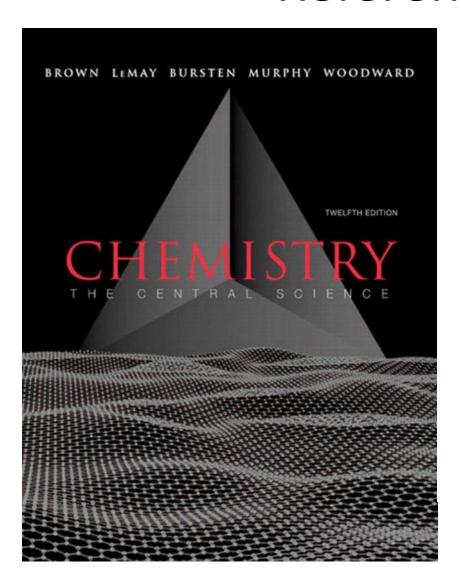
## **Properties of Solutions**

### Reference Book



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#### PATRICK M. WOODWARD

The Ohio State University

## Behavior in My Class

- Please enter in my class before I enter
- I will take attendance at the beginning of my class.
- If you are late for class, do not disturb me
- Keep silence
- Keep friendly relation in my class

## Types of Solution

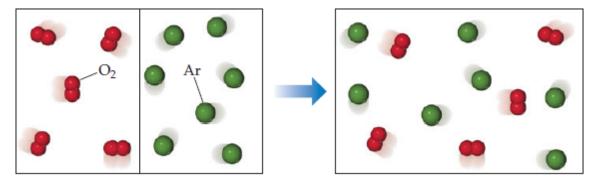
A solution should have at least two components solute + solvent = solution

- Gas in gas
- Gas in liquid
- Liquid in liquid
- Solid in liquid
- Solid in solid

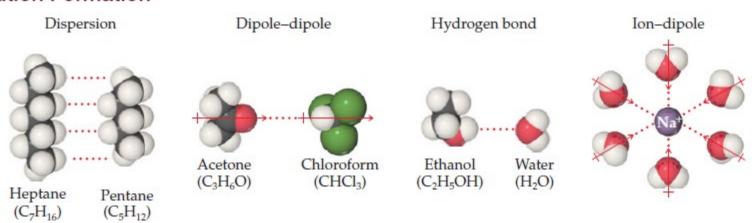
#### 13.1 THE SOLUTION PROCESS

A solution is formed when one substance disperses uniformly throughout another. The ability of substances to form solutions depends on two factors: (1) the natural tendency of substances to mix and spread into larger volumes when not restrained in some way and (2) the types of intermolecular interactions involved in the solution process.

#### The Natural Tendency toward Mixing



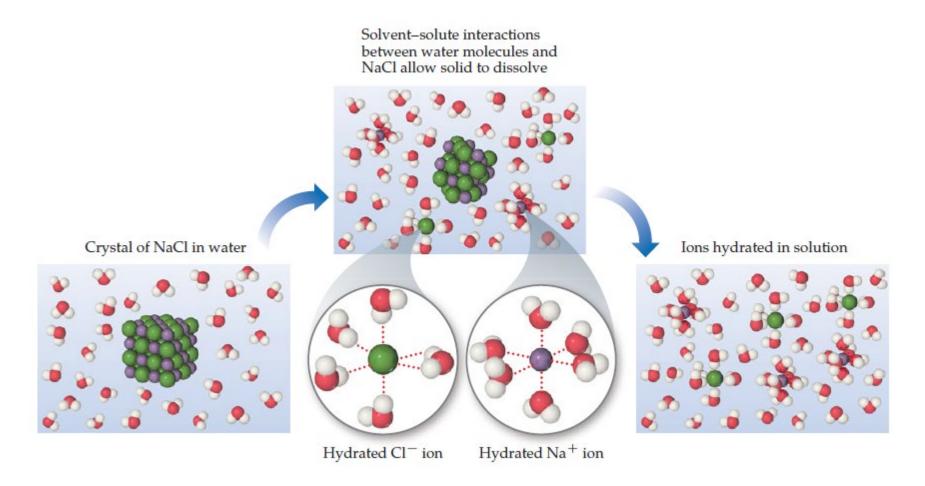
#### The Effect of Intermolecular Forces on Solution Formation



Three kinds of intermolecular interactions are involved in solution formation:

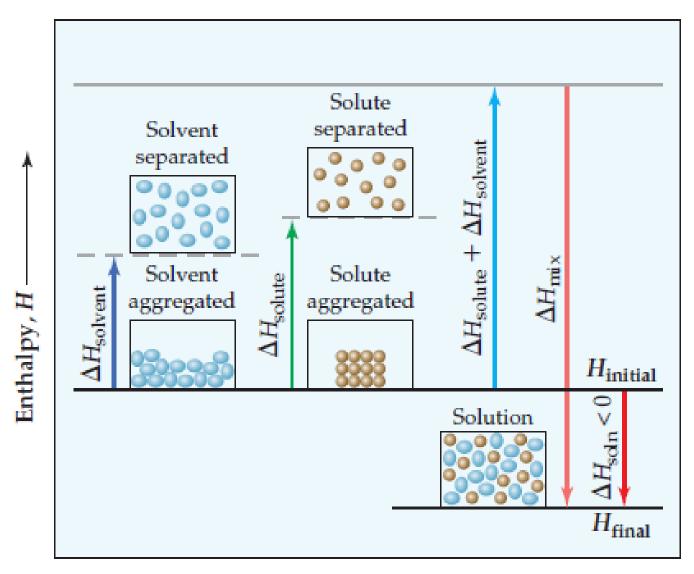
- Solute-solute interactions between solute particles must be overcome in order to disperse the solute particles through the solvent.
- Solvent-solvent interactions between solvent particles must be overcome to make room for the solute particles in the solvent.
- Solvent-solute interactions between solvent and solute particles occur as the particles mix.

#### **Energetics of Solution Formation**



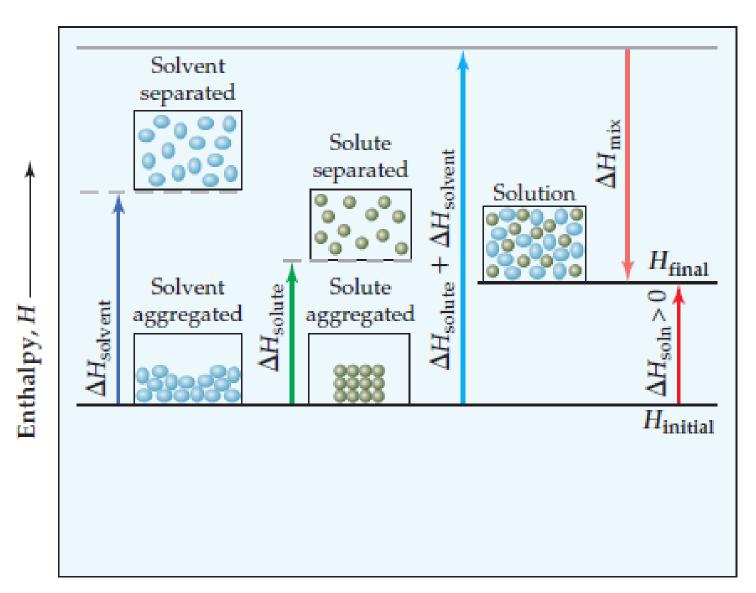
$$\Delta H_{\text{soln}} = \Delta H_{\text{solute}} + \Delta H_{\text{solvent}} + \Delta H_{\text{mix}}$$

#### **Energetics of Solution Formation**



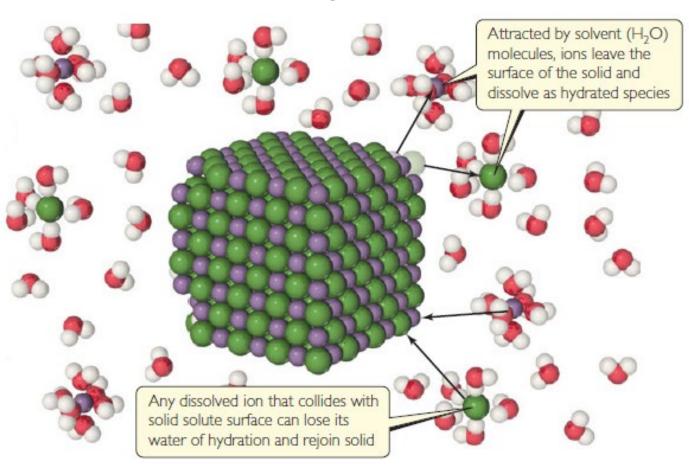
Exothermic solution process

#### **Energetics of Solution Formation**



Endothermic solution process

# 13.2 SATURATED SOLUTIONS AND SOLUBILITY



# 13.2 SATURATED SOLUTIONS AND SOLUBILITY

A solution that is in equilibrium with undissolved solute is **saturated**. Additional solute will not dissolve if added to a saturated solution. The amount of solute needed to form a saturated solution in a given quantity of solvent is known as the **solubility** of that solute. That is, the solubility of a given solute in a given solvent is the maximum amount of the solute that can dissolve in a given amount of the solvent at a specified temperature, given that excess solute is present. For example, the solubility of NaCl in water at 0 °C is 35.7 g per 100 mL of water. This is the maximum amount of NaCl that can be dissolved in water to give a stable equilibrium solution at that temperature.

