11 Properties of Solutions

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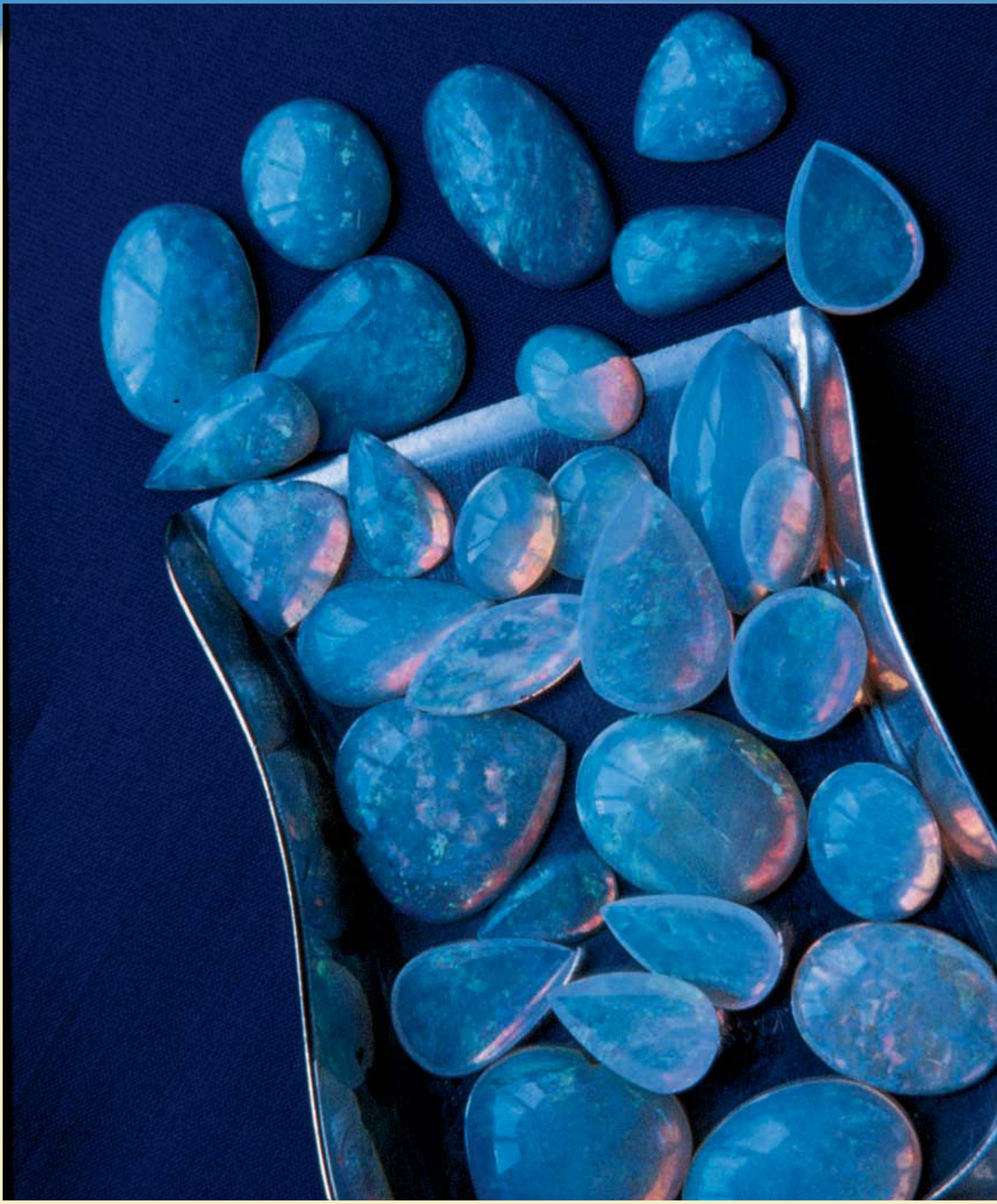


Opals are formed from colloidal suspensions of silica when the liquid evaporates.

Most of the substances we encounter in daily life are mixtures: Wood, milk, gasoline, champagne, seawater, shampoo, steel, and air are common examples. When the components of a mixture are uniformly intermingled—that is, when a mixture is homogeneous—it is called a *solution.* Solutions can be gases, liquids, or solids, as shown in Table 11.1. However, we will be concerned in this chapter with the properties of liquid solutions, particularly those containing water. As we saw in Chapter 4, many essential chemical reactions occur in aqueous solutions because water is capable of dissolving so many substances.

11.1 Solution Composition

A solute is the substance being dissolved. The solvent is the dissolving medium.

$$\text{Molarity} = \frac{\text{moles of solute}}{\text{liters of solution}}$$

Because a mixture, unlike a chemical compound, has a variable composition, the relative amounts of substances in a solution must be specified. The qualitative terms *dilute* (relatively little solute present) and *concentrated* (relatively large amount of solute) are often used to describe solution content, but we need to define solution composition more precisely to perform calculations. For example, in dealing with the stoichiometry of solution reactions in Chapter 4, we found it useful to describe solution composition in terms of **molarity,** or the number of moles of solute per liter of solution (symbolized by M).

Other ways of describing solution composition are also useful. **Mass percent** (sometimes called *weight percent*) is the percent by mass of the solute in the solution:

$$\text{Mass percent} = \left(\frac{\text{mass of solute}}{\text{mass of solution}}\right) \times 100\%$$

When liquids are mixed, the liquid present in the largest amount is called the *solvent.*

Another way of describing solution composition is the **mole fraction** (symbolized by the Greek lowercase letter chi, χ), the ratio of the number of moles of a given component to the total number of moles of solution. For a two-component solution, where n_A and n_B represent the number of moles of the two components,

$$\text{Mole fraction of component A} = \chi_A = \frac{n_A}{n_A + n_B}$$

TABLE 11.1 Various Types of Solutions

Example	State of Solution	State of Solute	State of Solvent
Air, natural gas	Gas	Gas	Gas
Vodka in water, antifreeze	Liquid	Liquid	Liquid
Brass	Solid	Solid	Solid
Carbonated water (soda)	Liquid	Gas	Liquid
Seawater, sugar solution	Liquid	Solid	Liquid
Hydrogen in platinum	Solid	Gas	Solid

In very dilute aqueous solutions, the magnitude of the molality and the molarity are almost the same.

Still another way of describing solution composition is **molality** (symbolized by *m*), the number of moles of solute per *kilogram of solvent:*

$$\text{Molality} = \frac{\text{moles of solute}}{\text{kilogram of solvent}}$$

Sample Exercise 11.1 Various Methods for Describing Solution Composition

A solution is prepared by mixing 1.00 g ethanol (C_2H_5OH) with 100.0 g water to give a final volume of 101 mL. Calculate the molarity, mass percent, mole fraction, and molality of ethanol in this solution.

Solution

Since molarity depends on the volume of the solution, it changes slightly with temperature. Molality is independent of temperature because it depends only on mass.

Molarity: The moles of ethanol can be obtained from its molar mass (46.07 g/mol):

$$1.00 \text{ g } C_2H_5OH \times \frac{1 \text{ mol } C_2H_5OH}{46.07 \text{ g } C_2H_5OH} = 2.17 \times 10^{-2} \text{ mol } C_2H_5OH$$

$$\text{Volume} = 101 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.101 \text{ L}$$

$$\text{Molarity of } C_2H_5OH = \frac{\text{moles of } C_2H_5OH}{\text{liters of solution}} = \frac{2.17 \times 10^{-2} \text{ mol}}{0.101 \text{ L}}$$

$$= 0.215\ M$$

Mass percent:

$$\text{Mass percent } C_2H_5OH = \left(\frac{\text{mass of } C_2H_5OH}{\text{mass of solution}}\right) \times 100\%$$

$$= \left(\frac{1.00 \text{ g } C_2H_5OH}{100.0 \text{ g } H_2O + 1.00 \text{ g } C_2H_5OH}\right) \times 100\%$$

$$= 0.990\% \ C_2H_5OH$$

Mole fraction:

$$\text{Mole fraction of } C_2H_5OH = \frac{n_{C_2H_5OH}}{n_{C_2H_5OH} + n_{H_2O}}$$

$$n_{H_2O} = 100.0 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.0 \text{ g } H_2O} = 5.56 \text{ mol}$$

$$\chi_{C_2H_5OH} = \frac{2.17 \times 10^{-2} \text{ mol}}{2.17 \times 10^{-2} \text{ mol} + 5.56 \text{ mol}}$$

$$= \frac{2.17 \times 10^{-2}}{5.58} = 0.00389$$

Molality:

$$\text{Molality of } C_2H_5OH = \frac{\text{moles of } C_2H_5OH}{\text{kilogram of } H_2O} = \frac{2.17 \times 10^{-2} \text{ mol}}{100.0 \text{ g} \times \frac{1 \text{ kg}}{1000 \text{ g}}}$$

$$= \frac{2.17 \times 10^{-2} \text{ mol}}{0.1000 \text{ kg}}$$

$$= 0.217\ m$$

See Exercises 11.25 through 11.27.

TABLE 11.2 The Molar Mass, Equivalent Mass, and Relationship of Molarity and Normality for Several Acids and Bases

Acid or Base	Molar Mass	Equivalent Mass	Relationship of Molarity and Normality
HCl	36.5	36.5	1 M = 1 N
H_2SO_4	98	$\frac{98}{2} = 49$	1 M = 2 N
NaOH	40	40	1 M = 1 N
$Ca(OH)_2$	74	$\frac{74}{2} = 37$	1 M = 2 N

The definition of an equivalent depends on the reaction taking place in the solution.

The quantity we call *equivalent mass* here traditionally has been called *equivalent weight.*

Oxidation–reduction half-reactions were discussed in Section 4.10.

Another concentration measure sometimes encountered is **normality** (symbolized by N). Normality is defined as the number of *equivalents* per liter of solution, where the definition of an equivalent depends on the reaction taking place in the solution. *For an acid–base reaction,* the equivalent is the mass of acid or base that can furnish or accept exactly 1 mole of protons (H^+ ions). In Table 11.2 note, for example, that the equivalent mass of sulfuric acid is the molar mass divided by 2, since each mole of H_2SO_4 can furnish 2 moles of protons. The equivalent mass of calcium hydroxide is also half the molar mass, since each mole of $Ca(OH)_2$ contains 2 moles of OH^- ions that can react with 2 moles of protons. The equivalent is defined so that 1 equivalent of acid will react with exactly 1 equivalent of base.

For oxidation–reduction reactions, the equivalent is defined as the quantity of oxidizing or reducing agent that can accept or furnish 1 mole of electrons. Thus 1 equivalent of reducing agent will react with exactly 1 equivalent of oxidizing agent. The equivalent mass of an oxidizing or reducing agent can be calculated from the number of electrons in its half-reaction. For example, MnO_4^- reacting in acidic solution absorbs five electrons to produce Mn^{2+}:

$$MnO_4^- + 5e^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$$

Since the MnO_4^- ion present in 1 mole of $KMnO_4$ consumes 5 moles of electrons, the equivalent mass is the molar mass divided by 5:

$$\text{Equivalent mass of KMnO}_4 = \frac{\text{molar mass}}{5} = \frac{158\text{ g}}{5} = 31.6\text{ g}$$

Sample Exercise 11.2

Calculating Various Methods of Solution Composition from the Molarity


A modern 12-volt lead storage battery of the type used in automobiles.

The electrolyte in automobile lead storage batteries is a 3.75 M sulfuric acid solution that has a density of 1.230 g/mL. Calculate the mass percent, molality, and normality of the sulfuric acid.

Solution

The density of the solution in grams per liter is

$$1.230\,\frac{\text{g}}{\text{mL}} \times \frac{1000\text{ mL}}{1\text{ L}} = 1.230 \times 10^3\text{ g/L}$$

Thus 1 liter of this solution contains 1230. g of the mixture of sulfuric acid and water. Since the solution is 3.75 M, we know that 3.75 mol H_2SO_4 is present per liter of solution. The number of grams of H_2SO_4 present is

$$3.75\text{ mol} \times \frac{98.1\text{ g H}_2\text{SO}_4}{1\text{ mol}} = 368\text{ g H}_2\text{SO}_4$$

CHEMICAL IMPACT

Electronic Ink

The printed page has been a primary means of communication for over 3000 years, and researchers at the Massachusetts Institute of Technology (MIT) believe they have discovered why. It seems that the brain responds positively to fixed images on a sheet of paper, particularly those areas of the brain that store and process "spatial maps." In comparison, information displayed on computer screens or TV screens seems to lack some of the visual signals that stimulate the learning centers of the brain to retain knowledge. While modern technology provides us with many other media by which we can communicate, the appeal of written words on a piece of paper remains. Surprisingly, the technology of printing has changed very little since the invention of the printing press—that is, until now.

In the past several years Joseph M. Jacobson and his students at MIT have developed a prototype of a self-printing page. The key to this self-printing "paper" is microencapsulation technology—the same technology that is used in "carbonless" carbon paper and "scratch-and-sniff" cologne and perfume advertisements in magazines. Jacobson's system involves the use of millions of transparent fluid-filled capsules containing microscopic particles. These particles are colored and positively charged on one side and white and negatively charged on the other. When an electric field is selectively applied to the capsules, the white side of the microparticles can be oriented upward or the colored side can be caused to flip up. Appropriate application of an electric field can orient the particles in such a way as to produce words, and once the words have been created, virtually no more energy is needed to keep the particles in place. An image can be maintained on a page with consumption of only 50 millionths of an amp of power! The entire display is about 200 μm thick (2.5 times that of paper)

The amount of water present in 1 liter of solution is obtained from the difference

$$1230.\text{ g solution} - 368\text{ g } H_2SO_4 = 862\text{ g } H_2O$$

Since we now know the masses of the solute and solvent, we can calculate the mass percent.

$$\text{Mass percent } H_2SO_4 = \frac{\text{mass of } H_2SO_4}{\text{mass of solution}} \times 100\% = \frac{368\text{ g}}{1230.\text{ g}} \times 100\%$$
$$= 29.9\%\ H_2SO_4$$

From the moles of solute and the mass of solvent we can calculate the molality.

$$\text{Molality of } H_2SO_4 = \frac{\text{moles } H_2SO_4}{\text{kilogram of } H_2O}$$
$$= \frac{3.75\text{ mol } H_2SO_4}{862\text{ g } H_2O \times \dfrac{1\text{ kg } H_2O}{1000\text{ g } H_2O}} = 4.35\ m$$

Since each sulfuric acid molecule can furnish two protons, 1 mol H_2SO_4 represents 2 equivalents. Thus a solution with 3.75 mol H_2SO_4 per liter contains 2 × 3.75 = 7.50 equivalents per liter, and the normality is 7.50 *N*.

See Exercise 11.31.

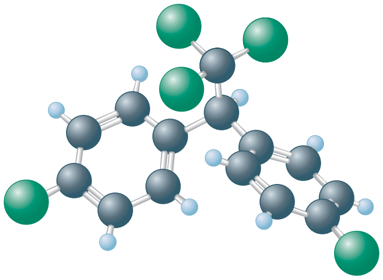
11.2 The Energies of Solution Formation

Dissolving solutes in liquids is very common. We dissolve salt in the water used to cook vegetables, sugar in iced tea, stains in cleaning fluid, gaseous carbon dioxide in water to make soda water, ethanol in gasoline to make gasohol, and so on.

and is so flexible and durable that it can be curled around a pencil and can operate at temperatures from −4 to 158°F. Presently, print resolution is not as good as a modern laser printer, but reduction of the microencapsulated particles from 50 to 40 μm should produce print that rivals the quality of the laser printer.

The first commercial applications of this technology are expected to appear in retail stores across the country in the form of electronic signs that can be updated instantly from a central location. The present technology is a long way from being able to create electronic books, but this is the eventual goal of Jacobson's research team. It seems very likely that this electronic ink technology will contribute greatly to the evolution of the printed page over the next century.

Signs like this one created by E Ink are the first to use electronic ink, which can be updated from a computer inside the store or from a remote location.



DDT

Polar solvents dissolve polar solutes; nonpolar solvents dissolve nonpolar solutes.

Solubility is important in other ways. For example, because the pesticide DDT is fat-soluble, it is retained and concentrated in animal tissues, where it causes detrimental effects. This is why DDT, even though it is effective for killing mosquitos, has been banned in the United States. Also, the solubility of various vitamins is important in determining correct dosages. The insolubility of barium sulfate means it can be used safely to improve X rays of the gastrointestinal tract, even though Ba^{2+} ions are quite toxic.

What factors affect solubility? The cardinal rule of solubility is *like dissolves like.* We find that we must use a polar solvent to dissolve a polar or ionic solute and a nonpolar solvent to dissolve a nonpolar solute. Now we will try to understand why this behavior occurs. To simplify the discussion, we will assume that the formation of a liquid solution takes place in three distinct steps.

➥ 1 **Separating the solute into its individual components (expanding the solute).**

➥ 2 **Overcoming intermolecular forces in the solvent to make room for the solute (expanding the solvent).**

➥ 3 **Allowing the solute and solvent to interact to form the solution.**

The enthalpy of solution is the sum of the energies used in expanding both solvent and solute and the energy of solvent–solute interaction.

These steps are illustrated in Fig. 11.1. Steps 1 and 2 require energy, since forces must be overcome to expand the solute and solvent. Step 3 usually releases energy. In other words, steps 1 and 2 are endothermic, and step 3 is often exothermic. The enthalpy change associated with the formation of the solution, called the **enthalpy (heat) of solution** (ΔH_{soln}), is the sum of the ΔH values for the steps:

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

where ΔH_{soln} may have a positive sign (energy absorbed) or a negative sign (energy released), as shown in Fig. 11.2.

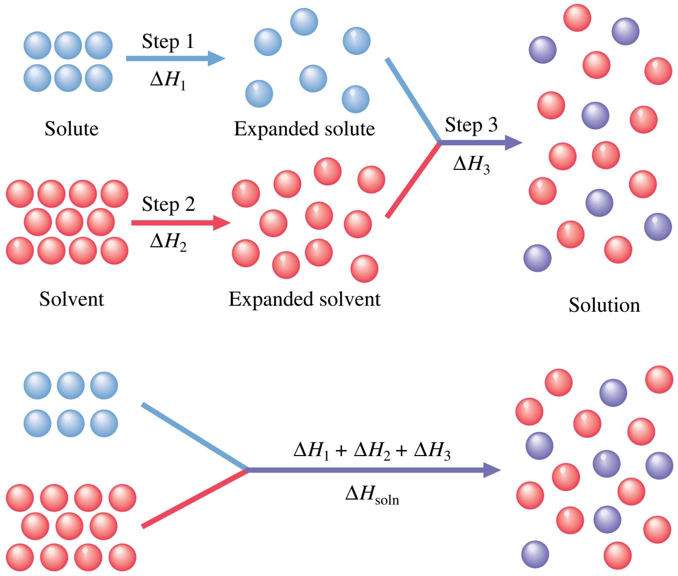


FIGURE 11.1 The formation of a liquid solution can be divided into three steps: (1) expanding the solute, (2) expanding the solvent, and (3) combining the expanded solute and solvent to form the solution.

To illustrate the importance of the various energy terms in the equation for ΔH_{soln}, we will consider two specific cases. First, we know that oil is not soluble in water. When oil tankers leak, the petroleum forms an oil slick that floats on the water and is eventually carried onto the beaches. We can explain the immiscibility of oil and water by considering the energy terms involved. Oil is a mixture of nonpolar molecules that interact through London dispersion forces, which depend on molecule size. We expect ΔH_1 to be small for a typical nonpolar solute, but it will be relatively large for the large oil molecules. The term ΔH_3 will be small, since interactions between the nonpolar solute molecules and the polar water molecules will be negligible. However, ΔH_2 will be large and positive because it takes considerable energy to overcome the hydrogen bonding forces among the water molecules to expand the solvent. Thus ΔH_{soln} will be large and positive because of the ΔH_1 and ΔH_2 terms. Since a large amount of energy would have to be expended to form an oil–water solution, this process does not occur to any appreciable extent. These same arguments hold true for any nonpolar solute and polar solvent—the combination of a nonpolar solute and a highly polar solvent is not expected to produce a solution.

