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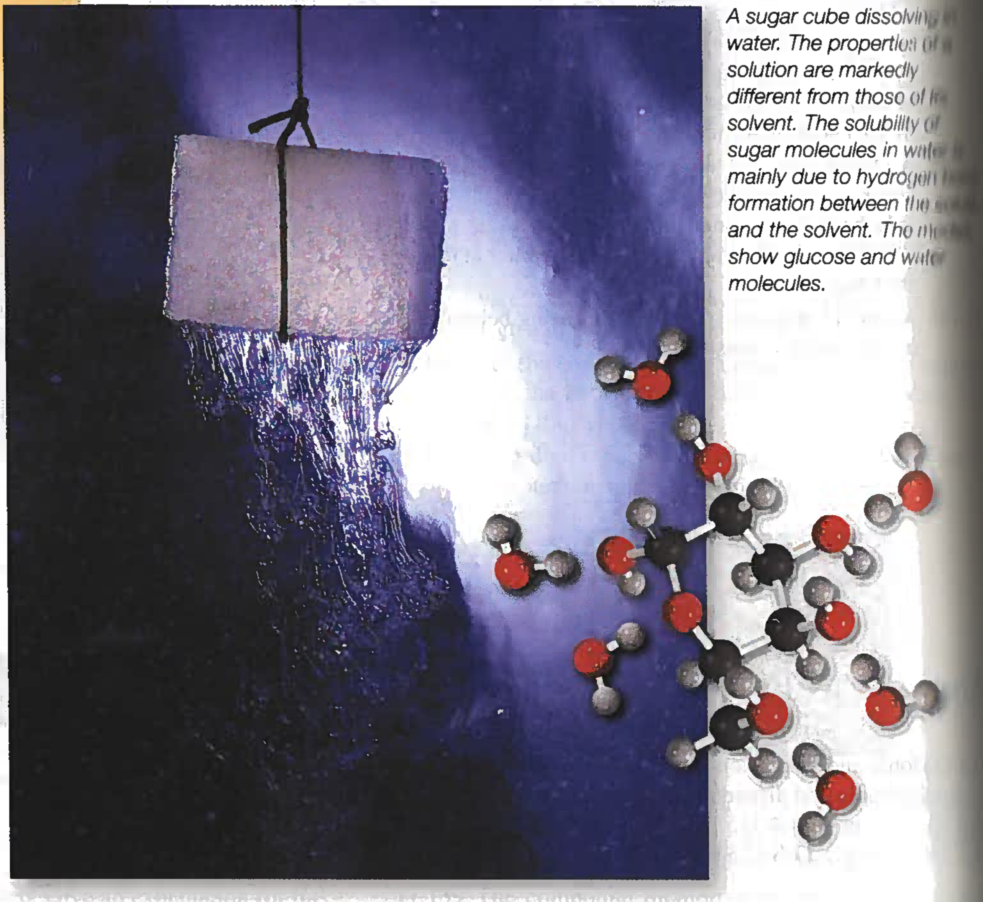


A sugar cube dissolving in water. The properties of a solution are markedly different from those of the solvent. The solubility of sugar molecules in water is mainly due to hydrogen bond formation between the solute and the solvent. The models show glucose and water molecules.

Physical Properties of Solutions

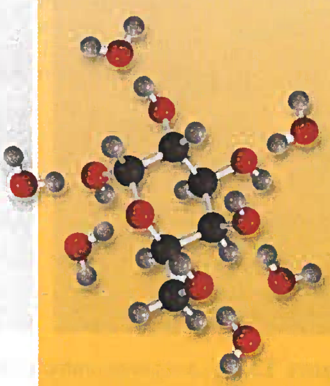
A LOOK AHEAD

- 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 on 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 the colligative 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)

Interactive Activity Summary

1. Animation: Dissolution of an Ionic and a Covalent Compound (12.2)
2. Animation: Osmosis (12.6)
3. Interactivity: Test Solution with Electrolytes (12.7)

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 solutions.



12.1 Types of Solutions

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

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

Chemists also characterize solutions by their capacity to dissolve a solute. A ***urated solution*** *contains the maximum amount of a solute that will dissolve in a solvent at a specific temperature.* An **unsaturated solution** *contains less solute has the capacity to dissolve.* A third type, a ***supersaturated solution,*** *contains solute than is present in a saturated solution.* Supersaturated solutions are not ve ble. In time, some of the solute will come out of a supersaturated solution as cry ***Crystallization*** *is the process in which dissolved solute comes out of solution and crystals* (Figure 12.1). Note that both precipitation and crystallization describ

TABLE 12.1 Types of Solutions

Component 1	Component 2	State of Resulting Solution	Examples
Gas	Gas	Gas	Air
Gas	Liquid	Liquid	Soda water (CO_2 in water)
Gas	Solid	Solid	H_2 gas in palladium
Liquid	Liquid	Liquid	Ethanol in wate
Solid	Liquid	Liquid	NaCl in water
Solid	Solid	Solid	Brass (Cu/Zn), solder (Sn/Pb)

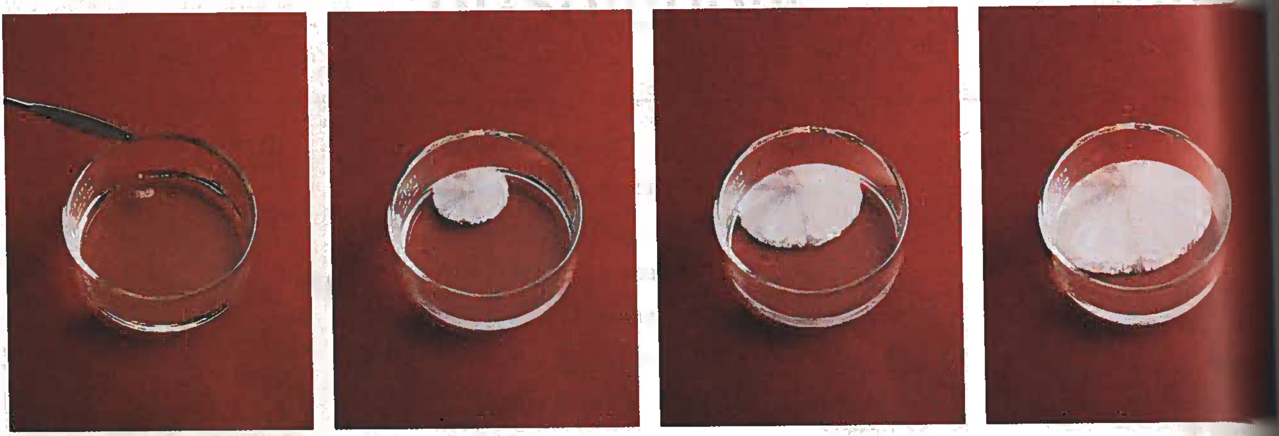


Figure 12.1 *In a supersaturated sodium acetate solution (left), sodium acetate crystals rapidly form when a small seed crystal is add*

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.

12.2 A Molecular View of the Solution Process

In Section 6.6 we discussed the solution process from a macroscopic point of view.

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

Animation:
Dissolution of an Ionic and a Covalent Compound
ARIS, Animation Center

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 ΔH_{soln} is given by

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

This equation is an application of Hess's law.

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

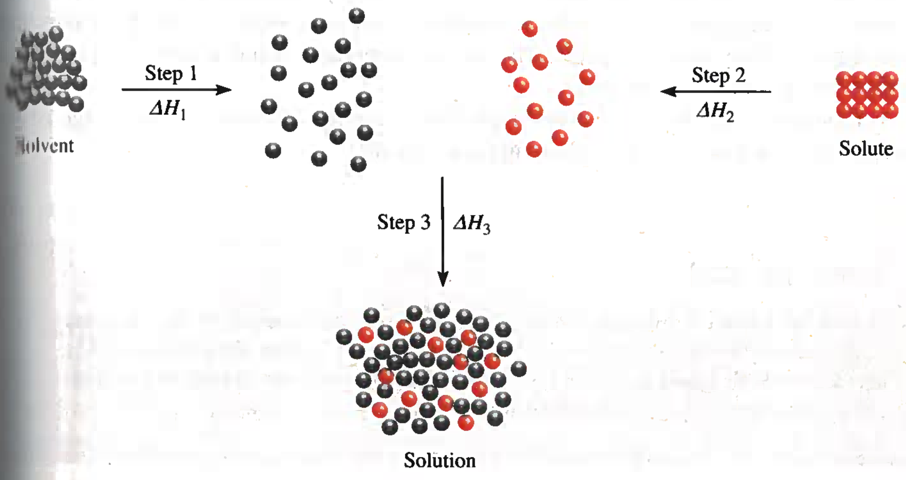
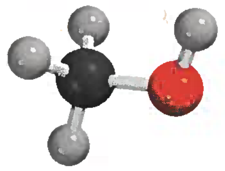


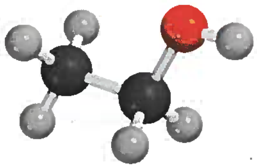
Figure 12.2 *A molecular view of the solution process portrayed as taking place in three steps: First the solvent and solute molecules are separated (steps 1 and 2). Then the solvent and solute molecules mix (step 3).*

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 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.

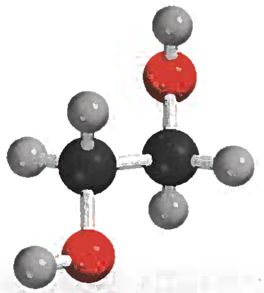
Solubility is a measure of how much solute will dissolve in a solvent at a specific temperature. The saying "like dissolves like" is helpful in predicting the solubility of a substance in a given solvent. What this expression means is that two substances with intermolecular forces of similar type and magnitude are likely to be soluble in each other. For example, both carbon tetrachloride (CCl_4) and benzene (C_6H_6) 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 CCl_4 and C_6H_6 molecules is comparable in magnitude to the forces between CCl_4 molecules and between C_6H_6 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:



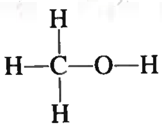
CH_3OH



C_2H_5OH

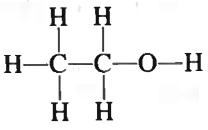


$CH_2(OH)CH_2(OH)$



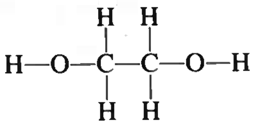
$$\begin{array}{c}\text{H}\\ |\\ \text{H—C—O—H}\\ |\\ \text{H}\end{array}$$

methanol



$$\begin{array}{c}\text{H H}\\ |\ \ |\\ \text{H—C—C—O—H}\\ |\ \ |\\ \text{H H}\end{array}$$

ethanol



$$\begin{array}{c}\text{H H}\\ |\ \ |\\ \text{H—O—C—C—O—H}\\ |\ \ |\\ \text{H H}\end{array}$$

1,2-ethylene glycol

The rules given in Table 4.2 (p. 123) enable us to predict the solubility of a particular ionic compound in water. 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 (Br_2) in benzene (C_6H_6, $\mu = 0$ D) and in water ($\mu = 1.87$ D), (b) KCl in carbon tetrachloride (CCl_4, $\mu = 0$ D) and in liquid ammonia (NH_3, $\mu = 1.46$ D), (c) formaldehyde (CH_2O) in carbon disulfide (CS_2, $\mu = 0$) and in water.

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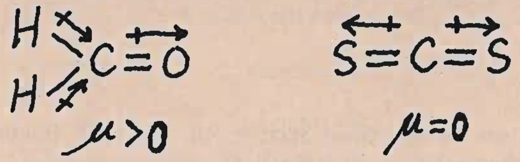
Strategy In predicting solubility, remember the saying: Like dissolves like. A nonpolar solute will dissolve in a nonpolar solvent; ionic compounds will generally dissolve in polar solvents due to favorable ion-dipole interaction; solutes that can form hydrogen bonds with the solvent will have high solubility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

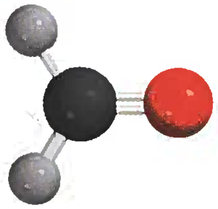
Solution (a) Br_2 is a nonpolar molecule and therefore should be more soluble in C_6H_6, which is also nonpolar, than in water. The only intermolecular forces between Br_2 and C_6H_6 are dispersion forces.

