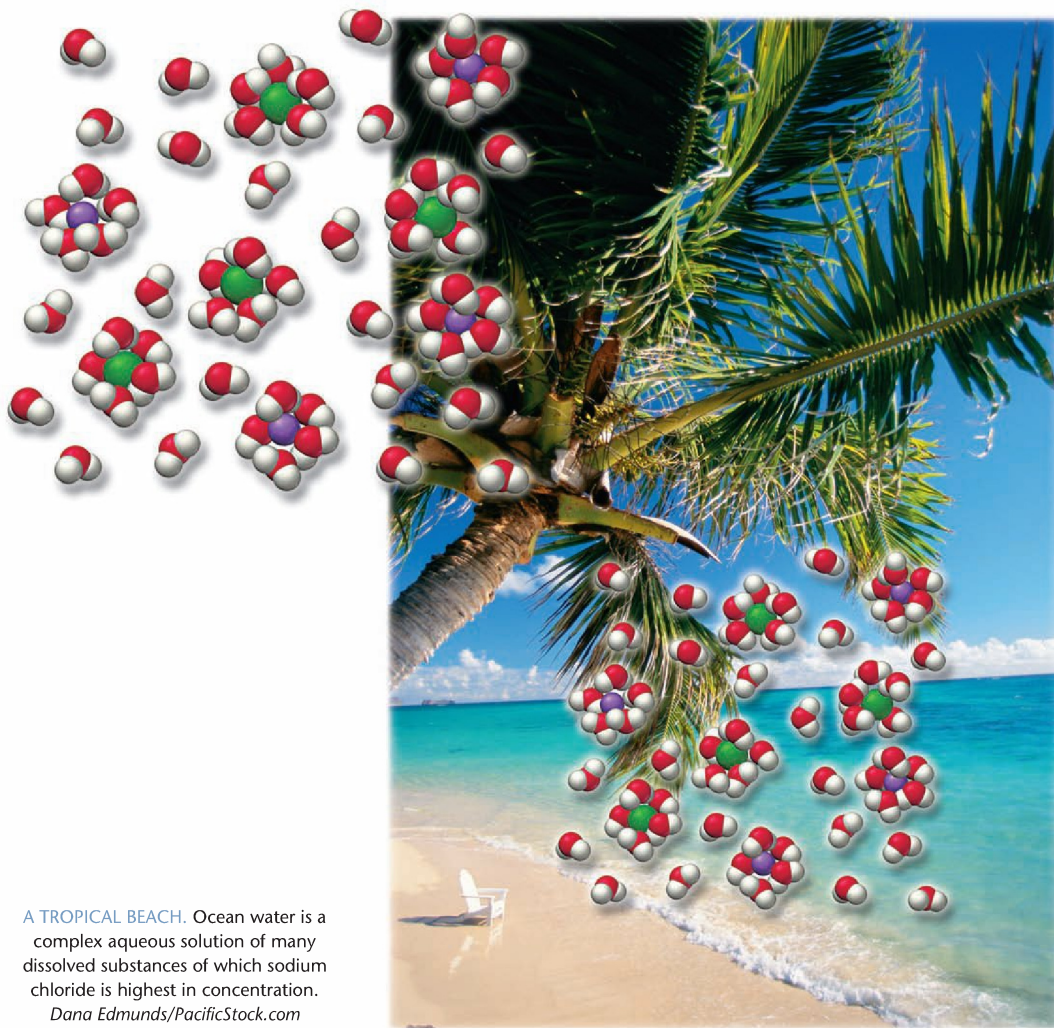


CHAPTER
13

PROPERTIES
OF SOLUTIONS



A TROPICAL BEACH. Ocean water is a complex aqueous solution of many dissolved substances of which sodium chloride is highest in concentration.
Dana Edmunds/PacificStock.com

13.1 The Solution Process

We begin by considering what happens at a molecular level when a substance dissolves, paying particular attention to the role of *intermolecular forces* in the process. Two important aspects of the solution process are the changes in *energy* and the changes in how particles are distributed in space as a result of the solution process.

13.2 Saturated Solutions and Solubility

We will see that in *saturated solutions* the dissolved and undissolved solutes are in *equilibrium*. The amount of solute in a saturated solution defines its *solubility*, the extent to which a particular solute dissolves in a particular solvent.

13.3 Factors Affecting Solubility

We next consider the major factors affecting solubility. The nature of the solute and solvent determines the kinds of intermolecular forces between and within them and strongly influences solubility. Temperature also influences solubility: Most solids are more soluble in water at higher temperatures, whereas gases are less soluble in water at higher temperatures. In addition, the solubility of gases increases with increasing pressure.

13.4 Ways of Expressing Concentration

We observe that many physical properties of solutions depend on their concentration, and we examine several common ways of expressing concentration.

13.5 Colligative Properties

We observe that solutes affect the properties of solutions. The physical properties of solutions that depend only on concentration and not on the identity of the solute are called *colligative properties*. These properties include the extent to which the solute lowers the vapor pressure, increases the boiling point, and decreases the freezing point of the solvent. The osmotic pressure of a solution is also a colligative property.

13.6 Colloids

We close the chapter by investigating *colloids*, mixtures in which particles larger than typical molecular sizes are dispersed in another component.

ON A WARM DAY AT THE BEACH, we are unlikely to consider chemistry while we enjoy the water and warmth of the sun. But as we breathe the air, swim in the water, and walk on the sand, we are experiencing the three states of matter.

In Chapter 10 and 11, we explored the properties

of gases, liquids, and solids. Most of the discussion focused on pure substances. However, the matter that we encounter in our daily lives, such as air, seawater, and sand, is usually composed of mixtures. In this chapter we examine mixtures, although we limit ourselves to those that are homogeneous. As we have noted in earlier chapters, a homogeneous mixture is called a *solution*. ∞ (Sections 1.2 and 4.1)

When we think of solutions, we usually first think about liquids, such as a solution of salt in water, like the seawater shown in this chapter's opening photo. Sterling silver, which is used in jewelry, is also a solution—a homogeneous distribution of about 7% copper in silver. Sterling silver is an example of

a solid solution. Numerous examples of solutions abound in the world around us—some solid, some liquid, and some gas. For example, the air we breathe is a solution of several gases; brass is a solid solution of zinc in copper; and the fluids that run through our bodies are solutions that carry a variety of essential nutrients, salts, and other materials.

Each of the substances in a solution is called a *component* of the solution. As we saw in Chapter 4, the *solvent* is normally the component present in the greatest amount. Other components are called *solutes*. Because liquid solutions are the most common, we will focus our attention on them in this chapter. Our primary goal is to examine the physical properties of solutions, comparing them with the properties of their components. We will be particularly concerned with *aqueous solutions*, which contain water as the solvent and a gas, liquid, or solid as a solute.

13.1 THE SOLUTION PROCESS

A solution is formed when one substance disperses uniformly throughout another. As we noted in the introduction, solutions may be gases, liquids, or solids. Each of these possibilities is listed in Table 13.1 ▼.

The ability of substances to form solutions depends on two general factors: (1) the types of intermolecular interactions involved in the solution process, and (2) the natural tendency of substances to spread into larger volumes when not restrained in some way. We begin our discussion of the solution process by examining the role of intermolecular interactions.

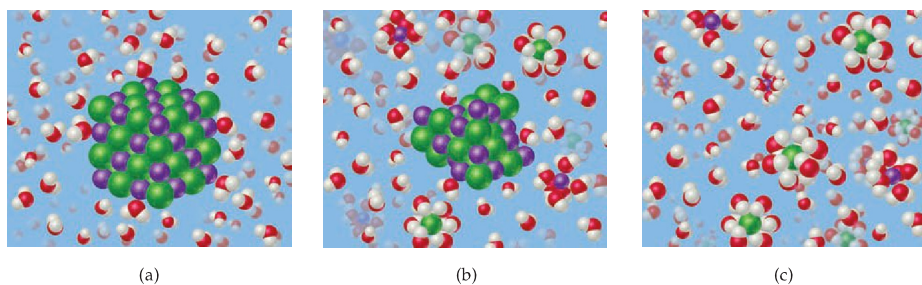
The Effect of Intermolecular Forces

Any of the various kinds of intermolecular forces that we discussed in Chapter 11 can operate between solute and solvent particles in a solution. Ion–dipole forces, for example, dominate in solutions of ionic substances in water. Dispersion forces, on the other hand, dominate when a nonpolar substance such as C_6H_{14} dissolves in another nonpolar one like CCl_4 . Indeed, a major factor determining whether a solution forms is the relative strengths of intermolecular forces between and among the solute and solvent particles. That is, the extent to which one substance is able to dissolve in another depends on the relative magnitudes of the solute–solvent, solute–solute, and solvent–solvent interactions involved in the solution process.

Solutions form when the magnitudes of the attractive forces between solute and solvent particles are comparable to or greater than those that exist between the solute particles themselves or between the solvent particles themselves. For example, the ionic substance $NaCl$ dissolves readily in water because the attractive interactions between the ions and the polar H_2O molecules (solute–solvent interactions) overcome the attraction between the ions in the solid $NaCl$

TABLE 13.1 ■ Examples of Solutions

State of Solution	State of Solvent	State of Solute	Example
Gas	Gas	Gas	Air
Liquid	Liquid	Gas	Oxygen in water
Liquid	Liquid	Liquid	Alcohol in water
Liquid	Liquid	Solid	Salt in water
Solid	Solid	Gas	Hydrogen in palladium
Solid	Solid	Liquid	Mercury in silver
Solid	Solid	Solid	Silver in gold



▲ **Figure 13.1 Dissolution of an ionic solid in water.** (a) A crystal of the ionic solid is hydrated by water molecules, with the oxygen atoms of the water molecules oriented toward the cations (purple) and the hydrogens oriented toward the anions (green). (b, c) As the solid dissolves, the individual ions are removed from the solid surface and become completely separate hydrated species in solution.

(solute–solute interactions) and between H_2O molecules in the solvent (solvent–solvent interactions). Let's examine this solution process more closely, paying attention to these various attractive forces.

When NaCl is added to water (Figure 13.1▲), the water molecules orient themselves on the surface of the NaCl crystals. The positive end of the water dipole is oriented toward the Cl^- ions, and the negative end of the water dipole is oriented toward the Na^+ ions. The ion–dipole attractions between the ions and water molecules are strong enough to pull the ions from their positions in the crystal.

Once separated from the crystal, the Na^+ and Cl^- ions are surrounded by water molecules, as shown in Figure 13.1(b and c) and Figure 13.2▶. We learned in Section 4.1 that interactions such as this between solute and solvent molecules are known as **solvation**. When the solvent is water, the interactions are also referred to as **hydration**.

In addition to the solvent–solute interactions (the ion–dipole attractions between H_2O molecules and the Na^+ and Cl^- ions) and the solute–solute interactions (between the Na^+ and Cl^- ions in the solid), we must consider one other interaction: the solvent–solvent interaction (in this case the hydrogen-bonding attractions between H_2O molecules). In forming the solution, the water molecules must make room for the hydrated Na^+ and Cl^- ions in their midst, causing some water molecules to move apart.

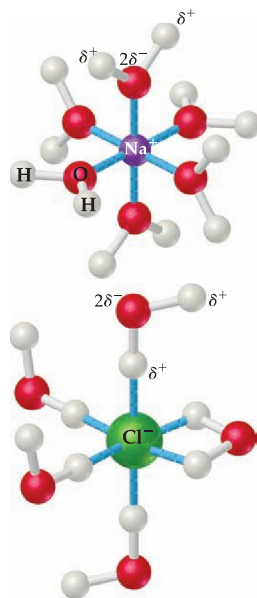
GIVE IT SOME THOUGHT

Why doesn't NaCl dissolve in nonpolar solvents such as hexane, C_6H_{14} ?

Energy Changes and Solution Formation

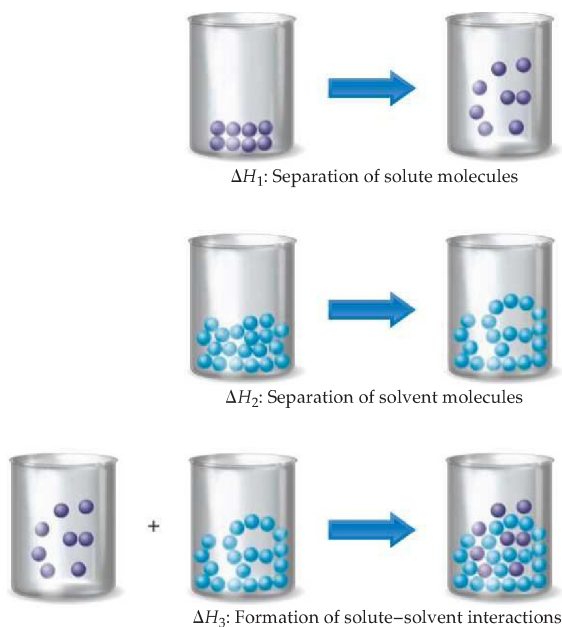
We can analyze the roles played by the solute–solvent, solute–solute, and solvent–solvent interactions by examining the energy changes associated with each. Let's continue to analyze the process of dissolving NaCl in water as an example of how energy considerations provide insight into the solution process.

We have observed that sodium chloride dissolves in water because the water molecules have a strong enough attraction for the Na^+ and Cl^- ions to overcome the attraction of these two ions for one another in the crystal. In addition, water molecules must separate from one another to form spaces in the solvent that the Na^+ and Cl^- ions will occupy. Thus, we can think of the overall energetics of solution formation as having three components—associated



▲ **Figure 13.2 Hydrated Na^+ and Cl^- ions.** The negative ends of the water dipoles point toward the positive ion, and the positive ends point toward the negative ion.

► **Figure 13.3 Enthalpy contributions to ΔH_{soln} .** The enthalpy changes ΔH_1 and ΔH_2 represent endothermic processes, requiring an input of energy, whereas ΔH_3 represents an exothermic process.



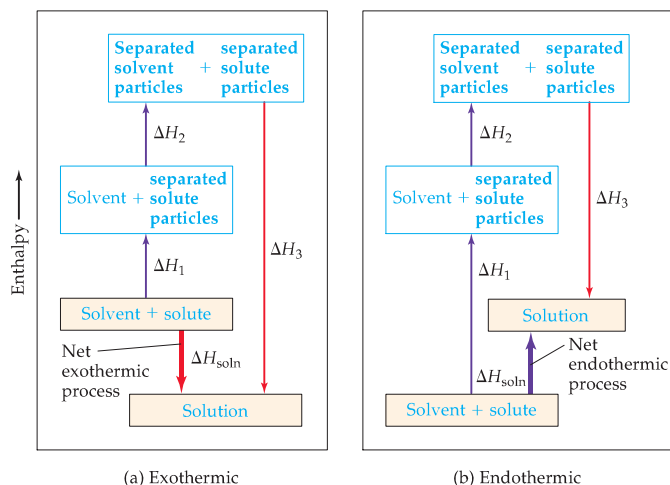
with breaking the solute-solute and the solvent-solvent interactions and forming the solute-solvent interactions—as illustrated schematically in Figure 13.3▲. The overall enthalpy change in forming a solution, ΔH_{soln} , is the sum of three terms associated with these three processes:

$$\Delta H_{\text{soln}} = \Delta H_1 + \Delta H_2 + \Delta H_3 \quad [13.1]$$

Regardless of the particular solute being considered, separation of the solute particles from one another requires an input of energy to overcome their attractive interactions. The process is therefore endothermic ($\Delta H_1 > 0$). Separation of solvent molecules to accommodate the solute also always requires energy ($\Delta H_2 > 0$). The third component, which arises from the attractive interactions between solute and solvent, is always exothermic ($\Delta H_3 < 0$).

As shown in Figure 13.4►, the three enthalpy terms in Equation 13.1 can be added together to give either a negative or a positive sum, depending on the relative magnitudes of the terms. Thus, the formation of a solution can be either exothermic or endothermic. For example, when magnesium sulfate, MgSO_4 , is added to water, the resultant solution gets quite warm: $\Delta H_{\text{soln}} = -91.2 \text{ kJ/mol}$. In contrast, the dissolution of ammonium nitrate (NH_4NO_3) is endothermic: $\Delta H_{\text{soln}} = 26.4 \text{ kJ/mol}$. These particular substances have been used to make the instant heat packs and ice packs that are used to treat athletic injuries (Figure 13.5►). The packs consist of a pouch of water and a dry chemical, MgSO_4 for hot packs and NH_4NO_3 for cold packs. When the pack is squeezed, the seal separating the solid from the water is broken and a solution forms, either increasing or decreasing the temperature.

In Chapter 5 we learned that the enthalpy change in a process can provide information about the extent to which a process will occur. ∞ (Section 5.4) Processes that are exothermic tend to proceed spontaneously. A solution will not form if ΔH_{soln} is too endothermic. The solvent-solute interaction must be



◀ **Figure 13.4 Enthalpy changes accompanying the solution process.** The three processes are illustrated in Figure 13.3. The diagram on the left (a) illustrates a net exothermic process ($\Delta H_{\text{soln}} < 0$); that on the right (b) shows a net endothermic process ($\Delta H_{\text{soln}} > 0$).

strong enough to make ΔH_3 comparable in magnitude to $\Delta H_1 + \Delta H_2$. This fact explains why ionic solutes such as NaCl do not dissolve in nonpolar liquids such as gasoline. The nonpolar hydrocarbon molecules of the gasoline would experience only weak attractive interactions with the ions, and these interactions would not compensate for the energies required to separate the ions from one another.

By similar reasoning, a polar liquid such as water does not form solutions with a nonpolar liquid such as octane (C_8H_{18}). The water molecules experience strong hydrogen-bonding interactions with one another. ∞ (Section 11.2) These attractive forces must be overcome to disperse the water molecules throughout the nonpolar liquid. The energy required to separate the H_2O molecules is not recovered in the form of attractive interactions between H_2O and C_8H_{18} molecules.

GIVE IT SOME THOUGHT

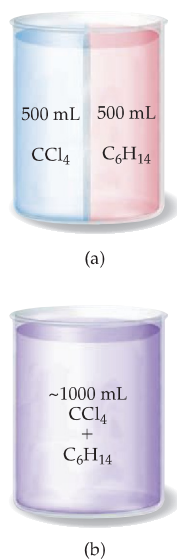
Label the following processes as exothermic or endothermic: (a) forming solvent-solute interactions, (b) breaking solvent-solvent interactions.

Solution Formation, Spontaneity, and Entropy

When carbon tetrachloride (CCl_4) and hexane (C_6H_{14}) are mixed, they dissolve in one another in all proportions. Both substances are nonpolar, and they have similar boiling points (77°C for CCl_4 and 69°C for C_6H_{14}). It is therefore reasonable to suppose that the magnitudes of the attractive forces (London dispersion forces) among molecules in the two substances and in their solution are comparable. When the two substances are mixed, dissolving occurs spontaneously; that is, it occurs without any extra input of energy from outside the system. Processes that occur spontaneously involve two distinct factors. The most obvious factor is energy, which we have used to analyze the dissolving of NaCl in water. The other factor is the distribution of each component into a larger volume—the tendency in nature for substances to mix and spread out into larger volumes.



▲ **Figure 13.5 Endothermic dissolution.** Ammonium nitrate instant ice packs are often used to treat athletic injuries. To activate the pack, the container is kneaded. The kneading breaks an interior seal separating solid NH_4NO_3 from water. The heat of solution of NH_4NO_3 is positive, so the temperature of the solution decreases.



▲ Figure 13.6 Increasing randomness in a solution process. A homogeneous solution of CCl_4 and C_6H_{14} forms when a barrier separating the two liquids is removed. Each CCl_4 molecule of the solution in (b) is more dispersed in space than it was in the left compartment in (a), and each C_6H_{14} molecule in (b) is more dispersed than it was in the right compartment in (a).

We see the influence of energy all around us. If you let go of a book, it falls to the floor because of gravity. At its initial height, the book has a higher potential energy than it has when it is on the floor. Unless the book is restrained, it falls; and as it does, potential energy is converted into kinetic energy. When the book strikes the floor, the kinetic energy is converted largely into heat energy, which is dispersed throughout the surroundings. The book has lost energy to its surroundings in this process. This fact leads us to the first basic principle identifying spontaneous processes and the direction they take: *Processes in which the energy content of the system decreases tend to occur spontaneously.* Spontaneous processes tend to be exothermic. (Section 5.4, “Strategies in Chemistry: Using Enthalpy as a Guide”) Change tends to occur in the direction that leads to a lower energy or lower enthalpy for the system.

Some spontaneous processes, however, do not result in lower energy for a system, and even some endothermic processes occur spontaneously. For example, NH_4NO_3 readily dissolves in water, even though the solution process is endothermic. Processes such as this are characterized by a more dispersed state of one or more components, resulting in an overall increase in the randomness of the system. In this example the densely ordered solid, NH_4NO_3 , is dispersed throughout the solution as separated NH_4^+ and NO_3^- ions. The mixing of CCl_4 and C_6H_{14} provides another simple example.