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

Under suitable conditions it is possible to form solutions that contain a greater amount of solute than needed to form a saturated solution. Such solutions are supersaturated. For example, when a saturated solution of sodium acetate is made at a

#### Solute-Solvent Interactions

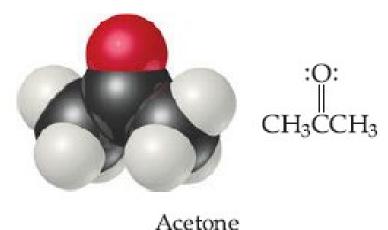
Solubility of gas increases with increasing polarity and molecular mass

TABLE 13.1 • Solubilities of Gases in Water at 20 °C, with 1 atm Gas Pressure

Gas	Solubility (M)		
$N_2$	$0.69 \times 10^{-3}$		
CO	$1.04 \times 10^{-3}$		
$O_2$	$1.38 \times 10^{-3}$		
Ar	$1.50 \times 10^{-3}$		
Kr	$2.79 \times 10^{-3}$		

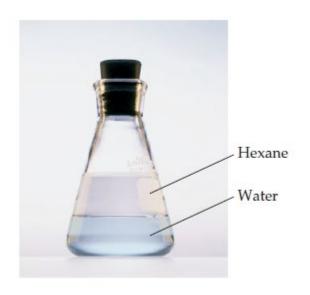
#### Solute-Solvent Interactions

Why acetone dissolves in water in all proportions?



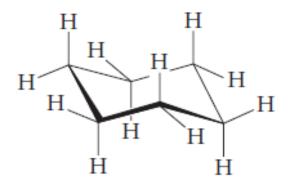
Because of favorable dipole–dipole attractions between solvent molecules and solute molecules, polar liquids tend to dissolve in polar solvents. Water is both polar and able to form hydrogen bonds.  $\infty$  (Section 11.2) Thus, polar molecules, especially those that can form hydrogen bonds with water molecules, tend to be soluble in water. For example, acetone, a polar molecule with the structural formula shown in the margin, mixes in all proportions with water. Acetone has a strongly polar C=O bond and pairs of nonbonding electrons on the O atom that can form hydrogen bonds with water.

#### Solute-Solvent Interactions

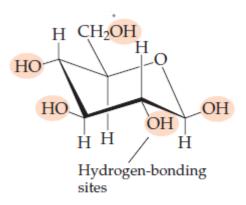


Pairs of liquids that mix in all proportions, such as acetone and water, are **miscible**, whereas those that do not dissolve in one another are **immiscible**. Gasoline, which is a mixture of hydrocarbons, is immiscible with water. Hydrocarbons are nonpolar substances because of several factors: The C-C bonds are nonpolar, the C-H bonds are nearly nonpolar, and the molecules are symmetrical enough to cancel much of the weak C-H bond dipoles. The attraction between the polar water molecules and the nonpolar hydrocarbon molecules is not sufficiently strong to allow the formation of a solution. Nonpolar liquids tend to be insoluble in polar liquids, as  $\blacktriangleright$  FIGURE 13.10 shows for hexane  $(C_6H_{14})$  and water.

#### Solute-Solvent Interactions



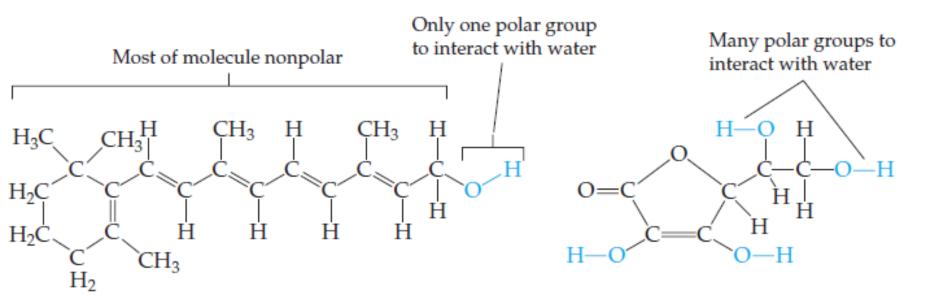
Cyclohexane, C<sub>6</sub>H<sub>12</sub>, which has no polar OH groups, is essentially insoluble in water



Glucose, C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>, has five OH groups and is highly soluble in water

One way to enhance the solubility of a substance in water is to increase the number of polar groups the substance contains. For example, increasing the number of OH groups in a solute increases the extent of hydrogen bonding between that solute and water, thereby increasing solubility. Glucose ( $C_6H_{12}O_6$ ,  $\triangleright$  FIGURE 13.12) has five OH groups on a six-carbon framework, which makes the molecule very soluble in water (83 g dissolves in 100 mL of water at 17.5 °C).