(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_2O is a polar molecule and CS_2 (a linear molecule) is nonpolar,



the forces between molecules of CH_2O and CS_2 are dipole-induced dipole and dispersion. On the other hand, CH_2O can form hydrogen bonds with water, so it should be more soluble in that solvent.



CH_2O

Similar problem: 12.11.

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

$$\text{percent by mass} = \frac{\text{mass of solute}}{\text{mass of soln}} \times 100\% \tag{12.1}$$

The percent by mass has no units 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?

(Continued)

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

Solution We write

$$\begin{aligned}\text{percent by mass of KCl} &= \frac{\text{mass of solute}}{\text{mass of soln}} \times 100\% \\ &= \frac{0.892\ \text{g}}{0.892\ \text{g} + 54.6\ \text{g}} \times 100\% \\ &= \boxed{1.61\%}\end{aligned}$$

Similar problem: 12.15.

Practice Exercise A sample of 6.44 g of naphthalene ($C_{10}H_8$) is dissolved in
of benzene (C_6H_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 com
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 has no units, because it too is a ratio of two similar quanti

Molarity (*M*)

For calculations involving molarity, see Examples 4.6 and 4.7 on p. 144.

In Section 4.5 molarity was defined as the number of moles of solute in 1 L of
tion; that is,

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

Thus, the units of molarity are mol/L.

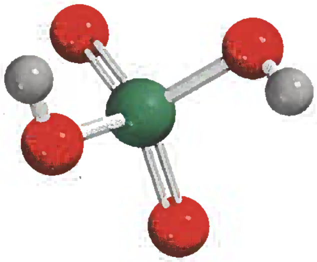
Molality (*m*)

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

$$\boxed{\text{molality} = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}}} \qquad (1$$

For example, to prepare a 1 molal, or 1 *m*, sodium sulfate (Na_2SO_4) aqueous
tion, we need to dissolve 1 mole (142.0 g) of the substance in 1000 g (1 kg) of
Depending on the nature of the solute-solvent interaction, the final volume of the
tion will be either greater or less than 1000 mL. It is also possible, though
unlikely, that the final volume could be equal to 1000 mL.

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



H_2SO_4

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 98.08 g.

(Continued

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.

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.

$$\begin{aligned}\text{moles of } H_2SO_4 &= 24.4\ \cancel{\text{g } H_2SO_4} \times \frac{1 \text{ mol } H_2SO_4}{98.09\ \cancel{\text{g } H_2SO_4}} \\ &= 0.249 \text{ mol } H_2SO_4\end{aligned}$$

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

$$\begin{aligned}m &= \frac{0.249 \text{ mol } H_2SO_4}{0.198 \text{ kg } H_2O} \\ &= \boxed{1.26\ m}\end{aligned}$$

Similar problem: 12.17.

Practice Exercise What is the molality of a solution containing 7.78 g of urea $[(NH_2)_2CO]$ in 203 g of water?

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. 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 ($C_6H_{12}O_6$) 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:

$$\left(0.396\ \cancel{\text{mol } C_6H_{12}O_6} \times \frac{180.2 \text{ g}}{1\ \cancel{\text{mol } C_6H_{12}O_6}}\right) + 1000 \text{ g } H_2O \text{ soln} = 1071 \text{ g}$$

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

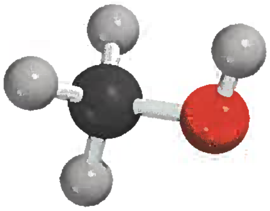
$$\begin{aligned} \text{volume} &= \frac{\text{mass}}{\text{density}} \\ &= \frac{1071\ \text{g}}{1.16\ \text{g/mL}} \times \frac{1\ \text{L}}{1000\ \text{mL}} \\ &= 0.923\ \text{L} \end{aligned}$$

Finally, the molarity of the solution is given by

$$\begin{aligned} \text{molarity} &= \frac{\text{moles of solute}}{\text{liters of soln}} \\ &= \frac{0.396\ \text{mol}}{0.923\ \text{L}} \\ &= 0.429\ \text{mol/L} = 0.429\ M \end{aligned}$$

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.



CH_3OH

Example 12.4

The density of a 2.45 M aqueous solution of methanol (CH_3OH) 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.

$$\underset{\text{want to calculate}}{\nearrow}\ m = \frac{\text{moles of solute}^{\ \swarrow\ \text{given}}}{\text{mass of solvent (kg)}_{\ \nwarrow\ \text{need to find}}}$$

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 M solution of methanol is

$$1\ \cancel{\text{L soln}} \times \frac{1000\ \cancel{\text{mL soln}}}{1\ \cancel{\text{L soln}}} \times \frac{0.976\ \text{g}}{1\ \cancel{\text{mL soln}}} = 976\ \text{g}$$

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

$$\begin{aligned} \text{mass of } H_2O &= \text{mass of soln} - \text{mass of solute} \\ &= 976\ \text{g} - \left(2.45\ \cancel{\text{mol } CH_3OH} \times \frac{32.04\ \text{g } CH_3OH}{1\ \cancel{\text{mol } CH_3OH}}\right) \\ &= 898\ \text{g} \end{aligned}$$

(Continued)

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

$$\text{molality} = \frac{2.45 \text{ mol } CH_3OH}{0.898 \text{ kg } H_2O}$$

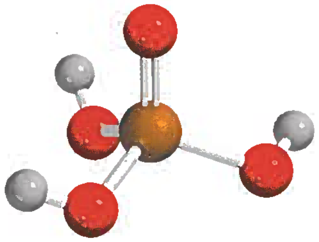
$$= \boxed{2.73\ m}$$

Similar problems: 12.18(a), 12.19.

Practice Exercise Calculate the molality of a 5.86 *M* ethanol (C_2H_5OH) 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_3PO_4). The molar mass of phosphoric acid is 98.00 g.



H_3PO_4

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% − 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

$$\text{moles of } H_3PO_4 = 35.4 \cancel{\text{ g } H_3PO_4} \times \frac{1 \text{ mol } H_3PO_4}{97.99 \cancel{\text{ g } H_3PO_4}}$$

$$= 0.361 \text{ mol } H_3PO_4$$

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

$$\text{molality} = \frac{0.361 \text{ mol } H_3PO_4}{0.0646 \text{ kg } H_2O}$$

$$= \boxed{5.59\ m}$$

Similar problem: 12.18(b).

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

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 ΔH_{soln} and the variation of solubility with temperature. For example, the solution process of $CaCl_2$ is exothermic, and that of NH_4NO_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.

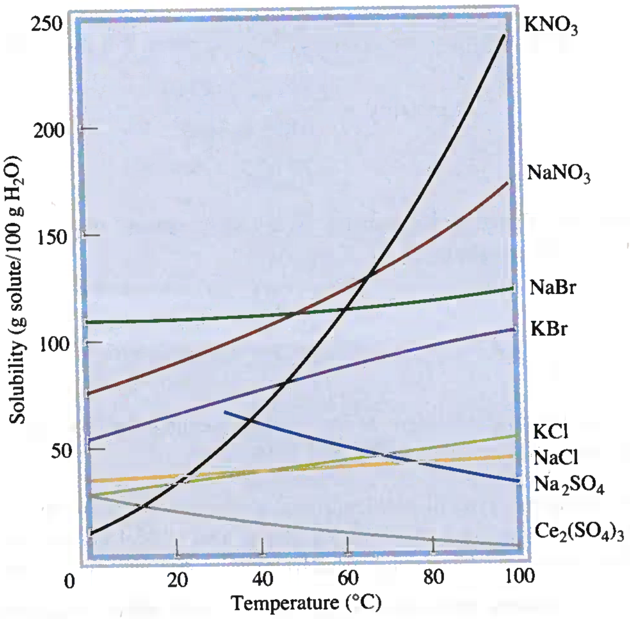


Figure 12.3 *Temperature dependence of the solubility of some ionic compounds in water.*

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_2O and 34.2 g/100 g H_2O, 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

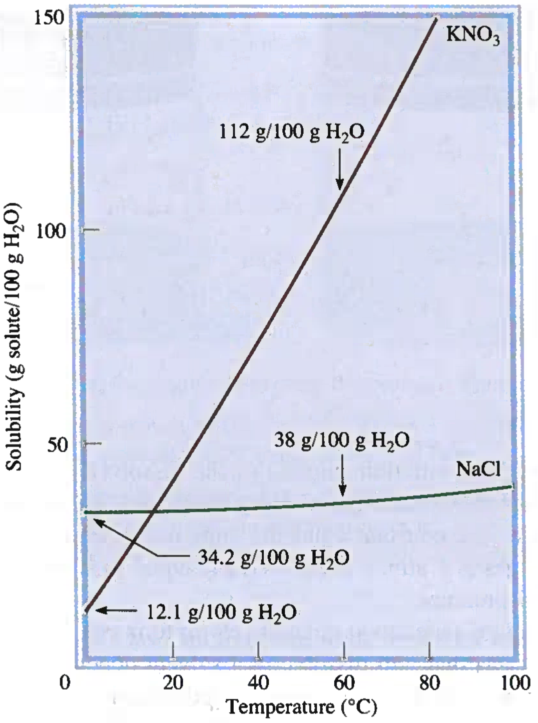


Figure 12.4 *The solubilities of KNO_3 and NaCl at 0°C and 60°C. The difference in temperature dependence enables us to isolate one of these compounds from a solution containing both of them, through fractional crystallization.*

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.

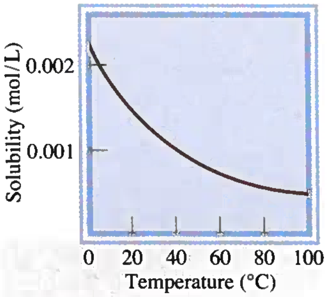


Figure 12.5 *Dependence on temperature of the solubility of O_2 gas in water. Note that the solubility decreases as temperature increases. The pressure of the gas over the solution is 1 atm.*

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:*

$$c \propto P$$

$$c = kP \qquad (12.3)$$

[†] 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.

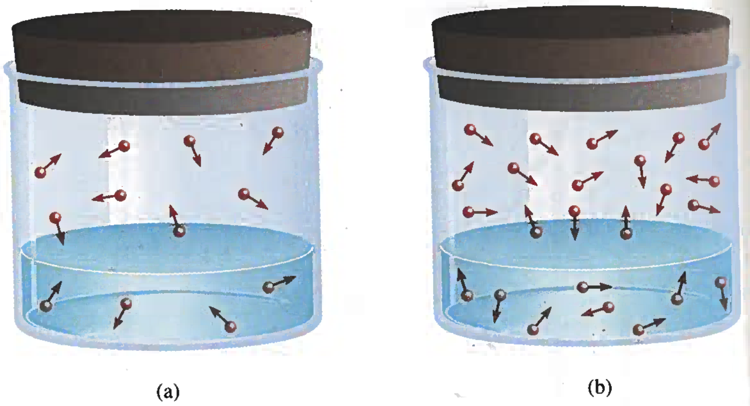


Figure 12.6 *A molecular interpretation of Henry's law. When the partial pressure of the gas over the solution increases from (a) to (b), the concentration of the dissolved gas also increases according to Equation (12.2).*

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

Here c is the molar concentration (mol/L) of the dissolved gas; P is the pressure (in atm) of the gas over the solution; 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 greater [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.

The effervescence of a soft drink. The bottle was shaken before being opened to dramatize the escape of CO_2.

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 bottle falls to atmospheric pressure, and the amount of CO_2 remaining in the beverage is determined only by the normal atmospheric partial pressure of CO_2, 0.0003 atm. The excess dissolved CO_2 comes out of solution, causing the effervescence.

Example 12.6 applies Henry's law to nitrogen gas.

Example 12.6

The solubility of nitrogen gas at 25°C and 1 atm is 6.8×10^{-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.

(Continued)

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

$$\begin{aligned} c &= kP \\ 6.8 \times 10^{-4}\ \text{mol/L} &= k\ (1\ \text{atm}) \\ k &= 6.8 \times 10^{-4}\ \text{mol/L} \cdot \text{atm} \end{aligned}$$

Therefore, the solubility of nitrogen gas in water is

$$\begin{aligned} c &= (6.8 \times 10^{-4}\ \text{mol/L} \cdot \text{atm})(0.78\ \text{atm}) \\ &= 5.3 \times 10^{-4}\ \text{mol/L} \\ &= 5.3 \times 10^{-4}\ M \end{aligned}$$

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 atm/1.0 atm = 0.78).

