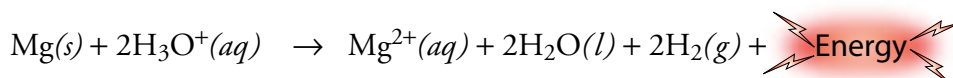# CHAPTER 15
SOLUTION DYNAMICS

For a chemical reaction to take place, the reacting particles must first collide– freely, frequently, and at high velocity. Particles in gases move freely and swiftly and collide continually, but gas phase reactions are difficult to contain and are sometimes dangerous. The particles in a liquid also move freely and quickly and have a high rate of collision, but very few pure substances are liquids at normal temperatures and pressures. Thus many important chemical reactions must take place in liquid solutions, where the reacting particles (dissolved gases, liquids, and solids) are free to move and collide in a medium that is very easy to contain. For example, "meals ready to eat" (MREs), which are used to feed soldiers in the field, include a packet that contains powdered magnesium metal and a solid acid. These substances are unable to react in the solid form. When water is added to dissolve the acid, hydronium ions are liberated, and they migrate throughout the mixture, colliding with magnesium metal, reacting with it in an extremely exothermic process, and releasing enough heat to cook the meal.

$$Mg(s) + 2H_3O^+(aq) \rightarrow Mg^{2+}(aq) + 2H_2O(l) + 2H_2(g) + \text{Energy}$$

We began to develop a mental image of how solutions form in Chapters 4 and 5, but there are still a lot of questions to be addressed. Let's look at some situations you might encounter in a day spent doing chores around the house.

8:43 After an early breakfast, you have time for some car maintenance. The fluid level in your cooling system is low, so you mix coolant and water and add it to the radiator. You wonder why the coolant and water mix so easily.

9:21 Next, the lawn needs attention, but before you can cut the grass, you need to gas up the mower. In the process, you spill a little gasoline on the garage floor and try unsuccessfully to clean it up with water. Why don't the gasoline and water mix?

12:40 Washing the lunch dishes gives you plenty of time to wonder why the dish soap helps clean grease away. You even have enough time to ask yourself why detergent works better than soap.

12:52 Your neighbor Hope drops by for a visit. You brew coffee for her and pour some iced tea for yourself. You seem to be out of granular sugar, so you raid the supply of sugar cubes that you usually save for dinner parties. Why does the sugar cube take longer to dissolve than the same amount of granular sugar, and why does powdered sugar dissolve even faster? Why do they all dissolve faster if you stir them? And why does sugar dissolve so much faster in the hot coffee than in the iced tea?

1:10 You convince Hope that it's time to get out of the kitchen and into the outside world, so it's off to Monterey Bay to do some scuba diving. On the way, you wonder about the reasons for some of the diving safety rules you've been taught. Why can diving too deep make you feel drowsy and disoriented? Why is it important to ascend from deep water slowly?

The discussion of solution dynamics in this chapter will answer these questions and many more.

Water dissolves the solids in this MRE packet, allowing them to mix and react.

Review Skills

The presentation of information in this chapter assumes that you can already perform the tasks listed below. You can test your readiness to proceed by answering the Review Questions at the end of the chapter. This might also be a good time to read the Chapter Objectives, which precede the Review Questions.

- Describe the structure of liquid water. (Section 3.3.)
- Given a description of a solution, identify the solute and solvent. (Section 4.2.)
- Describe the process by which an ionic compound dissolves in water, referring to the nature of the particles in solution and the kind of attractions that form between them. (Section 4.2.)
- Convert between names of compounds and their chemical formulas. (Section 5.3.)
- Write a general description of dynamic equilibrium. (Section 14.1.)

