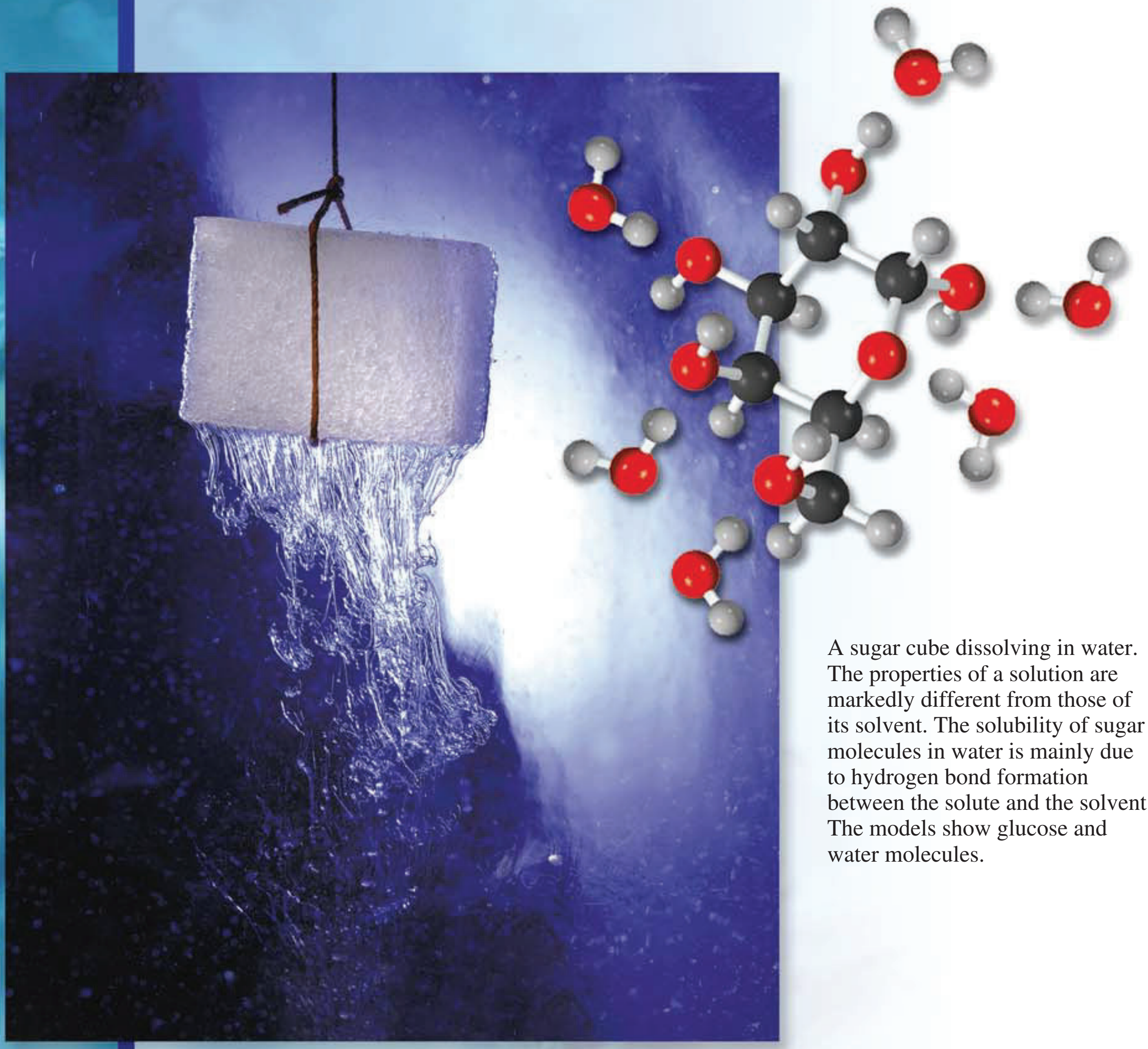
Physical Properties of Solutions



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

12

Chapter Outline

A Look Ahead

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

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

12.1 Types of Solutions

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

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

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

TABLE 12.1 Types of Solutions

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

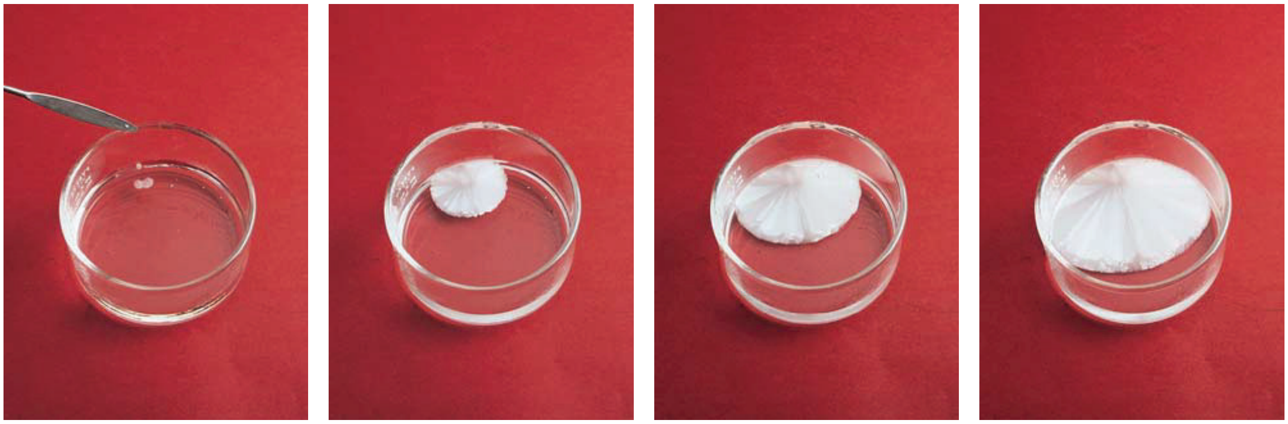


Figure 12.1 *In a supersaturated sodium acetate solution (left), sodium acetate crystals rapidly form when a small seed crystal is added.*

12.2 A Molecular View of the Solution Process

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

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