ΔH_1 is expected to be small for nonpolar solutes but can be large for large molecules.

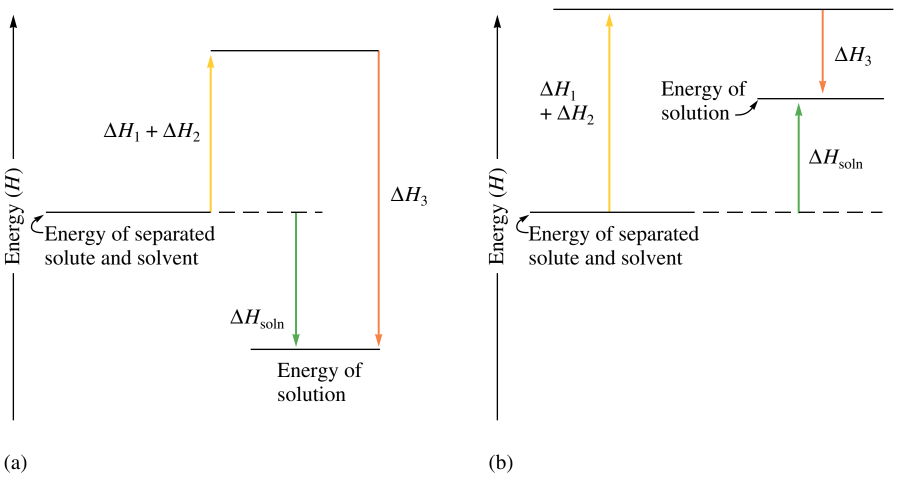


FIGURE 11.2 The heat of solution (a) ΔH_{soln} has a negative sign (the process is exothermic) if step 3 releases more energy than that required by steps 1 and 2. (b) ΔH_{soln} has a positive sign (the process is endothermic) if steps 1 and 2 require more energy than is released in step 3. (If the energy changes for steps 1 and 2 equal that for step 3, then ΔH_{soln} is zero.)

As a second case, let's consider the solubility of an ionic solute, such as sodium chloride, in water. Here the term ΔH_1 is large and positive because the strong ionic forces in the crystal must be overcome, and ΔH_2 is large and positive because hydrogen bonds must be broken in the water. Finally, ΔH_3 is large and negative because of the strong interactions between the ions and the water molecules. In fact, the exothermic and endothermic terms essentially cancel, as shown from the known values:

$$\begin{aligned} \text{NaCl}(s) &\longrightarrow \text{Na}^+(g) + \text{Cl}^-(g) & \Delta H_1 &= 786 \text{ kJ/mol} \\ \text{H}_2\text{O}(l) + \text{Na}^+(g) + \text{Cl}^-(g) &\longrightarrow \text{Na}^+(aq) + \text{Cl}^-(aq) & \Delta H_{\text{hyd}} &= \Delta H_2 + \Delta H_3 \\ & & &= -783 \text{ kJ/mol} \end{aligned}$$

Here the **enthalpy (heat) of hydration** (ΔH_{hyd}) combines the terms ΔH_2 (for expanding the solvent) and ΔH_3 (for solvent–solute interactions). The heat of hydration represents the enthalpy change associated with the dispersal of a gaseous solute in water. Thus the heat of solution for dissolving sodium chloride is the sum of ΔH_1 and ΔH_{hyd}:

$$\Delta H_{\text{soln}} = 786 \text{ kJ/mol} - 783 \text{ kJ/mol} = 3 \text{ kJ/mol}$$

The factors that act as driving forces for a process are discussed more fully in Chapter 16.

Note that ΔH_{soln} is small but positive; the dissolving process requires a small amount of energy. Then why is NaCl so soluble in water? The answer lies in nature's tendency toward higher probability of the mixed state. That is, processes naturally run in the direction that leads to the most probable state. For example, imagine equal numbers of orange and yellow spheres separated by a partition, as shown in Fig. 11.3(a). If we remove the partition and shake the container, the spheres will mix [Fig. 11.3(b)], and no amount of shaking will cause them to return to the state of separated orange and yellow. Why? The mixed state is simply much more likely to occur (more probable) than the original separate state because there are many more ways of placing the spheres to give a mixed state than a separated state. This is a general principle. *One factor that favors a process is an increase in probability.*

But energy considerations are also important. *Processes that require large amounts of energy tend not to occur.* Since dissolving 1 mole of solid NaCl requires only a small amount of energy, the solution forms, presumably because of the large increase in the probability of the state when the solute and solvent are mixed.

The various possible cases for solution formation are summarized in Table 11.3. Note that in two cases, polar–polar and nonpolar–nonpolar, the heat of solution is expected to be small. In these cases, the solution forms because of the increase in the probability of the mixed state. In the other cases (polar–nonpolar and nonpolar–polar), the heat of solution is expected to be large and positive, and the large quantity of energy required acts to prevent the solution from forming. Although this discussion has greatly oversimplified the complex driving forces for solubility, these ideas are a useful starting point for understanding the observation that *like dissolves like.*

Gasoline floating on water. Since gasoline is nonpolar, it is immiscible with water, because water contains polar molecules.

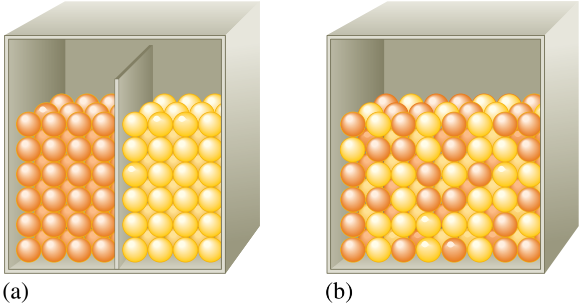


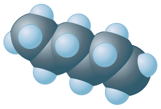
FIGURE 11.3
(a) Orange and yellow spheres separated by a partition in a closed container. (b) The spheres after the partition is removed and the container has been shaken for some time.

TABLE 11.3 The Energy Terms for Various Types of Solutes and Solvents

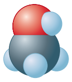
	ΔH_1	ΔH_2	ΔH_3	ΔH_{soln}	Outcome
Polar solute, polar solvent	Large	Large	Large, negative	Small	Solution forms
Nonpolar solute, polar solvent	Small	Large	Small	Large, positive	No solution forms
Nonpolar solute, nonpolar solvent	Small	Small	Small	Small	Solution forms
Polar solute, nonpolar solvent	Large	Small	Small	Large, positive	No solution forms

Sample Exercise 11.3

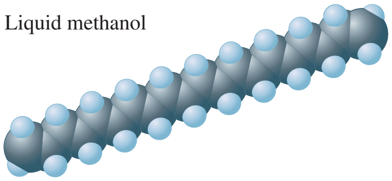
Differentiating Solvent Properties



Hexane



Liquid methanol



Grease

Decide whether liquid hexane (C_6H_{14}) or liquid methanol (CH_3OH) is the more appropriate solvent for the substances grease ($C_{20}H_{42}$) and potassium iodide (KI).

Solution

Hexane is a nonpolar solvent because it contains C—H bonds. Thus hexane will work best for the nonpolar solute grease. Methanol has an O—H group that makes it significantly polar. Thus it will serve as the better solvent for the ionic solid KI.

See Exercises 11.37 through 11.39.

11.3 Factors Affecting Solubility

Structure Effects

Visualization: Ammonia Fountain

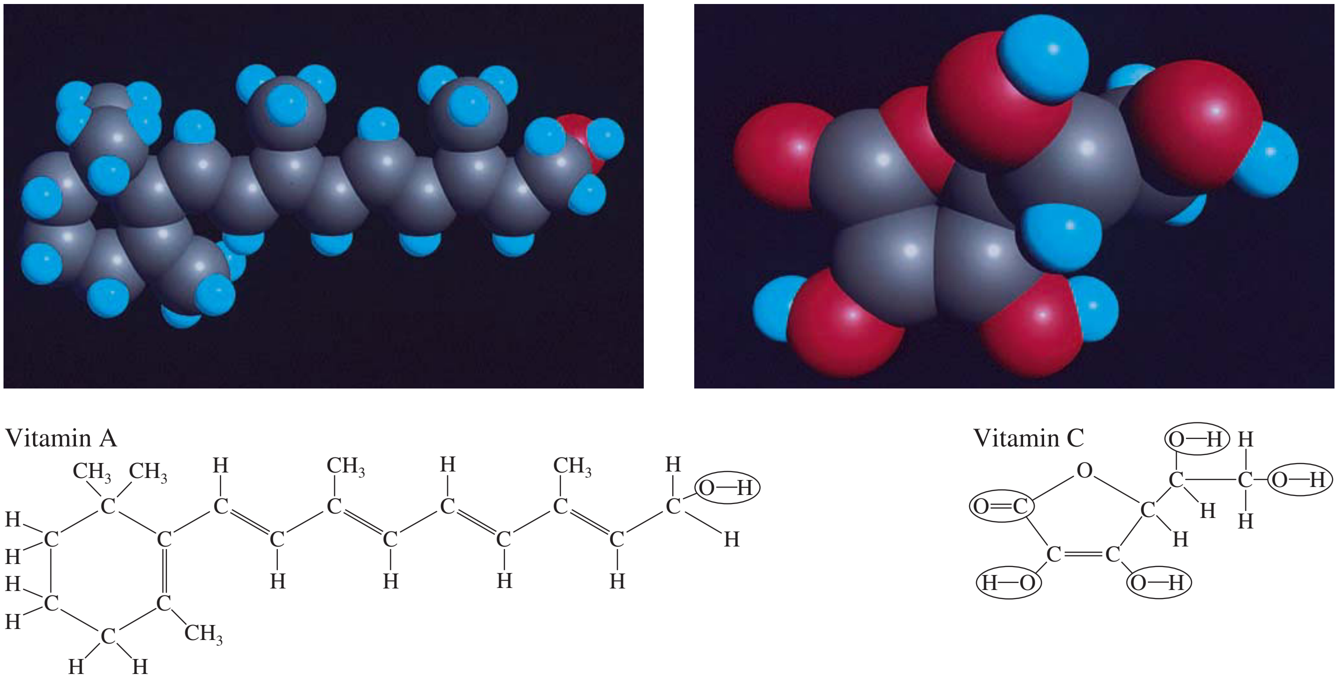
Visualization: Micelle Formation: The Cleansing Action of Soap

In the last section we saw that solubility is favored if the solute and solvent have similar polarities. Since it is the molecular structure that determines polarity, there should be a definite connection between structure and solubility. Vitamins provide an excellent example of the relationship among molecular structure, polarity, and solubility.

Recently, there has been considerable publicity about the pros and cons of consuming large quantities of vitamins. For example, large doses of vitamin C have been advocated to combat various illnesses, including the common cold. Vitamin E has been extolled as a youth-preserving elixir and a protector against the carcinogenic (cancer-causing) effects of certain chemicals. However, there are possible detrimental effects from taking large amounts of some vitamins, depending on their solubilities.

Vitamins can be divided into two classes: *fat-soluble* (vitamins A, D, E, and K) and *water-soluble* (vitamins B and C). The reason for the differing solubility characteristics can be seen by comparing the structures of vitamins A and C (Fig. 11.4). Vitamin A, composed mostly of carbon and hydrogen atoms that have similar electronegativities, is virtually nonpolar. This causes it to be soluble in nonpolar materials such as body fat, which is also largely composed of carbon and hydrogen, but not soluble in polar solvents such as water. On the other hand, vitamin C has many polar O—H and C—O bonds, making the molecule polar and thus water-soluble. We often describe nonpolar materials such as vitamin A as *hydrophobic* (water-fearing) and polar substances such as vitamin C as *hydrophilic* (water-loving).

Because of their solubility characteristics, the fat-soluble vitamins can build up in the fatty tissues of the body. This has both positive and negative effects. Since these vitamins



Vitamin A

Vitamin C

FIGURE 11.4
The molecular structures of (a) vitamin A (nonpolar, fat-soluble) and (b) vitamin C (polar, water-soluble). The circles in the structural formulas indicate polar bonds. Note that vitamin C contains far more polar bonds than vitamin A.

can be stored, the body can tolerate for a time a diet deficient in vitamins A, D, E, or K. Conversely, if excessive amounts of these vitamins are consumed, their buildup can lead to the illness *hypervitaminosis.*

In contrast, the water-soluble vitamins are excreted by the body and must be consumed regularly. This fact was first recognized when the British navy discovered that scurvy, a disease often suffered by sailors, could be prevented if the sailors regularly ate fresh limes (which are a good source of vitamin C) when aboard ship (hence the name “limey” for the British sailor).

Carbonation in a bottle of soda.

Pressure Effects

While pressure has little effect on the solubilities of solids or liquids, it does significantly increase the solubility of a gas. Carbonated beverages, for example, are always bottled at high pressures of carbon dioxide to ensure a high concentration of carbon dioxide in the liquid. The fizzing that occurs when you open a can of soda results from the escape of gaseous carbon dioxide because under these conditions the pressure of CO_2 above the solution is now much lower than that used in the bottling process.

The increase in gas solubility with pressure can be understood from Fig. 11.5. Figure 11.5(a) shows a gas in equilibrium with a solution; that is, the gas molecules are entering and leaving the solution at the same rate. If the pressure is suddenly increased [Fig. 11.5(b)], the number of gas molecules per unit volume increases, and the gas enters the solution at a higher rate than it leaves. As the concentration of dissolved gas increases, the rate of the escape of the gas also increases until a new equilibrium is reached [Fig. 11.5(c)], where the solution contains more dissolved gas than before.

CHEMICAL IMPACT

Ionic Liquids?

So far in this text, you have seen that ionic substances are stable solids with high melting points. For example, sodium chloride has a melting point near 800°C. One of the "hottest" areas of current chemical research is ionic liquids—substances composed of ions that are liquids at normal temperatures and pressures. This unusual behavior results from the differences in the sizes of the anions and cations in the ionic liquids. Dozens of small anions, such as BF_4^- (tetrafluoroborate) or PF_6^- (hexafluorophosphate), can be paired with thousands of large cations, such as 1-hexyl-3-methylimidazolium or 1-butyl-3-methylimidazolium (parts a and b respectively, in the accompanying figure). These substances remain liquids because the bulky, asymmetrical cations do not pack together efficiently with the smaller, symmetrical anions. In contrast, in sodium chloride the ions can pack very efficiently to form a compact, orderly arrangement, leading to maximum cation–anion attractions and thus a high melting point.

The excitement being generated by these ionic liquids arises from many factors. For one thing, almost an infinite variety of ionic liquids are possible due to the large variety of bulky cations and small anions available. According to Kenneth R. Seddon, Director of QUILL (Queen's University Ionic Liquid Laboratory) in Northern Ireland, a *trillion* ionic liquids are possible. Another great advantage of these liquids is their long liquid range, typically from −100°C to 200°C.

In addition, the cations in the liquids can be designed to perform specific functions. For example, chemist James

The relationship between gas pressure and the concentration of dissolved gas is given by **Henry's law:**

$$C = kP$$

where C represents the concentration of the dissolved gas, k is a constant characteristic of a particular solution, and P represents the partial pressure of the gaseous solute above the solution. In words, Henry's law states that *the amount of a gas dissolved in a solution is directly proportional to the pressure of the gas above the solution.*

William Henry (1774–1836), a close friend of John Dalton, formulated his law in 1801.

Henry's law holds only when there is no chemical reaction between the solute and solvent.

Henry's law is obeyed most accurately for dilute solutions of gases that do not dissociate in or react with the solvent. For example, Henry's law is obeyed by oxygen gas in water, but it does *not* correctly represent the behavior of gaseous hydrogen chloride in water because of the dissociation reaction

$$\mathrm{HCl}(g) \xrightarrow{\mathrm{H_2O}} \mathrm{H}^+(aq) + \mathrm{Cl}^-(aq)$$

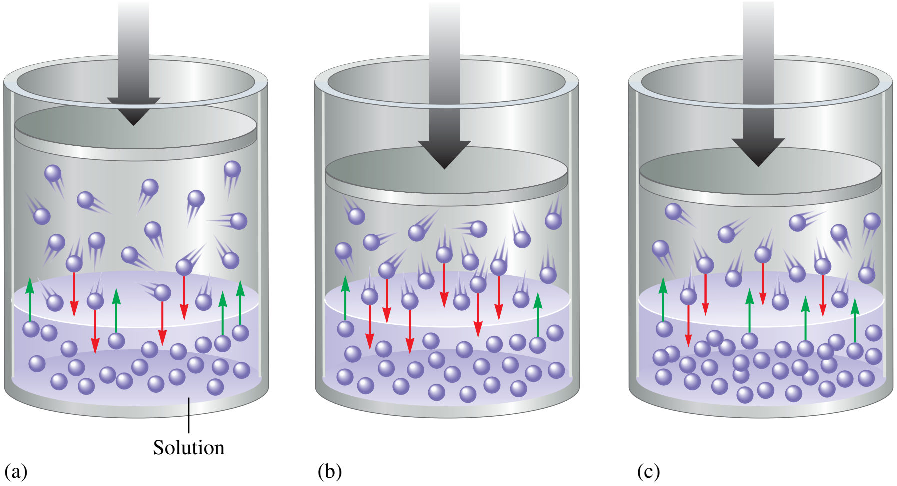
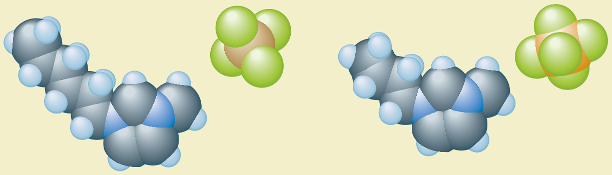


FIGURE 11.5
(a) A gaseous solute in equilibrium with a solution. (b) The piston is pushed in, which increases the pressure of the gas and the number of gas molecules per unit volume. This causes an increase in the rate at which the gas enters the solution, so the concentration of dissolved gas increases. (c) The greater gas concentration in the solution causes an increase in the rate of escape. A new equilibrium is reached.

H. Davis, of the University of South Alabama in Mobile, has designed various cations that will attract potentially harmful ions such as mercury, cadmium, uranium, and americium (the latter two are commonly found in nuclear waste materials) and leach them out of contaminated solutions. Davis has also developed cations that will remove H_2S (which produces SO_2 when the gas is burned) and CO_2 (which does not burn) from natural gas. Potentially, these ionic solutions might also be used to remove CO_2 from the exhaust gases of fossil-fuel–burning power plants to lessen the "greenhouse effect."

The biggest obstacle to the widespread use of ionic liquids is their cost. Normal organic solvents used in industry typically cost a few cents per liter, but ionic liquids can cost hundreds of times that amount. However, the environmentally friendly nature of ionic liquids (they produce no vapors because the ions are not volatile) and the flexibility of these substances as reaction media make them very attractive. As a consequence, efforts are under way to make their use economically feasible.

The term *ionic liquid* may have seemed like an oxymoron in the past, but these substances have a very promising future.


(a) (b)

Sample Exercise 11.4 Calculations Using Henry's Law

A certain soft drink is bottled so that a bottle at 25°C contains CO_2 gas at a pressure of 5.0 atm over the liquid. Assuming that the partial pressure of CO_2 in the atmosphere is 4.0×10^{-4} atm, calculate the equilibrium concentrations of CO_2 in the soda both before and after the bottle is opened. The Henry's law constant for CO_2 in aqueous solution is 3.1×10^{-2} mol/L · atm at 25°C.