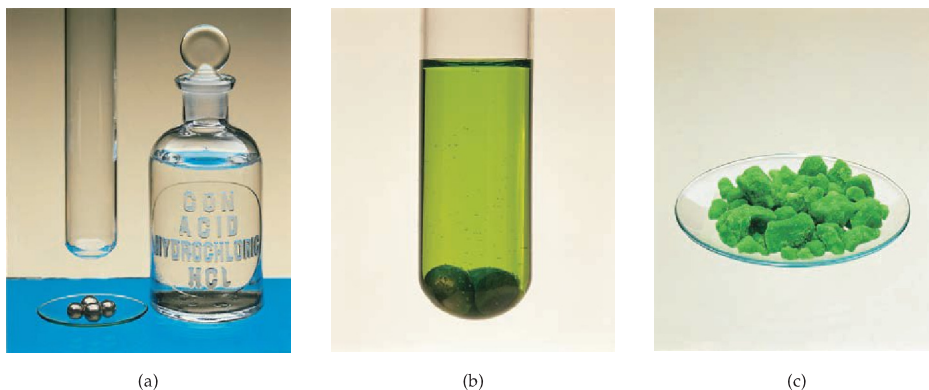
Suppose that we could suddenly remove a barrier that separates 500 mL of CCl_4 from 500 mL of C_6H_{14} , as shown in Figure 13.6(a). Before the barrier is removed, each liquid occupies a volume of 500 mL. All the CCl_4 molecules are in the 500 mL to the left of the barrier, and all the C_6H_{14} molecules are in the 500 mL to the right. When equilibrium has been established after the barrier has been removed, the two liquids together occupy a volume of about 1000 mL. Formation of a homogeneous solution has increased the degree of dispersal, or randomness, because the molecules of each substance are now mixed and distributed in a volume twice as large as that which they occupied individually before mixing. The degree of randomness in the system, sometimes referred to as disorder, is given by a thermodynamic quantity called **entropy**. This example illustrates our second basic principle: *Processes occurring at a constant temperature in which the randomness or dispersal in space (entropy) of the system increases tend to occur spontaneously.*

When molecules of different types are brought together, mixing—hence an increased dispersal—occurs spontaneously unless the molecules are restrained by sufficiently strong intermolecular forces or by physical barriers. Thus, gases spontaneously mix and expand unless restrained by their containers; in this case intermolecular forces are too weak to restrain the molecules. However, because strong bonds hold sodium and chloride ions together, sodium chloride does not spontaneously dissolve in gasoline.

We will discuss spontaneous processes again in Chapter 19. At that time we will consider the balance between the tendencies toward lower enthalpy and toward increased entropy in greater detail. For the moment, we need to be aware that the solution process involves two factors: a change in enthalpy and a change in entropy. In most cases the *formation of solutions is favored by the increase in entropy that accompanies mixing.* Consequently, a solution will form unless solute–solute or solvent–solvent interactions are too strong relative to the solute–solvent interactions.

GIVE IT SOME THOUGHT

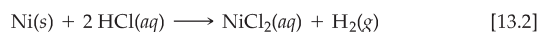
Silver chloride, AgCl , is essentially insoluble in water. Would you expect a significant change in the entropy of the system when 10 g of AgCl is added to 500 mL of water?



▲ **Figure 13.7 The nickel-acid reaction is not a simple dissolution.** (a) Nickel metal and hydrochloric acid. (b) Nickel reacts slowly with hydrochloric acid, forming $\text{NiCl}_2(aq)$ and $\text{H}_2(g)$. (c) $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$ is obtained when the solution from (b) is evaporated to dryness. Because the residue left after evaporation is chemically different from either reactant, we know what takes place is a chemical reaction rather than merely a solution process.

Solution Formation and Chemical Reactions

In all our discussions of solutions, we must be careful to distinguish the physical process of solution formation from chemical reactions that lead to a solution. For example, nickel metal is dissolved on contact with hydrochloric acid solution because the following chemical reaction occurs:



In this instance the chemical form of the substance being dissolved is changed from Ni to NiCl_2 . If the solution is evaporated to dryness, $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}(s)$, not $\text{Ni}(s)$, is recovered (Figure 13.7). When $\text{NaCl}(s)$ is dissolved in water, on the other hand, no chemical reaction occurs. If the solution is evaporated to dryness, NaCl is recovered. Our focus throughout this chapter is on solutions from which the solute can be recovered unchanged from the solution.

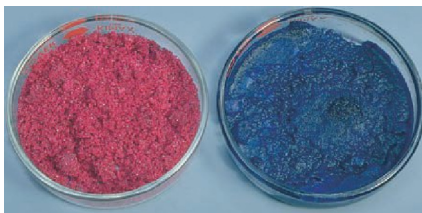


A Closer Look

HYDRATES

Frequently, hydrated ions remain in crystalline salts that are obtained by evaporation of water from aqueous solutions. Common examples include $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ [iron(III) chloride hexahydrate] and $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ [copper(II) sulfate pentahydrate]. The $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ consists of $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ and Cl^- ions; the $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ consists of $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ and $\text{SO}_4(\text{H}_2\text{O})_2^{2-}$ ions. Water molecules can also occur in positions in the crystal lattice that are not specifically associated with either a cation or an anion. $\text{BaCl}_2 \cdot 2 \text{H}_2\text{O}$ (barium chloride dihydrate) is an example. Compounds such as $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$, and $\text{BaCl}_2 \cdot 2 \text{H}_2\text{O}$, which contain a salt and water combined in definite proportions, are known as *hydrates*. The water associated with them is called *water of hydration*. Figure 13.8 shows an example of a hydrate and the corresponding anhydrous (water-free) substance.

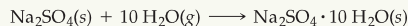
Related Exercises: 13.4, 13.107



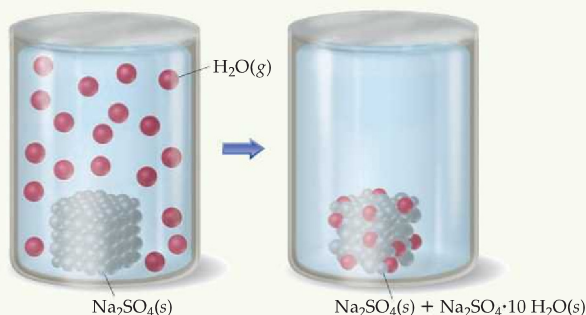
▲ **Figure 13.8 Hydrates and anhydrous salts.** Hydrated cobalt(II) chloride, $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$ (left), and anhydrous CoCl_2 (right).

SAMPLE EXERCISE 13.1 | Assessing Entropy Change

In the process illustrated below, water vapor reacts with excess solid sodium sulfate to form the hydrated form of the salt. The chemical reaction is



Essentially all of the water vapor in the closed container is consumed in this reaction. If we consider our system to consist initially of $\text{Na}_2\text{SO}_4(\text{s})$ and $10 \text{H}_2\text{O}(\text{g})$, (a) does the system become more or less ordered in this process, and (b) does the entropy of the system increase or decrease?

**SOLUTION**

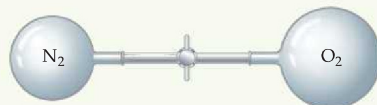
Analyze: We are asked to determine whether the reaction of water vapor with the solid salt causes the system to become more or less dispersed, or random, and to determine whether the process results in a higher or lower entropy for the system.

Plan: We need to examine the initial and final states and judge whether the process has made the system more or less dispersed. Depending on our answer to that question, we can determine whether the entropy has increased or decreased.

Solve: (a) In the course of forming the hydrate of $\text{Na}_2\text{SO}_4(\text{s})$, the water vapor moves from the vapor state, in which it is dispersed throughout the entire volume of the container, to the solid state, where it is confined to the $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}(\text{s})$ lattice. This means that the water vapor becomes less dispersed (more ordered, or less random). (b) When a system becomes less dispersed, or more ordered, its entropy is decreased.

PRACTICE EXERCISE

Does the entropy of the system increase or decrease when the stopcock is opened to allow mixing of the two gases in this apparatus?



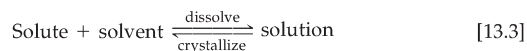
Answer: The entropy increases because each gas eventually becomes dispersed in twice the volume it originally occupied.



▲ **Figure 13.9 Dynamic equilibrium in a saturated solution.** In a solution in which excess ionic solute is present, ions on the surface of the solute are continuously passing into the solution as hydrated species, while hydrated ions from the solution are deposited on the surfaces of the solute. At equilibrium in a saturated solution, the two processes occur at equal rates.

13.2 SATURATED SOLUTIONS AND SOLUBILITY

As a solid solute begins to dissolve in a solvent, the concentration of solute particles in solution increases, thus increasing the chances of the solute particles colliding with the surface of the solid (Figure 13.9 ◀). Because of such a collision, the solute particle may become reattached to the solid. This process, which is the opposite of the solution process, is called **crystallization**. Thus, two opposing processes occur in a solution in contact with undissolved solute. This situation is represented in a chemical equation by use of two half arrows:





(a) A seed crystal of NaCH_3COO being added to the supersaturated solution. (b) Excess NaCH_3COO crystallizes from the solution. (c) The solution arrives at saturation.

▲ **Figure 13.10 Sodium acetate readily forms a supersaturated solution in water.**

When the rates of these opposing processes become equal, there is no further net increase in the amount of solute in solution. A dynamic equilibrium is established similar to the one between evaporation and condensation discussed in Section 11.5.

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

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

Under suitable conditions it is sometimes possible to form solutions that contain a greater amount of solute than that needed to form a saturated solution. Such solutions are **supersaturated**. For example, considerably more sodium acetate (NaCH_3COO) can dissolve in water at high temperatures than at low temperatures. When a saturated solution of sodium acetate is made at a high temperature and then slowly cooled, all of the solute may remain dissolved even though the solubility decreases as the temperature decreases. Because the solute in a supersaturated solution is present in a concentration higher than the equilibrium concentration, supersaturated solutions are unstable. Supersaturated solutions result for much the same reason as supercooled liquids (Section 11.4). For crystallization to occur, the molecules or ions of solute must arrange themselves properly to form crystals. The addition of a small crystal of the solute (a seed crystal) provides a template for crystallization of the excess solute, leading to a saturated solution in contact with excess solid (Figure 13.10 ▲).

GIVE IT SOME THOUGHT

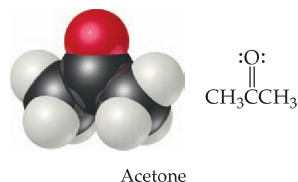
Is a supersaturated solution of sodium acetate a stable equilibrium solution?

13.3 FACTORS AFFECTING SOLUBILITY

The extent to which one substance dissolves in another depends on the nature of both the solute and the solvent. \rightleftharpoons (Section 13.1) It also depends on temperature and, at least for gases, on pressure. Let's consider these factors more closely.

TABLE 13.2 ■ Solubilities of Gases in Water at 20 °C, with 1 atm Gas Pressure

Gas	Solubility (M)
N ₂	0.69×10^{-3}
CO	1.04×10^{-3}
O ₂	1.38×10^{-3}
Ar	1.50×10^{-3}
Kr	2.79×10^{-3}

**Hexane is insoluble in water.** Hexane is the top layer because it is less dense than water.

Solute–Solvent Interactions

One factor determining solubility is the natural tendency of substances to mix (the tendency of systems to move toward a more dispersed, or random, state). ∞ (Section 13.2) If this were the only factor involved, however, we would expect all substances to be completely soluble in one another. This is clearly not the case. So what other factors are involved? As we saw in Section 13.1, the relative forces of attraction among the solute and solvent molecules also play very important roles in the solution process.

Although the tendency toward dispersal and the various interactions among solute and solvent particles are all involved in determining the solubilities, considerable insight can often be gained by focusing on the interaction between the solute and solvent. The data in Table 13.2 ◀ show, for example, that the solubilities of various simple gases in water increase with increasing molecular mass or polarity. The attractive forces between the gas and solvent molecules are mainly of the London dispersion type, which increase with increasing size and mass of the gas molecules. ∞ (Section 11.2) Thus, the data indicate that the solubilities of gases in water increase as the attraction between the solute (gas) and solvent (water) increases. In general, when other factors are comparable, *the stronger the attractions are between solute and solvent molecules, the greater the solubility.*

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

Pairs of liquids such as acetone and water that mix in all proportions are **miscible**, whereas those that do not dissolve in one another are **immiscible**. Gasoline, which is a mixture of hydrocarbons, is immiscible with water. Hydrocarbons are nonpolar substances because of several factors: The C—C bonds are nonpolar, the C—H bonds are nearly nonpolar, and the shapes of the molecules are symmetrical enough to cancel much of the weak C—H bond dipoles. The attraction between the polar water molecules and the nonpolar hydrocarbon molecules is not sufficiently strong to allow the formation of a solution. *Nonpolar liquids tend to be insoluble in polar liquids.* As a result, hexane (C₆H₁₄) does not dissolve in water, as the photo in the margin shows.

The series of compounds in Table 13.3 ▼ demonstrates that polar liquids tend to dissolve in other polar liquids and nonpolar liquids in nonpolar ones. These organic compounds all contain the OH group attached to a C atom. Organic compounds with this molecular feature are called *alcohols*. The O—H bond is polar and is able to form hydrogen bonds. For example, CH₃CH₂OH molecules can form hydrogen bonds with water molecules as well as with each other (Figure 13.11 ►). As a result, the solute–solute, solvent–solvent, and solute–solvent forces

TABLE 13.3 ■ Solubilities of Some Alcohols in Water and in Hexane*

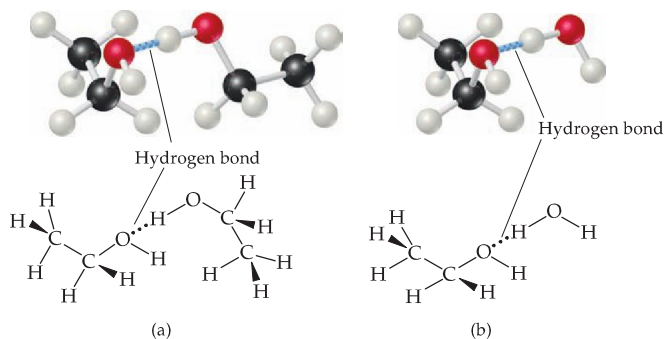
Alcohol	Solubility in H ₂ O	Solubility in C ₆ H ₁₄
CH ₃ OH (methanol)	∞	0.12
CH ₃ CH ₂ OH (ethanol)	∞	∞
CH ₃ CH ₂ CH ₂ OH (propanol)	∞	∞
CH ₃ CH ₂ CH ₂ CH ₂ OH (butanol)	0.11	∞
CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ OH (pentanol)	0.030	∞
CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ OH (hexanol)	0.0058	∞

*Expressed in mol alcohol/100 g solvent at 20 °C. The infinity symbol (∞) indicates that the alcohol is completely miscible with the solvent.

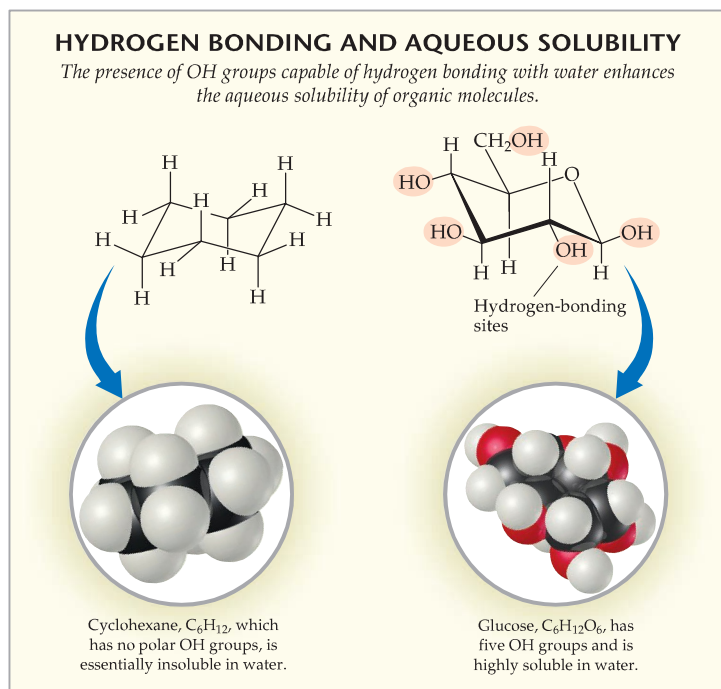
are not greatly different within a mixture of $\text{CH}_3\text{CH}_2\text{OH}$ and H_2O . No major change occurs in the environments of the molecules as they are mixed. Therefore, the increased dispersal (entropy) of the two components into a larger combined volume as they mix plays a significant role in the formation of the solution. Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), therefore, is completely miscible with water.

The number of carbon atoms in an alcohol affects its solubility in water. As the length of the carbon chain increases, the polar OH group becomes an ever smaller part of the molecule, and the molecule behaves more like a hydrocarbon. The solubility of the alcohol in water decreases correspondingly. On the other hand, the solubility of the alcohol in a nonpolar solvent like hexane (C_6H_{14}) increases as the nonpolar hydrocarbon chain increases in length.

One way to enhance the solubility of a substance in water is to increase the number of polar groups it contains. For example, increasing the number of OH groups along a carbon chain of a solute increases the extent of hydrogen bonding between that solute and water, thereby increasing solubility. Glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) has five OH groups on a six-carbon framework, which makes the molecule very soluble in water (83 g dissolves in 100 mL of water at 17.5 °C). The glucose molecule is shown in Figure 13.12 ▼.



▲ **Figure 13.11 Hydrogen-bonding interactions.** (a) Between two ethanol molecules and (b) between an ethanol molecule and a water molecule.



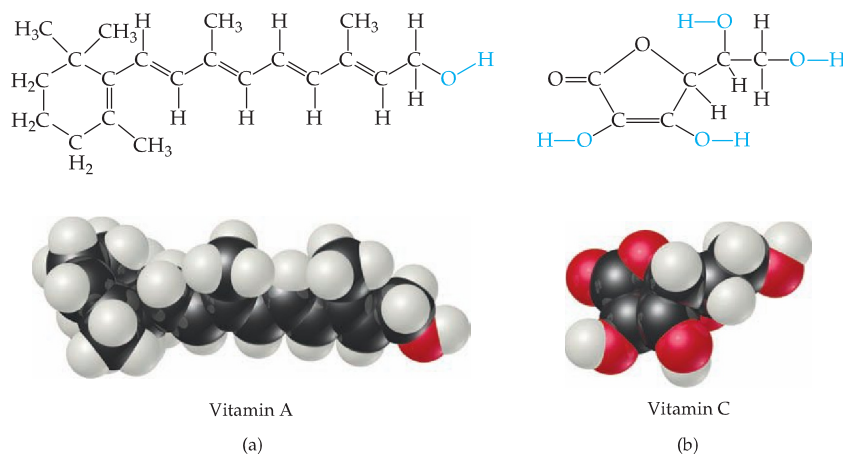
▲ **Figure 13.12 Structure and solubility.**

Vitamins have unique chemical structures that affect their solubilities in different parts of the human body. Vitamins B and C are water soluble, for example, whereas vitamins A, D, E, and K are soluble in nonpolar solvents and in the fatty tissue of the body (which is nonpolar). Because of their water solubility, vitamins B and C are not stored to any appreciable extent in the body, and so foods containing these vitamins should be included in the daily diet. In contrast, the fat-soluble vitamins are stored in sufficient quantities to keep vitamin-deficiency diseases from appearing even after a person has subsisted for a long period on a vitamin-deficient diet.

The different solubility patterns of the water-soluble vitamins and the fat-soluble ones can be rationalized in terms of

the structures of the molecules. The chemical structures of vitamin A (retinol) and of vitamin C (ascorbic acid) are shown in Figure 13.13. Notice that the vitamin A molecule is an alcohol with a very long carbon chain. Because the OH group is such a small part of the molecule, the molecule resembles the long-chain alcohols listed in Table 13.3. This vitamin is nearly nonpolar. In contrast, the vitamin C molecule is smaller and has more OH groups that can form hydrogen bonds with water. It is somewhat like glucose, which was discussed earlier. It is a more polar substance.

Related Exercises: 13.7, 13.44



▲ **Figure 13.13 Vitamins A and C.** (a) The molecular structure of vitamin A, a fat-soluble vitamin. The molecule is composed largely of carbon-carbon and carbon-hydrogen bonds, so it is nearly nonpolar. (b) The molecular structure of vitamin C, a water-soluble vitamin. Notice the OH groups and the other oxygen atoms in the molecule, which can interact with water molecules by hydrogen bonding.

Examination of different combinations of solvents and solutes such as those considered in the preceding paragraphs has led to an important generalization: *Substances with similar intermolecular attractive forces tend to be soluble in one another.* This generalization is often simply stated as “like dissolves like.” Nonpolar substances are more likely to be soluble in nonpolar solvents; ionic and polar solutes are more likely to be soluble in polar solvents. Network solids such as diamond and quartz are not soluble in either polar or nonpolar solvents because of the strong bonding forces within the solid.