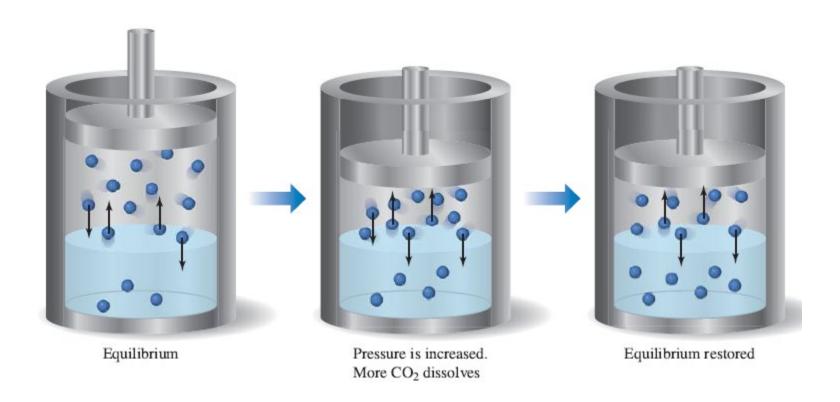
#### Solute-Solvent Interactions



Vitamin A Vitamin C

#### Pressure Effects

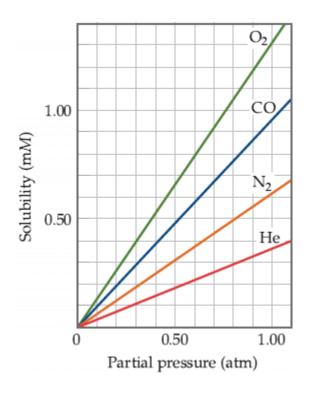
The solubilities of solids and liquids are not appreciably affected by pressure, whereas the solubility of a gas in any solvent is increased as the partial pressure of the gas above the solvent increases. We can understand the effect of pressure on gas solubility by considering **FIGURE 13.14**, which shows carbon dioxide gas distributed between the gas and



### Pressure Effects

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

$$S_{g} = kP_{g} \tag{13.4}$$





### Pressure Effects

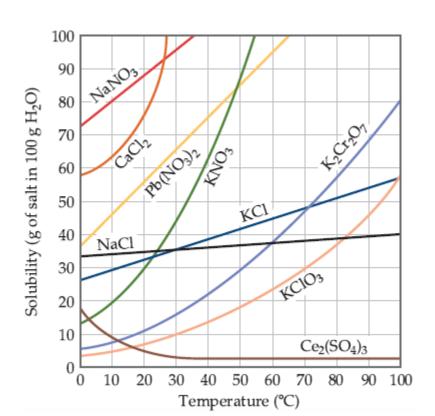


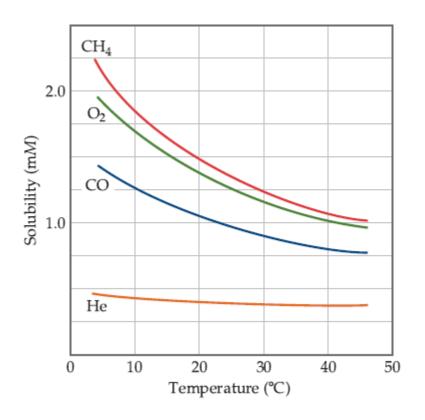
▲ FIGURE 13.17 Gas solubility increases as pressure increases. Divers who use compressed gases must be concerned about the solubility of the gases in their blood.

#### **Temperature Effects**

The solubility of most solid solutes in water increases as the solution temperature increases, as  $\nabla$  FIGURE 13.18 shows. There are exceptions to this rule, however, as seen for  $Ce_2(SO_4)_3$ , whose solubility curve slopes downward with increasing temperature.

In contrast to solid solutes, the solubility of gases in water decreases with increasing temperature (▼ FIGURE 13.19). If a glass of cold tap water is warmed, you can see bubbles on the inside of the glass because some of the dissolved air comes out of solution.





### **Expression solution concentrations**

#### Mass Percentage, ppm, and ppb

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

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

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

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

Thus, 1 ppm also corresponds to 1 mg of solute per liter of aqueous solution.

### Expression solution concentrations

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

#### SAMPLE EXERCISE 13.3 Calculation of Mass-Related Concentrations

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

### **Expression solution concentrations**

#### Mole Fraction, Molarity, and Molality

Concentration expressions are often based on the number of moles of one or more components of the solution. Recall from Section 10.6 that the *mole fraction* of a component of a solution is given by

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

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

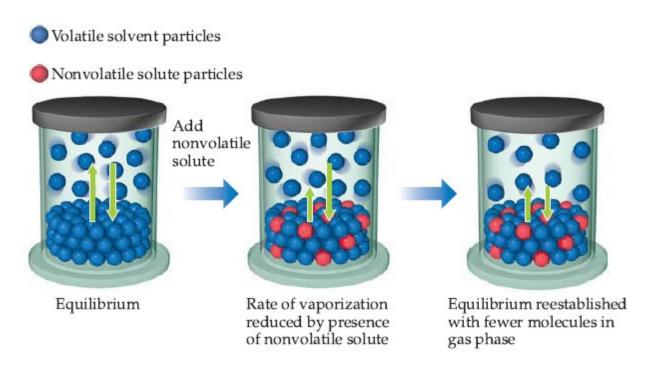
$$Molality = \frac{\text{moles of solute}}{\text{kilograms of solvent}}$$
[13.9]

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

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

- 1. Depression of Freezing Point
- 2. Elevation of Boiling Point
- 3. Lowering of Vapor Pressure
- 4. Osmotic Pressure

#### Vapor-Pressure Lowering



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

#### Vapor-Pressure Lowering

For example, the vapor pressure of pure water at 20 °C is  $P_{\rm H_2O}^{\rm o}=17.5$  torr. Imagine holding the temperature constant while adding glucose ( $C_6H_{12}O_6$ ) to the water so that the mole fractions in the resulting solution are  $X_{\rm H_2O}=0.800$  and  $X_{\rm C_6H_{12}O_6}=0.200$ . According to Equation 13.10, the vapor pressure of the water above this solution is 80.0% of that of pure water:

$$P_{\text{solution}} = (0.800)(17.5 \text{ torr}) = 14.0 \text{ torr}$$

The presence of the nonvolatile solute lowers the vapor pressure of the volatile solvent by 17.5 torr - 14.0 torr = 3.5 torr.