Similar problem: 12.37.

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 1.3×10^{-3} mol/L · 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

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

Carbon dioxide also reacts with water, as follows:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

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:

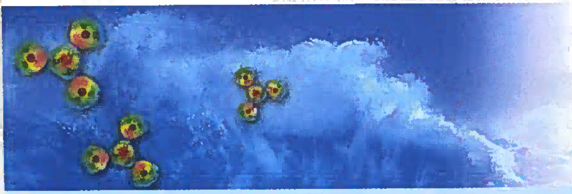
$$Hb + 4O_2 \rightleftharpoons Hb(O_2)_4$$

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

The Chemistry in Action essay on p. 516 explains a natural disaster with Henry's law.

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 ≤ 0.2 M.



CHEMISTRY *in Action*

The Killer Lake

Disaster struck swiftly and without warning. On August 21, 1986, Lake Nyos in Cameroon, a small nation on the west coast of Africa, suddenly belched a dense cloud of carbon dioxide. Speeding down a river valley, the cloud asphyxiated over 1700 people and many livestock.

How did this tragedy happen? Lake Nyos is stratified into layers that do not mix. A boundary separates the freshwater at the surface from the deeper, denser solution containing dissolved minerals and gases, including CO_2. The CO_2 gas comes from springs of carbonated groundwater that percolate upward into the bottom of the volcanically formed lake. Given the high water pressure at the bottom of the lake, the concentration of CO_2 gradually accumulated to a dangerously high level, in accordance with Henry's law. What triggered the release of CO_2 is not known for certain. It is believed that an earthquake, landslide, or even strong winds may have upset the delicate balance within the lake, creating waves that overturned the water layers. When the deep water rose, dissolved CO_2 came out of solution, just as a soft drink fizzes when the bottle is uncapped. Being heavier than air, the CO_2 traveled close to the ground and literally smothered an entire village 15 miles away.

Now, more than 20 years after the incident, scientists are concerned that the CO_2 concentration at the bottom of Lake Nyos is again reaching saturation level. To prevent a recurrence of the earlier tragedy, an attempt has been made to pump up the deep water, thus releasing the dissolved CO_2. In addition to being costly, this approach is controversial because it might disturb the waters near the bottom of the lake, leading to an uncontrollable release of CO_2 to the surface. In the meantime, a natural time bomb is ticking away.

Deep waters in Lake Nyos are pumped to the surface to remove dissolved CO_2 gas.

To review the concept of equilibrium vapor pressure as it applies to pure liquids, see Section 11.8.

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 partial pressure of a solvent over a solution, P_1, is given by the vapor pressure of the pure solvent, P_1°, times the mole fraction of the solvent in the solution, X_1*:

$$\boxed{P_1 = X_1 P_1^\circ} \qquad (12.4)$$

[†] François Marie Raoult (1830–1901). French chemist. Raoult's work was mainly in solution properties and electrochemistry.

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

$$P_1 = (1 - X_2)P_1^\circ$$

or

$$P_1 = P_1^\circ - X_2P_1^\circ$$

so that

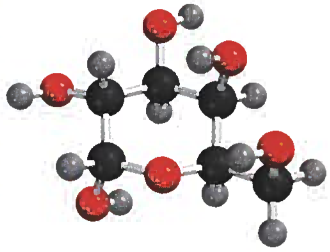
$$P_1^\circ - P_1 = \Delta P = X_2P_1^\circ \tag{12.5}$$

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

Example 12.7 illustrates the use of Raoult's law [Equation (12.5)].

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. 196). Assume the density of the solution is 1.00 g/mL.



$C_6H_{12}O_6$

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

$$\underset{\text{want to calculate}}{P_1} = \overset{\text{need to find}}{X_1}\underset{\text{given}}{P_1^\circ}$$

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

$$n_1(\text{water}) = 460\ \cancel{\text{mL}} \times \frac{1.00\ \cancel{\text{g}}}{1\ \cancel{\text{mL}}} \times \frac{1\ \text{mol}}{18.02\ \cancel{\text{g}}} = 25.5\ \text{mol}$$

$$n_2(\text{glucose}) = 218\ \cancel{\text{g}} \times \frac{1\ \text{mol}}{180.2\ \cancel{\text{g}}} = 1.21\ \text{mol}$$

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) mmHg, or 1.4 mmHg.

(Continued)

Similar problems: 12.51, 12.52.

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 mmHg) or 1.4 mmHg.

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

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:

$$P_A = X_A P_A^\circ$$
$$P_B = X_B P_B^\circ$$

where P_A and P_B are the partial pressures over the solution for components A and B; P_A° and P_B° 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

$$P_T = X_A P_A^\circ + X_B P_B^\circ$$

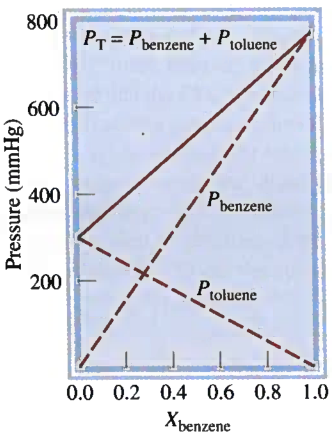
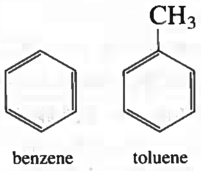


Figure 12.7 *The dependence of the partial pressures of benzene and toluene on their mole fractions in a benzene-toluene solution ($X_{toluene} = 1 - X_{benzene}$) at 80°C. This solution is said to be ideal because the vapor pressures obey Raoult's law.*

For example, benzene and toluene are volatile components that have similar structures and therefore similar intermolecular forces:



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 $X_{benzene}$, the mole fraction of toluene, $X_{toluene}$, is given by $(1 - X_{benzene})$. 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, ΔH_{soln}, is zero.

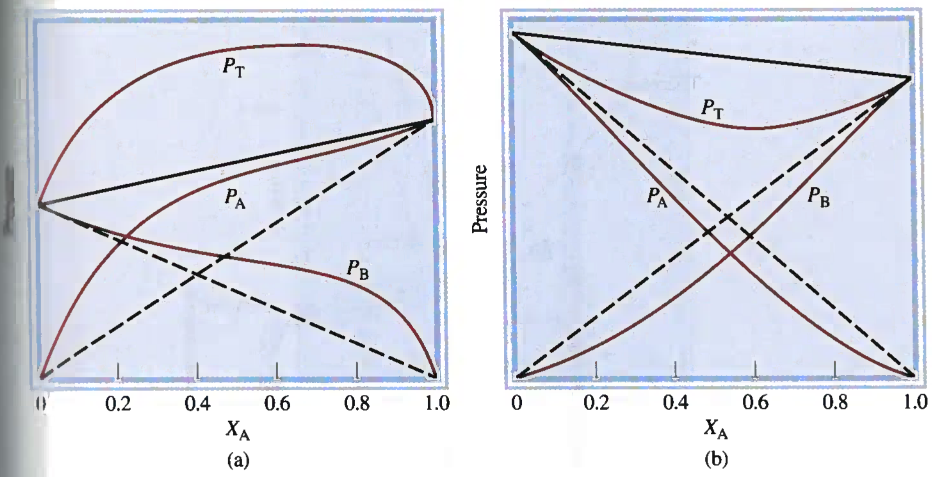


Figure 12.8 *Nonideal solutions. (a) Positive deviation occurs when P_T is greater than that predicted by Raoult's law (the solid black line). (b) Negative deviation. Here, P_T is less than that predicted by Raoult's law (the solid black line).*

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 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.

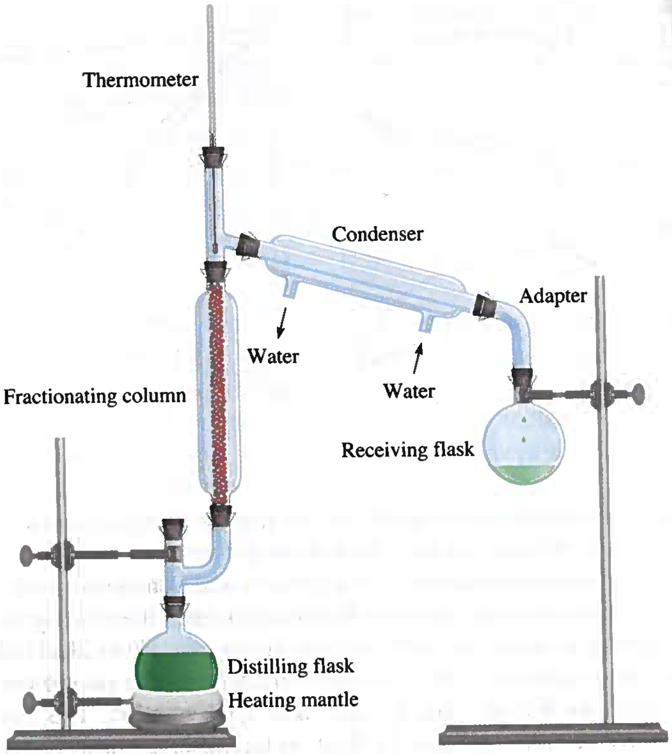


Figure 12.9 *An apparatus for small-scale fractional distillation. The fractionating column is packed with tiny glass beads. The longer the fractionating column, the more complete the separation of the volatile liquids.*

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 nonvolatile 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*** **(ΔT_b)** is defined as *the boiling point of the solution (T_b) minus the boiling point of the pure solvent (T_b°):*

$$\Delta T_b = T_b - T_b^\circ$$

Because $T_b > T_b^\circ$, ΔT_b is a positive quantity.

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

$$\Delta T_b \propto m$$

$$\Delta T_b = K_b m \qquad (12.6)$$

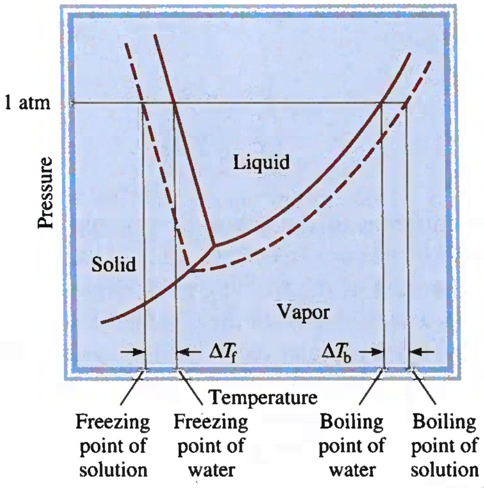


Figure 12.10 *Phase diagram illustrating the boiling-point elevation and freezing-point depression of aqueous solutions. The dashed curves pertain to the solution, and the solid curves to the pure solvent. As you can see, the boiling point of the solution is higher than that of water, and the freezing point of the solution is lower than that of water.*

where m is the molality of the solution and K_b is the *molal boiling-point elevation constant.* The units of K_b are °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.

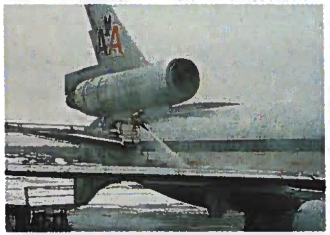
Table 12.2 lists values of K_b for several common solvents. Using the boiling-point elevation constant for water and Equation (12.6), you can see that if the molality of an aqueous solution is 1.00 m, the boiling point will be 100.52°C.

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 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*** **(ΔT_f)** is defined as *the freezing point of the pure solvent (T_f°) minus the freezing point of the solution (T_f):*

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



De-icing of airplanes is based on freezing-point depression.

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

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

*Measured at 1 atm.

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

$$\Delta T_f \propto m$$

$$\boxed{\Delta T_f = K_f m} \qquad (1[illegible])$$

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 (CH_3OH), 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.

In cold climate regions, antifreeze must be used in car radiators in winter.

Example 12.8

Ethylene glycol (EG), $CH_2(OH)CH_2(OH)$, 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.