GIVE IT SOME THOUGHT

Suppose the hydrogens on the OH groups in glucose (Figure 13.12) were replaced with methyl groups, CH₃. Would you expect the water solubility of the resulting molecule to be higher than, lower than, or about the same as the solubility of glucose?

SAMPLE EXERCISE 13.2 Predicting Solubility Patterns

Predict whether each of the following substances is more likely to dissolve in the nonpolar solvent carbon tetrachloride (CCl_4) or in water: C_7H_{16} , Na_2SO_4 , HCl , and I_2 .

SOLUTION

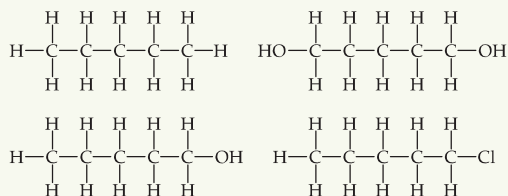
Analyze: We are given two solvents, one that is nonpolar (CCl_4) and the other that is polar (H_2O), and asked to determine which will be the best solvent for each solute listed.

Plan: By examining the formulas of the solutes, we can predict whether they are ionic or molecular. For those that are molecular, we can predict whether they are polar or nonpolar. We can then apply the idea that the nonpolar solvent will be best for the nonpolar solutes, whereas the polar solvent will be best for the ionic and polar solutes.

Solve: C_7H_{16} is a hydrocarbon, so it is molecular and nonpolar. Na_2SO_4 , a compound containing a metal and nonmetals, is ionic. HCl , a diatomic molecule containing two nonmetals that differ in electronegativity, is polar. I_2 , a diatomic molecule with atoms of equal electronegativity, is nonpolar. We would therefore predict that C_7H_{16} and I_2 (the nonpolar solutes) would be more soluble in the nonpolar CCl_4 than in polar H_2O , whereas water would be the better solvent for Na_2SO_4 and HCl (the ionic and polar covalent solutes).

PRACTICE EXERCISE

Arrange the following substances in order of increasing solubility in water:



Answer: $\text{C}_5\text{H}_{12} < \text{C}_5\text{H}_{11}\text{Cl} < \text{C}_5\text{H}_{11}\text{OH} < \text{C}_5\text{H}_{10}(\text{OH})_2$ (in order of increasing polarity and hydrogen-bonding ability)

Pressure Effects

The solubilities of solids and liquids are not appreciably affected by pressure, whereas the solubility of a gas in any solvent is increased as the pressure over the solvent increases. We can understand the effect of pressure on the solubility of a gas by considering the dynamic equilibrium illustrated in Figure 13.14. Suppose that we have a gaseous substance distributed between the gas and solution phases. When equilibrium is established, the rate at which gas molecules enter the solution equals the rate at which solute molecules escape from the solution to enter the gas phase. The small arrows in Figure 13.14(a) represent the rates of these opposing processes. Now suppose that we exert added pressure on the piston and compress the gas above the solution, as shown in Figure 13.14(b). If we reduced the volume to half its original value, the pressure of the gas would increase to about twice its original value. The rate at which gas molecules strike the surface to enter the solution phase would therefore increase. As a result, the solubility of the gas in the solution would increase until equilibrium is again established; that is, solubility increases until the rate at which gas molecules enter the solution equals the rate at which solute molecules escape from the solution. Thus, *the solubility of the gas increases in direct proportion to its partial pressure above the solution.*



▲ Figure 13.14 Effect of pressure on gas solubility. When the pressure is increased, as in (b), the rate at which gas molecules enter the solution increases. The concentration of solute molecules at equilibrium increases in proportion to the pressure.



▲ **Figure 13.15 Solubility decreases as pressure decreases.** CO₂ bubbles out of solution when a carbonated beverage is opened, because the CO₂ partial pressure above the solution is reduced.

The relationship between pressure and the solubility of a gas is expressed by a simple equation known as **Henry's law**:

$$S_g = kP_g \quad [13.4]$$

Here, S_g is the solubility of the gas in the solution phase (usually expressed as molarity), P_g is the partial pressure of the gas over the solution, and k is a proportionality constant known as the *Henry's law constant*. The Henry's law constant is different for each solute–solvent pair. It also varies with temperature. As an example, the solubility of N₂ gas in water at 25 °C and 0.78 atm pressure is $5.3 \times 10^{-4} M$. The Henry's law constant for N₂ in water at 25 °C is thus given by $(5.3 \times 10^{-4} \text{ mol/L})/0.78 \text{ atm} = 6.8 \times 10^{-4} \text{ mol/L-atm}$. If the partial pressure of N₂ is doubled, Henry's law predicts that the solubility in water at 25 °C will also double, to $1.36 \times 10^{-3} M$.

Bottlers use the effect of pressure on solubility in producing carbonated beverages such as beer and many soft drinks. These are bottled under a carbon dioxide pressure greater than 1 atm. When the bottles are opened to the air, the partial pressure of CO₂ above the solution decreases. Hence, the solubility of CO₂ decreases, and CO₂(g) escapes from the solution as bubbles (Figure 13.15 ◀).

■ SAMPLE EXERCISE 13.3 | A Henry's Law Calculation

Calculate the concentration of CO₂ in a soft drink that is bottled with a partial pressure of CO₂ of 4.0 atm over the liquid at 25 °C. The Henry's law constant for CO₂ in water at this temperature is $3.1 \times 10^{-2} \text{ mol/L-atm}$.

SOLUTION

Analyze: We are given the partial pressure of CO₂, P_{CO_2} , and the Henry's law constant, k , and asked to calculate the concentration of CO₂ in the solution.

Plan: With the information given, we can use Henry's law, Equation 13.4, to calculate the solubility, S_{CO_2} .

Chemistry and Life

BLOOD GASES AND DEEP-SEA DIVING

Because the solubility of gases increases with increasing pressure, divers who breathe compressed air (Figure 13.16 ▶) must be concerned about the solubility of gases in their blood. Although the gases are not very soluble at sea level, their solubilities can become appreciable at deep levels where their partial pressures are greater. Thus, deep-sea divers must ascend slowly to prevent dissolved gases from being released rapidly from blood and other fluids in the body. These bubbles affect nerve impulses and give rise to the affliction known as decompression sickness, or “the bends,” which is painful and potentially fatal. Nitrogen is the main problem because it has the highest partial pressure in air and because it can be removed only through the respiratory system. Oxygen, in contrast, is consumed in metabolism.

Deep-sea divers sometimes substitute helium for nitrogen in the air that they breathe, because helium has a much lower solubility in biological fluids than N₂. For example, divers working at a depth of 100 ft experience a pressure of about 4 atm. At this pressure a mixture of 95% helium and 5% oxygen will give an oxygen partial pressure of about 0.2 atm, which is the partial pressure of oxygen in normal air at 1 atm. If the oxygen partial pressure becomes too great, the urge to breathe is reduced, CO₂ is not removed from the body, and

CO₂ poisoning occurs. At excessive concentrations in the body, carbon dioxide acts as a neurotoxin, interfering with nerve conduction and transmission.

Related Exercises: 13.55, 13.56, 13.105



▲ **Figure 13.16 Solubility increases as pressure increases.** Divers who use compressed gases must be concerned about the solubility of the gases in their blood. *Doug Perrine/PacificStock.com*

Solve: $S_{\text{CO}_2} = kP_{\text{CO}_2} = (3.1 \times 10^{-2} \text{ mol/L}\cdot\text{atm})(4.0 \text{ atm}) = 0.12 \text{ mol/L} = 0.12 \text{ M}$

Check: The units are correct for solubility, and the answer has two significant figures consistent with both the partial pressure of CO_2 and the value of Henry's constant.

PRACTICE EXERCISE

Calculate the concentration of CO_2 in a soft drink after the bottle is opened and equilibrates at 25°C under a CO_2 partial pressure of $3.0 \times 10^{-4} \text{ atm}$.

Answer: $9.3 \times 10^{-6} \text{ M}$

Temperature Effects

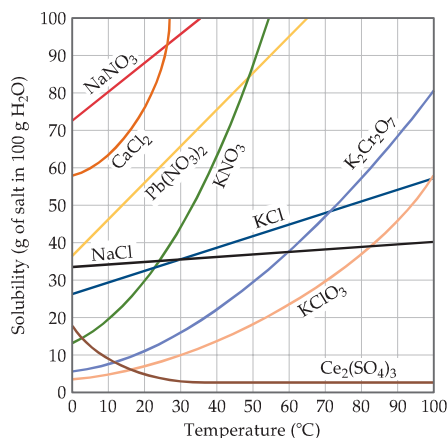
The solubility of most solid solutes in water increases as the temperature of the solution increases. Figure 13.17 shows this effect for several ionic substances in water. There are exceptions to this rule, however, as seen for $\text{Ce}_2(\text{SO}_4)_3$, whose solubility curve slopes downward with increasing temperature.

In contrast to solid solutes, the solubility of gases in water decreases with increasing temperature (Figure 13.18). If a glass of cold tap water is warmed, you can see bubbles of air on the inside of the glass. Similarly, carbonated beverages go flat as they are allowed to warm. As the temperature of the solution increases, the solubility of CO_2 decreases, and $\text{CO}_2(\text{g})$ escapes from the solution.

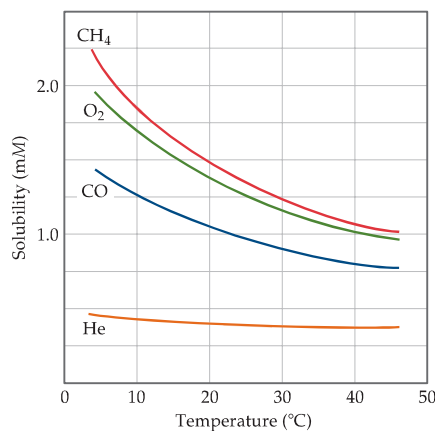
The decreased solubility of O_2 in water as temperature increases is one of the effects of thermal pollution of lakes and streams. The effect is particularly serious in deep lakes because warm water is less dense than cold water. It therefore tends to remain on top of cold water, at the surface. This situation impedes the dissolving of oxygen into the deeper layers, thus stifling the respiration of all aquatic life needing oxygen. Fish may suffocate and die under these conditions.

GIVE IT SOME THOUGHT

Why do bubbles form on the inside wall of a cooking pot when water is heated on the stove, even though the temperature is well below the boiling point of water?



▲ **Figure 13.17** Solubilities of several ionic compounds in water as a function of temperature.



▲ **Figure 13.18** Variation of gas solubility with temperature. Note that solubilities are in units of millimoles per liter (mmol/L), for a constant total pressure of 1 atm in the gas phase.

13.4 WAYS OF EXPRESSING CONCENTRATION

The concentration of a solution can be expressed either qualitatively or quantitatively. The terms *dilute* and *concentrated* are used to describe a solution qualitatively. A solution with a relatively small concentration of solute is said to be dilute; one with a large concentration is said to be concentrated. We use several different ways to express concentration in quantitative terms, and we examine four of these in this section: mass percentage, mole fraction, molarity, and molality.

Mass Percentage, ppm, and ppb

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

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

where we have abbreviated “solution” as “soln.” Percent means per hundred. Thus, a solution of hydrochloric acid that is 36% HCl by mass contains 36 g of HCl for each 100 g of solution.

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

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

A solution whose solute concentration is 1 ppm contains 1 g of solute for each million (10^6) grams of solution or, equivalently, 1 mg of solute per kilogram of solution. Because the density of water is 1 g/mL, 1 kg of a dilute aqueous solution will have a volume very close to 1 L. Thus, 1 ppm also corresponds to 1 mg of solute per liter of aqueous solution.

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

GIVE IT SOME THOUGHT

A solution of SO_2 in water contains 0.00023 g of SO_2 per liter of solution. What is the concentration of SO_2 in ppm? In ppb?

SAMPLE EXERCISE 13.4 | Calculation of Mass-Related Concentrations

(a) A solution is made by dissolving 13.5 g of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) in 0.100 kg of water. What is the mass percentage of solute in this solution? (b) A 2.5-g sample of groundwater was found to contain $5.4 \mu\text{g}$ of Zn^{2+} . What is the concentration of Zn^{2+} in parts per million?

SOLUTION

(a) Analyze: We are given the number of grams of solute (13.5 g) and the number of grams of solvent (0.100 kg = 100 g). From this we must calculate the mass percentage of solute.

Plan: We can calculate the mass percentage by using Equation 13.5. The mass of the solution is the sum of the mass of solute (glucose) and the mass of solvent (water).

Solve: Mass % of glucose = $\frac{\text{mass glucose}}{\text{mass soln}} \times 100 = \frac{13.5 \text{ g}}{13.5 \text{ g} + 100 \text{ g}} \times 100 = 11.9\%$

Comment: The mass percentage of water in this solution is $(100 - 11.9)\% = 88.1\%$.

(b) Analyze: In this case we are given the number of micrograms of solute. Because $1 \mu\text{g}$ is $1 \times 10^{-6} \text{ g}$, $5.4 \mu\text{g} = 5.4 \times 10^{-6} \text{ g}$.

Plan: We calculate the parts per million using Equation 13.6.

Solve: ppm = $\frac{\text{mass of solute}}{\text{mass of soln}} \times 10^6 = \frac{5.4 \times 10^{-6} \text{ g}}{2.5 \text{ g}} \times 10^6 = 2.2 \text{ ppm}$

■ PRACTICE EXERCISE

(a) Calculate the mass percentage of NaCl in a solution containing 1.50 g of NaCl in 50.0 g of water. (b) A commercial bleaching solution contains 3.62 mass % sodium hypochlorite, NaOCl. What is the mass of NaOCl in a bottle containing 2.50 kg of bleaching solution?

Answers: (a) 2.91%, (b) 90.5 g of NaOCl

Mole Fraction, Molarity, and Molality

Concentration expressions are often based on the number of moles of one or more components of the solution. The three most commonly used are mole fraction, molarity, and molality.

Recall from Section 10.6 that the *mole fraction* of a component of a solution is given by

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

The symbol X is commonly used for mole fraction, with a subscript to indicate the component of interest. For example, the mole fraction of HCl in a hydrochloric acid solution is represented as X_{HCl} . Thus, a solution containing 1.00 mol of HCl (36.5 g) and 8.00 mol of water (144 g) has a mole fraction of HCl of $X_{\text{HCl}} = (1.00 \text{ mol}) / (1.00 \text{ mol} + 8.00 \text{ mol}) = 0.111$. Mole fractions have no units because the units in the numerator and the denominator cancel. The sum of the mole fractions of all components of a solution must equal 1. Thus, in the aqueous HCl solution, $X_{\text{H}_2\text{O}} = 1.000 - 0.111 = 0.889$. Mole fractions are very useful when dealing with gases as we saw in Section 10.6 but have limited use when dealing with liquid solutions.

Recall from Section 4.5 that the *molarity* (M) of a solute in a solution is defined as

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

For example, if you dissolve 0.500 mol of Na_2CO_3 in enough water to form 0.250 L of solution, then the solution has a concentration of $(0.500 \text{ mol}) / (0.250 \text{ L}) = 2.00 \text{ M}$ in Na_2CO_3 . Molarity is especially useful for relating the volume of a solution to the quantity of solute it contains, as we saw in our discussions of titrations. ∞ (Section 4.6)

The **molality** of a solution, denoted m , is a unit that we have not encountered in previous chapters. This concentration unit equals the number of moles of solute per kilogram of solvent:

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

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

The definitions of molarity and molality are similar enough that they can be easily confused. Molarity depends on the *volume of solution*, whereas molality depends on the *mass of solvent*. When water is the solvent, the molality and molarity of dilute solutions are numerically about the same because 1 kg of solvent is nearly the same as 1 kg of solution, and 1 kg of the solution has a volume of about 1 L.

The molality of a given solution does not vary with temperature because masses do not vary with temperature. Molarity, however, changes with temperature because the expansion or contraction of the solution changes its volume. Thus molality is often the concentration unit of choice when a solution is to be used over a range of temperatures.

GIVE IT SOME THOUGHT

If an aqueous solution is very dilute, will the molality of the solution be (a) greater than its molarity, (b) nearly the same as its molarity, or (c) smaller than its molarity?

SAMPLE EXERCISE 13.5 | Calculation of Molality

A solution is made by dissolving 4.35 g glucose ($C_6H_{12}O_6$) in 25.0 mL of water at 25 °C. Calculate the molality of glucose in the solution. Water has a density of 1.00 g/mL.

SOLUTION

Analyze: We are asked to calculate a molality. To do this, we must determine the number of moles of solute (glucose) and the number of kilograms of solvent (water).

Plan: We use the molar mass of $C_6H_{12}O_6$ to convert grams to moles. We use the density of water to convert milliliters to kilograms. The molality equals the number of moles of solute divided by the number of kilograms of solvent (Equation 13.9).

Solve: Use the molar mass of glucose, 180.2 g/mol, to convert grams to moles:

$$\text{Mol } C_6H_{12}O_6 = (4.35 \text{ g } C_6H_{12}O_6) \left(\frac{1 \text{ mol } C_6H_{12}O_6}{180.2 \text{ g } C_6H_{12}O_6} \right) = 0.0241 \text{ mol } C_6H_{12}O_6$$

Because water has a density of 1.00 g/mL, the mass of the solvent is

$$(25.0 \text{ mL})(1.00 \text{ g/mL}) = 25.0 \text{ g} = 0.0250 \text{ kg}$$

Finally, use Equation 13.9 to obtain the molality:

$$\text{Molality of } C_6H_{12}O_6 = \frac{0.0241 \text{ mol } C_6H_{12}O_6}{0.0250 \text{ kg } H_2O} = 0.964 \text{ } m$$

PRACTICE EXERCISE

What is the molality of a solution made by dissolving 36.5 g of naphthalene ($C_{10}H_8$) in 425 g of toluene (C_7H_8)?

Answer: 0.670 *m*

Conversion of Concentration Units

Sometimes the concentration of a given solution needs to be known in several different concentration units. It is possible to interconvert concentration units as shown in Sample Exercises 13.6 and 13.7.

SAMPLE EXERCISE 13.6 | Calculation of Mole Fraction and Molality

An aqueous solution of hydrochloric acid contains 36% HCl by mass. (a) Calculate the mole fraction of HCl in the solution. (b) Calculate the molality of HCl in the solution.

SOLUTION

Analyze: We are asked to calculate the concentration of the solute, HCl, in two related concentration units, given only the percentage by mass of the solute in the solution.

Plan: In converting concentration units based on the mass or moles of solute and solvent (mass percentage, mole fraction, and molality), it is useful to assume a certain total mass of solution. Let's assume that there is exactly 100 g of solution. Because the solution is 36% HCl, it contains 36 g of HCl and $(100 - 36) \text{ g} = 64 \text{ g}$ of H_2O . We must convert grams of solute (HCl) to moles to calculate either mole fraction or molality. We must convert grams of solvent (H_2O) to moles to calculate mole fractions, and to kilograms to calculate molality.

Solve: (a) To calculate the mole fraction of HCl, we convert the masses of HCl and H_2O to moles and then use Equation 13.7:

$$\text{Moles HCl} = (36 \text{ g HCl}) \left(\frac{1 \text{ mol HCl}}{36.5 \text{ g HCl}} \right) = 0.99 \text{ mol HCl}$$

$$\text{Moles H}_2\text{O} = (64 \text{ g H}_2\text{O}) \left(\frac{1 \text{ mol H}_2\text{O}}{18 \text{ g H}_2\text{O}} \right) = 3.6 \text{ mol H}_2\text{O}$$

$$X_{\text{HCl}} = \frac{\text{moles HCl}}{\text{moles H}_2\text{O} + \text{moles HCl}} = \frac{0.99}{3.6 + 0.99} = \frac{0.99}{4.6} = 0.22$$

(b) To calculate the molality of HCl in the solution, we use Equation 13.9. We calculated the number of moles of HCl in part (a), and the mass of solvent is $64 \text{ g} = 0.064 \text{ kg}$:

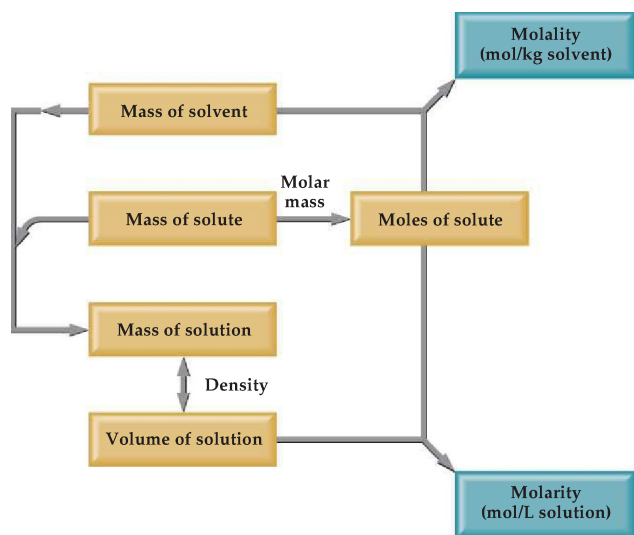
$$\text{Molality of HCl} = \frac{0.99 \text{ mol HCl}}{0.064 \text{ kg H}_2\text{O}} = 15 \text{ m}$$

■ PRACTICE EXERCISE

A commercial bleach solution contains 3.62 mass % NaOCl in water. Calculate (a) the mole fraction and (b) the molality of NaOCl in the solution.

