delta P = X_i P^o_i
\]  
(12.5) Vapor pressure lowering in terms of the concentration of solution.

\[\Delta T_b = K_b m\]
(12.6) Boiling-point elevation.

\[\Delta T_f = K_f m\]
(12.7) Freezing-point depression.

\[
\pi = MRT
\]  
(12.8) Osmotic pressure of a solution.

\[i = \frac{\text{actual number of particles in soln after dissociation}}{\text{number of formula units initially dissolved in soln}}\]
(12.9) Calculating the van’t Hoff factor for an electrolyte solution.

### Summary of Facts and Concepts

1. Solutions are homogeneous mixtures of two or more substances, which may be solids, liquids, or gases.

2. The ease of dissolving a solute in a solvent is governed by intermolecular forces. Energy and the disorder that results when molecules of the solute and solvent mix to form a solution are the forces driving the solution process.

3. The concentration of a solution can be expressed as percent by mass, mole fraction, molarity, and molality. The choice of units depends on the circumstances.

4. Increasing temperature usually increases the solubility of solid and liquid substances and usually decreases the solubility of gases in water.

5. According to Henry’s law, the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas over the solution.

6. Raoult’s law states that the partial pressure of a substance A over a solution is equal to the mole fraction \((X_A)\) of A times the vapor pressure \((P^o_A)\) of pure A. An ideal solution obeys Raoult’s law over the entire range of concentration. In practice, very few solutions exhibit ideal behavior.

7. Vapor-pressure lowering, boiling-point elevation, freezing-point depression, and osmotic pressure are colligative properties of solutions; that is, they depend only on the number of solute particles that are present and not on their nature.

8. In electrolyte solutions, the interaction between ions leads to the formation of ion pairs. The van’t Hoff factor provides a measure of the extent of dissociation of electrolytes in solution.

9. A colloid is a dispersion of particles (about \(1 \times 10^3\) pm to \(1 \times 10^6\) pm) of one substance in another substance. A colloid is distinguished from a regular solution by the Tyndall effect, which is the scattering of visible light by colloidal particles. Colloids in water are classified as hydrophilic colloids and hydrophobic colloids.

### Key Words

| Boiling-point elevation \((\Delta T_b)\), p. 531 | Freezing-point depression \((\Delta T_f)\), p. 532 | Molality, p. 518 |
| Colligative properties, p. 526 | Henry’s law, p. 524 | Nonvolatile, p. 527 |
| Colloid, p. 541 | Hydrophilic, p. 541 | Osmosis, p. 534 |
| Crystallization, p. 514 | Hydrophobic, p. 541 | Osmotic pressure \((\pi)\), p. 534 |
| Fractional crystallization, p. 522 | Ideal solution, p. 529 | Percent by mass, p. 517 |
| Fractional distillation, p. 529 | Ion pair, p. 539 | Raoult’s law, p. 527 |
| Miscible, p. 516 | Saturated solution, p. 514 | Supersaturated solution, p. 514 |
| Nonvolatile, p. 527 | Semipermeable membrane, p. 534 | Unsaturated solution, p. 514 |
| Osmosis, p. 534 | Solvation, p. 516 | Volatile, p. 528 |
| Supersaturated solution, p. 514 | van’t Hoff factor \((i)\), p. 539 | |