- Describe hydrogen bonds between molecules of H_2O and CH_3OH. (Section 14.3.)
- Given the name or chemical formula for a compound, (1) categorize the substance as an ionic compound, a polar molecular compound with hydrogen bonds, a polar molecular compound without hydrogen bonds, or a nonpolar molecular compound, (2) identify the type of particle that forms its basic structure, and (3) identify the type of attraction holding its particles in the solid and liquid form. (Section 14.3.)
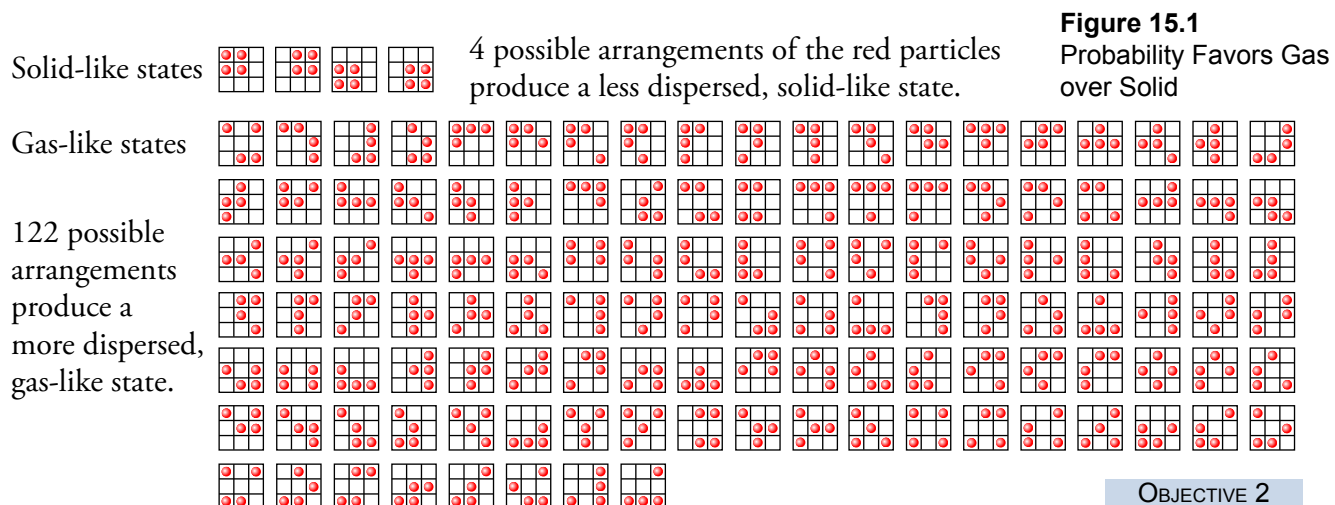
15.1 Why Solutions Form

We start this stage of our exploration of the nature of solutions by looking at some of the reasons why certain substances mix to form solutions and why others do not. When you are finished reading this section, you will have the necessary tools for predicting the solubility of substances in liquids.
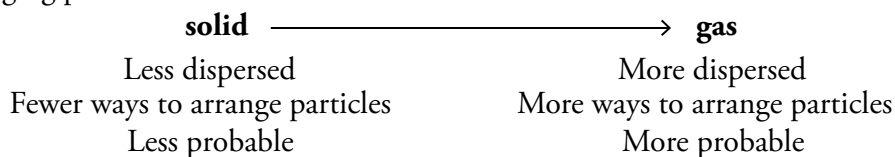
The Natural Tendency to Spread Out

OBJECTIVE 2

It is common for scientists to develop and explain their ideas by considering simplified systems first and then applying the ideas that relate to these simplified systems to more complex systems. Before we try to explain the more complicated changes that take place when solutions form, let's take a look at a much simpler system consisting of four particles that can each be found in one of nine positions. Figure 15.1 shows that there are 126 ways to arrange these four particles in the nine positions. We know that the particles in solids are closer together than the particles in a gas, so in our simple system, let's assume that any arrangement that has the four particles clustered together is like a solid. Figure 15.1 shows that there are four ways to do this. In our system, we will consider any other, more dispersed (more spread out) arrangement as being like a gas. Figure 15.1 shows that there are 122 ways to position the particles in a gas-like arrangement. Thus over 96% of the possible arrangements lead to gas-like states. Therefore, if we assume that the particles can move freely between positions, they are more likely to be found in a gas-like state than in a solid-like state.

Figure 15.1
Probability Favors Gas over Solid

Solid-like states

4 possible arrangements of the red particles produce a less dispersed, solid-like state.