Answers: (a) 9.00×10^{-3} , (b) 0.505 m.

To interconvert molality and molarity, we need to know the density of the solution. Figure 13.19 outlines the calculation of the molarity and molality of a solution from the mass of solute and the mass of solvent. The mass of the solution is the sum of masses of the solvent and solute. The volume of the solution can be calculated from its mass and density.



▲ **Figure 13.19 Calculating molality and molarity.** This diagram summarizes the calculation of molality and molarity from the mass of the solute, the mass of the solvent, and the density of the solution.

SAMPLE EXERCISE 13.7 | Calculation of Molarity Using the Density of the Solution

A solution with a density of 0.876 g/mL contains 5.0 g of toluene (C_7H_8) and 225 g of benzene. Calculate the molarity of the solution.

SOLUTION

Analyze: Our goal is to calculate the molarity of a solution, given the masses of solute (5.0 g) and solvent (225 g) and the density of the solution (0.876 g/mL).

Plan: The molarity of a solution is the number of moles of solute divided by the number of liters of solution (Equation 13.8). The number of moles of solute (C_7H_8) is calculated from the number of grams of solute and its molar mass. The volume of the solution is obtained from the mass of the solution (mass of solute + mass of solvent = 5.0 g + 225 g = 230 g) and its density.

Solve: The number of moles of solute is
$$\text{Moles } C_7H_8 = (5.0 \text{ g } C_7H_8) \left(\frac{1 \text{ mol } C_7H_8}{92 \text{ g } C_7H_8} \right) = 0.054 \text{ mol}$$

The density of the solution is used to convert the mass of the solution to its volume:
$$\text{Milliliters soln} = (230 \text{ g}) \left(\frac{1 \text{ mL}}{0.876 \text{ g}} \right) = 263 \text{ mL}$$

Molarity is moles of solute per liter of solution:
$$\text{Molarity} = \left(\frac{\text{moles } C_7H_8}{\text{liter soln}} \right) = \left(\frac{0.054 \text{ mol } C_7H_8}{263 \text{ mL soln}} \right) \left(\frac{1000 \text{ mL soln}}{1 \text{ L soln}} \right) = 0.21 \text{ M}$$

Check: The magnitude of our answer is reasonable. Rounding moles to 0.05 and liters to 0.25 gives a molarity of

$$(0.05 \text{ mol}) / (0.25 \text{ L}) = 0.2 \text{ M}$$

The units for our answer (mol/L) are correct, and the answer, 0.21 M, has two significant figures, corresponding to the number of significant figures in the mass of solute (2).

Comment: Because the mass of the solvent (0.225 kg) and the volume of the solution (0.263 L) are similar in magnitude, the molarity and molality are also similar in magnitude:

$$(0.054 \text{ mol } C_7H_8) / (0.225 \text{ kg solvent}) = 0.24 \text{ m}$$

PRACTICE EXERCISE

A solution containing equal masses of glycerol ($C_3H_8O_3$) and water has a density of 1.10 g/mL. Calculate (a) the molality of glycerol, (b) the mole fraction of glycerol, (c) the molarity of glycerol in the solution.

Answers: (a) 10.9 m, (b) $X_{C_3H_8O_3} = 0.163$, (c) 5.97 M

13.5 COLLIGATIVE PROPERTIES

Some physical properties of solutions differ in important ways from those of the pure solvent. For example, pure water freezes at 0 °C, but aqueous solutions freeze at lower temperatures. Ethylene glycol is added to the water in radiators of cars as an antifreeze to lower the freezing point of the solution. It also raises the boiling point of the solution above that of pure water, making it possible to operate the engine at a higher temperature.

The lowering of the freezing point and the raising of the boiling point are physical properties of solutions that depend on the *quantity* (concentration) but not the *kind* or *identity* of the solute particles. Such properties are called **colligative properties**. (*Colligative* means “depending on the collection”; colligative properties depend on the collective effect of the number of solute particles.) In addition to the decrease in freezing point and the increase in boiling point, vapor-pressure reduction and osmotic pressure are colligative properties. As we examine each of these, notice how the concentration of the solute affects the property relative to that of the pure solvent.

Lowering the Vapor Pressure

We learned in Section 11.5 that a liquid in a closed container will establish equilibrium with its vapor. When that equilibrium is reached, the pressure exerted by the vapor is called the *vapor pressure*. A substance that has no measurable vapor pressure is *nonvolatile*, whereas one that exhibits a vapor pressure is *volatile*.

When we compare the vapor pressures of various solvents with those of their solutions, we find that adding a nonvolatile solute to a solvent always lowers the vapor pressure. This effect is illustrated in Figure 13.20. The extent to which a nonvolatile solute lowers the vapor pressure is proportional to its concentration. This relationship is expressed by **Raoult's law**, which states that the partial pressure exerted by solvent vapor above a solution, P_A , equals the product of the mole fraction of the solvent in the solution, X_A , times the vapor pressure of the pure solvent, P_A° :

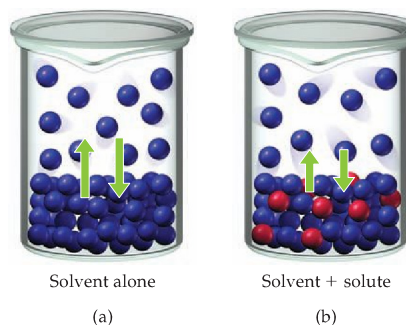
$$P_A = X_A P_A^\circ \quad [13.10]$$

For example, the vapor pressure of water is 17.5 torr at 20 °C. Imagine holding the temperature constant while adding glucose ($C_6H_{12}O_6$) to the water so that the resulting solution has $X_{H_2O} = 0.800$ and $X_{C_6H_{12}O_6} = 0.200$. According to Equation 13.10, the vapor pressure of water over the solution will be 80.0% of that of pure water:

$$P_{H_2O} = (0.800)(17.5 \text{ torr}) = 14.0 \text{ torr}$$

In other words, the presence of the nonvolatile solute lowers the vapor pressure of the volatile solvent by 17.5 torr – 14.0 torr = 3.5 torr.

Raoult's law predicts that when we increase the mole fraction of nonvolatile solute particles in a solution, the vapor pressure over the solution will be reduced. In fact, the reduction in vapor pressure depends on the total concentration of solute particles, regardless of whether they are molecules or ions. Remember that vapor-pressure lowering is a colligative property, so it depends on the concentration of solute particles and not on their kind.



▲ Figure 13.20 Vapor-pressure lowering. The vapor pressure over a solution formed by a volatile solvent and a nonvolatile solute (b) is lower than that of the solvent alone (a). The extent of the decrease in the vapor pressure upon addition of the solute depends on the concentration of the solute.

GIVE IT SOME THOUGHT

Adding 1 mol of NaCl to 1 kg of water reduces the vapor pressure of water more than adding 1 mol of $C_6H_{12}O_6$. Explain.

SAMPLE EXERCISE 13.8 | Calculation of Vapor-Pressure Lowering

Glycerin ($C_3H_8O_3$) is a nonvolatile nonelectrolyte with a density of 1.26 g/mL at 25 °C. Calculate the vapor pressure at 25 °C of a solution made by adding 50.0 mL of glycerin to 500.0 mL of water. The vapor pressure of pure water at 25 °C is 23.8 torr (Appendix B), and its density is 1.00 g/mL.

SOLUTION

Analyze: Our goal is to calculate the vapor pressure of a solution, given the volumes of solute and solvent and the density of the solute.

Plan: We can use Raoult's law (Equation 13.10) to calculate the vapor pressure of a solution. The mole fraction of the solvent in the solution, X_A , is the ratio of the number of moles of solvent (H_2O) to total moles of solution (moles $C_3H_8O_3$ + moles H_2O).

Solve: To calculate the mole fraction of water in the solution, we must determine the number of moles of $C_3H_8O_3$ and H_2O :

$$\text{Moles } C_3H_8O_3 = (50.0 \text{ mL } C_3H_8O_3) \left(\frac{1.26 \text{ g } C_3H_8O_3}{1 \text{ mL } C_3H_8O_3} \right) \left(\frac{1 \text{ mol } C_3H_8O_3}{92.1 \text{ g } C_3H_8O_3} \right) = 0.684 \text{ mol}$$

$$\text{Moles } H_2O = (500.0 \text{ mL } H_2O) \left(\frac{1.00 \text{ g } H_2O}{1 \text{ mL } H_2O} \right) \left(\frac{1 \text{ mol } H_2O}{18.0 \text{ g } H_2O} \right) = 27.8 \text{ mol}$$

$$X_{H_2O} = \frac{\text{mol } H_2O}{\text{mol } H_2O + \text{mol } C_3H_8O_3} = \frac{27.8}{27.8 + 0.684} = 0.976$$

We now use Raoult's law to calculate the vapor pressure of water for the solution: $P_{H_2O} = X_{H_2O} P_{H_2O}^\circ = (0.976)(23.8 \text{ torr}) = 23.2 \text{ torr}$

The vapor pressure of the solution has been lowered by 0.6 torr relative to that of pure water.

PRACTICE EXERCISE

The vapor pressure of pure water at 110 °C is 1070 torr. A solution of ethylene glycol and water has a vapor pressure of 1.00 atm at 110 °C. Assuming that Raoult's law is obeyed, what is the mole fraction of ethylene glycol in the solution?

Answer: 0.290

An ideal gas obeys the ideal-gas equation (Section 10.4), and an **ideal solution** obeys Raoult's law. Real solutions best approximate ideal behavior when the solute concentration is low and when the solute and solvent have similar molecular sizes and similar types of intermolecular attractions.

Many solutions do not obey Raoult's law exactly: They are not ideal solutions. If the intermolecular forces between solvent and solute are weaker than those between solvent and solvent and between solute and solute, then the vapor pressure tends to be greater than predicted by Raoult's law. Conversely, when the interactions between solute and solvent are exceptionally strong, as might be the case when hydrogen bonding exists, the vapor pressure is lower than Raoult's law predicts. Although you should be aware that these departures from ideal solution occur, we will ignore them for the remainder of this chapter.

GIVE IT SOME THOUGHT

In Raoult's law, $P_A = X_A P_A^\circ$, what are the meanings of P_A and P_A° ?

A Closer Look

IDEAL SOLUTIONS WITH TWO OR MORE VOLATILE COMPONENTS

Solutions sometimes have two or more volatile components. Gasoline, for example, is a complex solution containing several volatile substances. To gain some understanding of such mixtures, consider an ideal solution containing two components, A and B. The partial pressures of A and B vapors above the solution are given by Raoult's law:

$$P_A = X_A P_A^\circ \quad \text{and} \quad P_B = X_B P_B^\circ$$

The total vapor pressure over the solution is the sum of the partial pressures of each volatile component:

$$P_{\text{total}} = P_A + P_B = X_A P_A^\circ + X_B P_B^\circ$$

Consider, for example, a mixture of benzene (C_6H_6) and toluene (C_7H_8) containing 1.0 mol of benzene and 2.0 mol of toluene ($X_{\text{ben}} = 0.33$ and $X_{\text{tol}} = 0.67$). At 20 °C the vapor pressures of the pure substances are

$$\text{Benzene: } P_{\text{ben}}^\circ = 75 \text{ torr}$$

$$\text{Toluene: } P_{\text{tol}}^\circ = 22 \text{ torr}$$

Thus, the partial pressures of benzene and toluene above the solution are

$$P_{\text{ben}} = (0.33)(75 \text{ torr}) = 25 \text{ torr}$$

$$P_{\text{tol}} = (0.67)(22 \text{ torr}) = 15 \text{ torr}$$

The total vapor pressure is

$$P_{\text{total}} = 25 \text{ torr} + 15 \text{ torr} = 40 \text{ torr}$$

The vapor, therefore, is richer in benzene, the more volatile component. The mole fraction of benzene in the vapor is given by the ratio of its vapor pressure to the total pressure (Equation 10.15):

$$X_{\text{ben in vapor}} = \frac{P_{\text{ben}}}{P_{\text{total}}} = \frac{25 \text{ torr}}{40 \text{ torr}} = 0.63$$

Although benzene constitutes only 33% of the molecules in the solution, it makes up 63% of the molecules in the vapor.

When ideal solutions are in equilibrium with their vapor, the more volatile component of the mixture will be relatively

richer in the vapor. This fact forms the basis of *distillation*, a technique used to separate (or partially separate) mixtures containing volatile components. Distillation is the procedure by which a moonshiner obtains whiskey using a still and by which petrochemical plants achieve the separation of crude petroleum into gasoline, diesel fuel, lubricating oil, and so forth (Figure 13.21 ▽). Distillation is also used routinely on a small scale in the laboratory. A specially designed *fractional distillation* apparatus can achieve in a single operation a degree of separation that would be equivalent to several successive simple distillations.

Related Exercises: 13.63, 13.64



▲ **Figure 13.21 Separating volatile components.** In an industrial distillation tower, such as the ones shown here, the components of a volatile organic mixture are separated according to boiling-point range.

Boiling-Point Elevation

In Sections 11.5 and 11.6 we examined the vapor pressures of pure substances and how they can be used to construct phase diagrams. How will the phase diagram of a solution, and hence its boiling and freezing points, differ from those of the pure solvent? The addition of a nonvolatile solute lowers the vapor pressure of the solution. Thus, as shown in Figure 13.22, the vapor-pressure curve of the solution (blue line) will be shifted downward relative to the vapor-pressure curve of the pure liquid (black line); at any given temperature the vapor pressure of the solution is lower than that of the pure liquid. Recall that the normal boiling point of a liquid is the temperature at which its vapor pressure equals 1 atm. ∞ (Section 11.5) At the normal boiling point of the pure liquid, the vapor pressure of the solution will be less than 1 atm (Figure 13.22).

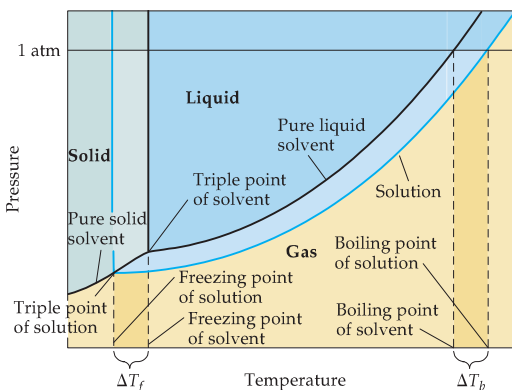
Therefore, a higher temperature is required to attain a vapor pressure of 1 atm. Thus, *the boiling point of the solution is higher than that of the pure liquid.*

The increase in boiling point relative to that of the pure solvent, ΔT_b , is a positive quantity obtained by subtracting the boiling point of the pure solvent from the boiling point of the solution. The value of ΔT_b is directly proportional to the concentration of the solution expressed by its molality, m :

$$\Delta T_b = K_b m \quad [13.11]$$

The magnitude of K_b , which is called the **molal boiling-point-elevation constant**, depends only on the solvent. Some typical values for several common solvents are given in Table 13.4. Because solutions generally do not behave ideally, however, the constants listed in Table 13.4 serve well only for solutions that are not too concentrated.

For water, K_b is $0.51\text{ }^\circ\text{C}/m$; therefore, a $1\text{ }m$ aqueous solution of sucrose or any other aqueous solution that is $1\text{ }m$ in nonvolatile solute particles will boil $0.51\text{ }^\circ\text{C}$ higher than pure water. The boiling-point elevation is proportional to the concentration of solute particles, regardless of whether the particles are molecules or ions. When NaCl dissolves in water, 2 mol of solute particles (1 mol of Na^+ and 1 mol of Cl^-) are formed for each mole of NaCl that dissolves. Therefore, a $1\text{ }m$ aqueous solution of NaCl is $1\text{ }m$ in Na^+ and $1\text{ }m$ in Cl^- , making it $2\text{ }m$ in total solute particles. As a result, the boiling-point elevation of a $1\text{ }m$ aqueous solution of NaCl is approximately $(2\text{ }m)(0.51\text{ }^\circ\text{C}/m) = 1\text{ }^\circ\text{C}$, twice as large as a $1\text{ }m$ solution of a nonelectrolyte such as sucrose. Thus, to properly predict the effect of a particular solute on the boiling point (or any other colligative property), it is important to know whether the solute is an electrolyte or a nonelectrolyte. ∞ (Sections 4.1 and 4.3)



▲ **Figure 13.22 Phase diagrams for a pure solvent and for a solution of a nonvolatile solute.** The vapor pressure of the solid solvent is unaffected by the presence of solute if the solid freezes out without containing a significant concentration of solute, as is usually the case.

GIVE IT SOME THOUGHT

An unknown solute dissolved in water causes the boiling point to increase by $0.51\text{ }^\circ\text{C}$. Does this mean that the concentration of the solute is $1.0\text{ }m$?

TABLE 13.4 ■ Molal Boiling-Point-Elevation and Freezing-Point-Depression Constants

Solvent	Normal Boiling Point ($^\circ\text{C}$)	K_b ($^\circ\text{C}/m$)	Normal Freezing Point ($^\circ\text{C}$)	K_f ($^\circ\text{C}/m$)
Water, H_2O	100.0	0.51	0.0	1.86
Benzene, C_6H_6	80.1	2.53	5.5	5.12
Ethanol, $\text{C}_2\text{H}_5\text{OH}$	78.4	1.22	-114.6	1.99
Carbon tetrachloride, CCl_4	76.8	5.02	-22.3	29.8
Chloroform, CHCl_3	61.2	3.63	-63.5	4.68

Freezing-Point Depression

When a solution freezes, crystals of pure solvent usually separate out; the solute molecules are not normally soluble in the solid phase of the solvent. When aqueous solutions are partially frozen, for example, the solid that separates out is almost always pure ice. As a result, the part of the phase diagram in Figure 13.22 that represents the vapor pressure of the solid is the same as that for the pure liquid. The vapor-pressure curves for the liquid and solid phases meet at the triple point. ∞ (Section 11.6) In Figure 13.22 we see that the triple point of the solution must be at a lower temperature than that in the pure liquid because the solution has a lower vapor pressure than the pure liquid.

The freezing point of a solution is the temperature at which the first crystals of pure solvent begin to form in equilibrium with the solution. Recall from Section 11.6 that the line representing the solid-liquid equilibrium rises nearly vertically from the triple point. Because the triple-point temperature of the solution is lower than that of the pure liquid, *the freezing point of the solution is lower than that of the pure liquid*. The decrease in freezing point, ΔT_f , is a positive quantity obtained by subtracting the freezing point of the solution from the freezing point of the pure solvent.

Like the boiling-point elevation, ΔT_f is directly proportional to the molality of the solute:

$$\Delta T_f = K_f m \quad [13.12]$$

The values of K_f , the **molal freezing-point-depression constant**, for several common solvents are given in Table 13.4. For water, K_f is $1.86^\circ\text{C}/m$; therefore, a $1\ m$ aqueous solution of sucrose or any other aqueous solution that is $1\ m$ in nonvolatile solute particles (such as $0.5\ m\ \text{NaCl}$) will freeze 1.86°C lower than pure water. The freezing-point lowering caused by solutes explains the use of antifreeze in cars and the use of calcium chloride (CaCl_2) to melt ice on roads during winter.



Antifreeze being added to an automobile radiator. Antifreeze consists of an aqueous solution of ethylene glycol, $\text{CH}_2(\text{OH})\text{CH}_2(\text{OH})$.

SAMPLE EXERCISE 13.9 | Calculation of Boiling-Point Elevation and Freezing-Point Lowering

Automotive antifreeze consists of ethylene glycol, $\text{CH}_2(\text{OH})\text{CH}_2(\text{OH})$, a nonvolatile nonelectrolyte. Calculate the boiling point and freezing point of a 25.0 mass % solution of ethylene glycol in water.

SOLUTION

Analyze: We are given that a solution contains 25.0 mass % of a nonvolatile, nonelectrolyte solute and asked to calculate the boiling and freezing points of the solution. To do this, we need to calculate the boiling-point elevation and freezing-point depression.

Plan: To calculate the boiling-point elevation and the freezing-point depression using Equations 13.11 and 12, we must express the concentration of the solution as molality. Let's assume for convenience that we have 1000 g of solution. Because the solution is 25.0 mass % ethylene glycol, the masses of ethylene glycol and water in the solution are 250 and 750 g, respectively. Using these quantities, we can calculate the molality of the solution, which we use with the molal boiling-point-elevation and freezing-point-depression constants (Table 13.4) to calculate ΔT_b and ΔT_f . We add ΔT_b to the boiling point and subtract ΔT_f from the freezing point of the solvent to obtain the boiling point and freezing point of the solution.