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

$$\underset{\nearrow \text{ want to calculate}}{\Delta T_f} = \overset{\text{constant} \swarrow}{\underset{\nwarrow \text{ need to find}}{K_f m}}$$

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:

$$651\ \cancel{\text{g EG}} \times \frac{1\ \text{mol EG}}{62.07\ \cancel{\text{g EG}}} = 10.5\ \text{mol EG}$$

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

$$= \frac{10.5\ \text{mol EG}}{2.505\ \text{kg}\ H_2O} = 4.19\ \text{mol EG/kg}\ H_2O$$

$$= 4.19\ m$$

(Continued)

From Equation (12.7) and Table 12.2 we write

$$\begin{aligned}\Delta T_f &= K_f m\\ &= (1.86°\text{C}/m)(4.19\ m)\\ &= 7.79°\text{C}\end{aligned}$$

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

$$\begin{aligned}\Delta T_b &= K_b m\\ &= (0.52°\text{C}/m)(4.19\ m)\\ &= 2.2°\text{C}\end{aligned}$$

Because the solution will boil at (100 + 2.2)°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.

Similar problems: 12.58, 12.61.

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

Osmotic Pressure

Animation:
Osmosis
ARIS

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*** ($\boldsymbol{\pi}$) 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.

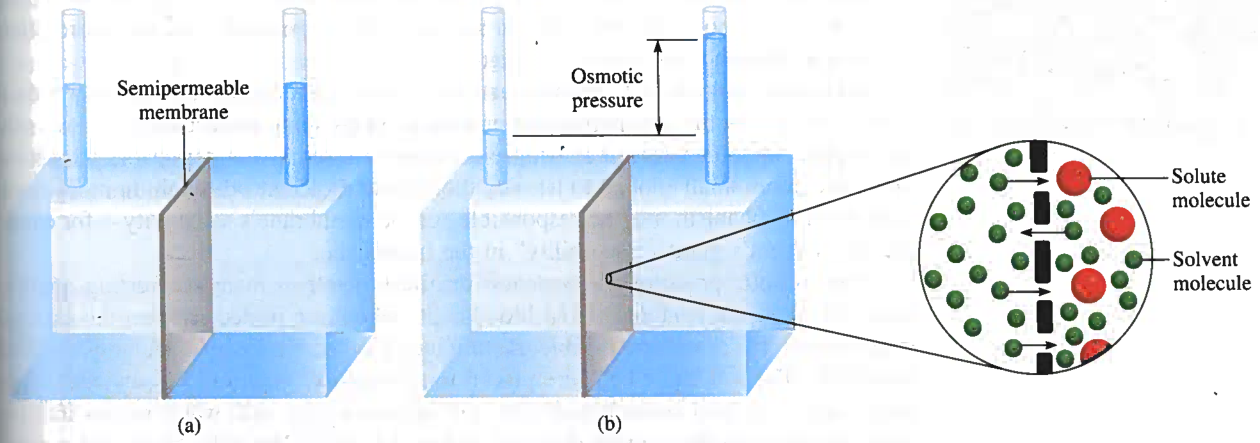
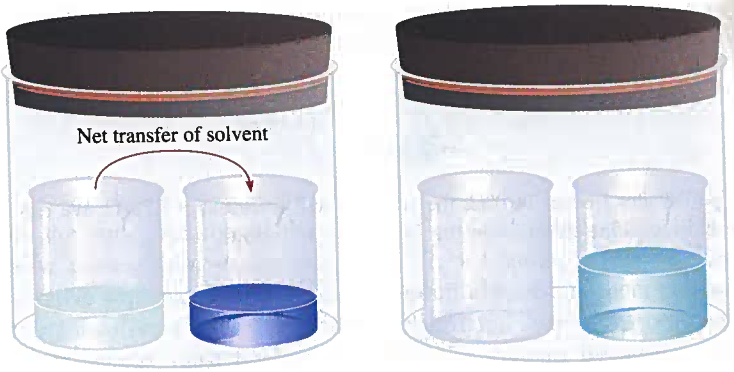


Figure 12.11 *Osmotic pressure. (a) The levels of the pure solvent (left) and of the solution (right) are equal at the start. (b) During osmosis, the level on the solution side rises as a result of the net flow of solvent from left to right. The osmotic pressure is equal to the hydrostatic pressure exerted by the column of fluid in the right tube at equilibrium. Basically the same effect occurs when the pure solvent is replaced by a more dilute solution than that on the right.*

Figure 12.12 *(a) Unequal vapor pressures inside the container lead to a net transfer of water from the left beaker (which contains pure water) to the right one (which contains a solution). (b) At equilibrium, all the water in the left beaker has been transferred to the right beaker. This driving force for solvent transfer is analogous to the osmotic phenomenon that is shown in Figure 12.11.*



(a) (b)

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

$$\pi = MRT \qquad (12.8)$$

where M is the molarity of solution, R is the gas constant (0.0821 L · atm/K · mol), and T is the absolute temperature. The osmotic pressure, π, 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

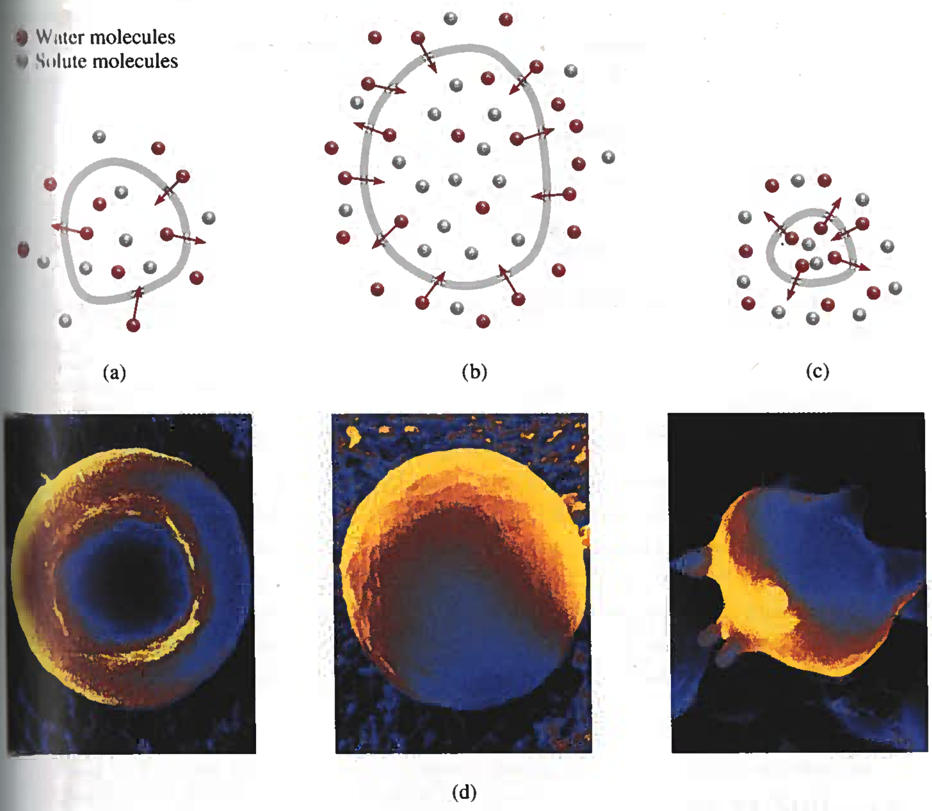


Figure 12.13 *A cell in (a) an isotonic solution, (b) a hypotonic solution, and (c) a hypertonic solution. The cell remains unchanged in (a), swells in (b), and shrinks in (c). (d) From left to right: a red blood cell in an isotonic solution, in a hypotonic solution, and in a hypertonic solution.*

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.

California redwoods.

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 ($C_{12}H_{22}O_{11}$) 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?

(Continued)

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

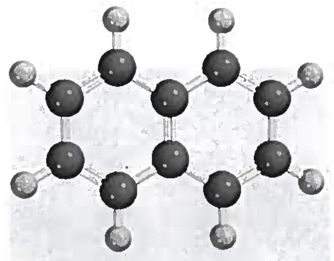
$$\begin{aligned} \pi &= MRT \\ M &= \frac{\pi}{RT} = \frac{30.0 \text{ atm}}{(0.0821 \text{ L}\cdot\text{atm/K}\cdot\text{mol})(298 \text{ K})} \\ &= 1.23 \text{ mol/L} \\ &= \boxed{1.23\ M} \end{aligned}$$

Similar problem: 12.65.

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

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.



$C_{10}H_8$

Example 12.10

A 7.85-g sample of a compound with the empirical formula C_5H_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

$$\text{freezing-point depression} \longrightarrow \text{molality} \longrightarrow \text{number of moles} \longrightarrow \text{molar mass}$$

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

$$\text{molality} = \frac{\Delta T_f}{K_f} = \frac{1.05°\text{C}}{5.12°\text{C}/m} = 0.205\ m$$

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

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

(Continued)

Thus, the molar mass of the solute is

$$\begin{aligned}\text{molar mass} &= \frac{\text{grams of compound}}{\text{moles of compound}}\\ &= \frac{7.85\text{ g}}{0.0617\text{ mol}} = 127\text{ g/mol}\end{aligned}$$

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 $(C_5H_4)_2$ or $C_{10}H_8$ (naphthalene).

Similar problem: 12.59.

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 π and temperature?

Solution The sequence of conversions is as follows:

$$\text{osmotic pressure} \longrightarrow \text{molarity} \longrightarrow \text{number of moles} \longrightarrow \text{molar mass}$$

First we calculate the molarity using Equation (12.8)

$$\begin{aligned}\pi &= MRT\\ M &= \frac{\pi}{RT}\\ &= \frac{10.0\text{ mmHg} \times \dfrac{1\text{ atm}}{760\text{ mmHg}}}{(0.0821\text{ L}\cdot\text{atm/K}\cdot\text{mol})(298\text{ K})}\\ &= 5.38 \times 10^{-4}\,M\end{aligned}$$

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

$$\begin{aligned}\text{moles of Hb} &= \frac{\text{mass of Hb}}{\text{molar mass of Hb}}\\ \text{molar mass of Hb} &= \frac{\text{mass of Hb}}{\text{moles of Hb}}\\ &= \frac{35.0\text{ g}}{5.38 \times 10^{-4}\text{ mol}}\\ &= 6.51 \times 10^{4}\text{ g/mol}\end{aligned}$$

Similar problems: 12.66, 12.68.

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.

The density of mercury is 13.6 g/mL. Therefore, 10 mmHg corresponding to a column of water 13.6 cm in height.

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

$$\begin{aligned}\Delta T_f &= (1.86^\circ\text{C}/m)(5.38 \times 10^{-4}\,m)\\ &= 1.00 \times 10^{-3}\,^\circ\text{C}\end{aligned}$$

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 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

Interactivity:
Test Solution with Electrolytes
ARIS, Interactives

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 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

$$i = \frac{\text{actual number of particles in soln after dissociation}}{\text{number of formula units initially dissolved in soln}} \tag{12.9}$$

Every unit of NaCl or KNO_3 that dissociates yields two ions ($i = 2$); every unit of Na_2SO_4 or $MgCl_2$ that dissociates produces three ions ($i = 3$).

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_2SO_4 and $CaCl_2$, i should be 3. Consequently, the equations for colligative properties must be modified as

$$\Delta T_b = iK_bm \tag{12.10}$$

$$\Delta T_f = iK_fm \tag{12.11}$$

$$\pi = iMRT \tag{12.12}$$

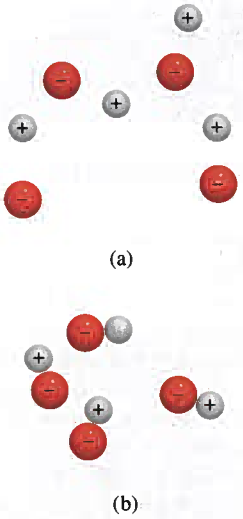
In reality, the colligative properties of electrolyte solutions are usually smaller than anticipated because at higher concentrations, electrostatic forces come into play.

[†] 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

Electrolyte	*i* (Measured)	*i* (Calculated)
Sucrose*	1.0	1.0
HCl	1.9	2.0
NaCl	1.9	2.0
$MgSO_4$	1.3	2.0
$MgCl_2$	2.7	3.0
$FeCl_3$	3.4	4.0

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


(a)

(b)

Figure 12.14 *(a) Free ions and (b) ion pairs in solution. Such an ion pair bears no net charge and therefore cannot conduct electricity in solution.*

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.