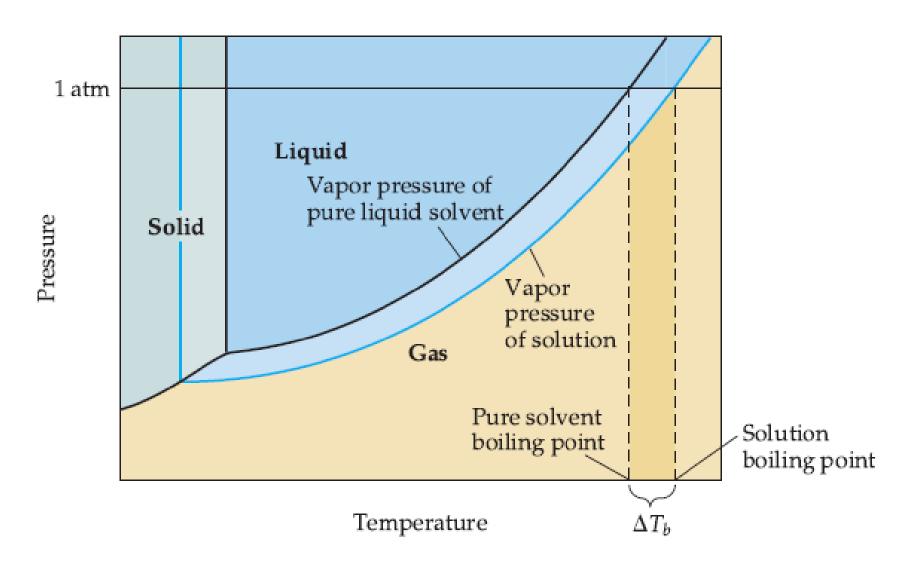
The vapor-pressure lowering,  $\Delta P$ , is directly proportional to the mole fraction of the solute,  $X_{\text{solute}}$ :

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

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

$$\Delta P = X_{\text{C}_6\text{H}_{12}\text{O}_6} P_{\text{H}_2\text{O}}^{\text{o}} = (0.200)(17.5 \text{ torr}) = 3.50 \text{ torr}$$

#### **Boiling-Point Elevation**



#### **Boiling-Point Elevation**

$$\Delta T_b = K_b m$$

 $K_h$ , which is called the **molal boiling-point-elevation constant**,

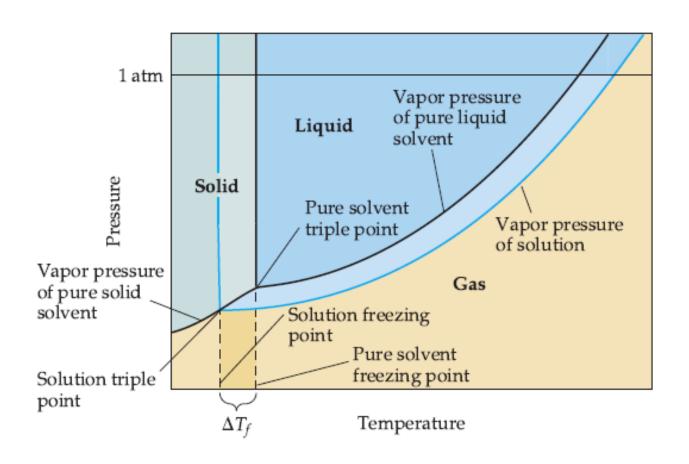
Solvent	Normal Boiling Point (°C)	$K_b\left(^{\circ}\mathrm{C}/m\right)$	Normal Freezing Point (°C)	$K_f(^{\circ}\mathbb{C}/m)$
Water, H <sub>2</sub> O	100.0	0.51	0.0	1.86
Benzene, C <sub>6</sub> H <sub>6</sub>	80.1	2.53	5.5	5.12
Ethanol, C <sub>2</sub> H <sub>5</sub> OH	78.4	1.22	-114.6	1.99
Carbon tetrachloride, CCl <sub>4</sub>	76.8	5.02	-22.3	29.8
Chloroform, CHCl <sub>3</sub>	61.2	3.63	-63.5	4.68