Solve: The molality of the solution is calculated as follows:

$$\begin{aligned} \text{Molality} &= \frac{\text{moles } \text{C}_2\text{H}_6\text{O}_2}{\text{kilograms } \text{H}_2\text{O}} = \left(\frac{250\ \text{g } \text{C}_2\text{H}_6\text{O}_2}{750\ \text{g } \text{H}_2\text{O}} \right) \left(\frac{1\ \text{mol } \text{C}_2\text{H}_6\text{O}_2}{62.1\ \text{g } \text{C}_2\text{H}_6\text{O}_2} \right) \left(\frac{1000\ \text{g } \text{H}_2\text{O}}{1\ \text{kg } \text{H}_2\text{O}} \right) \\ &= 5.37\ m \end{aligned}$$

We can now use Equations 13.11 and 13.12 to calculate the changes in the boiling and freezing points:

$$\begin{aligned} \Delta T_b &= K_b m = (0.51^\circ\text{C}/m)(5.37\ m) = 2.7^\circ\text{C} \\ \Delta T_f &= K_f m = (1.86^\circ\text{C}/m)(5.37\ m) = 10.0^\circ\text{C} \end{aligned}$$

Hence, the boiling and freezing points of the solution are

$$\begin{aligned}\text{Boiling point} &= (\text{normal bp of solvent}) + \Delta T_b \\ &= 100.0\text{ }^\circ\text{C} + 2.7\text{ }^\circ\text{C} = 102.7\text{ }^\circ\text{C}\end{aligned}$$

$$\begin{aligned}\text{Freezing point} &= (\text{normal fp of solvent}) - \Delta T_f \\ &= 0.0\text{ }^\circ\text{C} - 10.0\text{ }^\circ\text{C} = -10.0\text{ }^\circ\text{C}\end{aligned}$$

Comment: Notice that the solution is a liquid over a larger temperature range than the pure solvent.

■ PRACTICE EXERCISE

Calculate the freezing point of a solution containing 0.600 kg of CHCl_3 and 42.0 g of eucalyptol ($\text{C}_{10}\text{H}_{18}\text{O}$), a fragrant substance found in the leaves of eucalyptus trees. (See Table 13.4.)

Answer: $-65.6\text{ }^\circ\text{C}$

■ SAMPLE EXERCISE 13.10 | Freezing-Point Depression in Aqueous Solutions

List the following aqueous solutions in order of their expected freezing point: 0.050 m CaCl_2 , 0.15 m NaCl , 0.10 m HCl , 0.050 m CH_3COOH , 0.10 m $\text{C}_{12}\text{H}_{22}\text{O}_{11}$.

SOLUTION

Analyze: We must order five aqueous solutions according to expected freezing points, based on molalities and the solute formulas.

Plan: The lowest freezing point will correspond to the solution with the greatest concentration of solute particles. To determine the total concentration of solute particles in each case, we must determine whether the substance is a nonelectrolyte or an electrolyte and consider the number of ions formed when an electrolyte ionizes.

Solve: CaCl_2 , NaCl , and HCl are strong electrolytes, CH_3COOH (acetic acid) is a weak electrolyte, and $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ is a nonelectrolyte. The molality of each solution in total particles is as follows:

$$0.050\text{ }m\text{ CaCl}_2 \Rightarrow 0.050\text{ }m\text{ in Ca}^{2+}\text{ and }0.10\text{ }m\text{ in Cl}^- \Rightarrow 0.15\text{ }m\text{ in particles}$$

$$0.15\text{ }m\text{ NaCl} \Rightarrow 0.15\text{ }m\text{ Na}^+\text{ and }0.15\text{ }m\text{ in Cl}^- \Rightarrow 0.30\text{ }m\text{ in particles}$$

$$0.10\text{ }m\text{ HCl} \Rightarrow 0.10\text{ }m\text{ H}^+\text{ and }0.10\text{ }m\text{ in Cl}^- \Rightarrow 0.20\text{ }m\text{ in particles}$$

$$0.050\text{ }m\text{ CH}_3\text{COOH} \Rightarrow \text{weak electrolyte} \Rightarrow \text{between }0.050\text{ }m\text{ and }0.10\text{ }m\text{ in particles}$$

$$0.10\text{ }m\text{ C}_{12}\text{H}_{22}\text{O}_{11} \Rightarrow \text{nonelectrolyte} \Rightarrow 0.10\text{ }m\text{ in particles}$$

Because the freezing points depend on the total molality of particles in solution, the expected ordering is 0.15 m NaCl (lowest freezing point), 0.10 m HCl , 0.050 m CaCl_2 , 0.10 m $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, and 0.050 m CH_3COOH (highest freezing point).

■ PRACTICE EXERCISE

Which of the following solutes will produce the largest increase in boiling point upon addition to 1 kg of water: 1 mol of $\text{Co}(\text{NO}_3)_2$, 2 mol of KCl , 3 mol of ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$)?

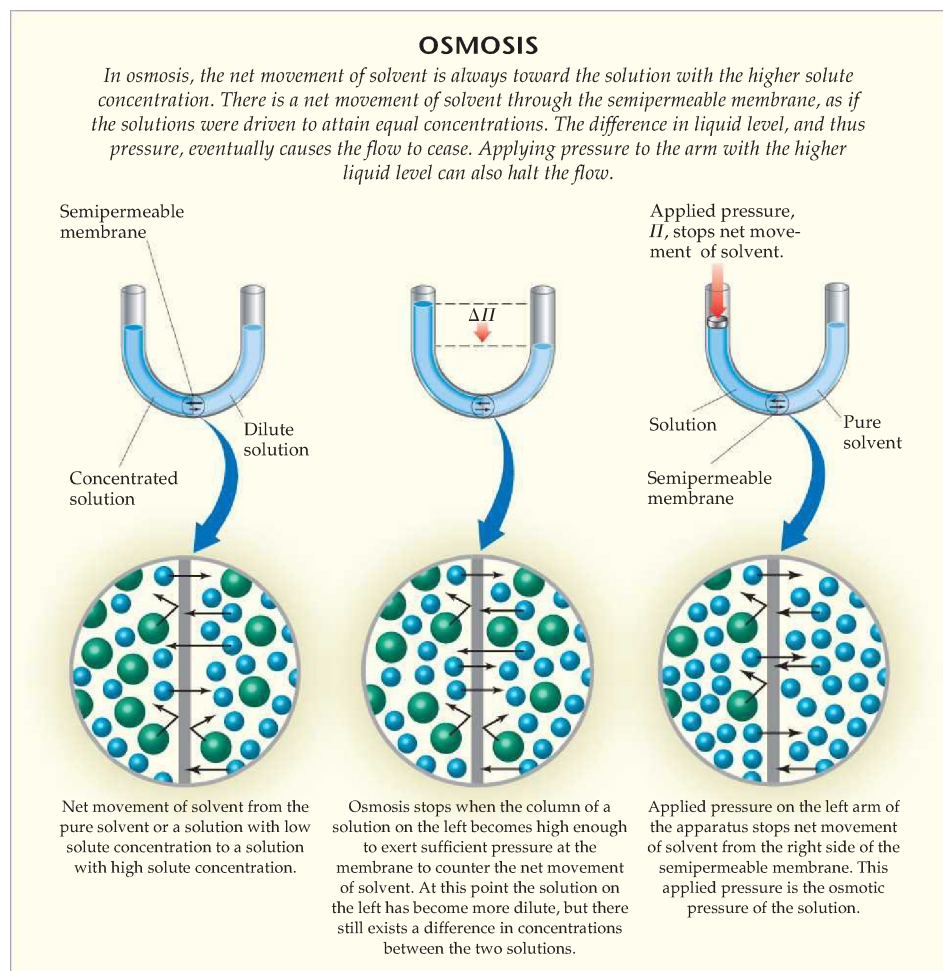
Answer: 2 mol of KCl because it contains the highest concentration of particles, 2 m K^+ and 2 m Cl^- , giving 4 m in all

Osmosis

Certain materials, including many membranes in biological systems and synthetic substances such as cellophane, are *semipermeable*. When in contact with a solution, they allow some molecules to pass through their network of tiny pores but not others. Most importantly, semipermeable membranes generally allow small solvent molecules such as water to pass through but block larger solute molecules or ions. This selectivity gives rise to some interesting and important applications.

Consider a situation in which only solvent molecules are able to pass through a membrane. If such a membrane is placed between two solutions of different concentration, solvent molecules move in both directions through the membrane. The concentration of *solvent* is higher in the solution containing less solute, however, so the rate with which solvent passes from the less concentrated (lower solute concentration) to the more concentrated solution (higher solute concentration) is greater than the rate in the opposite direction. Thus, there is a net movement of solvent molecules from the less concentrated solution into the more concentrated one. In this process, called **osmosis**, the net movement of solvent is always toward the solution with the higher solute concentration.

Osmosis is illustrated in Figure 13.23. Let's begin with two solutions of different concentration separated by a semipermeable membrane. Because the solution on the left is more concentrated than the one on the right, there is a net movement of *solvent* through the membrane from right to left, as if the solutions



▲ Figure 13.23 Osmosis.

were driven to attain equal concentrations. As a result, the liquid levels in the two arms become unequal. Eventually, the pressure difference resulting from the unequal heights of the liquid in the two arms becomes so large that the net flow of solvent ceases, as shown in the center panel. Alternatively, we may apply pressure to the left arm of the apparatus, as shown in the panel on the right, to halt the net flow of solvent. The pressure required to prevent osmosis by pure solvent is the **osmotic pressure**, Π of the solution. The osmotic pressure obeys a law similar in form to the ideal-gas law, $\Pi V = nRT$ where V is the volume of the solution, n is the number of moles of solute, R is the ideal-gas constant, and T is the temperature on the Kelvin scale. From this equation, we can write

$$\Pi = \left(\frac{n}{V}\right)RT = MRT \quad [13.13]$$

where M is the molarity of the solution.

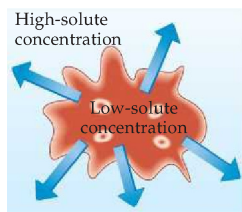
If two solutions of identical osmotic pressure are separated by a semipermeable membrane, no osmosis will occur. The two solutions are *isotonic*. If one solution is of lower osmotic pressure, it is *hypotonic* with respect to the more concentrated solution. The more concentrated solution is *hypertonic*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

GIVE IT SOME THOUGHT

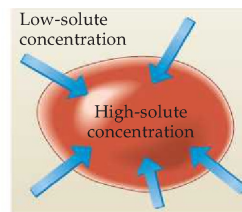
Of two KBr solutions, one 0.5 m and the other 0.20 m , which is hypotonic with respect to the other?

Osmosis plays a very important role in living systems. The membranes of red blood cells, for example, are semipermeable. Placing a red blood cell in a solution that is *hypertonic* relative to the intracellular solution (the solution within the cells) causes water to move out of the cell, as shown in Figure 13.24(a). This causes the cell to shrivel, a process called *crenation*. Placing the cell in a solution that is *hypotonic* relative to the intracellular fluid causes water to move into the cell, as illustrated in Figure 13.24(b). This may cause the cell to rupture, a process called *hemolysis*.

People who need body fluids or nutrients replaced but cannot be fed orally are given solutions by intravenous (IV) infusion, which feeds nutrients directly into the veins. To prevent crenation or hemolysis of red blood cells, the IV solutions must be isotonic with the intracellular fluids of the cells.



(a) Crenation



(b) Hemolysis

▲ **Figure 13.24 Osmosis through red blood cell wall.** The blue arrows represent the net movement of water molecules.

SAMPLE EXERCISE 13.11 | Calculations Involving Osmotic Pressure

The average osmotic pressure of blood is 7.7 atm at 25 °C. What molarity of glucose ($C_6H_{12}O_6$) will be isotonic with blood?

SOLUTION

Analyze: We are asked to calculate the concentration of glucose in water that would be isotonic with blood, given that the osmotic pressure of blood at 25 °C is 7.7 atm.

Plan: Because we are given the osmotic pressure and temperature, we can solve for the concentration, using Equation 13.13.

Solve:

$$\Pi = MRT$$

$$M = \frac{\Pi}{RT} = \frac{7.7 \text{ atm}}{\left(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(298 \text{ K})} = 0.31 \text{ M}$$

Comment: In clinical situations the concentrations of solutions are generally expressed as mass percentages. The mass percentage of a 0.31 M solution of glucose is 5.3%. The concentration of NaCl that is isotonic with blood is 0.16 M, because NaCl ionizes to form two particles, Na⁺ and Cl⁻ (a 0.155 M solution of NaCl is 0.310 M in particles). A 0.16 M solution of NaCl is 0.9 mass % in NaCl. This kind of solution is known as a physiological saline solution.

■ PRACTICE EXERCISE

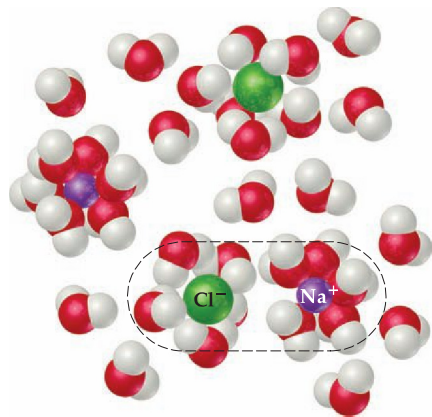
What is the osmotic pressure at 20 °C of a 0.0020 M sucrose (C₁₂H₂₂O₁₁) solution?
Answer: 0.048 atm, or 37 torr

A Closer Look

COLLIGATIVE PROPERTIES OF ELECTROLYTE SOLUTIONS

The colligative properties of solutions depend on the total concentration of solute particles, regardless of whether the particles are ions or molecules. Thus, we would expect a 0.100 *m* solution of NaCl to have a freezing-point depression of (0.200 *m*)(1.86 °C/*m*) = 0.372 °C because it is 0.100 *m* in Na⁺ (*aq*) and 0.100 *m* in Cl⁻ (*aq*). The measured freezing-point depression is only 0.348 °C, however, and the situation is similar for other strong electrolytes. A 0.100 *m* solution of KCl, for example, freezes at -0.344 °C.

The difference between the expected and observed colligative properties for strong electrolytes is due to electrostatic attractions between ions. As the ions move about in solution, ions of opposite charge collide and “stick together” for brief moments. While they are together, they behave as a single particle called an *ion pair* (Figure 13.25 ▼). The number of independent particles is thereby reduced, causing a reduction in the freezing-point depression (as well as in the boiling-point elevation, the vapor-pressure reduction, and the osmotic pressure).



▲ **Figure 13.25 Ion pairing and colligative properties.** A solution of NaCl contains not only separated Na⁺ (*aq*) and Cl⁻ (*aq*) ions but ion pairs as well. Ion pairing becomes more prevalent as the solution concentration increases and has an effect on all the colligative properties of the solution.

One measure of the extent to which electrolytes dissociate is the *van't Hoff factor*, *i*. This factor is the ratio of the actual value of a colligative property to the value calculated, assuming the substance to be a nonelectrolyte. Using the freezing-point depression, for example, we have

$$i = \frac{\Delta T_f \text{ (measured)}}{\Delta T_f \text{ (calculated for nonelectrolyte)}} \quad [13.14]$$

The ideal value of *i* can be determined for a salt from the number of ions per formula unit. For NaCl, for example, the ideal van't Hoff factor is 2 because NaCl consists of one Na⁺ and one Cl⁻ per formula unit; for K₂SO₄ it is 3 because K₂SO₄ consists of two K⁺ and one SO₄²⁻. In the absence of any information about the actual value of *i* for a solution, we will use the ideal value in calculations.

Table 13.5 ▼ gives the observed van't Hoff factors for several substances at different dilutions. Two trends are evident in these data. First, dilution affects the value of *i* for electrolytes; the more dilute the solution, the more closely *i* approaches the ideal or limiting value. Thus, the extent of ion pairing in electrolyte solutions decreases upon dilution. Second, the lower the charges on the ions, the less *i* departs from the limiting value because the extent of ion pairing decreases as the ionic charges decrease. Both trends are consistent with simple electrostatics: The force of interaction between charged particles decreases as their separation increases and as their charges decrease.

Related Exercises: 13.79, 13.80, 13.99, 13.102

TABLE 13.5 ■ van't Hoff Factors for Several Substances at 25 °C

Compound	Concentration			Limiting Value
	0.100 <i>m</i>	0.0100 <i>m</i>	0.00100 <i>m</i>	
Sucrose	1.00	1.00	1.00	1.00
NaCl	1.87	1.94	1.97	2.00
K ₂ SO ₄	2.32	2.70	2.84	3.00
MgSO ₄	1.21	1.53	1.82	2.00

There are many interesting biological examples of osmosis. A cucumber placed in concentrated brine loses water via osmosis and shrivels into a pickle. If a carrot that has become limp because of water loss to the atmosphere is placed in water, the water moves into the carrot through osmosis, making it firm once again. People who eat a lot of salty food retain water in tissue cells and intercellular space because of osmosis. The resultant swelling or puffiness is called *edema*. Water moves from soil into plant roots and subsequently into the upper portions of the plant at least in part because of osmosis. Bacteria on salted meat or candied fruit lose water through osmosis, shrivel, and die—thus preserving the food.

The movement of a substance from an area where its concentration is high to an area where it is low is spontaneous. Biological cells transport water and other select materials through their membranes, permitting nutrients to enter and waste materials to exit. In some cases substances must be moved across the cell membrane from an area of low concentration to one of high concentration. This movement—called *active transport*—is not spontaneous, so cells must expend energy to do it.

GIVE IT SOME THOUGHT

Is the osmotic pressure of a 0.10 M solution of NaCl greater than, less than, or equal to that of a 0.10 M solution of KBr?

Determination of Molar Mass

The colligative properties of solutions provide a useful means of experimentally determining molar mass. Any of the four colligative properties can be used, as shown in Sample Exercises 13.12 and 13.13.

SAMPLE EXERCISE 13.12 | Molar Mass from Freezing-Point Depression

A solution of an unknown nonvolatile nonelectrolyte was prepared by dissolving 0.250 g of the substance in 40.0 g of CCl_4 . The boiling point of the resultant solution was 0.357°C higher than that of the pure solvent. Calculate the molar mass of the solute.

SOLUTION

Analyze: Our goal is to calculate the molar mass of a solute based on knowledge of the boiling-point elevation of its solution in CCl_4 , $\Delta T_b = 0.357^\circ\text{C}$, and the masses of solute and solvent. Table 13.4 gives K_b for the solvent (CCl_4), $K_b = 5.02^\circ\text{C}/m$.

Plan: We can use Equation 13.11, $\Delta T_b = K_b m$, to calculate the molality of the solution. Then we can use molality and the quantity of solvent (40.0 g CCl_4) to calculate the number of moles of solute. Finally, the molar mass of the solute equals the number of grams per mole, so we divide the number of grams of solute (0.250 g) by the number of moles we have just calculated.

Solve: From Equation 13.11 we have

$$\text{Molality} = \frac{\Delta T_b}{K_b} = \frac{0.357^\circ\text{C}}{5.02^\circ\text{C}/m} = 0.0711 m$$

Thus, the solution contains 0.0711 mol of solute per kilogram of solvent. The solution was prepared using 40.0 g = 0.0400 kg of solvent (CCl_4). The number of moles of solute in the solution is therefore

$$(0.0400 \text{ kg } \text{CCl}_4) \left(0.0711 \frac{\text{mol solute}}{\text{kg } \text{CCl}_4} \right) = 2.84 \times 10^{-3} \text{ mol solute}$$

The molar mass of the solute is the number of grams per mole of the substance:

$$\text{Molar mass} = \frac{0.250 \text{ g}}{2.84 \times 10^{-3} \text{ mol}} = 88.0 \text{ g/mol}$$

PRACTICE EXERCISE

Camphor ($\text{C}_{10}\text{H}_{16}\text{O}$) melts at 179.8°C , and it has a particularly large freezing-point-depression constant, $K_f = 40.0^\circ\text{C}/m$. When 0.186 g of an organic substance of unknown molar mass is dissolved in 22.01 g of liquid camphor, the freezing point of the mixture is found to be 176.7°C . What is the molar mass of the solute?

Answer: 110 g/mol

SAMPLE EXERCISE 13.13 | Molar Mass from Osmotic Pressure

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

SOLUTION

Analyze: Our goal is to calculate the molar mass of a high-molecular-mass protein, based on its osmotic pressure and a knowledge of the mass of protein and solution volume.

Plan: The temperature ($T = 25\text{ }^\circ\text{C}$) and osmotic pressure ($\Pi = 1.54\text{ torr}$) are given, and we know the value of R so we can use Equation 13.13 to calculate the molarity of the solution, M . In doing so, we must convert temperature from $^\circ\text{C}$ to K and the osmotic pressure from torr to atm. We then use the molarity and the volume of the solution (5.00 mL) to determine the number of moles of solute. Finally, we obtain the molar mass by dividing the mass of the solute (3.50 mg) by the number of moles of solute.