As Example 12.12 shows, the van't Hoff factor can be determined from colligative properties measurements.

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

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

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.

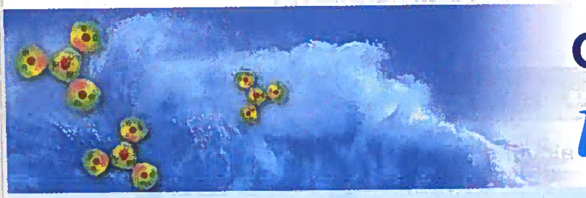
Solution From Equation (12.12) we have

$$\begin{aligned} i &= \frac{\pi}{MRT} \\ &= \frac{0.465\ \text{atm}}{(0.010\ M)(0.0821\ \text{L}\cdot\text{atm/K}\cdot\text{mol})(298\ \text{K})} \\ &= \boxed{1.90} \end{aligned}$$

Similar problem: 12.81.

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.

The Chemistry in Action essay on p. 530 describes three physical techniques for obtaining the pure solvent (water) from a solution (seawater).



CHEMISTRY *in Action*

Desalination

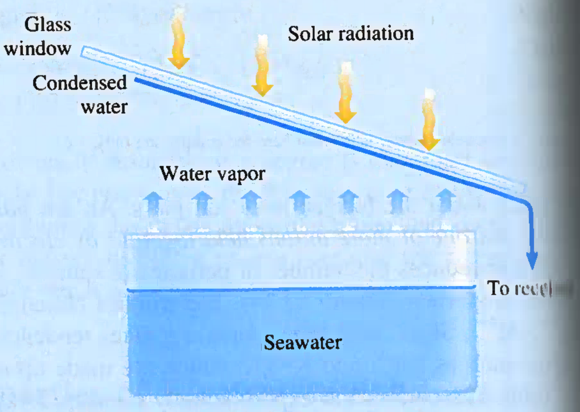
Over the centuries, scientists have sought ways of removing salts from seawater, a process called *desalination,* to augment the supply of fresh water. The ocean is an enormous and extremely complex aqueous solution. There are about 1.5×10^{21} L of seawater in the ocean, of which 3.5 percent (by mass) is dissolved material. The accompanying table lists the concentrations of seven substances that together comprise more than 99 percent of the dissolved constituents of ocean water. In an age when astronauts have landed on the moon and spectacular advances in science and medicine have been made, desalination may seem a simple enough objective. However, the technology is very costly. It is an interesting paradox that in our technological society, accomplishing something simple like desalination at a socially acceptable cost is often as difficult as achieving something complex, such as sending an astronaut to the moon.

Composition of Seawater

Ions	g/kg of Seawater
Chloride (Cl^-)	19.35
Sodium (Na^+)	10.76
Sulfate (SO_4^{2-})	2.71
Magnesium (Mg^{2+})	1.29
Calcium (Ca^{2+})	0.41
Potassium (K^+)	0.39
Bicarbonate (HCO_3^-)	0.14

Distillation

The oldest method of desalination, distillation, accounts for more than 90 percent of the approximately 500 million gallons per day capacity of the desalination systems currently in operation worldwide. The process involves vaporizing seawater and then condensing the pure water vapor. Most distillation systems use heat energy to do this. Attempts to reduce the cost of distillation include the use of solar radiation as the energy source.



A solar still for desalinating seawater.

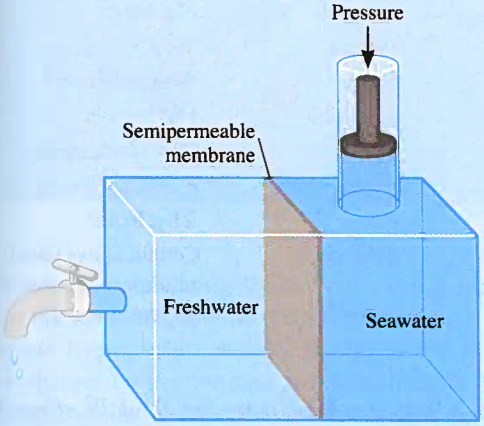
This approach is attractive because sunshine is normally mo intense in arid lands, where the need for water is also gre However, despite intensive research and development eff several engineering problems persist, and "solar stills" do n yet operate on a large scale.

Freezing

Desalination by freezing has also been under development f a number of years, but it has not yet become commercially fe sible. This method is based on the fact that when an aque solution (in this case, seawater) freezes, the solid that separa from solution is almost pure water. Thus, ice crystals fro frozen seawater at desalination plants could be rinsed off an thawed to provide usable water. The main advantage of free ing is its low energy consumption, as compared with distill tion. The heat of vaporization of water is 40.79 kJ/m whereas that of fusion is only 6.01 kJ/mol. Some scienti have even suggested that a partial solution to the water shorta in California would be to tow icebergs from the Arctic dow to the West Coast. The major disadvantages of freezing a

12.8 Colloids

The solutions discussed so far are true homogeneous mixtures. Now consider wh happens if we add fine sand to a beaker of water and stir. The sand particles are su pended at first but then gradually settle to the bottom. This is an example of a het erogeneous mixture. Between these two extremes is an intermediate state called colloidal suspension, or simply, a colloid. A ***colloid*** is *a dispersion of particles o one substance (the dispersed phase) throughout a dispersing medium made o another substance.* Colloidal particles are much larger than the normal solu



Reverse osmosis. By applying enough pressure on the solution side, freshwater can be made to flow from right to left. The semipermeable membrane allows the passage of water molecules but not of dissolved ions.

associated with the slow growth of ice crystals and with washing the salt deposits off the crystals.

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.

A small reverse-osmosis apparatus enables a person to obtain drinkable freshwater from seawater.

molecules; they range from 1×10^3 pm to 1×10^6 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.

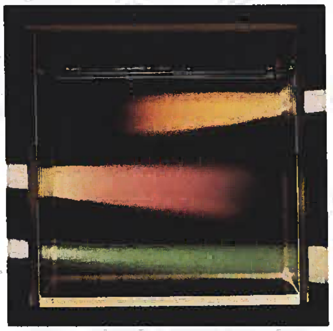


Figure 12.15 *Three beams of white light, passing through a colloid of sulfur particles in water, change to orange, pink, and bluish-green. The colors produced depend on the size of the particles and also on the position of the viewer. The smaller the dispersed particles, the shorter (and bluer) the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

TABLE 12.4 Types of Colloids

Dispersing Medium	Dispersed Phase	Name	Example
Gas	Liquid	Aerosol	Fog, mist
Gas	Solid	Aerosol	Smoke
Liquid	Gas	Foam	Whipped cream
Liquid	Liquid	Emulsion	Mayonnaise
Liquid	Solid	Sol	Milk of magnesia
Solid	Gas	Foam	Plastic foams
Solid	Liquid	Gel	Jelly, butter
Solid	Solid	Solid sol	Certain alloys (steel), gemstones (glass with dispersed metal)

One way to distinguish a solution from a colloid is by the *Tyndall*[†] *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).

Figure 12.16 *Sunlight scattered by dust particles in the air.*

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 interact

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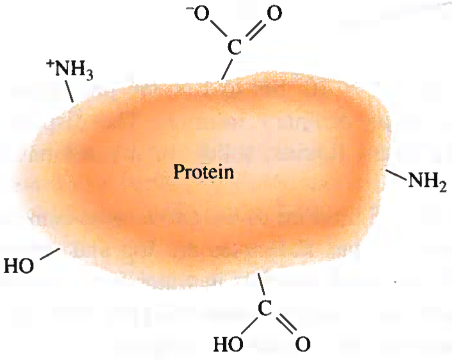
[†] John Tyndall (1820–1893). Irish physicist. Tyndall did important work in magnetism, and explained glacier motion.

Figure 12.17 *Hydrophilic groups on the surface of a large molecule such as protein stabilize the molecule in water. Note that all these groups can form hydrogen bonds with water.*



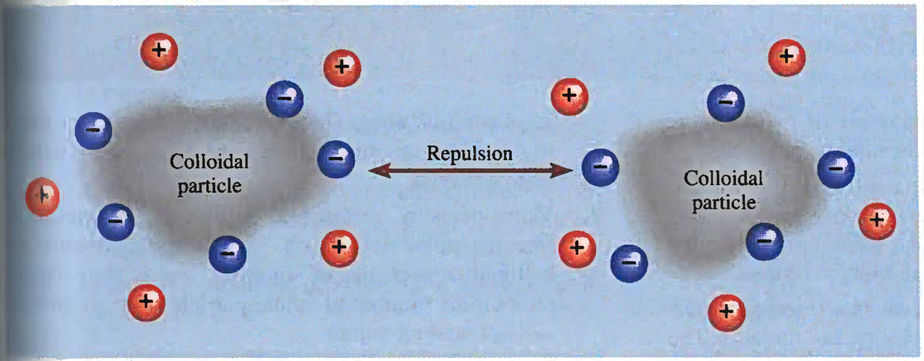
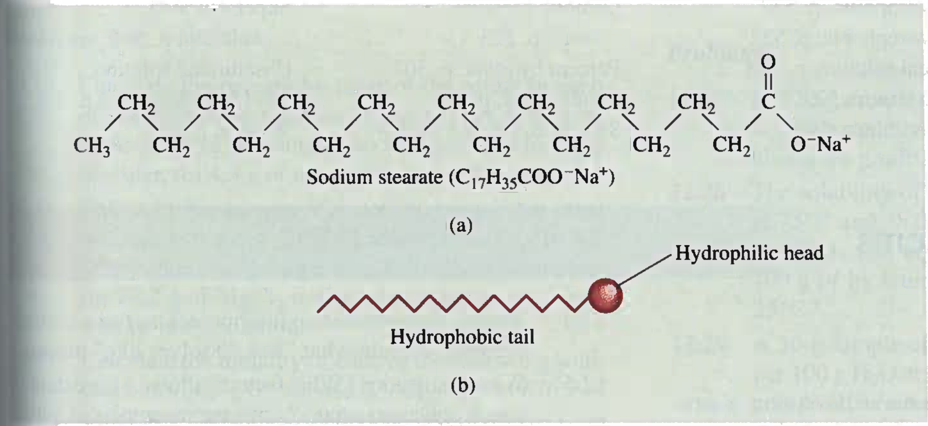


Figure 12.18 *Diagram showing the stabilization of hydrophobic colloids. Negative ions are adsorbed onto the surface and the repulsion between like charges prevents the clumping of the particles.*

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 this way. When the fresh water 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—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 stabilized in water because the exterior portion is now largely hydrophilic. This is how greasy substances are removed by the action of soap.

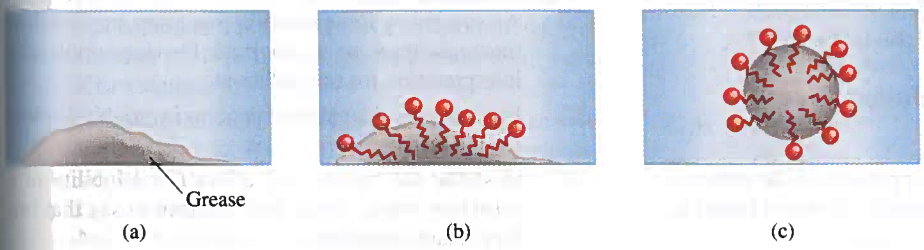


Sodium stearate ($C_{17}H_{35}COO^-Na^+$)

(a)

(b)

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



(a) (b) (c)

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.*

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_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 1×10^3 pm to 1×10^6 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 (ΔT_b), p. 520
Colligative properties, p. 515
Colloid, p. 530
Crystallization, p. 504
Fractional crystallization, p. 512
Fractional distillation, p. 519
Freezing-point depression (ΔT_f), p. 521
Henry's law, p. 513
Hydrophilic, p. 532
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Ideal solution, p. 518
Ion pair, p. 529
Miscible, p. 506
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Supersaturated solution, p. 504
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Volatile, p. 518

Questions and Problems

Types of Solutions

Review Questions

12.1 Distinguish between an unsaturated solution, a saturated solution, and a supersaturated solution.

12.2 From which type of solution listed in Question 12.1 does crystallization or precipitation occur? How does a crystal differ from a precipitate?

A Molecular View of the Solution Process

Review Questions

12.3 Briefly describe the solution process at the molecular level. Use the dissolution of a solid in a liquid as an example.