#### **Boiling-Point Elevation**

$$\Delta T_b = K_b m$$

It is important to remember that boiling-point elevation is proportional to the *total* concentration of solute particles, regardless of whether the particles are molecules or ions. When NaCl dissolves in water, 2 mol of solute particles (1 mol of Na<sup>+</sup> and 1 mol of Cl<sup>-</sup>) are formed for each mole of NaCl that dissolves. Therefore, a 1 m aqueous solution of NaCl is 1 m in Na<sup>+</sup> and 1 m in Cl<sup>-</sup>, making it 2 m in total solute particles. As a result, the boiling-point elevation of a 1 m aqueous solution of NaCl is approximately (2 m)(0.51 °C/m) = 1 °C, twice as large as the boiling-point elevation of a 1 m solution of a nonelectrolyte such as sucrose. Thus, to properly predict the effect of a particular solute on boiling-point elevation (or any other colligative property), it is important to know whether the solute is an electrolyte or a nonelectrolyte.  $\infty$  (Sections 4.1 and 4.3)

#### Freezing-Point Depression



#### Freezing-Point Depression

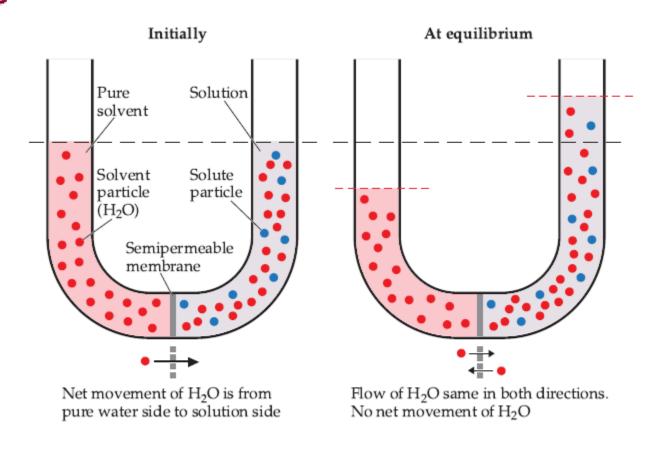
Like the boiling-point elevation,  $\Delta T_f$  is directly proportional to solute molality:

$$\Delta T_f = K_f m \tag{13.13}$$

The values of  $K_f$ , the **molal freezing-point-depression constant**, for several common solvents are given in Table 13.3. For water,  $K_f$  is 1.86 °C/m. Therefore, any aqueous solution that is 1 m in nonvolatile solute particles (such as 1 m C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> or 0.5 m NaCl) freezes at the temperature that is 1.86 °C lower than the freezing point of pure water.

The freezing-point depression caused by solutes explains the use of antifreeze in cars and the use of calcium chloride (CaCl<sub>2</sub>) to melt ice on roads during winter.

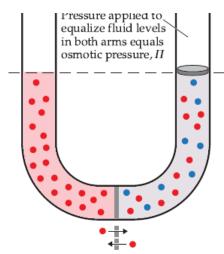
#### **Osmosis**



In this process, called **osmosis**, the net movement of solvent is always toward the solution with the higher solute concentration, as if the solutions were driven to attain equal concentrations.

#### Osmosis

▶ FIGURE 13.25 shows the osmosis that occurs between an aqueous solution and pure water. The U-tube contains water on the left and an aqueous solution on the right. There is a net movement of water through the membrane from left to right, As a result, the liquid levels in the two arms become unequal. Eventually, the pressure difference resulting from the unequal liquid heights becomes so large that the net flow of water ceases. The pressure required to stop osmosis from a pure solvent to a solution is the osmotic pressure of the solution. If an external pressure equal to the osmotic pressure is applied to the solution, the liquid levels in the two arms can be equalized, as shown in the right panel of Figure 13.25.



Flow of H<sub>2</sub>O same in both direction. No net movement of H<sub>2</sub>O

#### Osmosis

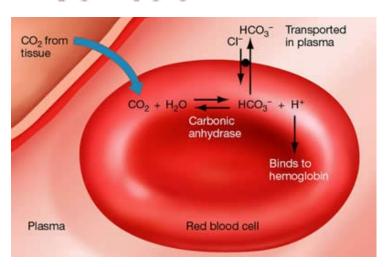
The osmotic pressure obeys a law similar in form to the ideal-gas law,  $\Pi V = nRT$ , where  $\Pi$  is the osmotic pressure, V is the volume of the solution, n is the number of moles of solute, R is the ideal-gas constant, and T is the Kelvin temperature. From this equation, we can write

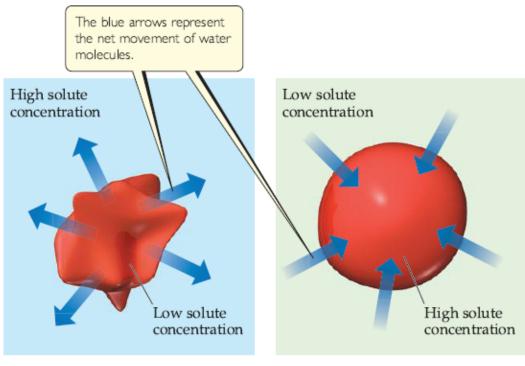
$$\Pi = \left(\frac{n}{V}\right)RT = MRT$$
 [13.14]