Solve: Solving Equation 13.13 for molarity gives

$$\text{Molarity} = \frac{\Pi}{RT} = \frac{(1.54\text{ torr})\left(\frac{1\text{ atm}}{760\text{ torr}}\right)}{\left(0.0821\frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(298\text{ K})} = 8.28 \times 10^{-5}\frac{\text{mol}}{\text{L}}$$

Because the volume of the solution is 5.00 mL = $5.00 \times 10^{-3}\text{ L}$, the number of moles of protein must be

$$\text{Moles} = (8.28 \times 10^{-5}\text{ mol/L})(5.00 \times 10^{-3}\text{ L}) = 4.14 \times 10^{-7}\text{ mol}$$

The molar mass is the number of grams per mole of the substance. The sample has a mass of 3.50 mg = $3.50 \times 10^{-3}\text{ g}$. The molar mass is the number of grams divided by the number of moles:

$$\text{Molar mass} = \frac{\text{grams}}{\text{moles}} = \frac{3.50 \times 10^{-3}\text{ g}}{4.14 \times 10^{-7}\text{ mol}} = 8.45 \times 10^3\text{ g/mol}$$

Comment: Because small pressures can be measured easily and accurately, osmotic pressure measurements provide a useful way to determine the molar masses of large molecules.

PRACTICE EXERCISE

A sample of 2.05 g of polystyrene of uniform polymer chain length was dissolved in enough toluene to form 0.100 L of solution. The osmotic pressure of this solution was found to be 1.21 kPa at 25 °C. Calculate the molar mass of the polystyrene.

Answer: $4.20 \times 10^4\text{ g/mol}$

13.6 COLLOIDS

When finely divided clay particles are dispersed throughout water, they eventually settle out of the water because of gravity. The dispersed clay particles are much larger than most molecules and consist of many thousands or even millions of atoms. In contrast, the dispersed particles of a solution are of molecular size. Between these extremes lie dispersed particles that are larger than typical molecules, but not so large that the components of the mixture separate under the influence of gravity. These intermediate types of dispersions or suspensions are called **colloidal dispersions**, or simply **colloids**. Colloids form the dividing line between solutions and heterogeneous mixtures. Like solutions, colloids can be gases, liquids, or solids. Examples of each are listed in Table 13.6 ▶.

TABLE 13.6 ■ Types of Colloids

Phase of Colloid	Dispersing (solutelike) Substance	Dispersed (solventlike) Substance	Colloid Type	Example
Gas	Gas	Gas	—	None (all are solutions)
Gas	Gas	Liquid	Aerosol	Fog
Gas	Gas	Solid	Aerosol	Smoke
Liquid	Liquid	Gas	Foam	Whipped cream
Liquid	Liquid	Liquid	Emulsion	Milk
Liquid	Liquid	Solid	Sol	Paint
Solid	Solid	Gas	Solid foam	Marshmallow
Solid	Solid	Liquid	Solid emulsion	Butter
Solid	Solid	Solid	Solid sol	Ruby glass

The size of the dispersed particles is used to classify a mixture as a colloid. Colloid particles range in diameter from approximately 5 to 1000 nm. Solute particles are smaller. The colloid particle may consist of many atoms, ions, or molecules, or it may even be a single giant molecule. The hemoglobin molecule, for example, which carries oxygen in blood, has molecular dimensions of $65 \text{ \AA} \times 55 \text{ \AA} \times 50 \text{ \AA}$ and a molar mass of 64,500 g/mol.

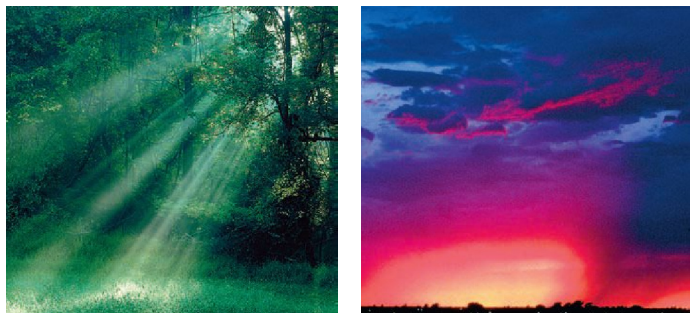
Although colloid particles may be so small that the dispersion appears uniform even under a microscope, they are large enough to scatter light very effectively. Consequently, most colloids appear cloudy or opaque unless they are very dilute. (Homogenized milk is a colloid.) Furthermore, because they scatter light, a light beam can be seen as it passes through a colloidal suspension, as shown in Figure 13.26 ▶. This scattering of light by colloidal particles, known as the **Tyndall effect**, makes it possible to see the light beam of an automobile on a dusty dirt road or the sunlight coming through a forest canopy [Figure 13.27(a) ▼]. Not all wavelengths are scattered to the same extent. As a result, brilliant red sunsets are seen when the sun is near the horizon and the air contains dust, smoke, or other particles of colloidal size [Figure 13.27(b)].

Hydrophilic and Hydrophobic Colloids

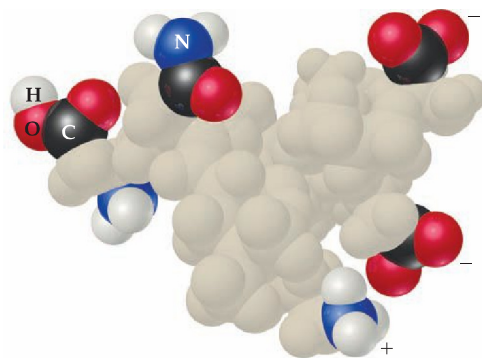
The most important colloids are those in which the dispersing medium is water. These colloids may be **hydrophilic** (water loving) or **hydrophobic** (water fearing). Hydrophilic colloids are most like the solutions that we have previously examined. In the human body the extremely large molecules that make up such important substances as enzymes and antibodies are kept in suspension by interaction with surrounding water molecules. The molecules fold in such a way that the hydrophobic groups are away from the water molecules,



▲ **Figure 13.26 Tyndall effect in the laboratory.** The glass on the left contains a colloidal suspension; that on the right contains a solution. The path of the beam through the colloidal suspension is visible because the light is scattered by the colloidal particles. Light is not scattered by the individual solute molecules in the solution.



◀ **Figure 13.27 Tyndall effect in nature.** (a) Scattering of sunlight by colloidal particles in the misty air of a forest. (b) The scattering of light by smoke or dust particles produces a rich red sunset.

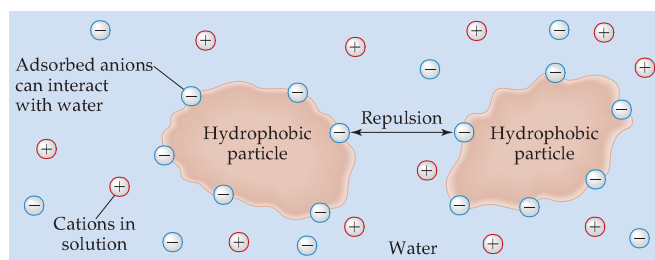


▲ **Figure 13.28 Hydrophilic colloids.** Examples of hydrophilic groups on the surface of a giant molecule (macromolecule) that help to keep the molecule suspended in water.

on the “inside” of the folded molecule, while the hydrophilic, polar groups are on the surface, interacting with the water molecules. These hydrophilic groups generally contain oxygen or nitrogen and often carry a charge. Some examples are shown in Figure 13.28 ◀.

Hydrophobic colloids can be prepared in water only if they are stabilized in some way. Otherwise, their natural lack of affinity for water causes them to separate from the water. Hydrophobic colloids can be stabilized by adsorption of ions on their surface, as shown in Figure 13.29 ▼. (*Adsorption* means to adhere to a surface. It differs from *absorption*, which means to pass into the interior, as when a sponge absorbs water.) These adsorbed ions can interact with water, thereby stabilizing the colloid. At the same time, the mutual repulsion between colloid particles with adsorbed ions of the same charge keeps the particles from colliding and getting larger.

Hydrophobic colloids can also be stabilized by the presence of hydrophilic groups on their surfaces. Small droplets of oil are hydrophobic, for example, so they do not remain suspended in water. Instead, they aggregate, forming an oil slick on the surface of the water. Sodium stearate (Figure 13.30 ◀), or any similar substance having one end that is hydrophilic (polar, or charged) and one that is hydrophobic (nonpolar), will stabilize a suspension of oil in water. Stabilization results from the interaction of the hydrophobic ends of the stearate ions with the oil droplet and the hydrophilic ends with the water as shown in Figure 13.31 ►.



▲ **Figure 13.29 Hydrophobic colloids.** Schematic illustration of how adsorbed ions stabilize a hydrophobic colloid in water.



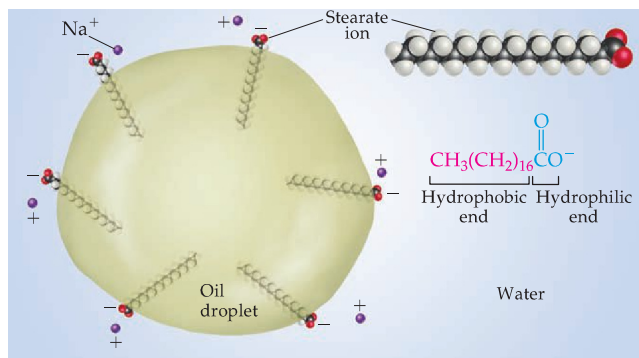
Sodium stearate

▲ **Figure 13.30 Sodium stearate.**

GIVE IT SOME THOUGHT

Why don't the oil droplets emulsified by sodium stearate coagulate to form larger oil droplets?

The stabilization of colloids has an interesting application in our own digestive system. When fats in our diet reach the small intestine, a hormone causes the gallbladder to excrete a fluid called bile. Among the components of bile are compounds that have chemical structures similar to sodium stearate; that is, they have a hydrophilic (polar) end and a hydrophobic (nonpolar) end. These compounds emulsify the fats present in the intestine and thus permit digestion and absorption of fat-soluble vitamins through the intestinal wall. The term *emulsify* means “to form an emulsion,” a suspension of one liquid in another, as in milk, for example (Table 13.6). A substance that aids in the formation of an emulsion is called an emulsifying agent. If you read the labels on foods and other materials, you will find that a variety of chemicals are used as emulsifying agents. These chemicals typically have a hydrophilic end and a hydrophobic end.



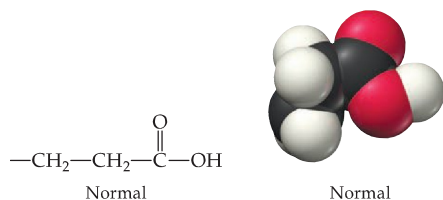
◀ **Figure 13.31** Stabilization of an emulsion of oil in water by stearate ions.

Chemistry and Life

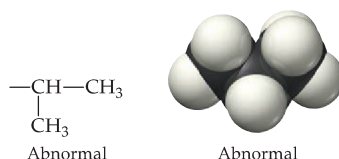
SICKLE-CELL ANEMIA

Our blood contains a complex protein called *hemoglobin* that carries oxygen from our lungs to other parts of our body. In the genetic disease known as *sickle-cell anemia*, hemoglobin molecules are abnormal and have a lower solubility, especially in their unoxygenated form. Consequently, as much as 85% of the hemoglobin in red blood cells crystallizes from solution.

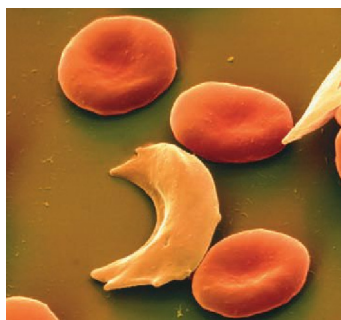
The reason for the insolubility of hemoglobin in sickle-cell anemia can be traced to a structural change in one part of an amino acid side chain. Normal hemoglobin molecules have an amino acid in their makeup that has the following side chain protruding from the main body of the molecule:



This side chain terminates in a polar group, which contributes to the solubility of the hemoglobin molecule in water. In the hemoglobin molecules of persons suffering from sickle-cell anemia, the side chain is of a different type:



This abnormal group of atoms is nonpolar (hydrophobic), and its presence leads to the aggregation of this defective form of hemoglobin into particles too large to remain suspended in biological fluids. It also causes the cells to distort into a sickle shape, as shown in Figure 13.32 ▼. The sickled cells tend to clog the capillaries, causing severe pain, physical weakness, and the gradual deterioration of the vital organs. The disease is hereditary, and if both parents carry the defective genes, it is likely that their children will possess only abnormal hemoglobin.



◀ **Figure 13.32** Normal and sickled red blood cells. Normal red blood cells are about 1×10^{-3} mm in diameter.

Removal of Colloidal Particles

Colloidal particles frequently must be removed from a dispersing medium, as in the removal of smoke from smokestacks or butterfat from milk. Because colloidal particles are so small, they cannot be separated by simple filtration. Instead, the colloidal particles must be enlarged in a process called *coagulation*. The resultant larger particles can then be separated by filtration or merely by allowing them to settle out of the dispersing medium.

Heating the mixture or adding an electrolyte may bring about coagulation. Heating the colloidal dispersion increases the particle motion and so the number of collisions. The particles increase in size as they stick together after colliding. The addition of electrolytes neutralizes the surface charges of the particles, thereby removing the electrostatic repulsions that prevent them from coming together. Wherever rivers empty into oceans or other salty bodies of water, for example, the suspended clay in the river is deposited as a delta when it mixes with the electrolytes in the salt water.

Semipermeable membranes can also be used to separate ions from colloidal particles because the ions can pass through the membrane but the colloidal particles cannot. This type of separation is known as *dialysis* and is used to purify blood in artificial kidney machines. Our kidneys normally remove the waste products of metabolism from blood. In a kidney machine, blood is circulated through a dialyzing tube immersed in a washing solution. The washing solution contains the same concentrations and kinds of ions as blood but is lacking the molecules and ions that are waste products. Wastes therefore dialyze out of the blood, but the ions and large colloidal particles such as proteins do not.

SAMPLE INTEGRATIVE EXERCISE | Putting Concepts Together

A 0.100-L solution is made by dissolving 0.441 g of $\text{CaCl}_2(\text{s})$ in water. (a) Calculate the osmotic pressure of this solution at 27°C , assuming that it is completely dissociated into its component ions. (b) The measured osmotic pressure of this solution is 2.56 atm at 27°C . Explain why it is less than the value calculated in (a), and calculate the van't Hoff factor, i , for the solute in this solution. (See the "A Closer Look" box on Colligative Properties of Electrolyte Solutions in Section 13.5.) (c) The enthalpy of solution for CaCl_2 is $\Delta H = -81.3 \text{ kJ/mol}$. If the final temperature of the solution is 27.0°C , what was its initial temperature? (Assume that the density of the solution is 1.00 g/mL , that its specific heat is $4.18 \text{ J/g}\cdot\text{K}$, and that the solution loses no heat to its surroundings.)

SOLUTION

(a) The osmotic pressure is given by Equation 13.13, $\Pi = MRT$. We know the temperature, $T = 27^\circ\text{C} = 300 \text{ K}$, and the gas constant, $R = 0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K}$. We can calculate the molarity of the solution from the mass of CaCl_2 and the volume of the solution:

$$\text{Molarity} = \left(\frac{0.441 \text{ g CaCl}_2}{0.100 \text{ L}} \right) \left(\frac{1 \text{ mol CaCl}_2}{111.0 \text{ g CaCl}_2} \right) = 0.0397 \text{ mol CaCl}_2/\text{L}$$

Soluble ionic compounds are strong electrolytes. \rightleftharpoons (Sections 4.1 and 4.3) Thus, CaCl_2 consists of metal cations (Ca^{2+}) and nonmetal anions (Cl^-). When completely dissociated, each CaCl_2 unit forms three ions (one Ca^{2+} and two Cl^-). Hence the total concentration of ions in the solution is $(3)(0.0397 \text{ M}) = 0.119 \text{ M}$, and the calculated osmotic pressure is

$$\Pi = MRT = (0.119 \text{ mol/L})(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(300 \text{ K}) = 2.93 \text{ atm}$$

(b) The actual values of colligative properties of electrolytes are less than those calculated, because the electrostatic interactions between ions limit their independent movements. In this case the van't Hoff factor, which measures the extent to which

electrolytes actually dissociate into ions, is given by

$$i = \frac{II(\text{measured})}{II(\text{calculated for nonelectrolyte})} = \frac{2.56 \text{ atm}}{(0.0397 \text{ mol/L})(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(300 \text{ K})} = 2.62$$

Thus, the solution behaves as if the CaCl_2 has dissociated into 2.62 particles instead of the ideal 3.

(c) If the solution is 0.0397 M in CaCl_2 and has a total volume of 0.100 L, the number of moles of solute is $(0.100 \text{ L})(0.0397 \text{ mol/L}) = 0.00397 \text{ mol}$. Hence the quantity of heat generated in forming the solution is $(0.00397 \text{ mol})(-81.3 \text{ kJ/mol}) = -0.323 \text{ kJ}$. The solution absorbs this heat, causing its temperature to increase. The relationship between temperature change and heat is given by Equation 5.22:

$$q = (\text{specific heat})(\text{grams})(\Delta T)$$

The heat absorbed by the solution is $q = +0.323 \text{ kJ} = 323 \text{ J}$. The mass of the 0.100 L of solution is $(100 \text{ mL})(1.00 \text{ g/mL}) = 100 \text{ g}$ (to 3 significant figures). Thus the temperature change is

$$\Delta T = \frac{q}{(\text{specific heat of solution})(\text{grams of solution})} = \frac{323 \text{ J}}{(4.18 \text{ J/g}\cdot\text{K})(100 \text{ g})} = 0.773 \text{ K}$$

A kelvin has the same size as a degree Celsius. ∞ (Section 1.4) Because the solution temperature increases by 0.773 °C, the initial temperature was 27.0 °C – 0.773 °C = 26.2 °C.

CHAPTER REVIEW

SUMMARY AND KEY TERMS

Section 13.1 Solutions form when one substance disperses uniformly throughout another. The attractive interaction of solvent molecules with solute is called **solvation**. When the solvent is water, the interaction is called **hydration**. The dissolution of ionic substances in water is promoted by hydration of the separated ions by the polar water molecules. The overall enthalpy change upon solution formation may be either positive or negative. Solution formation is favored both by a negative enthalpy change (exothermic process) and by an increased dispersal in space of the components of the solution, corresponding to a positive **entropy** change.

Section 13.2 The equilibrium between a saturated solution and undissolved solute is dynamic; the process of solution and the reverse process, **crystallization**, occur simultaneously. In a solution in equilibrium with undissolved solute, the two processes occur at equal rates, giving a **saturated** solution. If there is less solute present than is needed to saturate the solution, the solution is **unsaturated**. When solute concentration is greater than the equilibrium concentration value, the solution is **supersaturated**. This is an unstable condition, and separa-

tion of some solute from the solution will occur if the process is initiated with a solute seed crystal. The amount of solute needed to form a saturated solution at any particular temperature is the **solubility** of that solute at that temperature.

Section 13.3 The solubility of one substance in another depends on the tendency of systems to become more random, by becoming more dispersed in space, and on the relative intermolecular solute–solute and solvent–solvent energies compared with solute–solvent interactions. Polar and ionic solutes tend to dissolve in polar solvents, and nonpolar solutes tend to dissolve in nonpolar solvents (“like dissolves like”). Liquids that mix in all proportions are **miscible**; those that do not dissolve significantly in one another are **immiscible**. Hydrogen-bonding interactions between solute and solvent often play an important role in determining solubility; for example, ethanol and water, whose molecules form hydrogen bonds with each other, are miscible. The solubilities of gases in a liquid are generally proportional to the pressure of the gas over the solution, as expressed by **Henry’s law**: $S_g = kP_g$. The solubilities of most solid solutes in

water increase as the temperature of the solution increases. In contrast, the solubilities of gases in water generally decrease with increasing temperature.

Section 13.4 Concentrations of solutions can be expressed quantitatively by several different measures, including **mass percentage** [(mass solute/mass solution) $\times 10^2$], **parts per million (ppm)** [(mass solute/mass solution) $\times 10^6$], **parts per billion (ppb)** [(mass solute/mass solution) $\times 10^9$], and **mole fraction** [mol solute/(mol solute + mol solvent)]. Molarity, M , is defined as moles of solute per liter of solution; **molality**, m , is defined as moles of solute per kg of solvent. Molarity can be converted to these other concentration units if the density of the solution is known.

Section 13.5 A physical property of a solution that depends on the concentration of solute particles present, regardless of the nature of the solute, is a **colligative property**. Colligative properties include vapor-pressure lowering, freezing-point lowering, boiling-point elevation, and osmotic pressure. **Raoult's law** expresses the lowering of vapor pressure. An **ideal solution** obeys Raoult's law. Differences in solvent-solute as compared with solvent-solvent and solute-solute intermolecular forces cause many solutions to depart from ideal behavior.

A solution containing a nonvolatile solute possesses a higher boiling point than the pure solvent. The **molal boiling-point-elevation constant**, K_b , represents the increase in boiling point for a 1 m solution of solute particles as compared with the pure solvent. Similarly, the **molal freezing-point-depression constant**, K_f , measures the lowering of the freezing point of a solution for a 1 m solution of solute particles. The temperature changes are given by the equations $\Delta T_b = K_b m$ and $\Delta T_f = K_f m$.

When NaCl dissolves in water, two moles of solute particles are formed for each mole of dissolved salt. The boiling point or freezing point is thus elevated or depressed, respectively, approximately twice as much as that of a nonelectrolyte solution of the same concentration. Similar considerations apply to other strong electrolytes.