- solvent-solvent interaction
- solute-solute interaction
- solvent-solute interaction

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

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

This equation is an application of Hess's law.

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

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

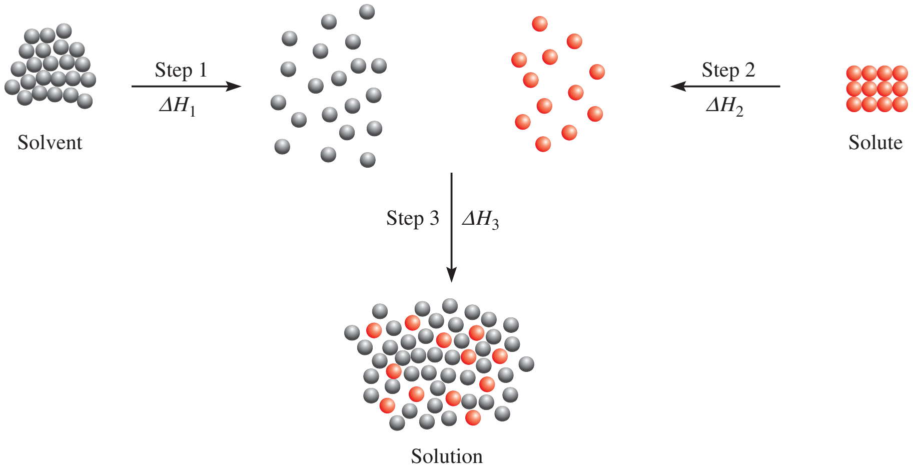
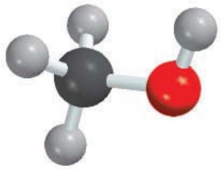


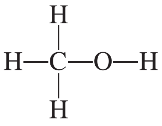
Figure 12.2 *A molecular view of the solution process portrayed as taking place in three steps: First the solvent and solute molecules are separated (steps 1 and 2). Then the solvent and solute molecules mix (step 3).*

solution process is accompanied by an increase in disorder. It is the increase in disorder of the system that favors the solubility of any substance, even if the solution process is endothermic.