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

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

#### **Osmosis**





Crenation of red blood cell placed in hypertonic environment

Hemolysis of red blood cell placed in hypotonic environment

#### Determination of Molar Mass

SAMPLE EXERCISE 13.11 Molar Mass from Freezing-Point Depression

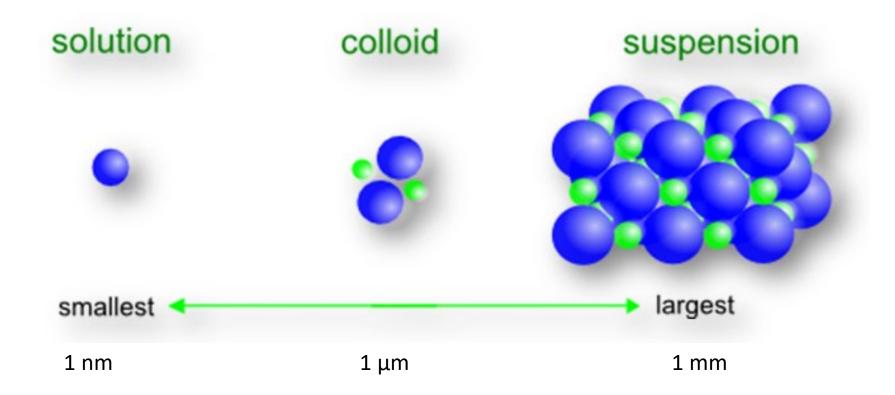
A solution of an unknown nonvolatile nonelectrolyte was prepared by dissolving 0.250 g of the substance in 40.0 g of CCl4. The boiling point of the resultant solution was 0.357 °C higher than that of the pure solvent. Calculate the molar mass of the solute.

$$\Delta T_b = K_b m$$

#### SAMPLE EXERCISE 13.12 Molar Mass from Osmotic Pressure

The osmotic pressure of an aqueous solution of a certain protein was measured to determine the protein's molar mass. The solution contained 3.50 mg of protein dissolved in sufficient water to form 5.00 mL of solution. The osmotic pressure of the solution at 25 °C was found to be 1.54 torr. Treating the protein as a nonelectrolyte, calculate its molar mass.

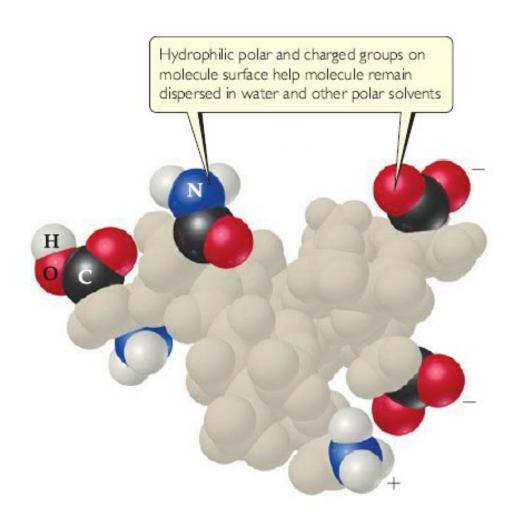
$$\Pi = \left(\frac{n}{V}\right)RT = MRT$$



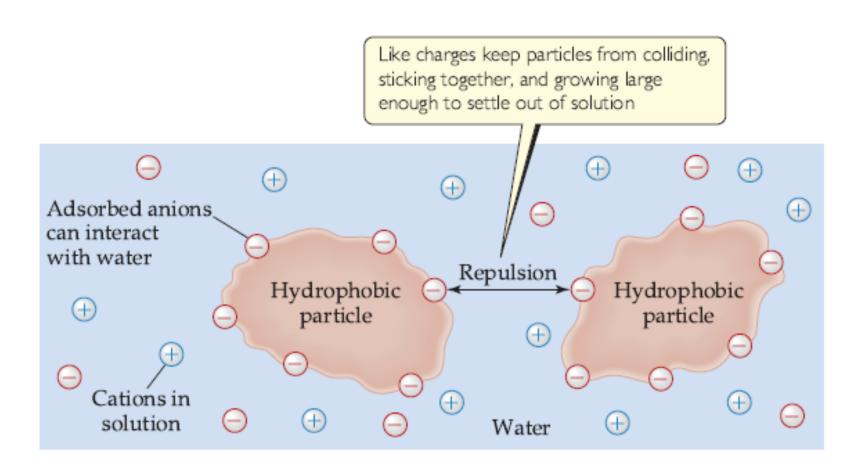
► FIGURE 13.28 Tyndall effect in the laboratory. The glass on the right contains a colloidal dispersion; that on the left contains a solution.