Solution

We can write Henry's law for CO_2 as

$$C_{CO_2} = k_{CO_2}P_{CO_2}$$

where $k_{CO_2} = 3.1 \times 10^{-2}$ mol/L · atm. In the *unopened* bottle, $P_{CO_2} = 5.0$ atm and

$$C_{CO_2} = k_{CO_2}P_{CO_2} = (3.1 \times 10^{-2}\ \text{mol/L} \cdot \text{atm})(5.0\ \text{atm}) = 0.16\ \text{mol/L}$$

In the *opened* bottle, the CO_2 in the soda eventually reaches equilibrium with the atmospheric CO_2, so $P_{CO_2} = 4.0 \times 10^{-4}$ atm and

$$C_{CO_2} = k_{CO_2}P_{CO_2} = \left(3.1 \times 10^{-2}\ \frac{\text{mol}}{\text{L} \cdot \text{atm}}\right)(4.0 \times 10^{-4}\ \text{atm}) = 1.2 \times 10^{-5}\ \text{mol/L}$$

Note the large change in concentration of CO_2. This is why soda goes "flat" after being open for a while.

See Exercises 11.43 and 11.44.

ΔH°_{soln} refers to the formation of a 1.0 *M* ideal solution and is not necessarily relevant to the process of dissolving a solid in a saturated solution. Thus ΔH°_{soln} is of limited use in predicting the variation of solubility with temperature.

Temperature Effects (for Aqueous Solutions)

Everyday experiences of dissolving substances such as sugar may lead you to think that solubility always increases with temperature. This is not the case. The dissolving of a solid occurs *more rapidly* at higher temperatures, but the amount of solid that can be dissolved may increase or decrease with increasing temperature. The effect of temperature on the solubility in water of several solids is shown in Fig. 11.6. Note that although the solubility of most solids in water increases with temperature, the solubilities of some substances (such as sodium sulfate and cerium sulfate) decrease with increasing temperature.

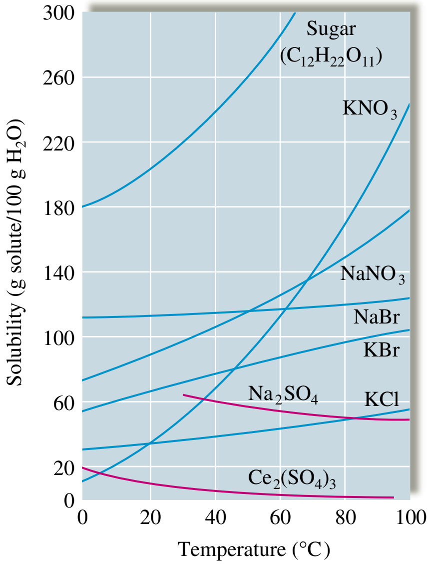


FIGURE 11.6
The solubilities of several solids as a function of temperature. Note that while most substances become more soluble in water with increasing temperature, sodium sulfate and cerium sulfate become less soluble.

Predicting the temperature dependence of solubility is very difficult. For example, although there is some correlation between the sign of $\Delta H^\circ_{\text{soln}}$ and the variation of solubility with temperature, important exceptions exist.* The only sure way to determine the temperature dependence of a solid's solubility is by experiment.

The behavior of gases dissolving in water appears less complex. The solubility of a gas in water typically decreases with increasing temperature,† as is shown for several cases in Fig. 11.7. This temperature effect has important environmental implications because of the widespread use of water from lakes and rivers for industrial cooling. After being used, the water is returned to its natural source at a higher than ambient temperature (**thermal pollution** has occurred). Because it is warmer, this water contains less than the normal concentration of oxygen and is also less dense; it tends to "float" on the colder water below, thus blocking normal oxygen absorption. This effect can be especially important in deep lakes. The warm upper layer can seriously decrease the amount of oxygen available to aquatic life in the deeper layers of the lake.

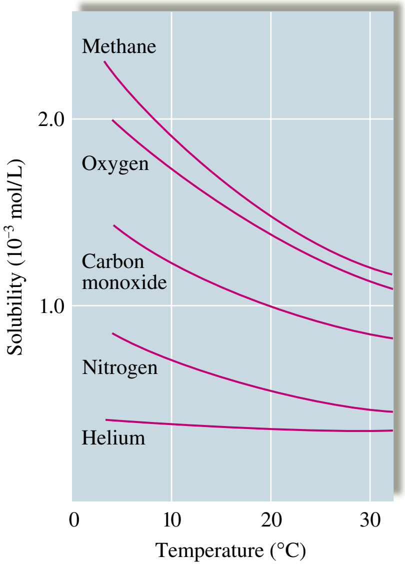


FIGURE 11.7
The solubilities of several gases in water as a function of temperature at a constant pressure of 1 atm of gas above the solution.

The decreasing solubility of gases with increasing temperature is also responsible for the formation of *boiler scale.* As we will see in more detail in Chapter 14, the bicarbonate ion is formed when carbon dioxide is dissolved in water containing the carbonate ion:

$$CO_3^{2-}(aq) + CO_2(aq) + H_2O(l) \longrightarrow 2HCO_3^-(aq)$$

When the water also contains Ca^{2+} ions, this reaction is especially important—calcium bicarbonate is soluble in water, but calcium carbonate is insoluble. When the water is heated, the carbon dioxide is driven off. For the system to replace the lost carbon dioxide, the reverse reaction must occur:

$$2HCO_3^-(aq) \longrightarrow H_2O(l) + CO_2(aq) + CO_3^{2-}(aq)$$

This reaction, however, also increases the concentration of carbonate ions, causing solid calcium carbonate to form. This solid is the boiler scale that coats the walls of containers such as industrial boilers and tea kettles. Boiler scale reduces the efficiency of heat transfer and can lead to blockage of pipes (see Fig. 11.8).

FIGURE 11.8
A pipe with accumulated mineral deposits. The cross section clearly indicates the reduction in pipe capacity.

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*For more information see R. S. Treptow, "Le Châtelier's Principle Applied to the Temperature Dependence of Solubility," *J. Chem. Ed.* **61** (1984): 499.

†The opposite behavior is observed for most nonaqueous solvents.

CHEMICAL IMPACT

The Lake Nyos Tragedy

On August 21, 1986, a cloud of gas suddenly boiled from Lake Nyos in Cameroon, killing nearly 2000 people. Although at first it was speculated that the gas was hydrogen sulfide, it now seems clear it was carbon dioxide. What would cause Lake Nyos to emit this huge, suffocating cloud of CO_2? Although the answer may never be known for certain, many scientists believe that the lake suddenly "turned over," bringing to the surface water that contained huge quantities of dissolved carbon dioxide. Lake Nyos is a deep lake that is thermally stratified: Layers of warm, less dense water near the surface float on the colder, denser water layers near the lake's bottom. Under normal conditions the lake stays this way; there is little mixing among the different layers. Scientists believe that over hundreds or thousands of years, carbon dioxide gas had seeped into the cold water at the lake's bottom and dissolved in great amounts because of the large pressure of CO_2 present (in accordance with Henry's law). For some reason on August 21, 1986, the lake apparently suffered an overturn, possibly due to wind or to unusual cooling of the lake's surface by monsoon clouds. This caused water that was greatly supersaturated with CO_2 to reach the surface and release tremendous quantities of gaseous CO_2 that suffocated thousands of humans and animals before they knew what hit them—a tragic, monumental illustration of Henry's law.

Lake Nyos in Cameroon.

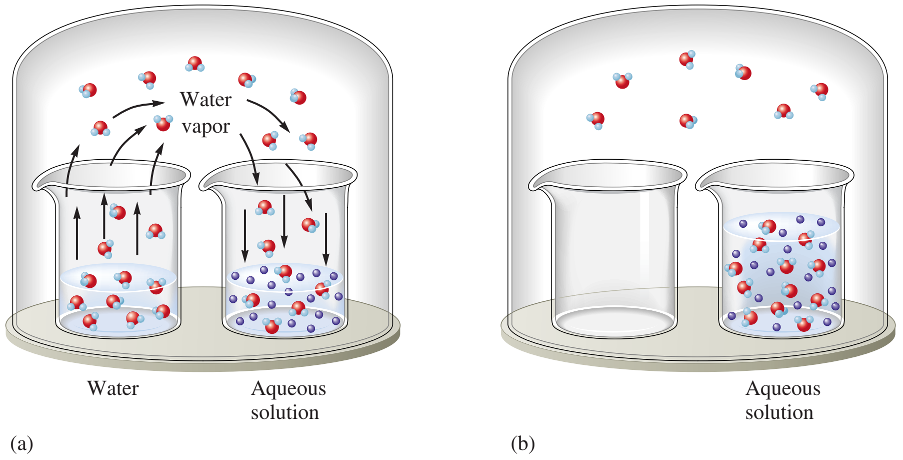
Since 1986 the scientists studying Lake Nyos and nearby Lake Monoun have observed a rapid recharging of the CO_2 levels in the deep waters of these lakes, causing concern that another deadly gas release could occur at any time. Apparently the only way to prevent such a disaster is to pump away the CO_2-charged deep water in the two lakes. Scientists at a conference to study this problem in 1994 recommended such a solution, but it has not yet been funded by Cameroon.

11.4 The Vapor Pressures of Solutions

Liquid solutions have physical properties significantly different from those of the pure solvent, a fact that has great practical importance. For example, we add antifreeze to the water in a car's cooling system to prevent freezing in winter and boiling in summer. We also melt ice on sidewalks and streets by spreading salt. These preventive measures work because of the solute's effect on the solvent's properties.

To explore how a nonvolatile solute affects a solvent, we will consider the experiment represented in Fig. 11.9, in which a sealed container encloses a beaker containing an aqueous sulfuric acid solution and a beaker containing pure water. Gradually, the volume of the sulfuric acid solution increases and the volume of the pure water decreases. Why? We can explain this observation if the vapor pressure of the pure solvent is greater than that of the solution. Under these conditions, the pressure of vapor necessary to achieve equilibrium with the pure solvent is greater than that required to reach equilibrium with the aqueous acid solution. Thus, as the pure solvent emits vapor to attempt to reach equilibrium, the aqueous sulfuric acid solution absorbs vapor to try to lower the vapor pressure toward its equilibrium value. This process results in a net transfer of water from the pure water through the vapor phase to the sulfuric acid solution. The system can reach an equilibrium vapor pressure only when all the water is transferred to the solution. This

A nonvolatile solute has no tendency to escape from solution into the vapor phase.



Water

Aqueous solution

(a)

Aqueous solution

(b)

FIGURE 11.9
An aqueous solution and pure water in a closed environment. (a) Initial stage. (b) After a period of time, the water is transferred to the solution.

experiment is just one of many observations indicating that the presence of a *nonvolatile solute lowers the vapor pressure of a solvent.*

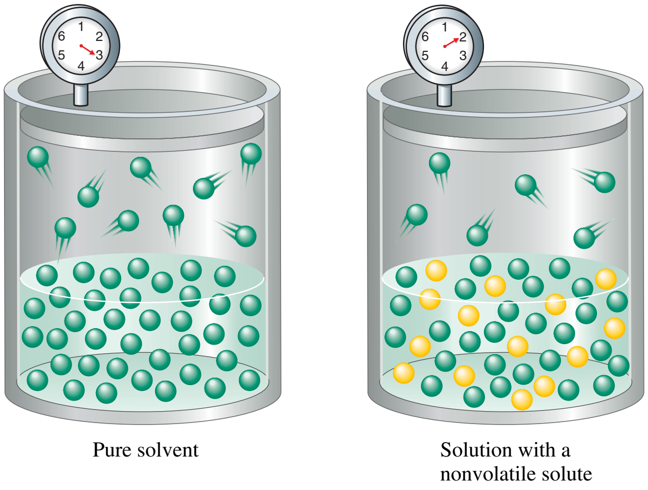
We can account for this behavior in terms of the simple model shown in Fig. 11.10. The dissolved nonvolatile solute decreases the number of solvent molecules per unit volume and it should proportionately lower the escaping tendency of the solvent molecules. For example, in a solution consisting of half nonvolatile solute molecules and half solvent molecules, we might expect the observed vapor pressure to be half that of the pure solvent, since only half as many molecules can escape. In fact, this is what is observed.

Visualization: Vapor Pressure Lowering: Liquid/Vapor Equilibrium
Visualization: Vapor Pressure Lowering: Addition of a Solute
Visualization: Vapor Pressure Lowering: Solution/Vapor Equilibrium

Detailed studies of the vapor pressures of solutions containing nonvolatile solutes were carried out by François M. Raoult (1830–1901). His results are described by the equation known as **Raoult's law:**

$$P_{\text{soln}} = \chi_{\text{solvent}} P^0_{\text{solvent}}$$

where P_{soln} is the observed vapor pressure of the solution, χ_{solvent} is the mole fraction of solvent, and P^0_{solvent} is the vapor pressure of the pure solvent. Note that for a solution of half solute and half solvent molecules, χ_{solvent} is 0.5, so the vapor pressure of the solution is half that of the pure solvent. On the other hand, for a solution in which three-fourths of the solution molecules are solvent, $\chi_{\text{solvent}} = \frac{3}{4} = 0.75$, and $P_{\text{soln}} = 0.75P^0_{\text{solvent}}$. The idea is that the nonvolatile solute simply dilutes the solvent.



Pure solvent

Solution with a nonvolatile solute

FIGURE 11.10
The presence of a nonvolatile solute inhibits the escape of solvent molecules from the liquid and so lowers the vapor pressure of the solvent.

Raoult's law states that the vapor pressure of a solution is directly proportional to the mole fraction of solvent present.

Raoult's law is a linear equation of the form $y = mx + b$, where $y = P_{\text{soln}}$, $x = \chi_{\text{solvent}}$, $m = P^0_{\text{solvent}}$, and $b = 0$. Thus a plot of P_{soln} versus χ_{solvent} gives a straight line with a slope equal to P^0_{solvent}, as shown in Fig. 11.11.

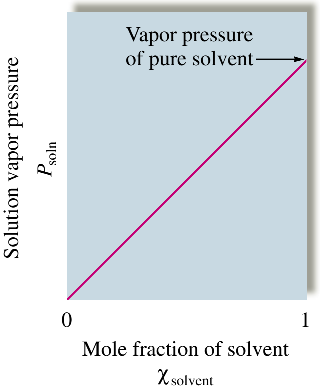


FIGURE 11.11
For a solution that obeys Raoult's law, a plot of P_{soln} versus χ_{solvent} gives a straight line.

Sample Exercise 11.5 Calculating the Vapor Pressure of a Solution

Calculate the expected vapor pressure at 25°C for a solution prepared by dissolving 158.0 g of common table sugar (sucrose, molar mass = 342.3 g/mol) in 643.5 cm^3 of water. At 25°C, the density of water is 0.9971 g/cm^3 and the vapor pressure is 23.76 torr.

Solution

We will use Raoult's law in the form

$$P_{\text{soln}} = \chi_{H_2O} P^0_{H_2O}$$

To calculate the mole fraction of water in the solution, we must first determine the number of moles of sucrose:

$$\text{Moles of sucrose} = 158.0 \text{ g sucrose} \times \frac{1 \text{ mol sucrose}}{342.3 \text{ g sucrose}}$$
$$= 0.4616 \text{ mol sucrose}$$

To determine the moles of water present, we first convert volume to mass using the density:

$$643.5 \text{ cm}^3 \text{ } H_2O \times \frac{0.9971 \text{ g } H_2O}{\text{cm}^3 \text{ } H_2O} = 641.6 \text{ g } H_2O$$

The number of moles of water is therefore

$$641.6 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.01 \text{ g } H_2O} = 35.63 \text{ mol } H_2O$$

The mole fraction of water in the solution is

$$\chi_{H_2O} = \frac{\text{mol } H_2O}{\text{mol } H_2O + \text{mol sucrose}} = \frac{35.63 \text{ mol}}{35.63 \text{ mol} + 0.4616 \text{ mol}}$$
$$= \frac{35.63 \text{ mol}}{36.09 \text{ mol}} = 0.9873$$

Then $$P_{\text{soln}} = \chi_{H_2O} P^0_{H_2O} = (0.9873)(23.76 \text{ torr}) = 23.46 \text{ torr}$$

Thus the vapor pressure of water has been lowered from 23.76 torr in the pure state to 23.46 torr in the solution. The vapor pressure has been lowered by 0.30 torr.

See Exercises 11.45 and 11.46.

The phenomenon of the lowering of the vapor pressure gives us a convenient way to "count" molecules and thus provides a means for experimentally determining molar masses. Suppose a certain mass of a compound is dissolved in a solvent and the vapor pressure of the resulting solution is measured. Using Raoult's law, we can determine the number of moles of solute present. Since the mass of this number of moles is known, we can calculate the molar mass.

The lowering of vapor pressure depends on the number of solute particles present in the solution.

We also can use vapor pressure measurements to characterize solutions. For example, 1 mole of sodium chloride dissolved in water lowers the vapor pressure approximately twice as much as expected because the solid has two ions per formula unit, which separate when it dissolves. Thus vapor pressure measurements can give valuable information about the nature of the solute after it dissolves.

CHEMICAL IMPACT

Spray Power

Products in aerosol cans are widely used in our society. We use hairsprays, mouth sprays, shaving cream, whipped cream, spray paint, spray cleaners, and many others. As in the case of most consumer products, chemistry plays an important role in making aerosol products work.

An aerosol is a mixture of small particles (solids or liquids) dispersed in some sort of medium (a gas or a liquid). An inspection of the ingredients in an aerosol can reveals a long list of chemical substances, all of which fall into one of three categories: (1) an active ingredient, (2) an inactive ingredient, or (3) a propellant. The active ingredients perform the functions for which the product was purchased (for example, the resins in hairspray). It is very important that the contents of an aerosol can be chemically compatible. If an undesired chemical reaction were to occur inside the can, it is likely that the product would be unable to perform its function. The inactive ingredients serve to keep the product properly mixed and prevent chemical reactions within the can prior to application. The propellant delivers the product out of the can.

Most aerosol products contain liquefied hydrocarbon propellants* such as propane (C_3H_8) and butane (C_4H_{10}). While these molecules are extremely flammable, they are excellent propellants, and they also help to disperse and mix the components of the aerosol can as they are delivered. These propellants have critical temperatures above room temperature,

Insecticide is sprayed from an aerosol can.

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*For foods delivered by aerosol cans, propane and butane are obviously not appropriate propellants. For substances such as whipped cream, the propellant N_2O is often used.

Sample Exercise 11.6

Calculating the Vapor Pressure of a Solution Containing Ionic Solute

Predict the vapor pressure of a solution prepared by mixing 35.0 g solid Na_2SO_4 (molar mass = 142 g/mol) with 175 g water at 25°C. The vapor pressure of pure water at 25°C is 23.76 torr.