12.4 Basing your answer on intermolecular force considerations, explain what "like dissolves like" means.

12.5 What is solvation? What factors influence the extent to which solvation occurs? Give two examples of solvation; include one that involves ion-dipole interaction and one in which dispersion forces come into play.

12.6 As you know, some solution processes are endothermic and others are exothermic. Provide a molecular interpretation for the difference.

12.7 Explain why the solution process invariably leads to an increase in disorder.

12.8 Describe the factors that affect the solubility of a solid in a liquid. What does it mean to say that two liquids are miscible?

Problems

12.9 Why is naphthalene ($C_{10}H_8$) more soluble than CsF in benzene?

12.10 Explain why ethanol (C_2H_5OH) is not soluble in cyclohexane (C_6H_{12}).

12.11 Arrange the following compounds in order of increasing solubility in water: O_2, LiCl, Br_2, methanol (CH_3OH).

12.12 Explain the variations in solubility in water of the alcohols listed here:

Compound	Solubility in Water (g/100 g) at 20°C
CH_3OH	∞
CH_3CH_2OH	∞
$CH_3CH_2CH_2OH$	∞
$CH_3CH_2CH_2CH_2OH$	9
$CH_3CH_2CH_2CH_2CH_2OH$	2.7

(*Note:* ∞ means that the alcohol and water are completely miscible in all proportions.)

Concentration Units

Review Questions

12.13 Define the following concentration terms and give their units: percent by mass, mole fraction, molarity, molality. Compare their advantages and disadvantages.

12.14 Outline the steps required for conversion between molarity, molality, and percent by mass.

Problems

12.15 Calculate the percent by mass of the solute in each of the following aqueous solutions: (a) 5.50 g of NaBr in 78.2 g of solution, (b) 31.0 g of KCl in 152 g of water, (c) 4.5 g of toluene in 29 g of benzene.

12.16 Calculate the amount of water (in grams) that must be added to (a) 5.00 g of urea $(NH_2)_2CO$ in the preparation of a 16.2 percent by mass solution, and (b) 26.2 g of $MgCl_2$ in the preparation of a 1.5 percent by mass solution.

12.17 Calculate the molality of each of the following solutions: (a) 14.3 g of sucrose ($C_{12}H_{22}O_{11}$) in 676 g of water, (b) 7.20 moles of ethylene glycol ($C_2H_6O_2$) in 3546 g of water.

12.18 Calculate the molality of each of the following aqueous solutions: (a) 2.50 *M* NaCl solution (density of solution = 1.08 g/mL), (b) 48.2 percent by mass KBr solution.

12.19 Calculate the molalities of the following aqueous solutions: (a) 1.22 *M* sugar ($C_{12}H_{22}O_{11}$) solution (density of solution = 1.12 g/mL), (b) 0.87 *M* NaOH solution (density of solution = 1.04 g/mL), (c) 5.24 *M* $NaHCO_3$ solution (density of solution = 1.19 g/mL).

12.20 For dilute aqueous solutions in which the density of the solution is roughly equal to that of the pure solvent, the molarity of the solution is equal to its molality. Show that this statement is correct for a 0.010 *M* aqueous urea $(NH_2)_2CO$ solution.

12.21 The alcohol content of hard liquor is normally given in terms of the "proof," which is defined as twice the percentage by volume of ethanol (C_2H_5OH) present. Calculate the number of grams of alcohol present in 1.00 L of 75-proof gin. The density of ethanol is 0.798 g/mL.

12.22 The concentrated sulfuric acid we use in the laboratory is 98.0 percent H_2SO_4 by mass. Calculate the molality and molarity of the acid solution. The density of the solution is 1.83 g/mL.

12.23 Calculate the molarity and the molality of an NH_3 solution made up of 30.0 g of NH_3 in 70.0 g of water. The density of the solution is 0.982 g/mL.

12.24 The density of an aqueous solution containing 10.0 percent of ethanol (C_2H_5OH) by mass is 0.984 g/mL. (a) Calculate the molality of this solution. (b) Calculate its molarity. (c) What volume of the solution would contain 0.125 mole of ethanol?

The Effect of Temperature on Solubility

Review Questions

12.25 How do the solubilities of most ionic compounds in water change with temperature? With pressure?

12.26 Describe the fractional crystallization process and its application.

Problems

12.27 A 3.20-g sample of a salt dissolves in 9.10 g of water to give a saturated solution at 25°C. What is the solubility (in g salt/100 g of H_2O) of the salt?

12.28 The solubility of KNO_3 is 155 g per 100 g of water at 75°C and 38.0 g at 25°C. What mass (in grams) of KNO_3 will crystallize out of solution if exactly 100 g of its saturated solution at 75°C is cooled to 25°C?

12.29 A 50-g sample of impure $KClO_3$ (solubility = 7.1 g per 100 g H_2O at 20°C) is contaminated with 10 percent of KCl (solubility = 25.5 g per 100 g of H_2O at 20°C). Calculate the minimum quantity of 20°C water needed to dissolve all the KCl from the sample. How much $KClO_3$ will be left after this treatment? (Assume that the solubilities are unaffected by the presence of the other compound.)

Gas Solubility

Review Questions

12.30 Discuss the factors that influence the solubility of a gas in a liquid.

12.31 What is thermal pollution? Why is it harmful to aquatic life?

12.32 What is Henry's law? Define each term in the equation, and give its units. How would you account for the law in terms of the kinetic molecular theory of gases? Give two exceptions to Henry's law.

12.33 A student is observing two beakers of water. One beaker is heated to 30°C, and the other is heated to 100°C. In each case, bubbles form in the water. Are these bubbles of the same origin? Explain.

12.34 A man bought a goldfish in a pet shop. Upon returning home, he put the goldfish in a bowl of recently boiled water that had been cooled quickly. A few minutes later the fish was found dead. Explain what happened to the fish.

Problems

12.35 A beaker of water is initially saturated with dissolved air. Explain what happens when He gas at 1 atm is bubbled through the solution for a long time.

12.36 A miner working 260 m below sea level opened a carbonated soft drink during a lunch break. To his surprise, the soft drink tasted rather "flat." Shortly afterward, the miner took an elevator to the surface. During the trip up, he could not stop belching. Why?

12.37 The solubility of CO_2 in water at 25°C and 1 atm is 0.034 mol/L. What is its solubility under atmospheric conditions? (The partial pressure of CO_2 in air is 0.0003 atm.) Assume that CO_2 obeys Henry's law.

12.38 The solubility of N_2 in blood at 37°C and at a partial pressure of 0.80 atm is 5.6×10^{-4} mol/L. A deep-sea diver breathes compressed air with the partial pressure of N_2 equal to 4.0 atm. Assume that the total volume of blood in the body is 5.0 L. Calculate the amount of N_2 gas released (in liters at 37°C and 1 atm) when the diver returns to the surface of the water, where the partial pressure of N_2 is 0.80 atm.

Colligative Properties of Nonelectrolyte Solutions

Review Questions

12.39 What are colligative properties? What is the meaning of the word "colligative" in this context?

12.40 Give two examples of (a) a volatile liquid and (b) a nonvolatile liquid.

12.41 Write the equation representing Raoult's law, and express it in words.

12.42 Use a solution of benzene in toluene to explain what is meant by an ideal solution.

12.43 Write the equations relating boiling-point elevation and freezing-point depression to the concentration of the solution. Define all the terms, and give their units.

12.44 How is vapor-pressure lowering related to a rise in the boiling point of a solution?

12.45 Use a phase diagram to show the difference in fre ing points and boiling points between an aqu urea solution and pure water.

12.46 What is osmosis? What is a semipermeable membrane?

12.47 Write the equation relating osmotic pressure to the concentration of a solution. Define all the terms and specify their units.

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

12.49 Explain why molality is used for boiling-point elevation and freezing-point depression calculations and molarity is used in osmotic pressure calculations.

12.50 Describe how you would use freezing-point depression and osmotic pressure measurements to determine the molar mass of a compound. Why are boiling-point elevation and vapor-pressure lowering normally not used for this purpose?

Problems

12.51 A solution is prepared by dissolving 396 g of sucrose ($C_{12}H_{22}O_{11}$) in 624 g of water. What is the vapor pressure of this solution at 30°C? (The vapor pressure of water is 31.8 mmHg at 30°C.)

12.52 How many grams of sucrose ($C_{12}H_{22}O_{11}$) must be added to 552 g of water to give a solution with a vapor pressure 2.0 mmHg less than that of pure water at 20°C? (The vapor pressure of water at 20°C is 17.5 mmHg.)

12.53 The vapor pressure of benzene is 100.0 mmHg at 26.1°C. Calculate the vapor pressure of a solution containing 24.6 g of camphor ($C_{10}H_{16}O$) dissolved in 98.5 g of benzene. (Camphor is a low-volatility solid.)

12.54 The vapor pressures of ethanol (C_2H_5OH) and 1-propanol (C_3H_7OH) at 35°C are 100 mmHg and 37.6 mmHg, respectively. Assume ideal behavior and calculate the partial pressures of ethanol and 1-propanol at 35°C over a solution of ethanol in 1-propanol, in which the mole fraction of ethanol is 0.300.

12.55 The vapor pressure of ethanol (C_2H_5OH) at 20°C is 44 mmHg, and the vapor pressure of methanol (CH_3OH) at the same temperature is 94 mmHg. A mixture of 30.0 g of methanol and 45.0 g of ethanol is prepared (and can be assumed to behave as an ideal solution). (a) Calculate the vapor pressure of methanol and ethanol above this solution at 20°C. (b) Calculate the mole fraction of methanol and ethanol in the vapor above this solution at 20°C. (c) Suggest a method for separating the two components of the solution.

12.56 How many grams of urea [$(NH_2)_2CO$] must be added to 450 g of water to give a solution with vapor pressure 2.50 mmHg less than that of pure water at 30°C? (The vapor pressure of water at 30°C is 31.8 mmHg.)

12.57 What are the boiling point and freezing point of a 2.47 *m* solution of naphthalene in benzene? (The boiling point and freezing point of benzene are 80.1°C and 5.5°C, respectively.)

12.58 An aqueous solution contains the amino acid glycine (NH_2CH_2COOH). Assuming that the acid does not ionize in water, calculate the molality of the solution if it freezes at −1.1°C.

12.59 Pheromones are compounds secreted by the females of many insect species to attract males. One of these compounds contains 80.78 percent C, 13.56 percent H, and 5.66 percent O. A solution of 1.00 g of this pheromone in 8.50 g of benzene freezes at 3.37°C. What are the molecular formula and molar mass of the compound? (The normal freezing point of pure benzene is 5.50°C.)

12.60 The elemental analysis of an organic solid extracted from gum arabic (a gummy substance used in adhesives, inks, and pharmaceuticals) showed that it contained 40.0 percent C, 6.7 percent H, and 53.3 percent O. A solution of 0.650 g of the solid in 27.8 g of the solvent diphenyl gave a freezing-point depression of 1.56°C. Calculate the molar mass and molecular formula of the solid. (K_f for diphenyl is 8.00°C/*m*.)

12.61 How many liters of the antifreeze ethylene glycol $[CH_2(OH)CH_2(OH)]$ would you add to a car radiator containing 6.50 L of water if the coldest winter temperature in your area is −20°C? Calculate the boiling point of this water-ethylene glycol mixture. (The density of ethylene glycol is 1.11 g/mL.)

12.62 A solution is prepared by condensing 4.00 L of a gas, measured at 27°C and 748 mmHg pressure, into 58.0 g of benzene. Calculate the freezing point of this solution.

12.63 The molar mass of benzoic acid (C_6H_5COOH) determined by measuring the freezing-point depression in benzene is twice what we would expect for the molecular formula, $C_7H_6O_2$. Explain this apparent anomaly.

12.64 A solution of 2.50 g of a compound having the empirical formula C_6H_5P in 25.0 g of benzene is observed to freeze at 4.3°C. Calculate the molar mass of the solute and its molecular formula.

12.65 What is the osmotic pressure (in atm) of a 1.36 *M* aqueous solution of urea $[(NH_2)_2CO]$ at 22.0°C?

12.66 A solution containing 0.8330 g of a polymer of unknown structure in 170.0 mL of an organic solvent was found to have an osmotic pressure of 5.20 mmHg at 25°C. Determine the molar mass of the polymer.