Gas-like states

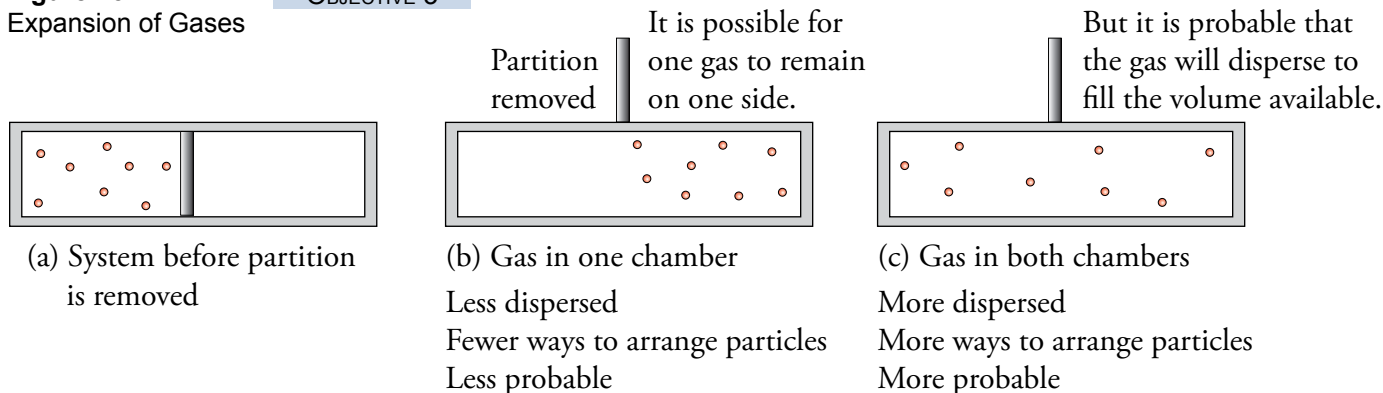122 possible arrangements produce a more dispersed, gas-like state.

OBJECTIVE 2

If the four particles had 16 possible positions, there would be 1820 possible combinations. Nine of these would be in solid-like states, and the other 1811 would be in gas-like states. Thus over 99.5% of the possible arrangements would represent gas-like states, as opposed to 96% for the system with 9 possible positions. This shows that an increase in the number of possible positions leads to an increase in the probability that the system will be in a more dispersed, gas-like state. In real systems, which provide a huge number of possible positions for particles, there is an extremely high probability that substances will shift from the less dispersed, solid form, which has fewer ways of arranging the particles, to the more dispersed, gas form, which has more ways of arranging particles.

solid $\longrightarrow$ **gas**

Less dispersed	More dispersed
Fewer ways to arrange particles	More ways to arrange particles
Less probable	More probable

In general, **particles of matter tend to become more dispersed (spread out).** The simple system shown in Figure 15.2 provides another example. It has two chambers that can be separated by a removable partition. Part *a* of the figure shows this system with gas on one side only. If the partition is lifted, the motion of the gas particles causes them to move back and forth between the chambers. Because there are more possible arrangements for the gas particles when they are dispersed throughout both chambers than when they are concentrated in one chamber, probability suggests that they will spread out to fill the total volume available to them.

OBJECTIVE 3

Figure 15.2
Expansion of Gases

OBJECTIVE 3

Partition removed

It is possible for one gas to remain on one side.

But it is probable that the gas will disperse to fill the volume available.