Osmosis is the movement of solvent molecules through a semipermeable membrane from a less concentrated to a more concentrated solution. This net movement of solvent generates an **osmotic pressure**, Π , which can be measured in units of gas pressure, such as atm. The osmotic pressure of a solution as compared with pure solvent is proportional to the solution molarity: $\Pi = MRT$. Osmosis is a very important process in living systems, in which cell walls act as semipermeable membranes, permitting the passage of water, but restricting the passage of ionic and macromolecular components.

Section 13.6 Particles that are large on the molecular scale but still small enough to remain suspended indefinitely in a solvent system form **colloids**, or **colloidal dispersions**. Colloids, which are intermediate between solutions and heterogeneous mixtures, have many practical applications. One useful physical property of colloids, the scattering of visible light, is referred to as the **Tyndall effect**. Aqueous colloids are classified as **hydrophilic** or **hydrophobic**. Hydrophilic colloids are common in living organisms, in which large molecular aggregates (enzymes, antibodies) remain suspended because they have many polar, or charged, atomic groups on their surfaces that interact with water. Hydrophobic colloids, such as small droplets of oil, may remain in suspension through adsorption of charged particles on their surfaces.

KEY SKILLS

- Understand how enthalpy and entropy changes affect solution formation.
- Understand the relationship between intermolecular forces and solubility, including use of the "like dissolves like" rule.
- Describe the effect of temperature on the solubility of solids and gases.
- Describe the relationship between the partial pressure of a gas and its solubility.
- Be able to calculate the concentration of a solution in terms of molarity, molality, mole fraction, percent composition, and parts per million and be able to interconvert between them.
- Describe what a colligative property is and explain the difference between the effects of nonelectrolytes and electrolytes on colligative properties.
- Be able to calculate the vapor pressure of a solvent over a solution.
- Be able to calculate the boiling point elevation and freezing point depression of a solution.
- Be able to calculate the osmotic pressure of a solution.

KEY EQUATIONS

$$S_g = kP_g \quad [13.4]$$

Henry's law, relating gas solubility to partial pressure

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

Defining concentration in terms of mass percent

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

Defining concentration in terms of parts per million (ppm)

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

Defining concentration in terms of mole fraction

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

Defining concentration in terms of molarity

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

Defining concentration in terms of molality

$$P_A = X_A P_A^\circ \quad [13.10]$$

Raoult's law, calculating vapor pressure of solvent above a solution

$$\Delta T_b = K_b m \quad [13.11]$$

Calculating the boiling point elevation of a solution

$$\Delta T_f = K_f m \quad [13.12]$$

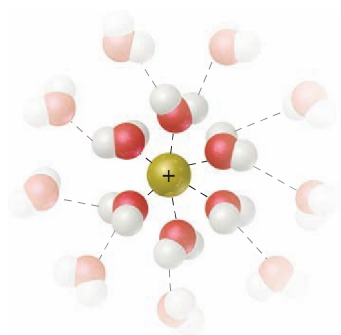
Calculating the freezing point depression of a solution

$$\Pi = \left(\frac{n}{V}\right)RT = MRT \quad [13.13]$$

Calculating the osmotic pressure of a solution

VISUALIZING CONCEPTS

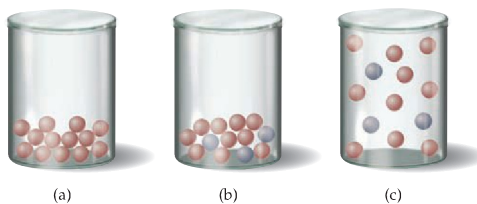
13.1 This figure shows the interaction of a cation with surrounding water molecules.



Would you expect the energy of ion-solvent interaction to be greater for Na^+ or Li^+ ? Explain. [Section 13.1]

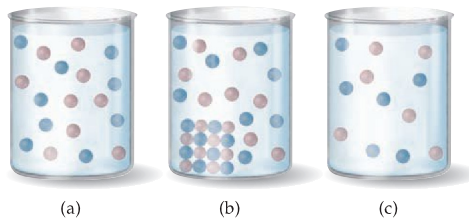
13.2 Why do ionic substances with higher lattice energies tend to be less soluble in water than those with lower lattice energies? [Section 13.1]

13.3 Rank the contents of the following containers in order of increasing entropy: [Section 13.1]



13.4 A quantity of the pink solid on the left in Figure 13.8 is placed in a warming oven and heated for a time. It slowly turns from pink to the deep blue color of the solid on the right. What has occurred? [Section 13.1]

13.5 Which of the following is the best representation of a saturated solution? Explain your reasoning. [Section 13.2]



13.6 The solubility of Xe in water at 20 °C is approximately $5 \times 10^{-3} M$. Compare this with the solubilities of Ar and Kr in water (Table 13.2) and explain what properties of the rare gas atoms account for the variation in solubility. [Section 13.3]

13.7 The structures of vitamins E and B₆ are shown below. Predict which is largely water soluble and which is largely fat soluble. Explain. [Section 13.3]



13.8 If you wanted to prepare a solution of CO in water at 25 °C in which the CO concentration was 2.5 mM, what pressure of CO would you need to use? (See Figure 13.18.) [Section 13.3]

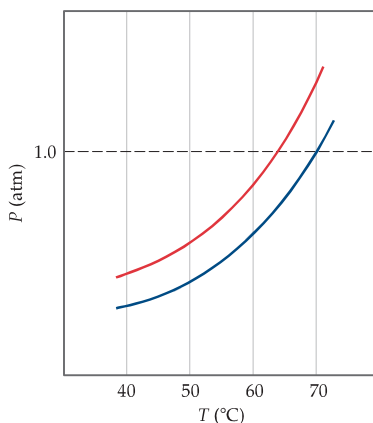
13.9 The figure shows two identical volumetric flasks containing the same solution at two temperatures.

(a) Does the molarity of the solution change with the change in temperature? Explain.

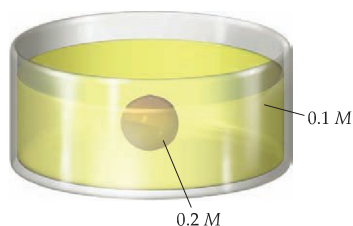
(b) Does the molality of the solution change with the change in temperature? Explain. [Section 13.4]



13.10 The following diagram shows the vapor pressure curves of a volatile solvent and a solution of that solvent containing a nonvolatile solute. (a) Which line represents the solution? (b) What are the normal boiling points of the solvent and the solution? [Section 13.5]

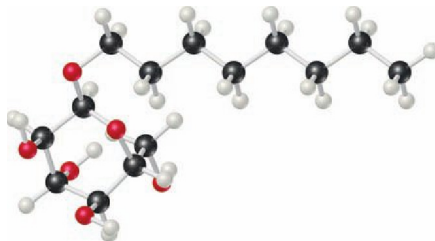


13.11 Suppose you had a balloon made of some highly flexible semipermeable membrane. The balloon is filled completely with a 0.2 M solution of some solute and is submerged in a 0.1 M solution of the same solute:



Initially, the volume of solution in the balloon is 0.25 L. Assuming the volume outside the semipermeable membrane is large, as the illustration shows, what would you expect for the solution volume inside the balloon once the system has come to equilibrium through osmosis? [Section 13.5]

13.12 The molecule *n*-octylglucoside, shown here, is widely used in biochemical research as a nonionic detergent for “solubilizing” large hydrophobic protein molecules. What characteristics of this molecule are important for its use in this way? [Section 13.6]



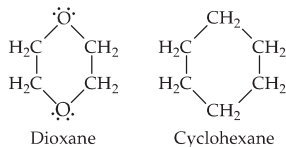
EXERCISES

The Solution Process

- 13.13** In general, the attractive intermolecular forces between solvent and solute particles must be comparable or greater than solute–solute interactions for significant solubility to occur. Explain this statement in terms of the overall energetics of solution formation.
- 13.14** (a) Considering the energetics of solute–solute, solvent–solvent, and solute–solvent interactions, explain why NaCl dissolves in water but not in benzene (C_6H_6). (b) What factors cause a cation to be strongly hydrated?
- 13.15** Indicate the type of solute–solvent interaction (Section 11.2) that should be most important in each of the following solutions: (a) CCl_4 in benzene (C_6H_6), (b) methanol (CH_3OH) in water, (c) KBr in water, (d) HCl in acetonitrile (CH_3CN).
- 13.16** Indicate the principal type of solute–solvent interaction in each of the following solutions, and rank the solutions from weakest to strongest solute–solvent interaction: (a) KCl in water, (b) CH_2Cl_2 in benzene (C_6H_6), (c) methanol (CH_3OH) in water.
- 13.17** (a) In Equation 13.1 which of the energy terms for dissolving an ionic solid would correspond to the lattice energy? (b) Which energy terms in this equation are always exothermic?
- 13.18** The schematic diagram of the solution process as the net sum of three steps in Figure 13.4 does not show the relative magnitudes of the three components because these will vary from case to case. For the dissolution of NH_4NO_3 in water, which of the three enthalpy changes would you expect to be much smaller than the other two? Explain.
- 13.19** When two nonpolar organic liquids such as hexane (C_6H_{14}) and heptane (C_7H_{16}) are mixed, the enthalpy change that occurs is generally quite small. (a) Use the energy diagram in Figure 13.4 to explain why. (b) Given that $\Delta H_{soln} \approx 0$, explain why hexane and heptane spontaneously form a solution.
- 13.20** The enthalpy of solution of KBr in water is about +198 kJ/mol. Nevertheless, the solubility of KBr in water is relatively high. Why does the solution process occur even though it is endothermic?

Saturated Solutions; Factors Affecting Solubility

- 13.21** The solubility of $Cr(NO_3)_3 \cdot 9H_2O$ in water is 208 g per 100 g of water at 15 °C. A solution of $Cr(NO_3)_3 \cdot 9H_2O$ in water at 35 °C is formed by dissolving 324 g in 100 g water. When this solution is slowly cooled to 15 °C, no precipitate forms. (a) What term describes this solution? (b) What action might you take to initiate crystallization? Use molecular-level processes to explain how your suggested procedure works.
- 13.22** The solubility of $MnSO_4 \cdot H_2O$ in water at 20 °C is 70 g per 100 mL of water. (a) Is a 1.22 M solution of $MnSO_4 \cdot H_2O$ in water at 20 °C saturated, supersaturated, or unsaturated? (b) Given a solution of $MnSO_4 \cdot H_2O$ of unknown concentration, what experiment could you perform to determine whether the new solution is saturated, supersaturated, or unsaturated?
- 13.23** By referring to Figure 13.17, determine whether the addition of 40.0 g of each of the following ionic solids to 100 g of water at 40 °C will lead to a saturated solution: (a) $NaNO_3$, (b) KCl, (c) $K_2Cr_2O_7$, (d) $Pb(NO_3)_2$.
- 13.24** By referring to Figure 13.17, determine the mass of each of the following salts required to form a saturated solution in 250 g of water at 30 °C: (a) $KClO_3$, (b) $Pb(NO_3)_2$, (c) $Ce_2(SO_4)_3$.
- 13.25** Water and glycerol, $CH_2(OH)CH(OH)CH_2OH$, are miscible in all proportions. What does this mean? How do the OH groups of the alcohol molecule contribute to this miscibility?
- 13.26** Oil and water are immiscible. What does this mean? Explain in terms of the structural features of their respective molecules and the forces between them.
- 13.27** (a) Would you expect stearic acid, $CH_3(CH_2)_{16}COOH$, to be more soluble in water or in carbon tetrachloride? Explain. (b) Which would you expect to be more soluble in water, cyclohexane or dioxane? Explain.



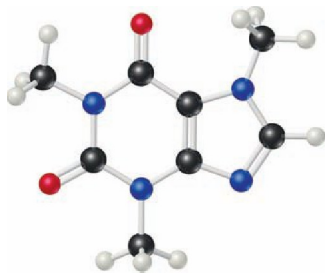
- 13.28** Consider a series of carboxylic acids whose general formula is $CH_3(CH_2)_nCOOH$. How would you expect the solubility of these compounds in water and in hexane to change as n increases? Explain.
- 13.29** Which of the following in each pair is likely to be more soluble in hexane, C_6H_{14} : (a) CCl_4 or $CaCl_2$; (b) benzene (C_6H_6) or glycerol, $CH_2(OH)CH(OH)CH_2OH$; (c) octanoic acid, $CH_3CH_2CH_2CH_2CH_2CH_2COOH$, or acetic acid, CH_3COOH . Explain your answer in each case.
- 13.30** Which of the following in each pair is likely to be more soluble in water: (a) cyclohexane (C_6H_{12}) or glucose ($C_6H_{12}O_6$) (Figure 13.12); (b) propionic acid (CH_3CH_2COOH) or sodium propionate (CH_3CH_2COONa); (c) HCl or ethyl chloride (CH_3CH_2Cl)? Explain in each case.

- 13.31** (a) Explain why carbonated beverages must be stored in sealed containers. (b) Once the beverage has been opened, why does it maintain more carbonation when refrigerated than at room temperature?
- 13.32** Explain why pressure affects the solubility of O_2 in water, but not the solubility of NaCl in water.
- 13.33** The Henry's law constant for helium gas in water at $30^\circ C$ is $3.7 \times 10^{-4} M/atm$ and the constant for N_2 at $30^\circ C$ is $6.0 \times 10^{-4} M/atm$. If the two gases are each present at 1.5 atm pressure, calculate the solubility of each gas.
- 13.34** The partial pressure of O_2 in air at sea level is 0.21 atm. Using the data in Table 13.2, together with Henry's law, calculate the molar concentration of O_2 in the surface water of a mountain lake saturated with air at $20^\circ C$ and an atmospheric pressure of 650 torr.

Concentrations of Solutions

- 13.35** (a) Calculate the mass percentage of Na_2SO_4 in a solution containing 10.6 g Na_2SO_4 in 483 g water. (b) An ore contains 2.86 g of silver per ton of ore. What is the concentration of silver in ppm?
- 13.36** (a) What is the mass percentage of iodine (I_2) in a solution containing 0.035 mol I_2 in 115 g of CCl_4 ? (b) Seawater contains 0.0079 g Sr^{2+} per kilogram of water. What is the concentration of Sr^{2+} measured in ppm?
- 13.37** A solution is made containing 14.6 g of CH_3OH in 184 g H_2O . Calculate (a) the mole fraction of CH_3OH , (b) the mass percent of CH_3OH , (c) the molality of CH_3OH .
- 13.38** A solution is made containing 25.5 g phenol (C_6H_5OH) in 425 g ethanol (C_2H_5OH). Calculate (a) the mole fraction of phenol, (b) the mass percent of phenol, (c) the molality of phenol.
- 13.39** Calculate the molarity of the following aqueous solutions: (a) 0.540 g $Mg(NO_3)_2$ in 250.0 mL of solution, (b) 22.4 g $LiClO_4 \cdot 3 H_2O$ in 125 mL of solution, (c) 25.0 mL of 3.50 M HNO_3 diluted to 0.250 L.
- 13.40** What is the molarity of each of the following solutions: (a) 15.0 g $Al_2(SO_4)_3$ in 0.350 L solution, (b) 5.25 g $Mn(NO_3)_2 \cdot 2 H_2O$ in 175 mL of solution, (c) 35.0 mL of 9.00 M H_2SO_4 diluted to 0.500 L?
- 13.41** Calculate the molarity of each of the following solutions: (a) 8.66 g benzene (C_6H_6) dissolved in 23.6 g carbon tetrachloride (CCl_4), (b) 4.80 g NaCl dissolved in 0.350 L of water.
- 13.42** (a) What is the molality of a solution formed by dissolving 1.25 mol of KCl in 16.0 mol of water? (b) How many grams of sulfur (S_8) must be dissolved in 100.0 g naphthalene ($C_{10}H_8$) to make a 0.12 m solution?
- 13.43** A sulfuric acid solution containing 571.6 g of H_2SO_4 per liter of solution has a density of $1.329 g/cm^3$. Calculate (a) the mass percentage, (b) the mole fraction, (c) the molality, (d) the molarity of H_2SO_4 in this solution.
- 13.44** Ascorbic acid (vitamin C, $C_6H_8O_6$) is a water-soluble vitamin. A solution containing 80.5 g of ascorbic acid dissolved in 210 g of water has a density of 1.22 g/mL at $55^\circ C$. Calculate (a) the mass percentage, (b) the mole fraction, (c) the molality, (d) the molarity of ascorbic acid in this solution.
- 13.45** The density of acetonitrile (CH_3CN) is 0.786 g/mL and the density of methanol (CH_3OH) is 0.791 g/mL. A solution is made by dissolving 22.5 mL CH_3OH in 98.7 mL CH_3CN . (a) What is the mole fraction of methanol in the solution? (b) What is the molality of the solution? (c) Assuming that the volumes are additive, what is the molarity of CH_3OH in the solution?
- 13.46** The density of toluene (C_7H_8) is 0.867 g/mL, and the density of thiophene (C_4H_4S) is 1.065 g/mL. A solution is made by dissolving 9.08 g of thiophene in 250.0 mL of toluene. (a) Calculate the mole fraction of thiophene in the solution. (b) Calculate the molality of thiophene in the solution. (c) Assuming that the volumes of the solute and solvent are additive, what is the molarity of thiophene in the solution?
- 13.47** Calculate the number of moles of solute present in each of the following aqueous solutions: (a) 600 mL of 0.250 M $SrBr_2$, (b) 86.4 g of 0.180 m KCl, (c) 124.0 g of a solution that is 6.45% glucose ($C_6H_{12}O_6$) by mass.
- 13.48** Calculate the number of moles of solute present in each of the following solutions: (a) 185 mL of 1.50 M $HNO_3(aq)$, (b) 50.0 mg of an aqueous solution that is 1.25 m NaCl, (c) 75.0 g of an aqueous solution that is 1.50% sucrose ($C_{12}H_{22}O_{11}$) by mass.
- 13.49** Describe how you would prepare each of the following aqueous solutions, starting with solid KBr: (a) 0.75 L of $1.5 \times 10^{-2} M$ KBr, (b) 125 g of 0.180 m KBr, (c) 1.85 L of a solution that is 12.0% KBr by mass (the density of the solution is 1.10 g/mL), (d) a 0.150 M solution of KBr that contains just enough KBr to precipitate 16.0 g of AgBr from a solution containing 0.480 mol of $AgNO_3$.
- 13.50** Describe how you would prepare each of the following aqueous solutions: (a) 1.50 L of 0.110 M $(NH_4)_2SO_4$ solution, starting with solid $(NH_4)_2SO_4$; (b) 120 g of a solution that is 0.65 m in Na_2CO_3 , starting with the solid solute; (c) 1.20 L of a solution that is 15.0% $Pb(NO_3)_2$ by mass (the density of the solution is 1.16 g/mL), starting with solid solute; (d) a 0.50 M solution of HCl that would just neutralize 5.5 g of $Ba(OH)_2$ starting with 6.0 M HCl.
- 13.51** Commercial aqueous nitric acid has a density of 1.42 g/mL and is 16 M. Calculate the percent HNO_3 by mass in the solution.
- 13.52** Commercial concentrated aqueous ammonia is 28% NH_3 by mass and has a density of 0.90 g/mL. What is the molarity of this solution?
- 13.53** Brass is a substitutional alloy consisting of a solution of copper and zinc. A particular sample of red brass consisting of 80.0% Cu and 20.0% Zn by mass has a density of 8750 kg/m³. (a) What is the molality of Zn in the solid solution? (b) What is the molarity of Zn in the solution?

- 13.54 Caffeine ($C_8H_{10}N_4O_2$) is a stimulant found in coffee and tea. If a solution of caffeine in chloroform ($CHCl_3$) as a solvent has a concentration of $0.0750\ m$, calculate (a) the percent caffeine by mass, (b) the mole fraction of caffeine.

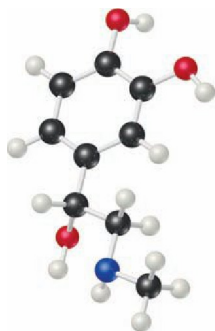


- 13.55 During a typical breathing cycle the CO_2 concentration in the expired air rises to a peak of 4.6% by volume. Calculate the partial pressure of the CO_2 at this point, assuming 1 atm pressure. What is the molarity of the CO_2 in air at this point, assuming a body temperature of $37\ ^\circ C$?
- 13.56 Breathing air that contains 4.0% by volume CO_2 over time causes rapid breathing, throbbing headache, and nausea, among other symptoms. What is the concentration of CO_2 in such air in terms of (a) mol percentage, (b) molarity, assuming 1 atm pressure, and a body temperature of $37\ ^\circ C$?