### Hydrophilic and Hydrophobic Colloids



#### Hydrophilic and Hydrophobic Colloids

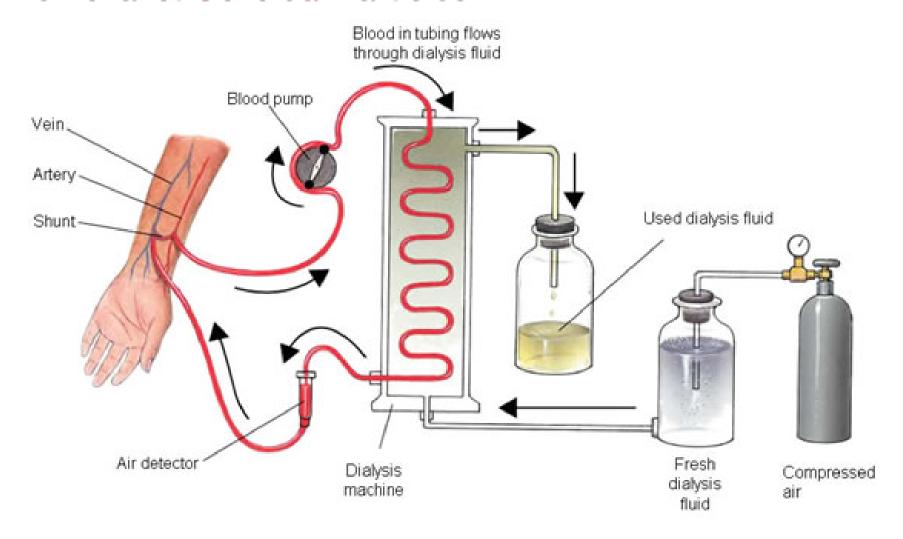


#### Removal of Colloidal Particles

Heating a colloidal dispersion or adding an electrolyte may bring about coagulation. Heating increases the particle motion and so the number of collisions. The particles get larger as they stick together after colliding. Addition of an electrolyte neutralizes the surface charges of the particles, thereby removing the electrostatic repulsions that prevent them from coming together. Wherever a river empties into the ocean, for example, the clay suspended in the river is deposited as a delta as it mixes with the electrolytes in the salt water.

A semipermeable membrane can be used to separate ions from colloidal particles because the ions can pass through the membrane but the colloidal particles cannot. This type of separation is known as *dialysis* and is used to purify blood in artificial kidney machines. Our kidneys normally remove waste products from blood. In a kidney machine, blood is circulated through a dialyzing tube immersed in a washing solution. The solution contains the same concentrations and kinds of ions as blood but no waste products. Dissolved wastes therefore dialyze out of the blood, but the large colloidal particles such as proteins do not.

#### Removal of Colloidal Particles



- 13.48 Ascorbic acid (vitamin C, C<sub>6</sub>H<sub>8</sub>O<sub>6</sub>) is a water-soluble vitamin. A solution containing 80.5 g of ascorbic acid dissolved in 210 g of water has a density of 1.22 g/mL at 55 °C. Calculate (a) the mass percentage, (b) the mole fraction, (c) the molality, (d) the molarity of ascorbic acid in this solution.
- 13.93 Most fish need at least 4 ppm dissolved O<sub>2</sub> for survival. (a) What is this concentration in mol/L? (b) What partial pressure of O<sub>2</sub> above the water is needed to obtain this concentration at 10 °C? (The Henry's law constant for O<sub>2</sub> at this temperature is 1.71 × 10<sup>-3</sup> mol/L-atm.)
- [13.105] A lithium salt used in lubricating grease has the formula LiC<sub>n</sub>H<sub>2n+1</sub>O<sub>2</sub>. The salt is soluble in water to the extent of 0.036 g per 100 g of water at 25 °C. The osmotic pressure of this solution is found to be 57.1 torr. Assuming that molality and molarity in such a dilute solution are the same and that the lithium salt is completely dissociated in the solution, determine an appropriate value of n in the formula for the salt.

[13.107] At ordinary body temperature (37 °C) the solubility of N<sub>2</sub> in water in contact with air at ordinary atmospheric pressure (1.0 atm) is 0.015 g/L. Air is approximately 78 mol % N2. Calculate the number of moles of N<sub>2</sub> dissolved per liter of blood, which is essentially an aqueous solution. At a depth of 100 ft in water, the pressure is 4.0 atm. What is the solubility of N<sub>2</sub> from air in blood at this pressure? If a scuba diver suddenly surfaces from this depth, how many milliliters of N2 gas, in the form of tiny bubbles, are released into the bloodstream from each liter of blood?

(a) A sample of hydrogen gas is generated in a closed con-13.110 tainer by reacting 2.050 g of zinc metal with 15.0 mL of 1.00 M sulfuric acid. Write the balanced equation for the reaction, and calculate the number of moles of hydrogen formed, assuming that the reaction is complete. (b) The volume over the solution is 122 mL. Calculate the partial pressure of the hydrogen gas in this volume at 25 °C, ignoring any solubility of the gas in the solution. (c) The Henry's law constant for hydrogen in water at 25 °C is  $7.8 \times 10^{-4} \,\mathrm{mol/L}$ -atm. Estimate the number of moles of hydrogen gas that remain dissolved in the solution. What fraction of the gas molecules in the system is dissolved in the solution? Was it reasonable to ignore any dissolved hydrogen in part (b)?