Solubility is a measure of how much solute will dissolve in a solvent at a specific temperature. The saying "like dissolves like" is helpful in predicting the solubility of a substance in a given solvent. What this expression means is that two substances with intermolecular forces of similar type and magnitude are likely to be soluble in each other. For example, both carbon tetrachloride (CCl_4) and benzene (C_6H_6) are nonpolar liquids. The only intermolecular forces present in these substances are dispersion forces (see Section 11.2). When these two liquids are mixed, they readily dissolve in each other, because the attraction between CCl_4 and C_6H_6 molecules is comparable in magnitude to the forces between CCl_4 molecules and between C_6H_6 molecules. Two liquids are said to be ***miscible*** if *they are completely soluble in each other in all proportions.* Alcohols such as methanol, ethanol, and 1,2-ethylene glycol are miscible with water because they can form hydrogen bonds with water molecules:

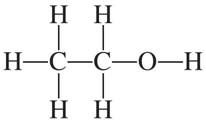


CH_3OH



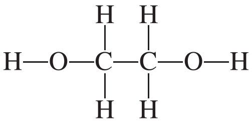
$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}O{-}H}$$

methanol



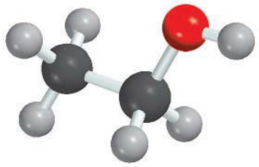
$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}O{-}H}$$

ethanol



$$\mathrm{H{-}O{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}O{-}H}$$

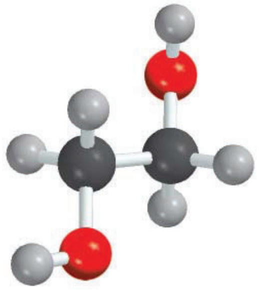
1,2-ethylene glycol



C_2H_5OH

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

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



$CH_2(OH)CH_2(OH)$

EXAMPLE 12.1

Predict the relative solubilities in the following cases: (a) Bromine (Br_2) in benzene (C_6H_6, $\mu = 0$ D) and in water ($\mu = 1.87$ D), (b) KCl in carbon tetrachloride (CCl_4, $\mu = 0$ D) and in liquid ammonia (NH_3, $\mu = 1.46$ D), (c) formaldehyde (CH_2O) in carbon disulfide (CS_2, $\mu = 0$ D) and in water.

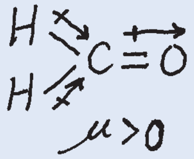
Strategy In predicting solubility, remember the saying: Like dissolves like. A nonpolar solute will dissolve in a nonpolar solvent; ionic compounds will generally dissolve in polar solvents due to favorable ion-dipole interaction; solutes that can form hydrogen bonds with the solvent will have high solubility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

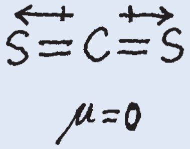
Solution (a) Br_2 is a nonpolar molecule and therefore should be more soluble in C_6H_6, which is also nonpolar, than in water. The only intermolecular forces between Br_2 and C_6H_6 are dispersion forces.

(Continued)

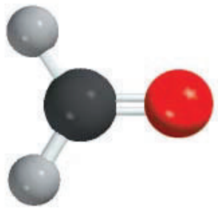
(b) KCl is an ionic compound. For it to dissolve, the individual K^+ and Cl^- ions must be stabilized by ion-dipole interaction. Because CCl_4 has no dipole moment, KCl should be more soluble in liquid NH_3, a polar molecule with a large dipole moment.