12.67 A quantity of 7.480 g of an organic compound is dissolved in water to make 300.0 mL of solution. The solution has an osmotic pressure of 1.43 atm at 27°C. The analysis of this compound shows that it contains 41.8 percent C, 4.7 percent H, 37.3 percent O, and 16.3 percent N. Calculate the molecular formula of the compound.

12.68 A solution of 6.85 g of a carbohydrate in 100.0 g of water has a density of 1.024 g/mL and an osmotic pressure of 4.61 atm at 20.0°C. Calculate the molar mass of the carbohydrate.

Colligative Properties of Electrolyte Solutions

Review Questions

12.69 Why is the discussion of the colligative properties of electrolyte solutions more involved than that of nonelectrolyte solutions?

12.70 What are ion pairs? What effect does ion-pair formation have on the colligative properties of a solution? How does the ease of ion-pair formation depend on (a) charges on the ions, (b) size of the ions, (c) nature of the solvent (polar versus nonpolar), (d) concentration?

12.71 Indicate which compound in each of the following pairs is more likely to form ion pairs in water: (a) NaCl or Na_2SO_4, (b) $MgCl_2$ or $MgSO_4$, (c) LiBr or KBr.

12.72 What is the van't Hoff factor? What information does it provide?

Problems

12.73 Which of the following aqueous solutions has (a) the higher boiling point, (b) the higher freezing point, and (c) the lower vapor pressure: 0.35 *m* $CaCl_2$ or 0.90 *m* urea? Explain. Assume $CaCl_2$ to undergo complete dissociation.

12.74 Consider two aqueous solutions, one of sucrose ($C_{12}H_{22}O_{11}$) and the other of nitric acid (HNO_3). Both solutions freeze at −1.5°C. What other properties do these solutions have in common?

12.75 Arrange the following solutions in order of decreasing freezing point: 0.10 *m* Na_3PO_4, 0.35 *m* NaCl, 0.20 *m* $MgCl_2$, 0.15 *m* $C_6H_{12}O_6$, 0.15 *m* CH_3COOH.

12.76 Arrange the following aqueous solutions in order of decreasing freezing point, and explain your reasoning: 0.50 *m* HCl, 0.50 *m* glucose, 0.50 *m* acetic acid.

12.77 What are the normal freezing points and boiling points of the following solutions? (a) 21.2 g NaCl in 135 mL of water and (b) 15.4 g of urea in 66.7 mL of water

12.78 At 25°C the vapor pressure of pure water is 23.76 mmHg and that of seawater is 22.98 mmHg. Assuming that seawater contains only NaCl, estimate its molal concentration.

12.79 Both NaCl and $CaCl_2$ are used to melt ice on roads and sidewalks in winter. What advantages do these substances have over sucrose or urea in lowering the freezing point of water?

12.80 A 0.86 percent by mass solution of NaCl is called "physiological saline" because its osmotic pressure is equal to that of the solution in blood cells. Calculate the osmotic pressure of this solution at normal body temperature (37°C). Note that the density of the saline solution is 1.005 g/mL.

12.81 The osmotic pressure of 0.010 *M* solutions of $CaCl_2$ and urea at 25°C are 0.605 atm and 0.245 atm, respectively. Calculate the van't Hoff factor for the $CaCl_2$ solution.

12.82 Calculate the osmotic pressure of a 0.0500 *M* $MgSO_4$ solution at 25°C. (*Hint:* See Table 12.3.)

Colloids

Review Questions

12.83 What are colloids? Referring to Table 12.4, why is there no colloid in which both the dispersed phase and the dispersing medium are gases?

12.84 Describe how hydrophilic and hydrophobic colloids are stabilized in water.

Additional Problems

12.85 Lysozyme is an enzyme that cleaves bacterial cell walls. A sample of lysozyme extracted from egg white has a molar mass of 13,930 g. A quantity of 0.100 g of this enzyme is dissolved in 150 g of water at 25°C. Calculate the vapor-pressure lowering, the depression in freezing point, the elevation in boiling point, and the osmotic pressure of this solution. (The vapor pressure of water at 25°C is 23.76 mmHg.)

12.86 Solutions A and B have osmotic pressures of 2.4 atm and 4.6 atm, respectively, at a certain temperature. What is the osmotic pressure of a solution prepared by mixing equal volumes of A and B at the same temperature?

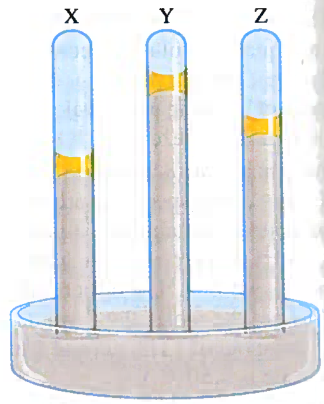
12.87 A cucumber placed in concentrated brine (salt water) shrivels into a pickle. Explain.

12.88 Two liquids A and B have vapor pressures of 76 mmHg and 132 mmHg, respectively, at 25°C. What is the total vapor pressure of the ideal solution made up of (a) 1.00 mole of A and 1.00 mole of B and (b) 2.00 moles of A and 5.00 moles of B?

12.89 Calculate the van't Hoff factor of Na_3PO_4 in a 0.40 *m* solution whose freezing point is −2.6°C.

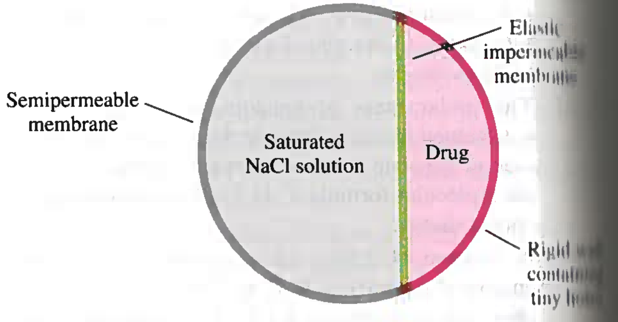
12.90 A 262-mL sample of a sugar solution containing 1.22 g of the sugar has an osmotic pressure of 30.3 mmHg at 35°C. What is the molar mass of the sugar?

12.91 Consider the three mercury manometers shown in the top right column. One of them has 1 mL of water on top of the mercury, another has 1 mL of a 1 *m* urea solution on top of the mercury, third one has 1 mL of a 1 *m* NaCl solution on top of the mercury. Which of these solu in the tube labeled X, which is in Y, and wh in Z?



12.92 A forensic chemist is given a white powder for sis. She dissolves 0.50 g of the substance in benzene. The solution freezes at 3.9°C. chemist conclude that the compound is ($C_{17}H_{21}NO_4$)? What assumptions are made analysis?

12.93 "Time-release" drugs have the advantage leasing the drug to the body at a constant that the drug concentration at any time is high as to have harmful side effects or to be ineffective. A schematic diagram of that works on this basis is shown below. how it works.



12.94 A solution of 1.00 g of anhydrous aluminum ride, $AlCl_3$, in 50.0 g of water freezes at −1.1 Does the molar mass determined from this point agree with that calculated from the form Why?

12.95 Explain why reverse osmosis is (theoretic more desirable as a desalination method than tillation or freezing. What minimum pressure be applied to seawater at 25°C in order for reverse osmosis to occur? (Treat seawater as a 0.70 *M* NaCl solution.)

12.96 What masses of sodium chloride, magnesium chloride, sodium sulfate, calcium chloride, potassium chloride, and sodium bicarbonate are needed to produce 1 L of artificial seawater for an aquarium? The required ionic concentrations are $[Na^+] = 2.56\ M$, $[K^+] = 0.0090\ M$, $[Mg^{2+}] = 0.054\ M$, $[Ca^{2+}] = 0.010\ M$, $[HCO_3^-] = 0.0020\ M$, $[Cl^-] = 2.60\ M$, $[SO_4^{2-}] = 0.051\ M$.

12.97 A protein has been isolated as a salt with the formula $Na_{20}P$ (this notation means that there are 20 Na^+ ions associated with a negatively charged protein P^{20-}). The osmotic pressure of a 10.0-mL solution containing 0.225 g of the protein is 0.257 atm at 25.0°C. (a) Calculate the molar mass of the protein from these data. (b) Calculate the actual molar mass of the protein.

12.98 A nonvolatile organic compound Z was used to make up two solutions. Solution A contains 5.00 g of Z dissolved in 100 g of water, and solution B contains 2.31 g of Z dissolved in 100 g of benzene. Solution A has a vapor pressure of 754.5 mmHg at the normal boiling point of water, and solution B has the same vapor pressure at the normal boiling point of benzene. Calculate the molar mass of Z in solutions A and B and account for the difference.

12.99 Hydrogen peroxide with a concentration of 3.0 percent (3.0 g of H_2O_2 in 100 mL of solution) is sold in drugstores for use as an antiseptic. For a 10.0-mL 3.0 percent H_2O_2 solution, calculate (a) the oxygen gas produced (in liters) at STP when the compound undergoes complete decomposition and (b) the ratio of the volume of O_2 collected to the initial volume of the H_2O_2 solution.

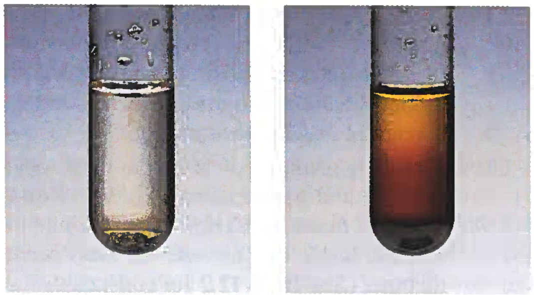
12.100 State which of the alcohols listed in Problem 12.12 you would expect to be the best solvent for each of the following substances, and explain why: (a) I_2, (b) KBr, (c) $CH_3CH_2CH_2CH_2CH_3$.

12.101 Before a carbonated beverage bottle is sealed, it is pressurized with a mixture of air and carbon dioxide. (a) Explain the effervescence that occurs when the cap of the bottle is removed. (b) What causes the fog to form near the mouth of the bottle right after the cap is removed?

12.102 Iodine (I_2) is only sparingly soluble in water (top left photo). Yet upon the addition of iodide ions (for example, from KI), iodine is converted to the triiodide ion, which readily dissolves (top right photo):

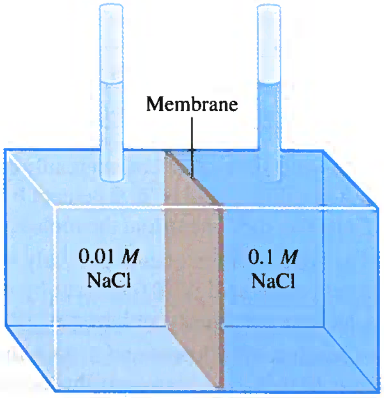
$$I_2(s) + I^-(aq) \rightleftharpoons I_3^-(aq)$$

Describe the change in solubility of I_2 in terms of the change in intermolecular forces.



12.103 Two beakers, one containing a 50-mL aqueous 1.0 *M* glucose solution and the other a 50-mL aqueous 2.0 *M* glucose solution, are placed under a tightly sealed bell jar at room temperature. What are the volumes in these two beakers at equilibrium?

12.104 In the apparatus shown below, what will happen if the membrane is (a) permeable to both water and the Na^+ and Cl^- ions, (b) permeable to water and Na^+ ions but not to Cl^- ions, (c) permeable to water but not to Na^+ and Cl^- ions?



12.105 Explain why it is essential that fluids used in intravenous injections have approximately the same osmotic pressure as blood.

12.106 Concentrated hydrochloric acid is usually available at a concentration of 37.7 percent by mass. What is its molar concentration? (The density of the solution is 1.19 g/mL.)

12.107 Explain each of the following statements: (a) The boiling point of seawater is higher than that of pure water. (b) Carbon dioxide escapes from the solution when the cap is removed from a carbonated soft-drink bottle. (c) Molal and molar concentrations of dilute aqueous solutions are approximately equal. (d) In discussing the colligative properties of a solution (other than osmotic pressure), it is preferable to express the concentration in units of molality rather than in molarity. (e) Methanol (b.p. 65°C) is useful as an antifreeze, but it should be removed from the car radiator during the summer season.