Solution

First, we need to know the mole fraction of H_2O.

$$n_{H_2O} = 175 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.0 \text{ g } H_2O} = 9.72 \text{ mol } H_2O$$

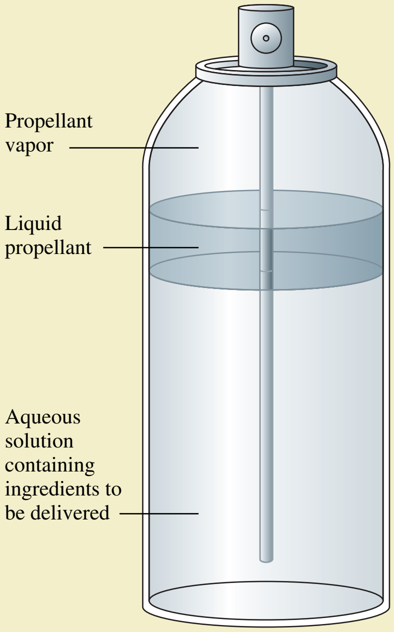
$$n_{Na_2SO_4} = 35.0 \text{ g } Na_2SO_4 \times \frac{1 \text{ mol } Na_2SO_4}{142 \text{ g } Na_2SO_4} = 0.246 \text{ mol } Na_2SO_4$$

It is essential to recognize that when 1 mole of solid Na_2SO_4 dissolves, it produces 2 mol Na^+ ions and 1 mol SO_4^{2-} ions. Thus the number of solute particles present in this solution is three times the number of moles of solute dissolved:

$$n_{\text{solute}} = 3(0.246) = 0.738 \text{ mol}$$

$$\chi_{H_2O} = \frac{n_{H_2O}}{n_{\text{solute}} + n_{H_2O}} = \frac{9.72 \text{ mol}}{0.738 \text{ mol} + 9.72 \text{ mol}} = \frac{9.72}{10.458} = 0.929$$

which means that the intermolecular forces among their molecules are strong enough to form a liquid when pressure is applied. In the highly pressurized aerosol can, the liquid phase of the propellant is in equilibrium with the gaseous phase of the propellant in the head space of the can. The ability of the propellant to maintain this equilibrium is the key to how the aerosol can works. All aerosol cans are constructed in a similar way (see accompanying diagram). At the top of the can is a valve (acts to open and seal the can) and an actuator (to open the valve). Pushing the actuator opens the valve, and the propellant gas escapes through a long tube (the dip tube) that extends from the bottom of the can. With the valve open, the propellant, at a greater pressure than the atmosphere, escapes through the dip tube, carrying the active ingredient(s) with it. The rapidly expanding gas propels the contents from the can and in some instances (for example, shaving cream, carpet shampoo) produces a foam. After each use, the remaining propellant in the can reestablishes equilibrium between the liquid and gaseous phases, keeping the pressure constant within the can as long as sufficient propellant remains. The trick is to have the active and inactive ingredients and the propellant run out at the same time. Given the nature of the most common propellants, you can understand the warning about not putting the "empty" cans in a fire.



An aerosol can for delivery of an active ingredient dissolved in an aqueous solution.

Now we can use Raoult's law to predict the vapor pressure:

$$P_{\mathrm{soln}} = \chi_{\mathrm{H_2O}} P^0_{\mathrm{H_2O}} = (0.929)(23.76 \text{ torr}) = 22.1 \text{ torr}$$

See Exercise 11.48.

Nonideal Solutions

So far we have assumed that the solute is nonvolatile and so does not contribute to the vapor pressure over the solution. However, for liquid–liquid solutions where both components are volatile, a modified form of Raoult's law applies:

$$P_{\mathrm{TOTAL}} = P_{\mathrm{A}} + P_{\mathrm{B}} = \chi_{\mathrm{A}} P^0_{\mathrm{A}} + \chi_{\mathrm{B}} P^0_{\mathrm{B}}$$

where P_{TOTAL} represents the total vapor pressure of a solution containing A and B, χ_{A} and χ_{B} are the mole fractions of A and B, P^0_{A} and P^0_{B} are the vapor pressures of pure A and pure B, and P_{A} and P_{B} are the partial pressures resulting from molecules of A and of B in the vapor above the solution (see Fig. 11.12).

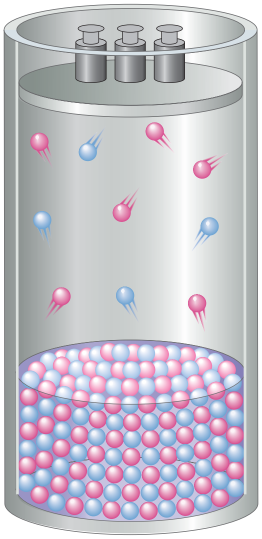
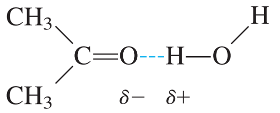


FIGURE 11.12
When a solution contains two volatile components, both contribute to the total vapor pressure. Note that in this case the solution contains equal numbers of the components 🔴 and 🔵 but the vapor contains more 🔴 than 🔵. This means that component 🔴 is more volatile (has a higher vapor pressure as a pure liquid) than component 🔵.

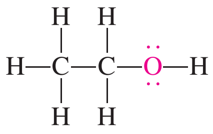
A liquid–liquid solution that obeys Raoult's law is called an **ideal solution.** Raoult's law is to solutions what the ideal gas law is to gases. As with gases, ideal behavior for solutions is never perfectly achieved but is sometimes closely approached. Nearly ideal behavior is often observed when the solute–solute, solvent–solvent, and solute–solvent interactions are very similar. That is, in solutions where the solute and solvent are very much alike, the solute simply acts to dilute the solvent. However, if the solvent has a special affinity for the solute, such as if hydrogen bonding occurs, the tendency of the solvent molecules to escape will be lowered more than expected. The observed vapor pressure will be *lower* than the value predicted by Raoult's law; there will be a *negative deviation from Raoult's law.*

When a solute and solvent release large quantities of energy in the formation of a solution, that is, when ΔH_{soln} is large and negative, we can assume that strong interactions exist between the solute and solvent. In this case we expect a negative deviation from Raoult's law, because both components will have a lower escaping tendency in the solution than in the pure liquids. This behavior is illustrated by an acetone–water solution, where the molecules can hydrogen-bond effectively:

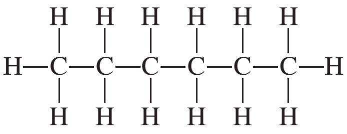
Strong solute–solvent interaction gives a vapor pressure lower than that predicted by Raoult's law.



In contrast, if two liquids mix endothermically, it indicates that the solute–solvent interactions are weaker than the interactions among the molecules in the pure liquids. More energy is required to expand the liquids than is released when the liquids are mixed. In this case the molecules in the solution have a higher tendency to escape than expected, and *positive* deviations from Raoult's law are observed (see Fig. 11.13). An example of this case is provided by a solution of ethanol and hexane, whose Lewis structures are as follows:



Ethanol



Hexane

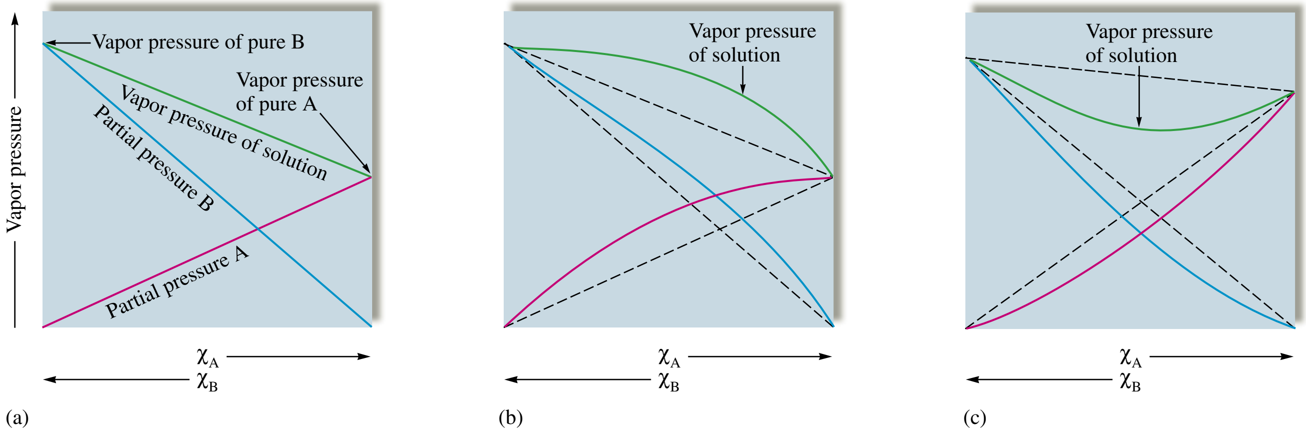


FIGURE 11.13

Vapor pressure for a solution of two volatile liquids. (a) The behavior predicted for an ideal liquid–liquid solution by Raoult's law. (b) A solution for which P_{TOTAL} is larger than the value calculated from Raoult's law. This solution shows a positive deviation from Raoult's law. (c) A solution for which P_{TOTAL} is smaller than the value calculated from Raoult's law. This solution shows a negative deviation from Raoult's law.

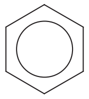
TABLE 11.4 Summary of the Behavior of Various Types of Solutions

Interactive Forces Between Solute (A) and Solvent (B) Particles	ΔH_{soln}	ΔT for Solution Formation	Deviation from Raoult's Law	Example
$A \leftrightarrow A, B \leftrightarrow B \equiv A \leftrightarrow B$	Zero	Zero	None (ideal solution)	Benzene–toluene
$A \leftrightarrow A, B \leftrightarrow B < A \leftrightarrow B$	Negative (exothermic)	Positive	Negative	Acetone–water
$A \leftrightarrow A, B \leftrightarrow B > A \leftrightarrow B$	Positive (endothermic)	Negative	Positive	Ethanol–hexane

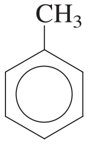
The polar ethanol and the nonpolar hexane molecules are not able to interact effectively. Thus the enthalpy of solution is positive, as is the deviation from Raoult's law.

Finally, for a solution of very similar liquids, such as benzene and toluene (shown in margin), the enthalpy of solution is very close to zero, and thus the solution closely obeys Raoult's law (ideal behavior).

A summary of the behavior of various types of solutions is given in Table 11.4.



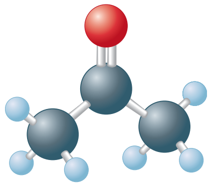
Benzene



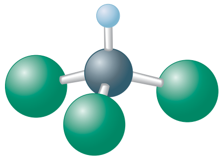
Toluene

Sample Exercise 11.7

Calculating the Vapor Pressure of a Solution Containing Two Liquids



Acetone



Chloroform

A solution is prepared by mixing 5.81 g acetone (C_3H_6O, molar mass = 58.1 g/mol) and 11.9 g chloroform ($HCCl_3$, molar mass = 119.4 g/mol). At 35°C, this solution has a total vapor pressure of 260. torr. Is this an ideal solution? The vapor pressures of pure acetone and pure chloroform at 35°C are 345 and 293 torr, respectively.

Solution

To decide whether this solution behaves ideally, we first calculate the expected vapor pressure using Raoult's law:

$$P_{\text{TOTAL}} = \chi_A P_A^0 + \chi_C P_C^0$$

where A stands for acetone and C stands for chloroform. The calculated value can then be compared with the observed vapor pressure.

First, we must calculate the number of moles of acetone and chloroform:

$$5.81 \text{ g acetone} \times \frac{1 \text{ mol acetone}}{58.1 \text{ g acetone}} = 0.100 \text{ mol acetone}$$

$$11.9 \text{ g chloroform} \times \frac{1 \text{ mol chloroform}}{119 \text{ g chloroform}} = 0.100 \text{ mol chloroform}$$

Since the solution contains equal numbers of moles of acetone and chloroform, that is,

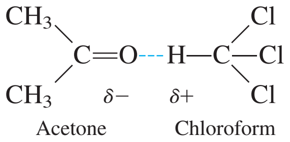
$$\chi_A = 0.500 \quad \text{and} \quad \chi_C = 0.500$$

the expected vapor pressure is

$$P_{\text{TOTAL}} = (0.500)(345 \text{ torr}) + (0.500)(293 \text{ torr}) = 319 \text{ torr}$$

In this case the usually nonpolar C—H bond is strongly polarized by the three attached, highly electronegative chlorine atoms, thus producing hydrogen bonding.

Comparing this value with the observed pressure of 260. torr shows that the solution does not behave ideally. The observed value is lower than that expected. This negative deviation from Raoult's law can be explained in terms of the hydrogen bonding interaction



which lowers the tendency of these molecules to escape from the solution.

See Exercises 11.55 and 11.56.

11.5 Boiling-Point Elevation and Freezing-Point Depression

In the preceding section we saw how a solute affects the vapor pressure of a liquid solvent. Because changes of state depend on vapor pressure, the presence of a solute also affects the freezing point and boiling point of a solvent. Freezing-point depression, boiling-point elevation, and osmotic pressure (discussed in Section 11.6) are called **colligative properties.** As we will see, they are grouped together because they depend only on the number, and not on the identity, of the solute particles in an ideal solution. Because of their direct relationship to the number of solute particles, the colligative properties are very useful for characterizing the nature of a solute after it is dissolved in a solvent and for determining molar masses of substances.

Boiling-Point Elevation

Normal boiling point was defined in Section 10.8.

Visualization: Boiling-Point Elevation: Liquid/Vapor Equilibrium
Visualization: Boiling-Point Elevation: Addition of a Solute
Visualization: Boiling-Point Elevation: Solution/Vapor Equilibrium

The normal boiling point of a liquid occurs at the temperature where the vapor pressure is equal to 1 atmosphere. We have seen that a nonvolatile solute lowers the vapor pressure of the solvent. Therefore, such a solution must be heated to a higher temperature than the boiling point of the pure solvent to reach a vapor pressure of 1 atmosphere. This means that *a nonvolatile solute elevates the boiling point of the solvent.* Figure 11.14 shows the phase diagram for an aqueous solution containing a nonvolatile solute. Note that the liquid/vapor line is shifted to higher temperatures than those for pure water.

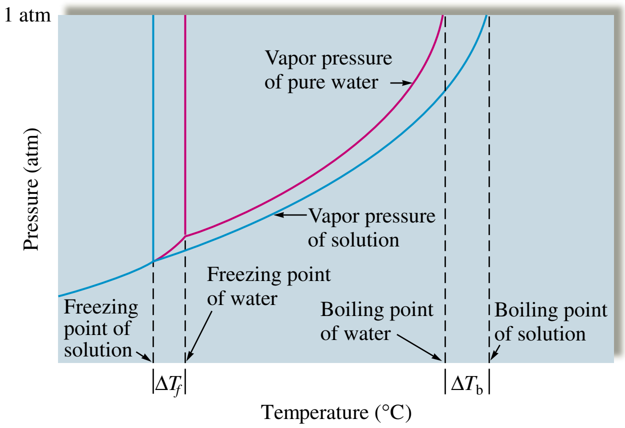


FIGURE 11.14
Phase diagrams for pure water (red lines) and for an aqueous solution containing a nonvolatile solute (blue lines). Note that the boiling point of the solution is higher than that of pure water. Conversely, the freezing point of the solution is lower than that of pure water. The effect of a nonvolatile solute is to extend the liquid range of a solvent.

TABLE 11.5 Molal Boiling-Point Elevation Constants (K_b) and Freezing-Point Depression Constants (K_f) for Several Solvents

Solvent	Boiling Point (°C)	K_b (°C · kg/mol)	Freezing Point (°C)	K_f (°C · kg/mol)
Water (H_2O)	100.0	0.51	0	1.86
Carbon tetrachloride (CCl_4)	76.5	5.03	−22.99	30.
Chloroform ($CHCl_3$)	61.2	3.63	−63.5	4.70
Benzene (C_6H_6)	80.1	2.53	5.5	5.12
Carbon disulfide (CS_2)	46.2	2.34	−111.5	3.83
Ethyl ether ($C_4H_{10}O$)	34.5	2.02	−116.2	1.79
Camphor ($C_{10}H_{16}O$)	208.0	5.95	179.8	40.

As you might expect, the magnitude of the boiling-point elevation depends on the concentration of the solute. The change in boiling point can be represented by the equation

$$\Delta T = K_b m_{\text{solute}}$$

where ΔT is the boiling-point elevation, or the difference between the boiling point of the solution and that of the pure solvent, K_b is a constant that is characteristic of the solvent and is called the **molal boiling-point elevation constant,** and m_{solute} is the *molality* of the solute in the solution.

Values of K_b for some common solvents are given in Table 11.5. The molar mass of a solute can be determined from the observed boiling-point elevation, as shown in Sample Exercise 11.8.

Sample Exercise 11.8 Calculating the Molar Mass by Boiling-Point Elevation

A solution was prepared by dissolving 18.00 g glucose in 150.0 g water. The resulting solution was found to have a boiling point of 100.34°C. Calculate the molar mass of glucose. Glucose is a molecular solid that is present as individual molecules in solution.

Sugar dissolved in water to make candy causes the boiling point to be elevated above 100°C.

Solution

We make use of the equation

$$\Delta T = K_b m_{\text{solute}}$$

where $$\Delta T = 100.34°\text{C} - 100.00°\text{C} = 0.34°\text{C}$$

From Table 11.5, for water $K_b = 0.51$. The molality of this solution then can be calculated by rearranging the boiling-point elevation equation to give

$$m_{\text{solute}} = \frac{\Delta T}{K_b} = \frac{0.34°\text{C}}{0.51°\text{C} \cdot \text{kg/mol}} = 0.67 \text{ mol/kg}$$

The solution was prepared using 0.1500 kg water. Using the definition of molality, we can find the number of moles of glucose in the solution.

$$m_{\text{solute}} = 0.67 \text{ mol/kg} = \frac{\text{mol solute}}{\text{kg solvent}} = \frac{n_{\text{glucose}}}{0.1500 \text{ kg}}$$

$$n_{\text{glucose}} = (0.67 \text{ mol/kg})(0.1500 \text{ kg}) = 0.10 \text{ mol}$$

Thus 0.10 mol glucose has a mass of 18.00 g, and 1.0 mol glucose has a mass of 180 g (10 × 18.00 g). The molar mass of glucose is 180 g/mol.

See Exercise 11.58.

Melting point and *freezing point* both refer to the temperature where the solid and liquid coexist.

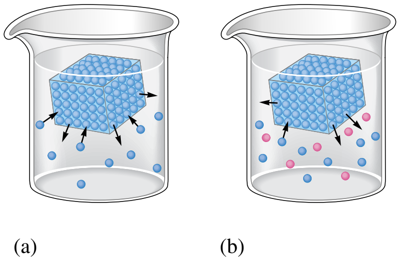


FIGURE 11.15
(a) Ice in equilibrium with liquid water.
(b) Ice in equilibrium with liquid water containing a dissolved solute (shown in pink).

Freezing-Point Depression

Visualization: Freezing-Point Depression: Solid/Liquid Equilibrium
Visualization: Freezing-Point Depression: Addition of a Solute
Visualization: Freezing-Point Depression: Solid/Solution Equilibrium

When a solute is dissolved in a solvent, the freezing point of the solution is lower than that of the pure solvent. Why? Recall that the vapor pressures of ice and liquid water are the same at 0°C. Suppose a solute is dissolved in water. The resulting solution will not freeze at 0°C because *the water in the solution has a lower vapor pressure than that of pure ice.* No ice will form under these conditions. However, the vapor pressure of ice decreases more rapidly than that of liquid water as the temperature decreases. Therefore, as the solution is cooled, the vapor pressure of the ice and that of the liquid water in the solution will eventually become equal. The temperature at which this occurs is the new freezing point of the solution and is below 0°C. The freezing point has been *depressed.*

We can account for this behavior in terms of the simple model shown in Fig. 11.15. The presence of the solute lowers the rate at which molecules in the liquid return to the solid state. Thus, for an aqueous solution, only the liquid state is found at 0°C. As the solution is cooled, the rate at which water molecules leave the solid ice decreases until this rate and the rate of formation of ice become equal and equilibrium is reached. This is the freezing point of the water in the solution.

Spreading salt on a highway.

Because a solute lowers the freezing point of water, compounds such as sodium chloride and calcium chloride are often spread on streets and sidewalks to prevent ice from forming in freezing weather. Of course, if the outside temperature is lower than the freezing point of the resulting salt solution, ice forms anyway. So this procedure is not effective at extremely cold temperatures.