(c) Because CH_2O is a polar molecule and CS_2 (a linear molecule) is nonpolar,





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



CH_2O

12.3 Concentration Units

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

Types of Concentration Units

Percent by Mass

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

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

or

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

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

Mole Fraction (X)

The mole fraction was introduced in Section 5.6. The mole fraction of a component of a solution, say, component A, is written X_A and is defined as

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

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

Molarity (M)

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

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

Thus, the units of molarity are mol/L.

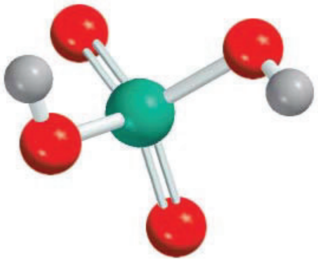
Molality (m)

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

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

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

Solutes will lower the freezing points of mixtures. The freezing points of solutions are depressed in proportion of molality of the total particles of solute in solutions. Thus ionic compounds that dissociate will lower freezing points more than nonionic compounds as they dissociate into a multiple of the molality of the solution.



H_2SO_4

Boiling points are elevated by nonvolatile solutes based on the same principles of molality and numbers of poarticles.

For the SAT Chemistry exam expects students to know about freezing point depression and boiling point elevation.

Fractional Distillation

Solution vapor pressure has a direct bearing on ***fractional distillation,*** *a procedure for separating liquid components of a solution based on their different boiling points.* Frac-tional distillation is somewhat analogous to fractional crystallization. Suppose we want to separate a *binary system* (a system with two components), say, benzene-toluene. Both benzene and toluene are relatively volatile, yet their boiling points are appreciably different (80.1°C and 110.6°C, respectively). When we boil a solution containing these two substances, the vapor formed is somewhat richer in the more volatile component, benzene. If the vapor is condensed in a separate container and that liquid is boiled again, a still higher concentration of benzene will be obtained in the vapor phase. By repeating this process many times, it is possible to separate benzene completely from toluene.

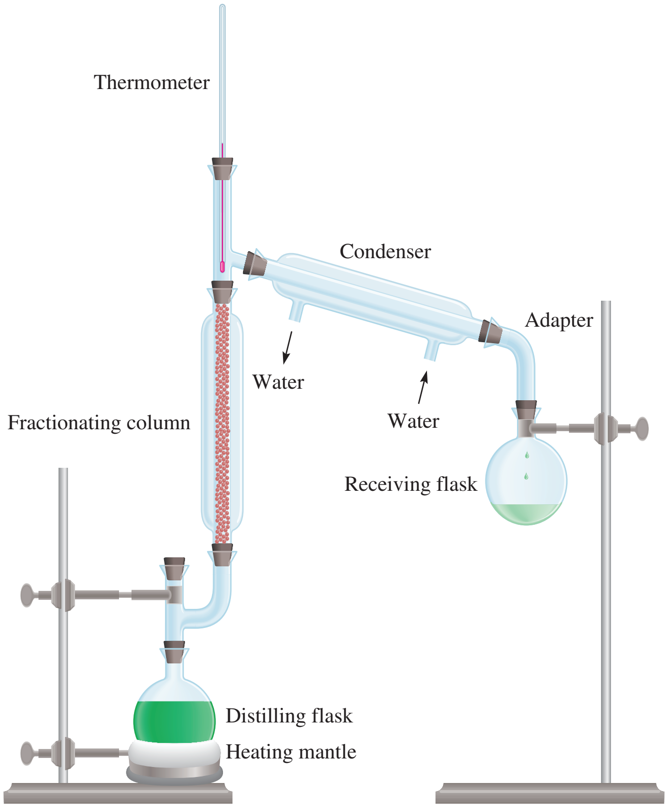


Figure 12.9 *An apparatus for small-scale fractional distillation. The fractionating column is packed with tiny glass beads. The longer the fractionating column, the more complete the separation of the volatile liquids.*

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