Colligative Properties

- 13.57 List four properties of a solution that depend on the total concentration but not the type of particle or particles present as solute. Write the mathematical expression that describes how each of these properties depends on concentration.
- 13.58 How does increasing the concentration of a nonvolatile solute in water affect the following properties: (a) vapor pressure, (b) freezing point, (c) boiling point; (d) osmotic pressure?
- 13.59 Consider two solutions, one formed by adding 10 g of glucose ($C_6H_{12}O_6$) to 1 L of water and the other formed by adding 10 g of sucrose ($C_{12}H_{22}O_{11}$) to 1 L of water. Are the vapor pressures over the two solutions the same? Why or why not?
- 13.60 (a) What is an *ideal solution*? (b) The vapor pressure of pure water at $60\ ^\circ C$ is 149 torr. The vapor pressure of water over a solution at $60\ ^\circ C$ containing equal numbers of moles of water and ethylene glycol (a nonvolatile solute) is 67 torr. Is the solution ideal according to Raoult's law? Explain.
- 13.61 (a) Calculate the vapor pressure of water above a solution prepared by adding 22.5 g of lactose ($C_{12}H_{22}O_{11}$) to 200.0 g of water at 338 K. (Vapor-pressure data for water are given in Appendix B.) (b) Calculate the mass of propylene glycol ($C_3H_8O_2$) that must be added to 0.340 kg of water to reduce the vapor pressure by 2.88 torr at $40\ ^\circ C$.
- [13.62] (a) Calculate the vapor pressure of water above a solution prepared by dissolving 32.5 g of glycerin ($C_3H_8O_3$) in 125 g of water at 343 K. (The vapor pressure of water is given in Appendix B.) (b) Calculate the mass of ethylene glycol ($C_2H_6O_2$) that must be added to 1.00 kg of ethanol (C_2H_5OH) to reduce its vapor pressure by 10.0 torr at $35\ ^\circ C$. The vapor pressure of pure ethanol at $35\ ^\circ C$ is 1.00×10^2 torr.
- [13.63] At $63.5\ ^\circ C$ the vapor pressure of H_2O is 175 torr, and that of ethanol (C_2H_5OH) is 400 torr. A solution is made by mixing equal masses of H_2O and C_2H_5OH . (a) What is the mole fraction of ethanol in the solution? (b) Assuming ideal-solution behavior, what is the vapor pressure of the solution at $63.5\ ^\circ C$? (c) What is the mole fraction of ethanol in the vapor above the solution?
- [13.64] At $20\ ^\circ C$ the vapor pressure of benzene (C_6H_6) is 75 torr, and that of toluene (C_7H_8) is 22 torr. Assume that benzene and toluene form an ideal solution. (a) What is the composition in mole fractions of a solution that has a vapor pressure of 35 torr at $20\ ^\circ C$? (b) What is the mole fraction of benzene in the vapor above the solution described in part (a)?
- 13.65 (a) Why does a $0.10\ m$ aqueous solution of NaCl have a higher boiling point than a $0.10\ m$ aqueous solution of $C_6H_{12}O_6$? (b) Calculate the boiling point of each solution. (c) The experimental boiling point of the NaCl solution is lower than that calculated, assuming that NaCl is completely dissociated in solution. Why is this the case?
- 13.66 Arrange the following aqueous solutions, each 10% by mass in solute, in order of increasing boiling point: glucose ($C_6H_{12}O_6$), sucrose ($C_{12}H_{22}O_{11}$), sodium nitrate ($NaNO_3$).
- 13.67 List the following aqueous solutions in order of increasing boiling point: $0.120\ m$ glucose, $0.050\ m$ LiBr, $0.050\ m$ $Zn(NO_3)_2$.
- 13.68 List the following aqueous solutions in order of decreasing freezing point: $0.040\ m$ glycerin ($C_3H_8O_3$), $0.020\ m$ KBr, $0.030\ m$ phenol (C_6H_5OH).
- 13.69 Using data from Table 13.4, calculate the freezing and boiling points of each of the following solutions: (a) $0.22\ m$ glycerol ($C_3H_8O_3$) in ethanol, (b) $0.240\ mol$ of naphthalene ($C_{10}H_8$) in $2.45\ mol$ of chloroform, (c) $2.04\ g$ KBr and $4.82\ g$ glucose ($C_6H_{12}O_6$) in $188\ g$ of water.
- 13.70 Using data from Table 13.4, calculate the freezing and boiling points of each of the following solutions: (a) $0.30\ m$ glucose in ethanol; (b) $20.0\ g$ of decane, $C_{10}H_{22}$, in $45.5\ g$ $CHCl_3$; (c) $0.45\ mol$ ethylene glycol and $0.15\ mol$ KBr in $150\ g$ H_2O .

- 13.71** How many grams of ethylene glycol ($C_2H_6O_2$) must be added to 1.00 kg of water to produce a solution that freezes at $-5.00\text{ }^\circ\text{C}$?
- 13.72** What is the freezing point of an aqueous solution that boils at $105.0\text{ }^\circ\text{C}$?
- 13.73** What is the osmotic pressure formed by dissolving 44.2 mg of aspirin ($C_9H_8O_4$) in 0.358 L of water at $25\text{ }^\circ\text{C}$?
- 13.74** Seawater contains 3.4 g of salts for every liter of solution. Assuming that the solute consists entirely of NaCl (over 90% is), calculate the osmotic pressure of seawater at $20\text{ }^\circ\text{C}$.
- 13.75** Adrenaline is the hormone that triggers the release of extra glucose molecules in times of stress or emergency. A solution of 0.64 g of adrenaline in 36.0 g of CCl_4 elevates the boiling point by $0.49\text{ }^\circ\text{C}$. Is the molar mass of adrenaline calculated from the boiling point elevation in agreement with the following structural formula?



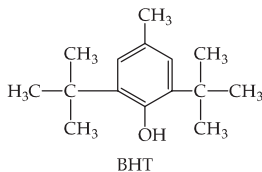
- 13.76** Lauryl alcohol is obtained from coconut oil and is used to make detergents. A solution of 5.00 g of lauryl alcohol in 0.100 kg of benzene freezes at $4.1\text{ }^\circ\text{C}$. What is the approximate molar mass of lauryl alcohol?
- 13.77** Lysozyme is an enzyme that breaks bacterial cell walls. A solution containing 0.150 g of this enzyme in 210 mL of solution has an osmotic pressure of 0.953 torr at $25\text{ }^\circ\text{C}$. What is the molar mass of lysozyme?
- 13.78** A dilute aqueous solution of an organic compound soluble in water is formed by dissolving 2.35 g of the compound in water to form 0.250 L solution. The resulting solution has an osmotic pressure of 0.605 atm at $25\text{ }^\circ\text{C}$. Assuming that the organic compound is a nonelectrolyte, what is its molar mass?
- [13.79]** The osmotic pressure of a 0.010 *M* aqueous solution of $CaCl_2$ is found to be 0.674 atm at $25\text{ }^\circ\text{C}$. (a) Calculate the van't Hoff factor, *i*, for the solution. (b) How would you expect the value of *i* to change as the solution becomes more concentrated? Explain.
- [13.80]** Based on the data given in Table 13.5, which solution would give the larger freezing-point lowering, a 0.030 *m* solution of NaCl or a 0.020 *m* solution of K_2SO_4 ? How do you explain the departure from ideal behavior and the differences observed between the two salts?

Colloids

- 13.81** (a) Why is there no colloid in which both the dispersed substance and the dispersing substance are gases? (b) Michael Faraday first prepared ruby-red colloids of gold particles in water that were stable for indefinite times. ∞ (Section 12.6) To the unaided eye these brightly colored colloids are not distinguishable from solutions. How could you determine whether a given colored preparation is a solution or colloid?
- 13.82** (a) Many proteins that remain homogeneously distributed in water have molecular masses in the range of 30,000 amu and larger. In what sense is it appropriate to consider such suspensions to be colloids rather than solutions? Explain. (b) What general name is given to a colloidal dispersion of one liquid in another? What is an emulsifying agent?
- 13.83** Indicate whether each of the following is a hydrophilic or a hydrophobic colloid: (a) butterfat in homogenized milk, (b) hemoglobin in blood, (c) vegetable oil in a salad dressing, (d) colloidal gold particles in water.
- 13.84** Explain how each of the following factors helps determine the stability or instability of a colloidal dispersion: (a) particulate mass, (b) hydrophobic character, (c) charges on colloidal particles.
- 13.85** Colloidal suspensions of proteins, such as a gelatin, can often be caused to separate into two layers by addition of a solution of an electrolyte. Given that protein molecules may carry electrical charges on their outer surface as illustrated in Figure 13.28, what do you believe happens when the electrolyte solution is added?
- 13.86** Explain how (a) a soap such as sodium stearate stabilizes a colloidal dispersion of oil droplets in water; (b) milk curdles upon addition of an acid.

ADDITIONAL EXERCISES

- 13.87 Butylated hydroxytoluene (BHT) has the following molecular structure:



It is widely used as a preservative in a variety of foods, including dried cereals. Based on its structure, would you expect BHT to be more soluble in water or in hexane (C_6H_{14})? Explain.

- 13.88 A saturated solution of sucrose ($C_{12}H_{22}O_{11}$) is made by dissolving excess table sugar in a flask of water. There are 50 g of undissolved sucrose crystals at the bottom of the flask in contact with the saturated solution. The flask is stoppered and set aside. A year later a single large crystal of mass 50 g is at the bottom of the flask. Explain how this experiment provides evidence for a dynamic equilibrium between the saturated solution and the undissolved solute.
- 13.89 Fish need at least 4 ppm dissolved O_2 for survival. (a) What is this concentration in mol/L? (b) What partial pressure of O_2 above the water is needed to obtain this concentration at $10^\circ C$? (The Henry's law constant for O_2 at this temperature is 1.71×10^{-3} mol/L-atm.)
- 13.90 The presence of the radioactive gas radon (Rn) in well water obtained from aquifers that lie in rock deposits presents a possible health hazard in parts of the United States. (a) Assuming that the solubility of radon in water with 1 atm pressure of the gas over the water at $30^\circ C$ is 7.27×10^{-3} M, what is the Henry's law constant for radon in water at this temperature? (b) A sample consisting of various gases contains 3.5×10^{-6} mole fraction of radon. This gas at a total pressure of 32 atm is shaken with water at $30^\circ C$. Calculate the molar concentration of radon in the water.
- 13.91 Glucose makes up about 0.10% by mass of human blood. Calculate the concentration in (a) ppm, (b) molality. What further information would you need to determine the molarity of the solution?
- 13.92 The maximum allowable concentration of lead in drinking water is 9.0 ppb. (a) Calculate the molarity of lead in a 9.0-ppb solution. What assumption did you have to make in your calculation? (b) How many grams of lead are in a swimming pool containing 9.0 ppb lead in $60 m^3$ of water?
- 13.93 Acetonitrile (CH_3CN) is a polar organic solvent that dissolves a wide range of solutes, including many salts. The density of a 1.80 M LiBr solution in acetonitrile is $0.826 g/cm^3$. Calculate the concentration of the solution in (a) molality, (b) mole fraction of LiBr, (c) mass percentage of CH_3CN .
- 13.94 A "canned heat" product used to warm chafing dishes consists of a homogeneous mixture of ethanol (C_2H_5OH) and paraffin that has an average formula of $C_{24}H_{50}$. What mass of C_2H_5OH should be added to 620 kg of the paraffin in formulating the mixture if the vapor pressure of ethanol at $35^\circ C$ over the mixture is to be 8 torr? The vapor pressure of pure ethanol at $35^\circ C$ is 100 torr.
- 13.95 Two beakers are placed in a sealed box at $25^\circ C$. One beaker contains 30.0 mL of a 0.050 M aqueous solution of a nonvolatile nonelectrolyte. The other beaker contains 30.0 mL of a 0.035 M aqueous solution of NaCl. The water vapor from the two solutions reaches equilibrium. (a) In which beaker does the solution level rise, and in which one does it fall? (b) What are the volumes in the two beakers when equilibrium is attained, assuming ideal behavior?
- 13.96 A solution contains 0.115 mol H_2O and an unknown number of moles of sodium chloride. The vapor pressure of the solution at $30^\circ C$ is 25.7 torr. The vapor pressure of pure water at this temperature is 31.8 torr. Calculate the number of moles of sodium chloride in the solution. (Hint: remember that sodium chloride is a strong electrolyte.)
- 13.97 Show that the vapor-pressure reduction, $\Delta P_{\text{solvent}}$, associated with the addition of a nonvolatile solute to a volatile solvent is given by the equation $\Delta P_{\text{solvent}} = X_{\text{solute}} \times P_{\text{solvent}}^\circ$.
- 13.98 A car owner who knows no chemistry has to put antifreeze in his car's radiator. The instructions recommend a mixture of 30% ethylene glycol and 70% water. Thinking he will improve his protection he uses pure ethylene glycol. He is saddened to find that the solution does not provide as much protection as he hoped. Why not?
- 13.99 Calculate the freezing point of a 0.100 m aqueous solution of K_2SO_4 , (a) ignoring interionic attractions, and (b) taking interionic attractions into consideration by using the van't Hoff factor (Table 13.5).
- 13.100 When 10.0 g of mercuric nitrate, $Hg(NO_3)_2$, is dissolved in 1.00 kg of water, the freezing point of the solution is $-0.162^\circ C$. When 10.0 g of mercuric chloride ($HgCl_2$) is dissolved in 1.00 kg of water, the solution freezes at $-0.0685^\circ C$. Use these data to determine which is the stronger electrolyte, $Hg(NO_3)_2$ or $HgCl_2$.

- 13.101** Carbon disulfide (CS_2) boils at 46.30°C and has a density of 1.261 g/mL . (a) When 0.250 mol of a nondissociating solute is dissolved in 400.0 mL of CS_2 , the solution boils at 47.46°C . What is the molal boiling-point-elevation constant for CS_2 ? (b) When 5.39 g of a nondissociating unknown is dissolved in 50.0 mL of CS_2 , the solution boils at 47.08°C . What is the molecular weight of the unknown?
- [13.102]** A 40.0% by weight solution of KSCN in water at 20°C has a density of 1.22 g/mL . (a) What is the mole fraction of KSCN in the solution, and what are the molarity and molality? (b) Given the calculated mole fraction of salt in the solution, comment on the total number of water molecules available to hydrate each anion and cation.

INTEGRATIVE EXERCISES

- 13.104** Fluorocarbons (compounds that contain both carbon and fluorine) were, until recently, used as refrigerants. The compounds listed in the following table are all gases at 25°C , and their solubilities in water at 25°C and 1 atm fluorocarbon pressure are given as mass percentages. (a) For each fluorocarbon, calculate the molality of a saturated solution. (b) Explain why the molarity of each of the solutions should be very close numerically to the molality. (c) Based on their molecular structures, account for the differences in solubility of the four fluorocarbons. (d) Calculate the Henry's law constant at 25°C for CHClF_2 , and compare its magnitude to that for N_2 ($6.8 \times 10^{-4}\text{ mol/L}\cdot\text{atm}$). Can you account for the difference in magnitude?

Fluorocarbon	Solubility (mass %)
CF_4	0.0015
CClF_3	0.009
CCl_2F_2	0.028
CHClF_2	0.30

- [13.105]** At ordinary body temperature (37°C) the solubility of N_2 in water in contact with air at ordinary atmospheric pressure (1.0 atm) is 0.015 g/L . Air is approximately $78\text{ mol}\%$ N_2 . Calculate the number of moles of N_2 dissolved per liter of blood, which is essentially an aqueous solution. At a depth of 100 ft in water, the pressure is 4.0 atm . What is the solubility of N_2 from air in blood at this pressure? If a scuba diver suddenly surfaces from this depth, how many milliliters of N_2 gas, in the form of tiny bubbles, are released into the bloodstream from each liter of blood?
- [13.106]** Consider the following values for enthalpy of vaporization (kJ/mol) of several organic substances:

$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{C}-\text{H} \end{array}$	30.4	$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{H}_2\text{C} \quad \text{CH}_2 \end{array}$	28.5
Acetaldehyde		Ethylene oxide	
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CCH}_3 \end{array}$	32.0	$\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{H}_2\text{C} \quad \text{CH}_2 \end{array}$	24.7
Acetone		Cyclopropane	

What ion pairing (if any) would you expect to find in the solution? Would you expect the colligative properties of such a solution to be those predicted by the formulas given in this chapter? Explain.

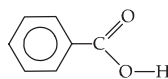
- [13.103]** A lithium salt used in lubricating grease has the formula $\text{LiC}_n\text{H}_{2n+1}\text{O}_2$. The salt is soluble in water to the extent of 0.036 g per 100 g of water at 25°C . The osmotic pressure of this solution is found to be 57.1 torr . Assuming that molality and molarity in such a dilute solution are the same and that the lithium salt is completely dissociated in the solution, determine an appropriate value of n in the formula for the salt.
- (a) Use variations in the intermolecular forces operating in these organic liquids to account for their variations in heats of vaporization. (b) How would you expect the solubilities of these substances to vary in hexane as solvent? In ethanol? Use intermolecular forces, including hydrogen-bonding interactions where applicable, to explain your responses.
- [13.107]** The enthalpies of solution of hydrated salts are generally more positive than those of anhydrous materials. For example, ΔH of solution for KOH is -57.3 kJ/mol whereas that for $\text{KOH} \cdot \text{H}_2\text{O}$ is -14.6 kJ/mol . Similarly, ΔH_{soln} for NaClO_4 is $+13.8\text{ kJ/mol}$, whereas that for $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ is $+22.5\text{ kJ/mol}$. Use the enthalpy contributions to the solution process depicted in Figure 13.4 to explain this effect.
- [13.108]** A textbook on chemical thermodynamics states, "The heat of solution represents the difference between the lattice energy of the crystalline solid and the solvation energy of the gaseous ions." (a) Draw a simple energy diagram to illustrate this statement. (b) A salt such as NaBr is insoluble in most polar nonaqueous solvents such as acetonitrile (CH_3CN) or nitromethane (CH_3NO_2), but salts of large cations, such as tetramethylammonium bromide [$(\text{CH}_3)_4\text{NBr}$], are generally more soluble. Use the thermochemical cycle you drew in part (a) and the factors that determine the lattice energy (Section 8.2) to explain this fact.
- 13.109** (a) A sample of hydrogen gas is generated in a closed container by reacting 2.050 g of zinc metal with 15.0 mL of 1.00 M sulfuric acid. Write the balanced equation for the reaction, and calculate the number of moles of hydrogen formed, assuming that the reaction is complete. (b) The volume over the solution is 122 mL . Calculate the partial pressure of the hydrogen gas in this volume at 25°C , ignoring any solubility of the gas in the solution. (c) The Henry's law constant for hydrogen in water at 25°C is $7.8 \times 10^{-4}\text{ mol/L}\cdot\text{atm}$. Estimate the number of moles of hydrogen gas that remain dissolved in the solution. What fraction of the gas molecules in the system is dissolved in the solution? Was it reasonable to ignore any dissolved hydrogen in part (b)?
- [13.110]** The following table presents the solubilities of several gases in water at 25°C under a total pressure of gas and water vapor of 1 atm . (a) What volume of $\text{CH}_4(\text{g})$ under

standard conditions of temperature and pressure is contained in 4.0 L of a saturated solution at 25 °C? (b) Explain the variation in solubility among the hydrocarbons listed (the first three compounds), based on their molecular structures and intermolecular forces. (c) Compare the solubilities of O₂, N₂, and NO, and account for the variations based on molecular structures and intermolecular forces. (d) Account for the much larger values observed for H₂S and SO₂ as compared with the other gases listed. (e) Find several pairs of substances with the same or nearly the same molecular masses (for example, C₂H₄ and N₂), and use intermolecular interactions to explain the differences in their solubilities.

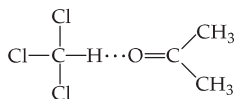
Gas	Solubility (mM)
CH ₄ (methane)	1.3
C ₂ H ₆ (ethane)	1.8
C ₂ H ₄ (ethylene)	4.7
N ₂	0.6
O ₂	1.2
NO	1.9
H ₂ S	99
SO ₂	1476

- [13.111] Consider the process illustrated in Figure 13.23, the net movement of solvent from the more dilute to the more concentrated solution through the semipermeable membrane. Is there a change in entropy of the system in going from the left to center panels? Explain. (*Hint*: Imagine that the more dilute solution on the right hand side of the apparatus is pure solvent.)

- [13.112] When 0.55 g of pure benzoic acid (C₆H₅COOH) is dissolved in 32.0 g of benzene (C₆H₆), the freezing point of the solution is 0.36 °C lower than the freezing point value of 5.5 °C for the pure solvent. (a) Calculate the molecular weight of benzoic acid in benzene. (b) Use the structure of the solute to account for the observed value:



- [13.113] At 35 °C the vapor pressure of acetone, (CH₃)₂CO, is 360 torr, and that of chloroform, CHCl₃, is 300 torr. Acetone and chloroform can form weak hydrogen bonds between one another as follows:



A solution composed of an equal number of moles of acetone and chloroform has a vapor pressure of 250 torr at 35 °C. (a) What would be the vapor pressure of the solution if it exhibited ideal behavior? (b) Use the existence of hydrogen bonds between acetone and chloroform molecules to explain the deviation from ideal behavior. (c) Based on the behavior of the solution, predict whether the mixing of acetone and chloroform is an exothermic ($\Delta H_{\text{soln}} < 0$) or endothermic ($\Delta H_{\text{soln}} > 0$) process.