The solid/liquid line for an aqueous solution is shown on the phase diagram for water in Fig. 11.14. Since the presence of a solute elevates the boiling point and depresses the freezing point of the solvent, adding a solute has the effect of extending the liquid range.

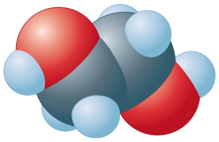
The equation for freezing-point depression is analogous to that for boiling-point elevation:

$$\Delta T = K_f m_{\text{solute}}$$

where ΔT is the freezing-point depression, or the difference between the freezing point of the pure solvent and that of the solution, and K_f is a constant that is characteristic of a particular solvent and is called the **molal freezing-point depression constant.** Values of K_f for common solvents are listed in Table 11.5.

Like the boiling-point elevation, the observed freezing-point depression can be used to determine molar masses and to characterize solutions.

Sample Exercise 11.9 Freezing-Point Depression



Ethylene glycol

What mass of ethylene glycol ($C_2H_6O_2$, molar mass = 62.1 g/mol), the main component of antifreeze, must be added to 10.0 L of water to produce a solution for use in a car's radiator that freezes at −10.0°F (−23.3°C)? Assume the density of water is exactly 1 g/mL.

The addition of antifreeze lowers the freezing point of water in a car's radiator.

Solution

The freezing point must be lowered from 0°C to −23.3°C. To determine the molality of ethylene glycol needed to accomplish this, we can use the equation

$$\Delta T = K_f m_{\text{solute}}$$

where $\Delta T = 23.3°\text{C}$ and $K_f = 1.86$ (from Table 11.5). Solving for the molality gives

$$m_{\text{solute}} = \frac{\Delta T}{K_f} = \frac{23.3°\text{C}}{1.86°\text{C} \cdot \text{kg/mol}} = 12.5 \text{ mol/kg}$$

This means that 12.5 mol ethylene glycol must be added per kilogram of water. We have 10.0 L, or 10.0 kg, of water. Therefore, the total number of moles of ethylene glycol needed is

$$\frac{12.5 \text{ mol}}{\text{kg}} \times 10.0 \text{ kg} = 1.25 \times 10^2 \text{ mol}$$

The mass of ethylene glycol needed is

$$1.25 \times 10^2 \text{ mol} \times \frac{62.1 \text{ g}}{\text{mol}} = 7.76 \times 10^3 \text{ g (or 7.76 kg)}$$

See Exercises 11.61 and 11.62.

Sample Exercise 11.10 Determining Molar Mass by Freezing-Point Depression

A chemist is trying to identify a human hormone that controls metabolism by determining its molar mass. A sample weighing 0.546 g was dissolved in 15.0 g benzene, and the freezing-point depression was determined to be 0.240°C. Calculate the molar mass of the hormone.

Solution

From Table 11.5, K_f for benzene is 5.12°C · kg/mol, so the molality of the hormone is

$$m_{\text{hormone}} = \frac{\Delta T}{K_f} = \frac{0.240°\text{C}}{5.12°\text{C} \cdot \text{kg/mol}} = 4.69 \times 10^{-2} \text{ mol/kg}$$

The moles of hormone can be obtained from the definition of molality:

$$4.69 \times 10^{-2} \text{ mol/kg} = m_{\text{solute}} = \frac{\text{mol hormone}}{0.0150 \text{ kg benzene}}$$

or

$$\text{mol hormone} = \left(4.69 \times 10^{-2} \frac{\text{mol}}{\text{kg}}\right)(0.0150 \text{ kg}) = 7.04 \times 10^{-4} \text{ mol}$$

Since 0.546 g hormone was dissolved, 7.04×10^{-4} mol hormone has a mass of 0.546 g, and

$$\frac{0.546 \text{ g}}{7.04 \times 10^{-4} \text{ mol}} = \frac{x \text{ g}}{1.00 \text{ mol}}$$

$$x = 776 \text{ g/mol}$$

Thus the molar mass of the hormone is 776 g/mol.

See Exercises 11.63 and 11.64.

11.6 Osmotic Pressure

Visualization: Osmosis

Osmotic pressure, another of the colligative properties, can be understood from Fig. 11.16. A solution and pure solvent are separated by a **semipermeable membrane,** which allows *solvent but not solute* molecules to pass through. As time passes, the volume of the solution increases and that of the solvent decreases. This flow of solvent into the solution through the semipermeable membrane is called **osmosis.** Eventually the liquid levels stop changing, indicating that the system has reached equilibrium. Because the liquid levels are different at this point, there is a greater hydrostatic pressure on the solution than on the pure solvent. This excess pressure is called the **osmotic pressure.**

We can take another view of this phenomenon, as illustrated in Fig. 11.17. Osmosis can be prevented by applying a pressure to the solution. *The minimum pressure that stops the osmosis is equal to the osmotic pressure of the solution.* A simple model to explain osmotic pressure can be constructed as shown in Fig. 11.18. The membrane allows only solvent molecules to pass through. However, the initial rates of solvent transfer to and from the solution are not the same. The solute particles interfere with the passage of solvent, so the rate of transfer is slower from the solution to the solvent than in the reverse direction. Thus there is a net transfer of solvent molecules into the solution, which causes the solution volume to increase. As the solution level rises in the tube, the resulting pressure exerts an extra "push" on the solvent molecules in the solution, forcing them back through the membrane. Eventually, enough pressure develops so that the solvent transfer becomes equal in both directions. At this point, equilibrium is achieved and the levels stop changing.

Osmotic pressure can be used to characterize solutions and determine molar masses, as can the other colligative properties, but osmotic pressure is particularly useful because a small concentration of solute produces a relatively large osmotic pressure.

Experiments show that the dependence of the osmotic pressure on solution concentration is represented by the equation

$$\Pi = MRT$$

where Π is the osmotic pressure in atmospheres, M is the molarity of the solution, R is the gas law constant, and T is the Kelvin temperature.

A molar mass determination using osmotic pressure is illustrated in Sample Exercise 11.11.

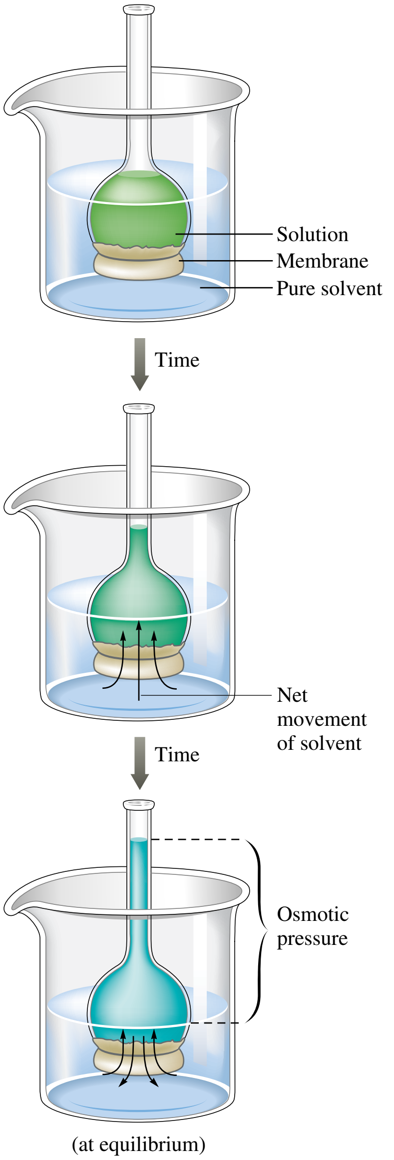


FIGURE 11.16
A tube with a bulb on the end that is covered by a semipermeable membrane. The solution is inside the tube and is bathed in the pure solvent. There is a net transfer of solvent molecules into the solution until the hydrostatic pressure equalizes the solvent flow in both directions.

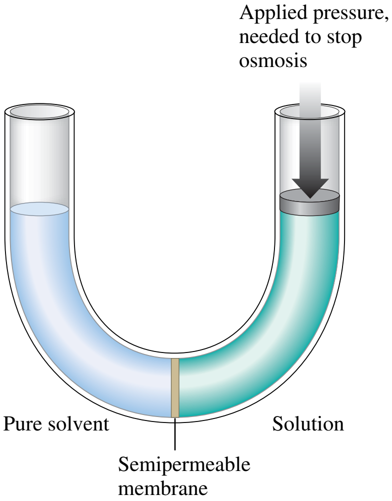


FIGURE 11.17
The normal flow of solvent into the solution (osmosis) can be prevented by applying an external pressure to the solution. The minimum pressure required to stop the osmosis is equal to the osmotic pressure of the solution.

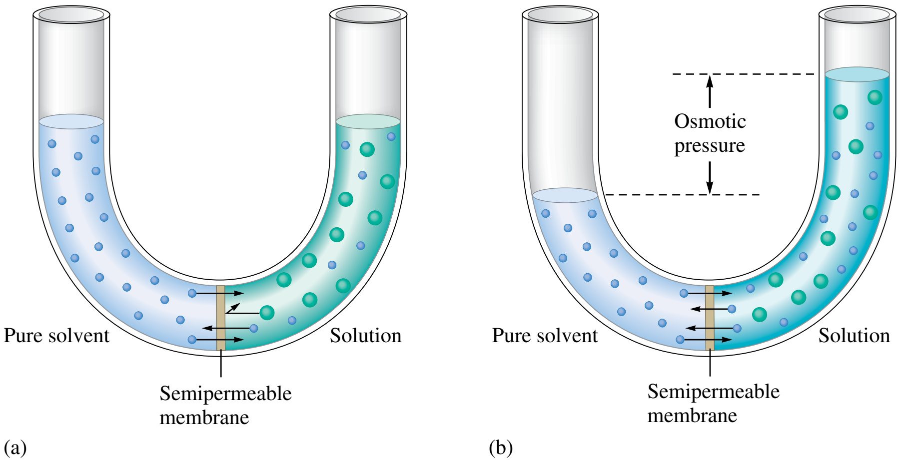


FIGURE 11.18
(a) A pure solvent and its solution (containing a nonvolatile solute) are separated by a semipermeable membrane through which solvent molecules (blue) can pass but solute molecules (green) cannot. The rate of solvent transfer is greater from solvent to solution than from solution to solvent. (b) The system at equilibrium, where the rate of solvent transfer is the same in both directions.

Sample Exercise 11.11 Determining Molar Mass from Osmotic Pressure

To determine the molar mass of a certain protein, 1.00×10^{-3} g of it was dissolved in enough water to make 1.00 mL of solution. The osmotic pressure of this solution was found to be 1.12 torr at 25.0°C. Calculate the molar mass of the protein.

Solution

We use the equation

$$\Pi = MRT$$

In this case we have

$$\Pi = 1.12 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 1.47 \times 10^{-3} \text{ atm}$$

$$R = 0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol}$$

$$T = 25.0 + 273 = 298 \text{ K}$$

Note that the osmotic pressure must be converted to atmospheres because of the units of *R*.

Solving for *M* gives

$$M = \frac{1.47 \times 10^{-3} \text{ atm}}{(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})} = 6.01 \times 10^{-5} \text{ mol/L}$$

Since 1.00×10^{-3} g protein was dissolved in 1 mL solution, the mass of protein per liter of solution is 1.00 g. The solution's concentration is 6.01×10^{-5} mol/L. This concentration is produced from 1.00×10^{-3} g protein per milliliter, or 1.00 g/L. Thus 6.01×10^{-5} mol protein has a mass of 1.00 g and

$$\frac{1.00 \text{ g}}{6.01 \times 10^{-5} \text{ mol}} = \frac{x \text{ g}}{1.00 \text{ mol}}$$

$$x = 1.66 \times 10^{4} \text{ g}$$

The molar mass of the protein is 1.66×10^4 g/mol. This molar mass may seem very large, but it is relatively small for a protein.

Measurements of osmotic pressure generally give much more accurate molar mass values than those from freezing-point or boiling-point changes.

See Exercise 11.66.

In osmosis, a semipermeable membrane prevents transfer of *all* solute particles. A similar phenomenon, called **dialysis,** occurs at the walls of most plant and animal cells.

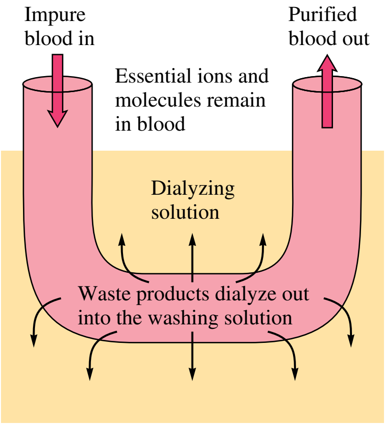
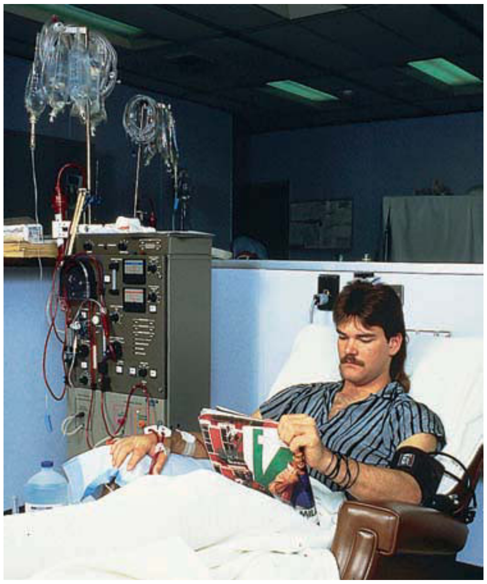


FIGURE 11.19
Representation of the functioning of an artificial kidney.



Patient undergoing dialysis.

However, in this case the membrane allows transfer of both solvent molecules and *small* solute molecules and ions. One of the most important applications of dialysis is the use of artificial kidney machines to purify the blood. The blood is passed through a cellophane tube, which acts as the semipermeable membrane. The tube is immersed in a dialyzing solution (see Fig. 11.19). This "washing" solution contains the same concentrations of ions and small molecules as blood but has none of the waste products normally removed by the kidneys. The resulting dialysis (movement of waste molecules into the washing solution) cleanses the blood.

Solutions that have identical osmotic pressures are said to be **isotonic solutions.** Fluids administered intravenously must be isotonic with body fluids. For example, if red blood cells are bathed in a hypertonic solution, which is a solution having an osmotic pressure higher than that of the cell fluids, the cells will shrivel because of a net transfer of water out of the cells. This phenomenon is called *crenation.* The opposite phenomenon, called *hemolysis,* occurs when cells are bathed in a hypotonic solution, a solution with an osmotic pressure lower than that of the cell fluids. In this case, the cells rupture because of the flow of water into the cells.

We can use the phenomenon of crenation to our advantage. Food can be preserved by treating its surface with a solute that gives a solution that is hypertonic to bacteria cells. Bacteria on the food then tend to shrivel and die. This is why salt can be used to protect meat and sugar can be used to protect fruit.

The brine used in pickling causes the cucumbers to shrivel.

Sample Exercise 11.12 Isotonic Solutions

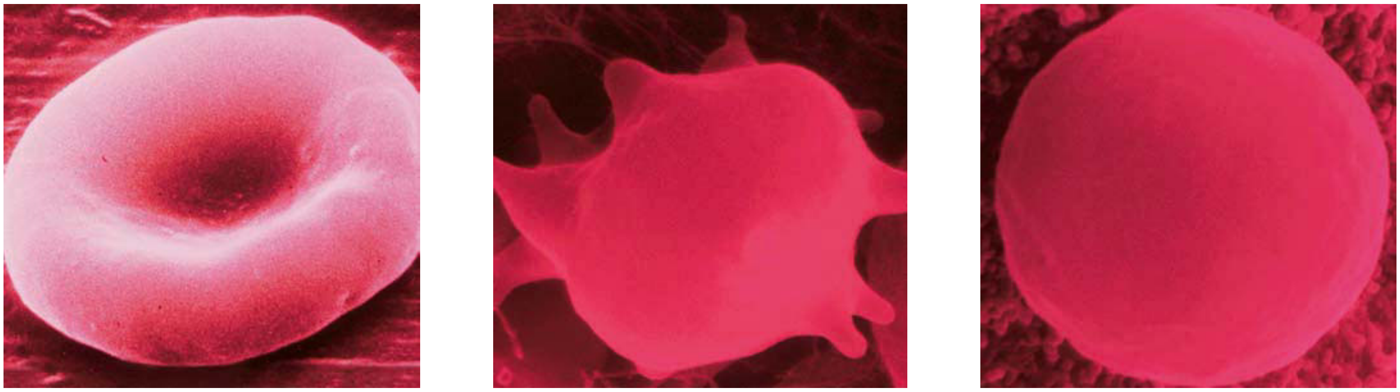
What concentration of sodium chloride in water is needed to produce an aqueous solution isotonic with blood ($\Pi = 7.70$ atm at 25°C)?

Solution

We can calculate the molarity of the solute from the equation

$$\Pi = MRT \quad \text{or} \quad M = \frac{\Pi}{RT}$$

$$M = \frac{7.70 \text{ atm}}{(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})} = 0.315 \text{ mol/L}$$



Red blood cells in three stages of osmosis. (a) The normal shape of a red blood cell. (b) This cell has shrunk because water moved out of it by osmosis. (c) This cell is swollen with water that has moved into it by osmosis.

This represents the total molarity of solute particles. But NaCl gives two ions per formula unit. Therefore, the concentration of NaCl needed is $\frac{0.315\ M}{2} = 0.1575\ M = 0.158\ M$. That is,

$$\underset{0.1575\ M}{\text{NaCl}} \longrightarrow \underbrace{\underset{0.1575\ M}{\text{Na}^+} + \underset{0.1575\ M}{\text{Cl}^-}}_{0.315\ M}$$

See Exercise 11.68.

Reverse Osmosis

If a solution in contact with pure solvent across a semipermeable membrane is subjected to an external pressure larger than its osmotic pressure, **reverse osmosis** occurs. The pressure will cause a net flow of solvent from the solution to the solvent, as shown in Fig. 11.20. In reverse osmosis, the semipermeable membrane acts as a "molecular filter" to remove solute particles. This fact is applicable to the **desalination** (removal of dissolved salts) of seawater, which is highly hypertonic to body fluids and thus is not drinkable.