12.108 A mixture of NaCl and sucrose ($C_{12}H_{22}O_{11}$) of combined mass 10.2 g is dissolved in enough water to make up a 250 mL solution. The osmotic pressure of the solution is 7.32 atm at 23°C. Calculate the mass percent of NaCl in the mixture.

12.109 A 1.32-g sample of a mixture of cyclohexane (C_6H_{12}) and naphthalene ($C_{10}H_8$) is dissolved in 18.9 g of benzene (C_6H_6). The freezing point of the solution is 2.2°C. Calculate the mass percent of the mixture. (See Table 12.2 for constants.)

12.110 How does each of the following affect the solubility of an ionic compound? (a) lattice energy, (b) solvent (polar versus nonpolar), (c) enthalpies of hydration of cation and anion

12.111 A solution contains two volatile liquids A and B. Complete the following table, in which the symbol $\longleftrightarrow$ indicates attractive intermolecular forces.

Attractive Forces	Deviation from Raoult's Law	ΔH_{soln}
$A \longleftrightarrow A$, $B \longleftrightarrow B >$ $A \longleftrightarrow B$		
	Negative	
		Zero

12.112 The concentration of commercially available concentrated sulfuric acid is 98.0 percent by mass, or 18 *M*. Calculate the density and the molality of the solution.

12.113 The concentration of commercially available concentrated nitric acid is 70.0 percent by mass, or 15.9 *M*. Calculate the density and the molality of the solution.

12.114 A mixture of ethanol and 1-propanol behaves ideally at 36°C and is in equilibrium with its vapor. If the mole fraction of ethanol in the solution is 0.62, calculate its mole fraction in the vapor phase at this temperature. (The vapor pressures of pure ethanol and 1-propanol at 36°C are 108 mmHg and 40.0 mmHg, respectively.)

12.115 For ideal solutions, the volumes are additive. This means that if 5 mL of A and 5 mL of B form an ideal solution, the volume of the solution is 10 mL. Provide a molecular interpretation for this observation. When 500 mL of ethanol (C_2H_5OH) are mixed with 500 mL of water, the final volume is less than 1000 mL. Why?

12.116 Ammonia (NH_3) is very soluble in water, but nitrogen trichloride (NCl_3) is not. Explain.

12.117 Aluminum sulfate [$Al_2(SO_4)_3$] is sometimes used in municipal water treatment plants to remove undesirable particles. Explain how this process works.

12.118 Acetic acid is a weak acid that ionizes in solution as follows:

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

If the freezing point of a 0.106 m CH_3COOH
tion is −0.203°C, calculate the percent of the
that has undergone ionization.

12.119 Making mayonnaise involves beating oil into
droplets in water, in the presence of egg yolk. W
is the purpose of the egg yolk? (*Hint:* Egg yolk
tains lecithins, which are molecules with a
head and a long nonpolar hydrocarbon tail.)

12.120 Acetic acid is a polar molecule and can form h
gen bonds with water molecules. Therefore, it
high solubility in water. Yet acetic acid is also
ble in benzene (C_6H_6), a nonpolar solvent that
the ability to form hydrogen bonds. A solution of
of CH_3COOH in 80 g C_6H_6 has a freezing p
3.5°C. Calculate the molar mass of the solute
suggest what its structure might be. (*Hint:* A
acid molecules can form hydrogen bonds bet
themselves.)

12.121 A 2.6-L sample of water contains 192 μg of
Does this concentration of lead exceed the
limit of 0.050 ppm of lead per liter of drin
water? [*Hint:* 1 μg = 1×10^{-6} g. Parts per
lion (ppm) is defined as (mass of component
of solution) $\times 10^6$.]

12.122 Fishes in the Antarctic Ocean swim in water at
−2°C. (a) To prevent their blood from freez
what must be the concentration (in molality) of
blood? Is this a reasonable physiological conce
tion? (b) In recent years scientists have discove
special type of protein in these fishes' blood wh
although present in quite low concentra
($\leq 0.001\ m$), has the ability to prevent the bl
from freezing. Suggest a mechanism for its actio

12.123 As we know, if a soft drink can is shaken and
opened, the drink escapes violently. However
after shaking the can we tap it several times wi
metal spoon, no such "explosion" of the drink
curs. Why?

12.124 Why are ice cubes (for example, those you see in
trays in the freezer of a refrigerator) cloudy insid

12.125 Two beakers are placed in a closed container. Be
A initially contains 0.15 mole of naphtha
($C_{10}H_8$) in 100 g of benzene (C_6H_6) and beaker
initially contains 31 g of an unknown compo
dissolved in 100 g of benzene. At equilibri
beaker A is found to have lost 7.0 g of benze

Assuming ideal behavior, calculate the molar mass of the unknown compound. State any assumptions made.

12.126 At 27°C, the vapor pressure of pure water is 23.76 mmHg and that of an urea solution is 22.98 mmHg. Calculate the molality of solution.

12.127 An example of the positive deviation shown in Figure 12.8(a) is a solution made of acetone (CH_3COCH_3) and carbon disulfide (CS_2). (a) Draw Lewis structures of these molecules. Explain the deviation from ideal behavior in terms of intermolecular forces. (b) A solution composed of 0.60 mole of acetone and 0.40 mole of carbon disulfide has a vapor pressure of 615 mmHg at 35.2°C. What would be the vapor pressure if the solution behaved ideally? The vapor pressure of the pure solvents at the same temperature are: acetone: 349 mmHg; carbon disulfide: 501 mmHg. (c) Predict the sign of ΔH_{soln}.

12.128 Liquids A (molar mass 100 g/mol) and B (molar mass 110 g/mol) form an ideal solution. At 55°C, A has a vapor pressure of 95 mmHg and B has a vapor pressure of 42 mmHg. A solution is prepared by mixing equal masses of A and B. (a) Calculate the mole fraction of each component in the solution. (b) Calculate the partial pressures of A and B over the solution at 55°C. (c) Suppose that some of the vapor described in (b) is condensed to a liquid. Calculate the mole fraction of each component in this liquid and the vapor pressure of each component above this liquid at 55°C.

Special Problems

12.129 A very long pipe is capped at one end with a semipermeable membrane. How deep (in meters) must the pipe be immersed into the sea for fresh water to begin to pass through the membrane? Assume the water to be at 20°C and treat it as a 0.70 *M* NaCl solution. The density of seawater is 1.03 g/cm^3 and the acceleration due to gravity is 9.81 m/s^2.

12.130 Two beakers, 1 and 2, containing 50 mL of 0.10 *M* urea and 50 mL of 0.20 *M* urea, respectively, are placed under a tightly sealed container (see Figure 12.12) at 298 K. Calculate the mole fraction of urea in the solutions at equilibrium. Assume ideal behavior.

12.131 A mixture of liquids A and B exhibits ideal behavior. At 84°C, the total vapor pressure of a solution containing 1.2 moles of A and 2.3 moles of B is 331 mmHg. Upon the addition of another mole of B to the solution, the vapor pressure increases to 347 mmHg. Calculate the vapor pressures of pure A and B at 84°C.

12.132 Using Henry's law and the ideal gas equation to prove the statement that the volume of a gas that dissolves in a given amount of solvent is *independent* of the pressure of the gas. (*Hint:* Henry's law can be modified as $n = kP$, where n is the number of moles of the gas dissolved in the solvent.)

12.133 (a) Derive the equation relating the molality (m) of a solution to its molarity (M)

$$m = \frac{M}{d - \dfrac{M\mathcal{M}}{1000}}$$

where d is the density of the solution (g/mL) and $\mathcal{M}$ is the molar mass of the solute (g/mol). (*Hint:* Start by expressing the solvent in kilograms in terms of the difference between the mass of the solution and the mass of the solute.) (b) Show that, for dilute aqueous solutions, m is approximately equal to M.

12.134 At 298 K, the osmotic pressure of a glucose solution is 10.50 atm. Calculate the freezing point of the solution. The density of the solution is 1.16 g/mL.

Answers to Practice Exercises

12.1 Carbon disulfide. **12.2** 7.44 percent. **12.3** 0.638 *m*. **12.4** 8.92 *m*. **12.5** 13.8 *m*. **12.6** 2.9×10^{-4} *M*. **12.7** 37.8 mmHg; 4.4 mmHg. **12.8** T_b: 101.3°C; T_f: −4.48°C. **12.9** 21.0 atm. **12.10** 0.066 *m* and 1.3×10^2 g/mol. **12.11** 2.60×10^4 g. **12.12** 1.21.

CHEMICAL Mystery

The Wrong Knife[†]

Dr. Thomas Noguchi, the renowned Los Angeles coroner, was performing an autopsy on a young man in his twenties who had been stabbed to death. A Los Angeles Police Department homicide detective entered the room, carrying a brown bag that held the fatal weapon. "Do you want to take a look at it?" he asked.

"No," Dr. Noguchi said. "I'll tell *you* exactly what it looks like."

Dr. Noguchi wasn't showing off. He wanted to demonstrate an important forensic technique to the pathology residents who were observing the autopsy. The traditional method of measuring a knife was to pour barium sulfate ($BaSO_4$) solution into the wound and X-ray it. Dr. Noguchi thought he had found a better way.

He lit a little Bunsen burner and melted some Wood's metal over it while the detective and the residents watched. (Wood's metal is an alloy of bismuth, lead, tin, and cadmium that has a low melting point of 71°C.) Then he selected a wound in the victim's chest above the location of the liver and poured the liquid metal into it. The metal slid down through the wound into the punctured liver. When it was cool he removed an exact mold of the tip of the murder weapon. He added the length of this tip to the distance between the liver and the skin surface of the chest. Then he said to the homicide detective, "It's a knife five and a half inches long, one inch wide and one sixteenth of an inch thick."

The detective smiled and reached into his bag. "Sorry, Dr. Noguchi." He pulled out a much smaller pocketknife, only about three inches in length.

"That's the wrong knife," Dr. Noguchi said at once.

"Oh, now, come on," the detective said. "We found the knife that killed him right at the scene."

"You don't have the murder weapon," Dr. Noguchi insisted.

The detective didn't believe him. But two days later police found a blood-stained knife in a trash can two blocks from the crime scene. That weapon was exactly five and a half inches long, one inch wide, and one sixteenth of an inch thick. And the blood on its blade matched the victim's.

It turned out to be the murder weapon. The pocketknife the police discovered at the scene had been used by the victim in self-defense. And two knives indicated a knife fight. Was it part of a gang war? The police investigated and found out that the victim was a member of a gang that was at war with another gang. By interrogating members of the rival gang, they eventually identified the murderer.

[†] Adapted with the permission of Simon & Schuster from "Coroner," by Thomas T. Noguchi, M.D., Copyright 1984 by Thomas Noguchi and Joseph DiMona.

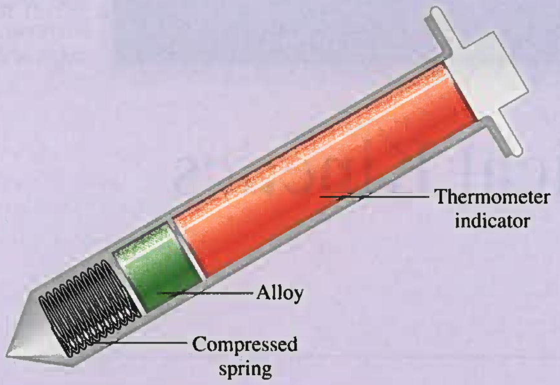
Composition of Wood's Metal*

Component	Melting Point (°C)
Bismuth (50%)	271
Cadmium (12.5%)	321
Lead (25%)	328
Tin (12.5%)	232

*The components are shown in percent by mass, and the melting point is that of the pure metal.

Chemical Clues

1. What is the function of the $BaSO_4$ solution as a traditional method for measuring a knife wound in a homicide victim's body? Describe a medical application of $BaSO_4$.
2. As the table shows, the melting points of the pure metals are much higher than that of Wood's metal. What phenomenon accounts for its low melting point?
3. Wood's metal is used in automatic sprinklers in the ceilings of hotels and stores. Explain how such a sprinkling system works.
4. The melting point of an alloy can be altered by changing the composition. Certain organic materials have also been developed for the same purpose. Shown below is a simplified diagram of the pop-up thermometer used in cooking turkeys. Describe how this thermometer works.



A pop-up thermometer used for cooking turkeys.