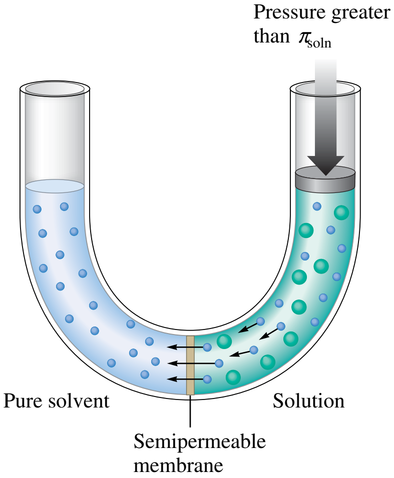
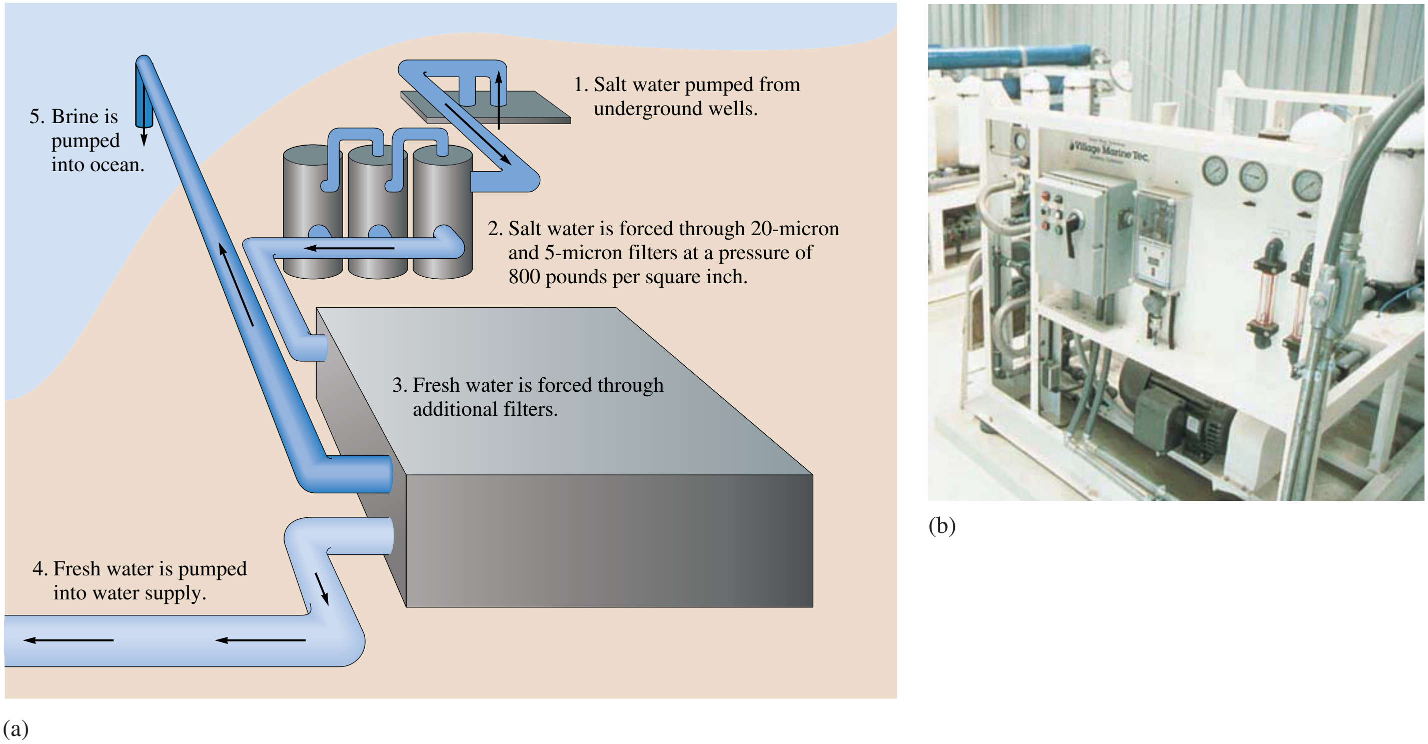


FIGURE 11.20
Reverse osmosis. A pressure greater than the osmotic pressure of the solution is applied, which causes a net flow of solvent molecules (blue) from the solution to the pure solvent. The solute molecules (green) remain behind.

As the population of the Sun Belt areas of the United States increases, more demand will be placed on the limited supplies of fresh water there. One obvious source of fresh water is from the desalination of seawater. Various schemes have been suggested, including solar evaporation, reverse osmosis, and even a plan for towing icebergs from Antarctica. The problem, of course, is that all the available processes are expensive. However, as water shortages increase, desalination is becoming necessary. For example, the first full-time public desalination plant in the United States started operations on Catalina Island, just off the coast of California (see Fig. 11.21). This plant, which can produce 132,000 gallons of drinkable water from the Pacific Ocean every day, operates by reverse osmosis. Powerful pumps, developing over 800 lb/in^2 of pressure, are employed to force seawater through synthetic semipermeable membranes.

Catalina Island's plant may be just the beginning. The city of Santa Barbara opened a $40 million desalination plant in 1992 that can produce 8 million gallons of drinking water per day, and other plants are in the planning stages.

A small-scale, manually operated reverse osmosis desalinator has been developed by the U.S. Navy to provide fresh water on life rafts. Potable water can be supplied by this desalinator at the rate of 1.25 gallons of water per hour—enough to keep 25 people alive. This compact desalinator, which weighs only 10 pounds, can now replace the bulky cases of fresh water formerly stored in Navy life rafts.



(a)

(b)

FIGURE 11.21
(a) Residents of Catalina Island off the coast of southern California are benefiting from a new desalination plant that can supply 132,000 gallons a day, or one-third of the island's daily needs. (b) Machinery in the desalination plant for Catalina Island.

11.7 Colligative Properties of Electrolyte Solutions

As we have seen previously, the colligative properties of solutions depend on the total concentration of solute particles. For example, a 0.10 m glucose solution shows a freezing point depression of 0.186°C:

$$\Delta T = K_f m = (1.86^\circ\text{C} \cdot \text{kg/mol})(0.100\ \text{mol/kg}) = 0.186^\circ\text{C}$$

On the other hand, a 0.10 m sodium chloride solution should show a freezing-point depression of 0.37°C, since the solution is 0.10 m Na^+ ions and 0.10 m Cl^- ions. Therefore, the solution contains a total of 0.20 m solute particles, and $\Delta T = (1.86^\circ\text{C} \cdot \text{kg/mol})(0.20\ \text{mol/kg}) = 0.37^\circ\text{C}$.

Dutch chemist J. H. van't Hoff (1852–1911) received the first Nobel Prize in chemistry in 1901.

The relationship between the moles of solute dissolved and the moles of particles in solution is usually expressed using the **van't Hoff factor,** i:

$$i = \frac{\text{moles of particles in solution}}{\text{moles of solute dissolved}}$$

The *expected* value for i can be calculated for a salt by noting the number of ions per formula unit. For example, for NaCl, i is 2; for K_2SO_4, i is 3; and for $Fe_3(PO_4)_2$, i is 5. These calculated values assume that when a salt dissolves, it completely dissociates into its component ions, which then move around independently. This assumption is not always true. For example, the freezing-point depression observed for 0.10 m NaCl is 1.87 times that for 0.10 m glucose rather than twice as great. That is, for a 0.10 m NaCl solution the observed value for i is 1.87 rather than 2. Why? The best explanation is that **ion pairing** occurs in solution (see Fig. 11.22). At a given instant a small percentage of the sodium and chloride ions are paired and thus count as a single particle. In general, ion pairing is most important in concentrated solutions. As the solution becomes more dilute,

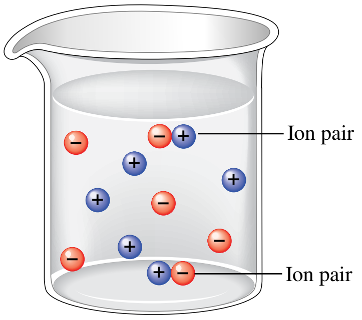


FIGURE 11.22
In an aqueous solution a few ions aggregate, forming ion pairs that behave as a unit.

TABLE 11.6 Expected and Observed Values of the van't Hoff Factor for 0.05 *m* Solutions of Several Electrolytes

Electrolyte	*i* (expected)	*i* (observed)
NaCl	2.0	1.9
$MgCl_2$	3.0	2.7
$MgSO_4$	2.0	1.3
$FeCl_3$	4.0	3.4
HCl	2.0	1.9
Glucose*	1.0	1.0

*A nonelectrolyte shown for comparison.

the ions are farther apart and less ion pairing occurs. For example, in a 0.0010 *m* NaCl solution, the observed value of *i* is 1.97, which is very close to the expected value.

Ion pairing occurs to some extent in all electrolyte solutions. Table 11.6 shows expected and observed values of *i* for a given concentration of various electrolytes. Note that the deviation of *i* from the expected value tends to be greatest where the ions have multiple charges. This is expected because ion pairing ought to be most important for highly charged ions.

The colligative properties of electrolyte solutions are described by including the van't Hoff factor in the appropriate equation. For example, for changes in freezing and boiling points, the modified equation is

$$\Delta T = imK$$

where *K* represents the freezing-point depression or boiling-point elevation constant for the solvent.

For the osmotic pressure of electrolyte solutions, the equation is

$$\Pi = iMRT$$

Sample Exercise 11.13

Osmotic Pressure

The observed osmotic pressure for a 0.10 *M* solution of $Fe(NH_4)_2(SO_4)_2$ at 25°C is 10.8 atm. Compare the expected and experimental values for *i*.

Solution

The ionic solid $Fe(NH_4)_2(SO_4)_2$ dissociates in water to produce 5 ions:

$$Fe(NH_4)_2(SO_4)_2 \xrightarrow{H_2O} Fe^{2+} + 2NH_4^+ + 2SO_4^{2-}$$

Thus the expected value for *i* is 5. We can obtain the experimental value for *i* by using the equation for osmotic pressure:

$$\Pi = iMRT \qquad \text{or} \qquad i = \frac{\Pi}{MRT}$$

where $\Pi = 10.8$ atm, $M = 0.10$ mol/L, $R = 0.08206$ L · atm/K · mol, and $T = 25 + 273 = 298$ K. Substituting these values into the equation gives

$$i = \frac{\Pi}{MRT} = \frac{10.8 \text{ atm}}{(0.10 \text{ mol/L})(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})} = 4.4$$

The experimental value for *i* is less than the expected value, presumably because of ion pairing.

See Exercises 11.73 and 11.74.

CHEMICAL IMPACT

The Drink of Champions—Water

In 1965, the University of Florida football team, the Gators, participated in a research program to test a sports drink formula containing a mixture of carbohydrates and electrolytes. The drink was used to help prevent dehydration caused by extreme workouts in the hot Florida climate. The Gators' success that season was in part attributed to their use of the sports drink formula. In 1967, a modified form of this formula was marketed with the name Gatorade. Today, Gatorade leads sales in sports drinks, but many other brands have entered a market where annual sales exceed $700 million!

During moderate- to high-intensity exercise, glycogen (a fuel reserve that helps maintain normal body processes) can be depleted within 60 to 90 minutes. Blood sugar levels drop as the glycogen reserves are used up, and lactic acid (a by-product of glucose metabolism) builds up in muscle tissue causing fatigue and muscle cramps. Muscles also generate a large amount of heat that must be dissipated. Water, which has a large specific heat capacity, is used to take heat away from these muscles. Sweating and evaporative cooling help the body maintain a constant temperature, but at a huge cost. During a high-intensity workout in hot weather, anywhere from 1 to 3 quarts of water can be lost from sweating per hour. Sweating away more than 2% of your body weight—a quart for every 100 pounds—can put a large stress on the heart, increasing body temperature and decreasing performance. Excessive sweating also results in the loss of sodium and potassium ions—two very important electrolytes that are present in the fluids inside and outside cells.

All the major sports drinks contain three main ingredients—carbohydrates in the form of simple sugars such as

FIGURE 11.23
The Tyndall effect.

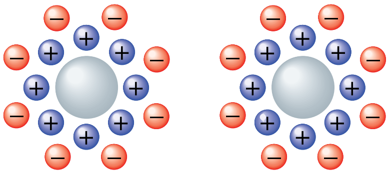


FIGURE 11.24
A representation of two colloidal particles. In each the center particle is surrounded by a layer of positive ions, with negative ions in the outer layer. Thus, although the particles are electrically neutral, they still repel each other because of their outer negative layer of ions.

11.8 Colloids

Mud can be suspended in water by vigorous stirring. When the stirring stops, most of the particles rapidly settle out, but even after several days some of the smallest particles remain suspended. Although undetected in normal lighting, their presence can be demonstrated by shining a beam of intense light through the suspension. The beam is visible from the side because the light is scattered by the suspended particles (Fig. 11.23). In a true solution, on the other hand, the beam is invisible from the side because the individual ions and molecules dispersed in the solution are too small to scatter visible light.

The scattering of light by particles is called the **Tyndall effect** and is often used to distinguish between a suspension and a true solution.

A suspension of tiny particles in some medium is called a **colloidal dispersion,** or a **colloid.** The suspended particles are single large molecules or aggregates of molecules or ions ranging in size from 1 to 1000 nm. Colloids are classified according to the states of the dispersed phase and the dispersing medium. Table 11.7 summarizes various types of colloids.

What stabilizes a colloid? Why do the particles remain suspended rather than forming larger aggregates and precipitating out? The answer is complicated, but the main factor seems to be *electrostatic repulsion.* A colloid, like all other macroscopic substances, is electrically neutral. However, when a colloid is placed in an electric field, the dispersed particles all migrate to the same electrode and thus must all have the same charge. How is this possible? The center of a colloidal particle (a tiny ionic crystal, a group of molecules, or a single large molecule) attracts from the medium a layer of ions, all of the same charge. This group of ions, in turn, attracts another layer of oppositely charged ions, as shown in Fig. 11.24. Because the colloidal particles all have an outer layer of ions with the same charge, they repel each other and do not easily aggregate to form particles that are large enough to precipitate.

sucrose, glucose, and fructose; electrolytes, including sodium and potassium ions; and water. Because these are the three major substances lost through sweating, good scientific reasoning suggests that drinking sports drinks should improve performance. But just how effectively do sports drinks deliver on their promises?

Recent studies have confirmed that athletes who eat a balanced diet and drink plenty of water are just as well off as those who consume sports drinks. A sports drink may have only one advantage over drinking water—it tastes better than water to most athletes. And if a drink tastes better, it will encourage more consumption, thus keeping cells hydrated.

Since most of the leading sports drinks contain the same ingredients in similar concentrations, taste may be the single most important factor in choosing your drink. If you are not interested in any particular sports drink, drink plenty of water. The key to quality performance is to keep your cells hydrated.

For healthy athletes, drinking water during exercise may be as effective as drinking sports drinks.

Adapted with permission from “Sports Drinks: Don’t Sweat the Small Stuff,” by Tim Graham, *ChemMatters,* February 1999, p. 11.

TABLE 11.7 Types of Colloids

Examples	Dispersing Medium	Dispersed Substance	Colloid Type
Fog, aerosol sprays	Gas	Liquid	Aerosol
Smoke, airborne bacteria	Gas	Solid	Aerosol
Whipped cream, soap suds	Liquid	Gas	Foam
Milk, mayonnaise	Liquid	Liquid	Emulsion
Paint, clays, gelatin	Liquid	Solid	Sol
Marshmallow, polystyrene foam	Solid	Gas	Solid foam
Butter, cheese	Solid	Liquid	Solid emulsion
Ruby glass	Solid	Solid	Solid sol

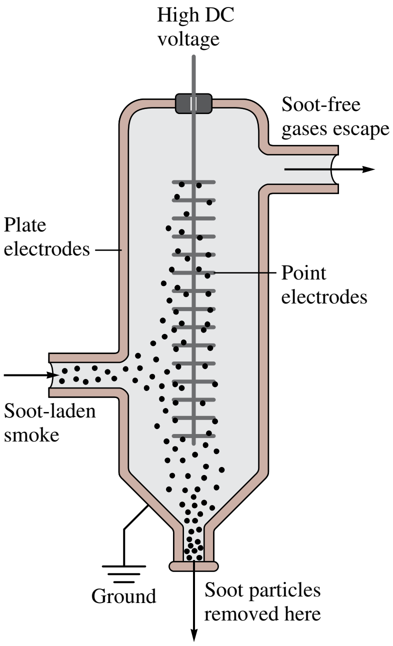


FIGURE 11.25
The Cottrell precipitator installed in a smokestack. The charged plates attract the colloidal particles because of their ion layers and thus remove them from the smoke.

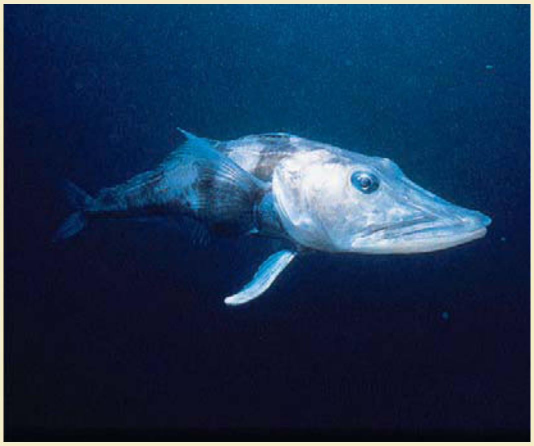
The destruction of a colloid, called **coagulation,** usually can be accomplished either by heating or by adding an electrolyte. Heating increases the velocities of the colloidal particles, causing them to collide with enough energy that the ion barriers are penetrated and the particles can aggregate. Because this process is repeated many times, the particle grows to a point where it settles out. Adding an electrolyte neutralizes the adsorbed ion layers. This is why clay suspended in rivers is deposited where the river reaches the ocean, forming the deltas characteristic of large rivers like the Mississippi. The high salt content of the seawater causes the colloidal clay particles to coagulate.

The removal of soot from smoke is another example of the coagulation of a colloid. When smoke is passed through an electrostatic precipitator (Fig. 11.25), the suspended solids are removed. The use of precipitators has produced an immense improvement in the air quality of heavily industrialized cities.

CHEMICAL IMPACT

Organisms and Ice Formation

The ice-cold waters of the polar oceans are teeming with fish that seem immune to freezing. One might think that these fish have some kind of antifreeze in their blood. However, studies show that they are protected from freezing in a very different way from the way antifreeze protects our cars. As we have seen in this chapter, solutes such as sugar, salt, and ethylene glycol lower the temperature at which the solid and liquid phases of water can coexist. However, the fish could not tolerate high concentrations of solutes in their blood because of the osmotic pressure effects. Instead, they are protected by proteins in their blood. These proteins allow the water in the bloodstream to be supercooled—exist below 0°C—without forming ice. They apparently coat the surface of each tiny ice crystal, as soon as it begins to form, preventing it from growing to a size that would cause biologic damage.



An Antarctic fish, *Chaerophalus aceratus.*

Although it might at first seem surprising, this research on polar fish has attracted the attention of ice cream manufacturers. Premium quality ice cream is smooth; it does not have large ice crystals in it. The makers of ice cream would like to incorporate these polar fish proteins, or molecules that behave similarly, into ice cream to prevent the growth of ice crystals during storage.

Fruit and vegetable growers have a similar interest: They also want to prevent ice formation that damages their crops during an unusual cold wave. However, this is a very different kind of problem than keeping polar fish from freezing. Many types of fruits and vegetables are colonized by bacteria that manufacture a protein that *encourages* freezing by acting as a nucleating agent to start an ice crystal. Chemists have identified the offending protein in the bacteria and the gene that is responsible for making it. They have learned to modify the genetic material of these bacteria in a way that removes their ability to make the protein that encourages ice crystal formation. If testing shows that these modified bacteria have no harmful effects on the crop or the environment, the original bacteria strain will be replaced with the new form so that ice crystals will not form so readily when a cold snap occurs.

Key Terms

Section 11.1

molarity
mass percent
mole fraction
molality
normality

Section 11.2

enthalpy (heat) of solution
enthalpy (heat) of hydration

Section 11.3

Henry's law
thermal pollution

Section 11.4

Raoult's law
ideal solution

For Review

Solution composition

- Molarity (M): moles solute per liter of solution
- Mass percent: ratio of mass of solute to mass of solution times 100%
- Mole fraction (χ): ratio of moles of a given component to total moles of all components
- Molality (m): moles solute per mass of solvent (in kg)
- Normality (N): number of equivalents per liter of solution

Enthalpy of solution (ΔH_{soln})

- The enthalpy change accompanying solution formation
- Can be partitioned into
  - The energy required to overcome the solute–solute interactions
  - The energy required to "make holes" in the solvent
  - The energy associated with solute–solvent interactions

Section 11.5
colligative properties
molal boiling-point elevation constant
molal freezing-point depression constant

Section 11.6
semipermeable membrane
osmosis
osmotic pressure
dialysis
isotonic solution
reverse osmosis
desalination

Section 11.7
van't Hoff factor
ion pairing

Section 11.8
Tyndall effect
colloid (colloidal dispersion)
coagulation

Factors That affect solubility

- Polarity of solute and solvent
  - "Like dissolves like" is a useful generalization
- Pressure increases the solubility of gases in a solvent
  - Henry's law: $C = kP$
- Temperature effects
  - Increased temperature decreases the solubility of a gas in water
  - Most solids are more soluble at higher temperatures but important exceptions exist

Vapor pressure of solutions

- A solution containing a nonvolatile solute has a lower vapor pressure than a solution of the pure solvent
- Raoult's law defines an ideal solution

  $P_{\text{vapor}}^{\text{soln}} = \chi_{\text{solvent}} P_{\text{vapor}}^{\text{solvent}}$

  - Solutions in which the solute–solvent attractions differ from the solute–solute and solvent–solvent attractions violate Raoult's law

Colligative properties

- Depend on the number of solute particles present
- Boiling-point elevation: $\Delta T = K_b m_{\text{solute}}$
- Freezing-point lowering: $\Delta T = K_f m_{\text{solute}}$
- Osmotic pressure: $\Pi = MRT$
  - Osmosis occurs when a solution and pure solvent are separated by a semipermeable membrane that allows solvent molecules to pass but not solute particles
  - Reverse osmosis occurs when the applied pressure is greater than the osmotic pressure of the solution
- Because colligative properties depend on the number of particles, solutes that break into several ions when they dissolve have an effect proportional to the number of ions produced
  - The van't Hoff factor *i* represents the number of ions produced by each formula unit of solute

Colloids

- A suspension of tiny particles stabilized by electrostatic repulsion among the ion layers surrounding the individual particles
- Can be coagulated (destroyed) by heating or adding an electrolyte

REVIEW QUESTIONS

1. The four most common ways to describe solution composition are mass percent, mole fraction, molarity, and molality. Define each of these solution composition terms. Why is molarity temperature-dependent, whereas the other three solution composition terms are temperature-independent?
2. Using KF as an example, write equations that refer to ΔH_{soln} and ΔH_{hyd}. Lattice energy was defined in Chapter 8 as ΔH for the reaction $K^+(g) + F^-(g) \longrightarrow KF(s)$. Show how you would utilize Hess's law to calculate ΔH_{soln} from ΔH_{hyd} and ΔH_{LE} for KF, where ΔH_{LE} = lattice energy ΔH_{soln} for KF, as for other soluble ionic compounds, is a relatively small number. How can this be since ΔH_{hyd} and ΔH_{LE} are relatively large negative numbers?
3. What does the axiom "like dissolves like" mean? There are four types of solute/solvent combinations: polar solutes in polar solvents, nonpolar solutes in polar solvents, and so on. For each type of solution, discuss the magnitude of ΔH_{soln}.
4. Structure, pressure, and temperature all have an effect on solubility. Discuss each of their effects. What is Henry's law? Why does Henry's law not work for $HCl(g)$? What do the terms *hydrophobic* and *hydrophilic* mean?

5. Define the terms in Raoult's law. Figure 11.9 illustrates the net transfer of water molecules from pure water to an aqueous solution of a nonvolatile solute. Explain why eventually all of the water from the beaker of pure water will transfer to the aqueous solution. If the experiment illustrated in Fig. 11.9 was performed using a volatile solute, what would happen? How do you calculate the total vapor pressure when both the solute and solvent are volatile?
6. In terms of Raoult's law, distinguish between an ideal liquid–liquid solution and a nonideal liquid–liquid solution. If a solution is ideal, what is true about ΔH_{soln}, ΔT for the solution formation, and the interactive forces within the pure solute and pure solvent as compared to the interactive forces within the solution. Give an example of an ideal solution. Answer the previous two questions for solutions that exhibit either negative or positive deviations from Raoult's law.
7. Vapor-pressure lowering is a colligative property, as are freezing-point depression and boiling-point elevation. What is a colligative property? Why is the freezing point depressed for a solution as compared to the pure solvent? Why is the boiling point elevated for a solution as compared to the pure solvent? Explain how to calculate ΔT for a freezing-point depression problem or a boiling-point elevation problem. Of the solvents listed in Table 11.5, which would have the largest freezing-point depression for a 0.50 molal solution? Which would have the smallest boiling-point elevation for a 0.50 molal solution?

   A common application of freezing-point depression and boiling-point elevation experiments is to provide a means to calculate the molar mass of a nonvolatile solute. What data are needed to calculate the molar mass of a nonvolatile solute? Explain how you would manipulate these data to calculate the molar mass of the nonvolatile solute.
8. What is osmotic pressure? How is osmotic pressure calculated? Molarity units are used in the osmotic pressure equation. When does the molarity of a solution approximately equal the molality of the solution? Before refrigeration was common, many foods were preserved by salting them heavily, and many fruits were preserved by mixing them with a large amount of sugar (fruit preserves). How do salt and sugar act as preservatives? Two applications of osmotic pressure are dialysis and desalination. Explain these two processes.
9. Distinguish between a strong electrolyte, a weak electrolyte, and a nonelectrolyte. How can colligative properties be used to distinguish between them? What is the van't Hoff factor? Why is the observed freezing-point depression for electrolyte solutions sometimes less than the calculated value? Is the discrepancy greater for concentrated or dilute solutions?
10. What is a colloidal dispersion? Give some examples of colloids. The Tyndall effect is often used to distinguish between a colloidal suspension and a true solution. Explain. The destruction of a colloid is done through a process called coagulation. What is coagulation?

Active Learning Questions

These questions are designed to be used by groups of students in class. The questions allow students to explore their understanding of concepts through discussion and peer teaching. The real value of these questions is the learning that occurs while students talk to each other about chemical concepts.

1. Consider Fig. 11.9. According to the caption and picture, water seems to go from one beaker to another.

   a. Explain why this occurs.
   b. The explanation in the text uses terms such as *vapor pressure* and *equilibrium.* Explain what these have to do with the phenomenon. For example, what is coming to equilibrium?
   c. Does all the water end up in the second beaker?
   d. Is water evaporating from the beaker containing the solution? If so, is the rate of evaporation increasing, decreasing, or staying constant?

   Draw pictures to illustrate your explanations.

2. Once again, consider Fig. 11.9. Suppose instead of having a nonvolatile solute in the solvent in one beaker, the two beakers contain different volatile liquids. That is, suppose one beaker contains liquid A (P_{vap} = 50 torr) and the other beaker contains liquid B (P_{vap} = 100 torr). Explain what happens as time passes. How is this similar to the first case (shown in the figure)? How is it different?

3. Assume that you place a freshwater plant into a saltwater solution and examine it under a microscope. What happens to the plant cells? What if you placed a saltwater plant in pure water? Explain. Draw pictures to illustrate your explanations.

4. How does ΔH_{soln} relate to deviations from Raoult's law? Explain.

5. You have read that adding a solute to a solvent can both increase the boiling point and decrease the freezing point. A friend of yours explains it to you like this: "The solute and solvent can be like salt in water. The salt gets in the way of freezing in that it blocks the water molecules from joining together. The salt acts like a strong bond holding the water molecules together so that it is harder to boil." What do you say to your friend?

6. You drop an ice cube (made from pure water) into a saltwater solution at 0°C. Explain what happens and why.

7. Using the phase diagram for water and Raoult's law, explain why salt is spread on the roads in winter (even when it is below freezing).

8. You and your friend are each drinking cola from separate 2-L bottles. Both colas are equally carbonated. You are able to drink 1 L of cola, but your friend can drink only about half a liter. You each close the bottles and place them in the refrigerator. The next day when you each go to get the colas, whose will be more carbonated and why?

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

Solution Review

If you have trouble with these exercises, review Sections 4.1 to 4.3 in Chapter 4.

9. Rubbing alcohol contains 585 g of isopropanol (C_3H_7OH) per liter (aqueous solution). Calculate the molarity.

10. What volume of a 0.580 *M* solution of $CaCl_2$ contains 1.28 g of solute?

11. Calculate the sodium ion concentration when 70.0 mL of 3.0 *M* sodium carbonate is added to 30.0 mL of 1.0 *M* sodium bicarbonate.

12. Write equations showing the ions present after the following strong electrolytes are dissolved in water.

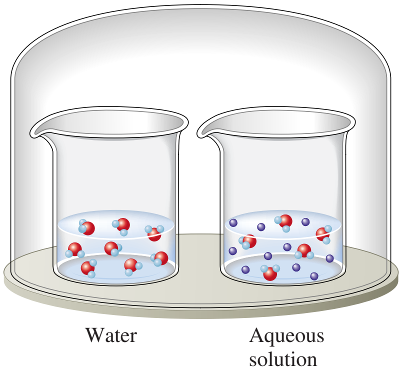
a. HNO_3
b. Na_2SO_4
c. $Al(NO_3)_3$
d. $SrBr_2$
e. $KClO_4$
f. NH_4Br
g. NH_4NO_3
h. $CuSO_4$
i. NaOH

Questions

13. Rationalize the temperature dependence of the solubility of a gas in water in terms of the kinetic molecular theory.

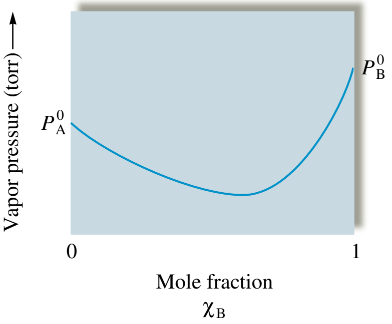
14. The weak electrolyte $NH_3(g)$ does not obey Henry's law. Why? $O_2(g)$ obeys Henry's law in water but not in blood (an aqueous solution). Why?

15. The two beakers in the sealed container illustrated below contain pure water and an aqueous solution of a volatile solute.



If the solute is less volatile than water, explain what will happen to the volumes in the two containers as time passes.

16. The following plot shows the vapor pressure of various solutions of components A and B at some temperature.



Which of the following statements is false concerning solutions of A and B?

a. The solutions exhibit negative deviations from Raoult's law.
b. ΔH_{mix} for the solutions should be exothermic.
c. The intermolecular forces are stronger in solution than in either pure A or pure B.
d. Pure liquid B is more volatile than pure liquid A.
e. The solution with χ_B = 0.6 will have a lower boiling point than either pure A or pure B.

17. When pure methanol is mixed with water, the resulting solution feels warm. Would you expect this solution to be ideal? Explain.

18. Detergent molecules can stabilize the emulsion of oil in water as well as remove dirt from soiled clothes. A typical detergent is sodium dodecylsulfate, or SDS, and it has a formula of $CH_3(CH_2)_{10}CH_2SO_4^-Na^+$. In aqueous solution, SDS suspends oil or dirt by forming small aggregates of detergent anions called *micelles*. Propose a structure for micelles.

19. For an acid or a base, when is the normality of a solution equal to the molarity of the solution and when are the two concentration units different?

20. In order for sodium chloride to dissolve in water, a small amount of energy must be added during solution formation. This is not energetically favorable. Why is NaCl so soluble in water?

21. Which of the following statements is(are) true? Correct the false statements.

a. The vapor pressure of a solution is directly related to the mole fraction of solute.

b. When a solute is added to water, the water in solution has a lower vapor pressure than that of pure ice at 0°C.

c. Colligative properties depend only on the identity of the solute and not on the number of solute particles present.

d. When sugar is added to water, the boiling point of the solution increases above 100°C because sugar has a higher boiling point than water.

22. Is the following statement true of false? Explain your answer. When determining the molar mass of a solute using boiling point of freezing point data, camphor would be the best solvent choice of all of the solvents listed in Table 11.5.

23. Explain the terms isotonic solution, crenation, and hemolysis.

24. What is ion pairing?

Exercises

In this section similar exercises are paired.

Concentration of Solutions

25. A solution of phosphoric acid was made by dissolving 10.0 g of H_3PO_4 in 100.0 mL of water. The resulting volume was 104 mL. Calculate the density, mole fraction, molarity, and molality of the solution. Assume water has a density of 1.00 g/cm^3.

26. An aqueous antifreeze solution is 40.0% ethylene glycol ($C_2H_6O_2$) by mass. The density of the solution is 1.05 g/cm^3.Calculate the molality, molarity, and mole fraction of the ethylene glycol.

27. Common commercial acids and bases are aqueous solutions with the following properties:

	Density (g/cm^3)	Mass Percent of Solute
Hydrochloric acid	1.19	38
Nitric acid	1.42	70.
Sulfuric acid	1.84	95
Acetic acid	1.05	99
Ammonia	0.90	28

Calculate the molarity, molality, and mole fraction of each of the preceding reagents.

28. In lab you need to prepare at least 100 mL of each of the following solutions. Explain how you would proceed using the given information.

a. 2.0 *m* KCl in water (density of H_2O = 1.00 g/cm^3)

b. 15% NaOH by mass in water (d = 1.00 g/cm^3)

c. 25% NaOH by mass in CH_3OH (d = 0.79 g/cm^3)

d. 0.10 mole fraction of $C_6H_{12}O_6$ in water (d = 1.00 g/cm^3)

29. A solution is prepared by mixing 25 mL pentane (C_5H_{12}, d = 0.63 g/cm^3) with 45 mL hexane (C_6H_{14}, d = 0.66 g/cm^3). Assuming that the volumes add on mixing, calculate the mass percent, mole fraction, molality, and molarity of the pentane.

30. A bottle of wine contains 12.5% ethanol by volume. The density of ethanol (C_2H_5OH) is 0.789 g/cm^3. Calculate the concentration of ethanol in wine in terms of mass percent and molality.

31. A 1.37 *M* solution of citric acid ($H_3C_6H_5O_7$) in water has a density of 1.10 g/cm^3. Calculate the mass percent, molality, mole fraction, and normality of the citric acid. Citric acid has three acidic protons.

32. Calculate the molarity and mole fraction of acetone in a 1.00 *m* solution of acetone (CH_3COCH_3) in ethanol (C_2H_5OH). (Density of acetone = 0.788 g/cm^3; density of ethanol = 0.789 g/cm^3.) Assume that the volumes of acetone and ethanol add.

Energetics of Solutions and Solubility

33. The lattice energy* of NaI is −686 kJ/mol, and the enthalpy of hydration is −694 kJ/mol. Calculate the enthalpy of solution per mole of solid NaI. Describe the process to which this enthalpy change applies.

34. **a.** Use the following data to calculate the enthalpy of hydration for calcium chloride and calcium iodide.

	Lattice Energy	ΔH_{soln}
$CaCl_2(s)$	−2247 kJ/mol	−46 kJ/mol
$CaI_2(s)$	−2059 kJ/mol	−104 kJ/mol

b. Based on your answers to part a, which ion, Cl^- or I^-, is more strongly attracted to water?

35. Although $Al(OH)_3$ is insoluble in water, NaOH is very soluble. Explain in terms of lattice energies.

36. The high melting points of ionic solids indicate that a lot of energy must be supplied to separate the ions from one another. How is it possible that the ions can separate from one another when soluble ionic compounds are dissolved in water, often with essentially no temperature change?

37. Which solvent, water or carbon tetrachloride, would you choose to dissolve each of the following?

a. KrF_2

b. SF_2

c. SO_2

d. CO_2

e. MgF_2

f. CH_2O

g. $CH_2{=}CH_2$

38. Which solvent, water or hexane (C_6H_{14}), would you choose to dissolve each of the following?

a. NaCl

b. HF

c. octane (C_8H_{18})

d. $(NH_4)_2SO_4$

39. What factors cause one solute to be more strongly attracted to water than another? For each of the following pairs, predict which substance would be more soluble in water.

a. CH_3CH_2OH or $CH_3CH_2CH_3$

b. $CHCl_3$ or CCl_4

c. CH_3CH_2OH or $CH_3(CH_2)_{14}CH_2OH$

---

*Lattice energy was defined in Chapter 8 as the energy change for the process $M^+(g) + X^-(g) \rightarrow MX(s)$.

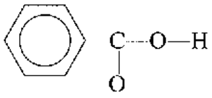
40. Which ion in each of the following pairs would you expect to be more strongly hydrated? Why?

- **a.** Na^+ or Mg^{2+}
- **b.** Mg^{2+} or Be^{2+}
- **c.** Fe^{2+} or Fe^{3+}
- **d.** F^- or Br^-
- **e.** Cl^- or ClO_4^-
- **f.** ClO_4^- or SO_4^{2-}

41. Rationalize the trend in water solubility for the following simple alcohols:

Alcohol	Solubility (g/100 g H_2O at 20°C)
Methanol, CH_3OH	Soluble in all proportions
Ethanol, CH_3CH_2OH	Soluble in all proportions
Propanol, $CH_3CH_2CH_2OH$	Soluble in all proportions
Butanol, $CH_3(CH_2)_2CH_2OH$	8.14
Pentanol, $CH_3(CH_2)_3CH_2OH$	2.64
Hexanol, $CH_3(CH_2)_4CH_2OH$	0.59
Heptanol, $CH_3(CH_2)_5CH_2OH$	0.09

42. The solubility of benzoic acid ($HC_7H_5O_2$),



is 0.34 g/100 mL in water at 25°C and is 10.0 g/100 mL in benzene (C_6H_6) at 25°C. Rationalize this solubility behavior. (*Hint:* Benzoic acid forms a dimer in benzene.) Would benzoic acid be more or less soluble in a 0.1 *M* NaOH solution than it is in water? Explain.

43. The solubility of nitrogen in water is 8.21×10^{-4} mol/L at 0°C when the N_2 pressure above water is 0.790 atm. Calculate the Henry's law constant for N_2 in units of mol/L · atm for Henry's law in the form $C = kP$, where C is the gas concentration in mol/L. Calculate the solubility of N_2 in water when the partial pressure of nitrogen above water is 1.10 atm at 0°C.

44. In Exercise 107 in Chapter 5, the pressure of CO_2 in a bottle of sparkling wine was calculated assuming that the CO_2 was insoluble in water. This was a bad assumption. Redo this problem by assuming that CO_2 obeys Henry's law. Use the data given in that problem to calculate the partial pressure of CO_2 in the gas phase and the solubility of CO_2 in the wine at 25°C. The Henry's law constant for CO_2 is 3.1×10^{-2} mol/L · atm at 25°C with Henry's law in the form $C = kP$, where C is the concentration of the gas in mol/L.

Vapor Pressures of Solutions

45. Glycerin, $C_3H_8O_3$, is a nonvolatile liquid. What is the vapor pressure of a solution made by adding 164 g of glycerin to 338 mL of H_2O at 39.8°C? The vapor pressure of pure water at 39.8°C is 54.74 torr and its density is 0.992 g/cm^3.

46. The vapor pressure of a solution containing 53.6 g glycerin ($C_3H_8O_3$) in 133.7 g ethanol (C_2H_5OH) is 113 torr at 40°C. Calculate the vapor pressure of pure ethanol at 40°C assuming that glycerin is a nonvolatile, nonelectrolyte solute in ethanol.

47. At a certain temperature, the vapor pressure of pure benzene (C_6H_6) is 0.930 atm. A solution was prepared by dissolving 10.0 g of a nondissociating, nonvolatile solute in 78.11 g of benzene at that temperature. The vapor pressure of the solution was found to be 0.900 atm. Assuming the solution behaves ideally, determine the molar mass of the solute.

48. A solution of sodium chloride in water has a vapor pressure of 19.6 torr at 25°C. What is the mole fraction of NaCl solute particles in this solution? What would be the vapor pressure of this solution at 45°C? The vapor pressure of pure water is 23.8 torr at 25°C and 71.9 torr at 45°C and assume sodium chloride exists as Na^+ and Cl^- ions in solution.

49. Pentane (C_5H_{12}) and hexane (C_6H_{14}) form an ideal solution. At 25°C the vapor pressures of pentane and hexane are 511 and 150. torr, respectively. A solution is prepared by mixing 25 mL pentane (density, 0.63 g/mL) with 45 mL hexane (density, 0.66 g/mL).

- **a.** What is the vapor pressure of the resulting solution?
- **b.** What is the composition by mole fraction of pentane in the vapor that is in equilibrium with this solution?

50. A solution is prepared by mixing 0.0300 mol CH_2Cl_2 and 0.0500 mol CH_2Br_2 at 25°C. Assuming the solution is ideal, calculate the composition of the vapor (in terms of mole fractions) at 25°C. At 25°C, the vapor pressures of pure CH_2Cl_2 and pure CH_2Br_2 are 133 and 11.4 torr, respectively.

51. What is the composition of a methanol (CH_3OH)–propanol ($CH_3CH_2CH_2OH$) solution that has a vapor pressure of 174 torr at 40°C? At 40°C, the vapor pressures of pure methanol and pure propanol are 303 and 44.6 torr, respectively. Assume the solution is ideal.

52. Benzene and toluene form an ideal solution. Consider a solution of benzene and toluene prepared at 25°C. Assuming the mole fractions of benzene and toluene in the vapor phase are equal, calculate the composition of the solution. At 25°C the vapor pressures of benzene and toluene are 95 and 28 torr, respectively.

53. Which of the following will have the lowest total vapor pressure at 25°C?

- **a.** pure water (vapor pressure = 23.8 torr at 25°C)
- **b.** a solution of glucose in water with $\chi_{C_6H_{12}O_6} = 0.01$
- **c.** a solution of sodium chloride in water with $\chi_{NaCl} = 0.01$
- **d.** a solution of methanol in water with $\chi_{CH_3OH} = 0.2$ (Consider the vapor pressure of both methanol [143 torr at 25°C] and water.)

54. Which of the choices in Exercise 53 has the highest vapor pressure?

55. A solution is made by mixing 50.0 g acetone (CH_3COCH_3) and 50.0 g methanol (CH_3OH). What is the vapor pressure of this solution at 25°C? What is the composition of the vapor expressed as a mole fraction? Assume ideal solution and gas behavior. (At 25°C the vapor pressures of pure acetone and pure methanol are 271 and 143 torr, respectively.) The actual vapor pressure of this solution is 161 torr. Explain any discrepancies.

56. The vapor pressures of several solutions of water–propanol ($CH_3CH_2CH_2OH$) were determined at various compositions, with the following data collected at 45°C:

χ_{H_2O}	Vapor pressure (torr)
0	74.0
0.15	77.3
0.37	80.2
0.54	81.6
0.69	80.6
0.83	78.2
1.00	71.9

a. Are solutions of water and propanol ideal? Explain.
b. Predict the sign of ΔH_{soln} for water–propanol solutions.
c. Are the interactive forces between propanol and water molecules weaker than, stronger than, or equal to the interactive forces between the pure substances? Explain.
d. Which of the solutions in the data would have the lowest normal boiling point?

Colligative Properties

57. A solution is prepared by dissolving 27.0 g of urea, $(NH_2)_2CO$, in 150.0 g of water. Calculate the boiling point of the solution. Urea is a nonelectrolyte.

58. A 2.00-g sample of a large biomolecule was dissolved in 15.0 g of carbon tetrachloride. The boiling point of this solution was determined to be 77.85°C. Calculate the molar mass of the biomolecule. For carbon tetrachloride, the boiling-point constant is 5.03°C · kg/mol, and the boiling point of pure carbon tetrachloride is 76.50°C.

59. What mass of glycerin ($C_3H_8O_3$), a nonelectrolyte, must be dissolved in 200.0 g water to give a solution with a freezing point of −1.50°C?

60. The freezing point of *t*-butanol is 25.50°C and K_f is 9.1°C · kg/mol. Usually *t*-butanol absorbs water on exposure to air. If the freezing point of a 10.0-g sample of *t*-butanol is 24.59°C, how many grams of water are present in the sample?

61. Calculate the freezing point and boiling point of an antifreeze solution that is 50.0% by mass of ethylene glycol ($HOCH_2CH_2OH$) in water. Ethylene glycol is a nonelectrolyte.

62. What volume of ethylene glycol ($C_2H_6O_2$), a nonelectrolyte, must be added to 15.0 L of water to produce an antifreeze solution with a freezing point of −25.0°C? What is the boiling point of this solution? (The density of ethylene glycol is 1.11 g/cm^3, and the density of water is 1.00 g/cm^3.)

63. Thyroxine, an important hormone that controls the rate of metabolism in the body, can be isolated from the thyroid gland. When 0.455 g of thyroxine is dissolved in 10.0 g of benzene, the freezing point of the solution is depressed by 0.300°C. What is the molar mass of thyroxine? See Table 11.5.

64. Anthraquinone contains only carbon, hydrogen, and oxygen and has an empirical formula of C_7H_4O. The freezing point of camphor is lowered by 22.3°C when 1.32 g anthraquinone is dissolved in 11.4 g camphor. Determine the molecular formula of anthraquinone.

65. a. Calculate the freezing-point depression and osmotic pressure at 25°C of an aqueous solution containing 1.0 g/L of a protein (molar mass $= 9.0 \times 10^4$ g/mol) if the density of the solution is 1.0 g/cm^3.
b. Considering your answer to part a, which colligative property, freezing-point depression or osmotic pressure, would be better used to determine the molar masses of large molecules? Explain.

66. An aqueous solution of 10.00 g of catalase, an enzyme found in the liver, has a volume of 1.00 L at 27°C. The solution's osmotic pressure at 27°C is found to be 0.74 torr. Calculate the molar mass of catalase.

67. If the human eye has an osmotic pressure of 8.00 atm at 25°C, what concentration of solute particles in water will provide an isotonic eyedrop solution (a solution with equal osmotic pressure)?

68. How would you prepare 1.0 L of an aqueous solution of sodium chloride having an osmotic pressure of 15 atm at 22°C? Assume sodium chloride exists as Na^+ and Cl^- ions in solution.

Properties of Electrolyte Solutions

69. Consider the following solutions:
0.010 *m* Na_3PO_4 in water
0.020 *m* $CaBr_2$ in water
0.020 *m* KCl in water
0.020 *m* HF in water (HF is a weak acid.)
a. Assuming complete dissociation of the soluble salts, which solution(s) would have the same boiling point as 0.040 *m* $C_6H_{12}O_6$ in water? $C_6H_{12}O_6$ is a nonelectrolyte.
b. Which solution would have the highest vapor pressure at 28°C?
c. Which solution would have the largest freezing-point depression?

70. From the following:

pure water
solution of $C_{12}H_{22}O_{11}$ ($m = 0.01$) in water
solution of NaCl ($m = 0.01$) in water
solution of $CaCl_2$ ($m = 0.01$) in water
choose the one with the

a. highest freezing point.
b. lowest freezing point.
c. highest boiling point.
d. lowest boiling point.
e. highest osmotic pressure.

71. Calculate the freezing point and the boiling point of each of the following aqueous solutions. (Assume complete dissociation.)
a. 0.050 *m* $MgCl_2$
b. 0.050 *m* $FeCl_3$

72. A water desalination plant is set up near a salt marsh containing water that is 0.10 *M* NaCl. Calculate the minimum pressure that must be applied at 20.°C to purify the water by reverse osmosis. Assume NaCl is completely dissociated.

73. Use the following data for three aqueous solutions of $CaCl_2$ to calculate the apparent value of the van't Hoff factor.

Molality	Freezing-Point Depression (°C)
0.0225	0.110
0.0910	0.440
0.278	1.330

74. Calculate the freezing point and the boiling point of each of the following solutions using the observed van't Hoff factors in Table 11.6.
a. 0.050 m $MgCl_2$ **b.** 0.050 m $FeCl_3$

75. In the winter of 1994, record low temperatures were registered throughout the United States. For example, in Champaign, Illinois, a record low of −29°F was registered. At this temperature can salting icy roads with $CaCl_2$ be effective in melting the ice?
a. Assume $i = 3.00$ for $CaCl_2$.
b. Assume the average value of i from Exercise 73.
(The solubility of $CaCl_2$ in cold water is 74.5 g per 100.0 g of water.)

76. A 0.500-g sample of a compound is dissolved in enough water to form 100.0 mL of solution. This solution has an osmotic pressure of 2.50 atm at 25°C. If each molecule of the solute dissociates into two particles (in this solvent), what is the molar mass of this solute?

Additional Exercises

77. In a coffee-cup calorimeter, 1.60 g of NH_4NO_3 was mixed with 75.0 g of water at an initial temperature of 25.00°C. After dissolution of the salt, the final temperature of the calorimeter contents was 23.34°C.
a. Assuming the solution has a heat capacity of 4.18 J/g · °C, and assuming no heat loss to the calorimeter, calculate the enthalpy of solution (ΔH_{soln}) for the dissolution of NH_4NO_3 in units of kJ/mol.
b. If the enthalpy of hydration for NH_4NO_3 is −630. kJ/mol, calculate the lattice energy of NH_4NO_3.

78. In flushing and cleaning columns used in liquid chromatography to remove adsorbed contaminants, a series of solvents is used. Hexane (C_6H_{14}), chloroform ($CHCl_3$), methanol (CH_3OH), and water are passed through the column in that order. Rationalize the order in terms of intermolecular forces and the mutual solubility (miscibility) of the solvents.

79. Explain the following on the basis of the behavior of atoms and/or ions.
a. Cooking with water is faster in a pressure cooker than in an open pan.
b. Salt is used on icy roads.
c. Melted sea ice from the Artic Ocean produces fresh water.
d. $CO_2(s)$ (dry ice) does not have a normal boiling point under normal atmospheric conditions, even though CO_2 is a liquid in fire extinguishers.
e. Adding a solute to a solvent extends the liquid phase over a larger temperature range.

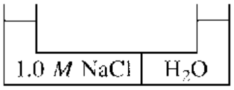
80. The term "proof" is defined as twice the percent by volume of pure ethanol in solution. Thus, a solution that is 95% (by volume) ethanol is 190 proof. What is the molarity of ethanol in a 92 proof ethanol/water solution? Assume the density of ethanol, C_2H_5OH, is 0.79 g/cm^3 and the density of water is 1.0 g/cm^3.

81. At 25°C, the vapor in equilibrium with a solution containing carbon disulfide and acetonitrile has a total pressure of 263 torr and is 85.5 mole percent carbon disulfide. What is the mole fraction of carbon disulfide in the solution? At 25°C, the vapor pressure of carbon disulfide is 375 torr. Assume the solution and vapor exhibit ideal behavior.

82. If the fluid inside a tree is about 0.1 M more concentrated in solute than the groundwater that bathes the roots, how high will a column of fluid rise in the tree at 25°C? Assume that the density of the fluid is 1.0 g/cm^3. (The density of mercury is 13.6 g/cm^3.)

83. An unknown compound contains only carbon, hydrogen, and oxygen. Combustion analysis of the compound gives mass percents of 31.57% C and 5.30% H. The molar mass is determined by measuring the freezing-point depression of an aqueous solution. A freezing point of −5.20°C is recorded for a solution made by dissolving 10.56 g of the compound in 25.0 g water. Determine the empirical formula, molar mass, and molecular formula of the compound. Assume that the compound is a nonelectrolyte.

84. Consider the following:



What would happen to the level of liquid in the two arms if the semipermeable membrane separating the two liquids were permeable to
a. H_2O only? **b.** H_2O, Na^+, and Cl^-?

85. Consider an aqueous solution containing sodium chloride that has a density of 1.01 g/mL. Assume the solution behaves ideally. The freezing point of this solution at 1.0 atm is −1.28°C. Calculate the percent composition of this solution (by mass).

86. What stabilizes a colloidal suspension? Explain why adding heat or adding an electrolyte can cause the suspended particles to settle out.

87. The freezing point of an aqueous solution is −2.79°C.
a. Determine the boiling point of this solution.
b. Determine the vapor pressure (in mm Hg) of this solution at 25°C (the vapor pressure of pure water at 25°C is 23.76 mm Hg).
c. Explain any assumptions you make in solving parts a and b.

Challenge Problems

88. The vapor pressure of pure benzene is 750.0 torr and the vapor pressure of toluene is 300.0 torr at a certain temperature. You make a solution by pouring "some" benzene with "some" toluene. You then place this solution in a closed container and wait for the vapor to come into equilibrium with the solution. Next, you condense the vapor. You put this liquid (the condensed vapor) in a closed container and wait for the vapor to come into equilibrium with the solution. You then condense this vapor and find the mole fraction of benzene in this vapor to be 0.714. Determine the mole fraction of benzene in the original solution assuming the solution behaves ideally.

89. Liquid A has vapor pressure x, and liquid B has vapor pressure y. What is the mole fraction of the liquid mixture if the vapor above the solution is 30.% A by moles? 50.% A? 80.% A? (Calculate in terms of x and y.)

Liquid A has vapor pressure x, liquid B has vapor pressure y. What is the mole fraction of the vapor above the solution if the liquid mixture is 30.% A by moles? 50.% A? 80.% A? (Calculate in terms of x and y.)

90. Erythrocytes are red blood cells containing hemoglobin. In a saline solution they shrivel when the salt concentration is high and swell when the salt concentration is low. In a 25°C aqueous solution of NaCl, whose freezing point is −0.406°C, erythrocytes neither swell nor shrink. If we want to calculate the osmotic pressure of the solution inside the erythrocytes under these conditions, what do we need to assume? Why? Estimate how good (or poor) of an assumption this is. Make this assumption and calculate the osmotic pressure of the solution inside the erythrocytes.

91. You make 20.0 g of a sucrose ($C_{12}H_{22}O_{11}$) and NaCl mixture and dissolve it in 1.00 kg of water. The freezing point of this solution is found to be −0.426°C. Assuming ideal behavior, calculate the mass percent composition of the original mixture, and the mole fraction of sucrose in the original mixture.

92. An aqueous solution is 1.00% NaCl by mass and has a density of 1.071 g/cm^3 at 25°C. The observed osmotic pressure of this solution is 7.83 atm at 25°C.

a. What fraction of the moles of NaCl in this solution exist as ion pairs?

b. Calculate the freezing point that would be observed for this solution.

93. The vapor in equilibrium with a pentane–hexane solution at 25°C has a mole fraction of pentane equal to 0.15 at 25°C. What is the mole fraction of pentane in the solution? (See Exercise 49 for the vapor pressures of the pure liquids.)

94. A forensic chemist is given a white solid that is suspected of being pure cocaine ($C_{17}H_{21}NO_4$, molar mass = 303.35 g/mol). She dissolves 1.22 ± 0.01 g of the solid in 15.60 ± 0.01 g benzene. The freezing point is lowered by 1.32 ± 0.04°C.

a. What is the molar mass of the substance? Assuming that the percent uncertainty in the calculated molar mass is the same as the percent uncertainty in the temperature change, calculate the uncertainty in the molar mass.

b. Could the chemist unequivocally state that the substance is cocaine? For example, is the uncertainty small enough to distinguish cocaine from codeine ($C_{18}H_{21}NO_3$, molar mass = 299.36 g/mol)?

c. Assuming that the absolute uncertainties in the measurements of temperature and mass remain unchanged, how could the chemist improve the precision of her results?

95. A 1.60-g sample of a mixture of naphthalene ($C_{10}H_8$) and anthracene ($C_{14}H_{10}$) is dissolved in 20.0 g benzene (C_6H_6). The freezing point of the solution is 2.81°C. What is the composition as mass percent of the sample mixture? The freezing point of benzene is 5.51°C, and K_f is 5.12°C · kg/mol.

96. A solid mixture contains $MgCl_2$ and NaCl. When 0.5000 g of this solid is dissolved in enough water to form 1.000 L of solution, the osmotic pressure at 25.0°C is observed to be 0.3950 atm. What is the mass percent of $MgCl_2$ in the solid? (Assume ideal behavior for the solution.)

97. Formic acid (HCO_2H) is a monoprotic acid that ionizes only partially in aqueous solutions. A 0.10 *M* formic acid solution is 4.2% ionized. Assuming that the molarity and molality of the solution are the same, calculate the freezing point and the boiling point of 0.10 *M* formic acid.

98. Specifications for lactated Ringer's solution, which is used for intravenous (IV) injections, are as follows to reach 100. mL of solution:

285–315 mg Na^+
14.1–17.3 mg K^+
4.9–6.0 mg Ca^{2+}
368–408 mg Cl^-
231–261 mg lactate, $C_3H_5O_3^-$

a. Specify the amounts of NaCl, KCl, $CaCl_2 \cdot 2H_2O$, and $NaC_3H_5O_3$ needed to prepare 100. mL of lactated Ringer's solution.

b. What is the range of the osmotic pressure of the solution at 37°C, given the above specifications?

99. In some regions of the southwest United States, the water is very hard. For example, in Las Cruces, New Mexico, the tap water contains about 560 μg of dissolved solids per milliliter. Reverse osmosis units are marketed in this area to soften water. A typical unit exerts a pressure of 8.0 atm and can produce 45 L of water per day.

a. Assuming all of the dissolved solids are $MgCO_3$ and assuming a temperature of 27°C, what total volume of water must be processed to produce 45 L of pure water?

b. Would the same system work for purifying seawater? (Assume seawater is 0.60 *M* NaCl.)

Integrative Problems

These problems require the integration of multiple concepts to find the solutions.

100. Creatinine, $C_4H_7N_3O$, is a by-product of muscle metabolism, and creatinine levels in the body are known to be a fairly reliable indicator of kidney function. The normal level of creatinine in the blood for adults is approximately 1.0 mg per deciliter (dL) of blood. If the density of blood is 1.025 g/mL, calculate the molality of a normal creatinine level in a 10.0-mL blood sample. What is the osmotic pressure of this solution at 25.0°C?

101. An aqueous solution containing 0.250 mol of Q, a strong electrolyte, in 5.00×10^2 g of water freezes at −2.79°C. What is the van't Hoff factor for Q? The molal freezing-point depression constant for water is 1.86°C · kg/mol. What is the formula of Q if it is 38.68% chlorine by mass and there are twice as many anions as cations in one formula unit of Q?

102. Patients undergoing an upper gastrointestinal tract laboratory test are typically given an X-ray contrast agent that aids with the radiologic imaging of the anatomy. One such contrast agent is sodium diatrizoate, a nonvolatile water-soluble compound. A 0.378 *m* solution is prepared by dissolving 38.4 g of sodium diatrizoate (NaDTZ) in 1.60×10^2 mL of water at 31.2°C (the density of water at 31.2°C is 0.995 g/mL). What is the molar mass of sodium diatrizoate? What is the vapor pressure of this solution if the vapor pressure of pure water at 31.2°C is 34.1 torr?

Marathon Problem*

This problem is designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

103. Using the following information, identify the strong electrolyte whose general formula is

$$M_x(A)_y \cdot zH_2O$$

Ignore the effect of interionic attractions in the solution.

a. A^{n-} is a common oxyanion. When 30.0 mg of the anhydrous sodium salt containing this oxyanion (Na_nA, where $n = 1, 2,$ or 3) is reduced, 15.26 mL of 0.02313 *M* reducing agent is required to react completely with the Na_nA present. Assume a 1:1 mole ratio in the reaction.

b. The cation is derived from a silvery white metal that is relatively expensive. The metal itself crystallizes in a body-centered cubic unit cell and has an atomic radius of 198.4 pm. The solid, pure metal has a density of 5.243 g/cm^3. The oxidation number of M in the strong electrolyte in question is +3.

c. When 33.45 mg of the compound is present (dissolved) in 10.0 mL of aqueous solution at 25°C, the solution has an osmotic pressure of 558 torr.

Get help understanding core concepts and visualizing molecular-level interactions, and practice problem solving, by visiting the Online Study Center at **college.hmco.com/PIC/zumdahl7e.**

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