(a) System before partition is removed

(b) Gas in one chamber

Less dispersed
Fewer ways to arrange particles
Less probable

(c) Gas in both chambers

More dispersed
More ways to arrange particles
More probable

We can apply the conclusions derived from the consideration of simplified systems to real systems. For example, we can use the information about the simple systems described above to explain the behavior of a small amount of dry ice, $CO_2(s)$, in a closed container. The movement of particles in the solid CO_2 allows some of the CO_2 molecules at the surface of the solid to break their attractions to other molecules and escape into the space above the solid. Like all particles in the gas form, the escaped CO_2 molecules are constantly moving, colliding with other particles, and changing their direction and velocity. This gives them the possibility of moving anywhere in the container. Because the most spread out or dispersed arrangement of particles is the most probable state, the gaseous CO_2 spreads out to fill the total space available to it. Because of the movement of the gaseous molecules, each molecule eventually collides with the surface of the solid. When this happens the particle is attracted to the other particles on the surface of the solid and is likely to return to the solid. Therefore, particles are able to move back and forth between the solid and gaseous form, and we expect to find them in the more probable, more dispersed gas state, which has more equivalent ways to arrange the particles.
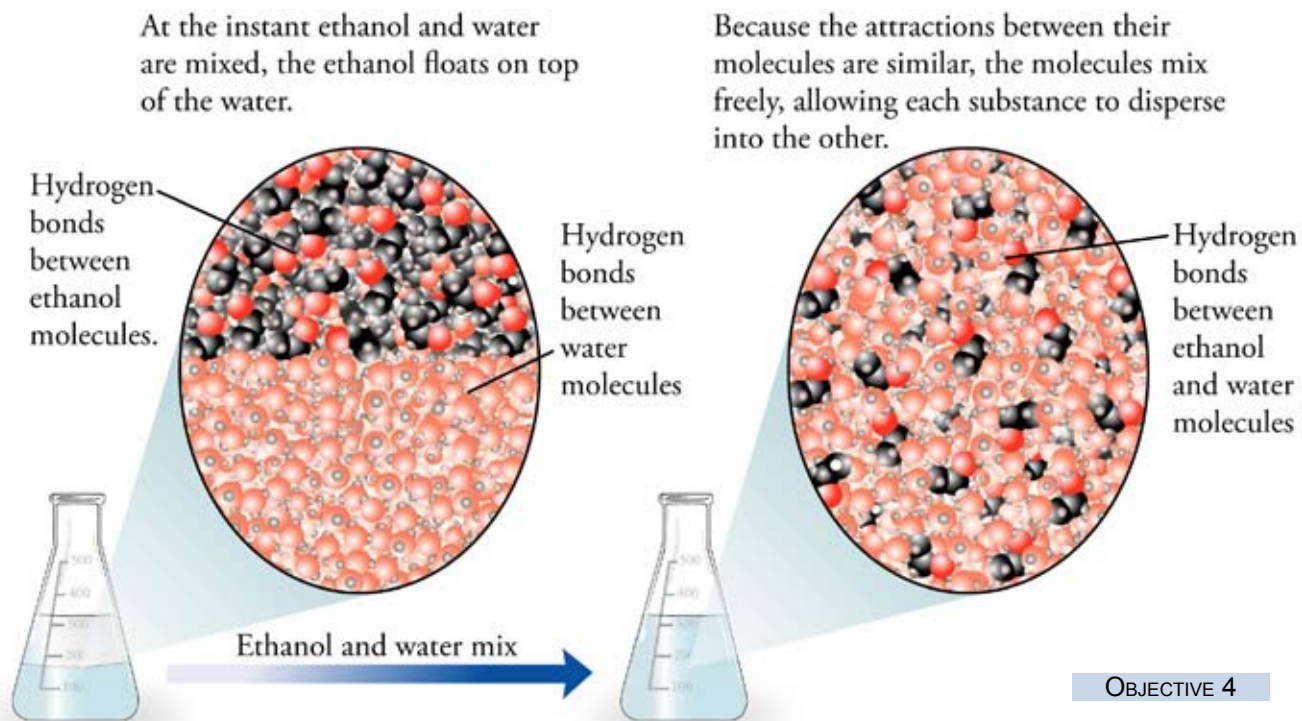
Why Do Solutions Form?

Although much of the explanation for why certain substances mix and form solutions and why others do not is beyond the scope of this text, we can get a glimpse at why solutions form by taking a look at the process by which ethanol, C_2H_5OH, dissolves in water. Ethanol is actually **miscible** in water, which means that the two liquids can be mixed in any proportion without any limit to their solubility. Much of what we now know about the tendency of particles to become more dispersed can be used to understand this kind of change as well.
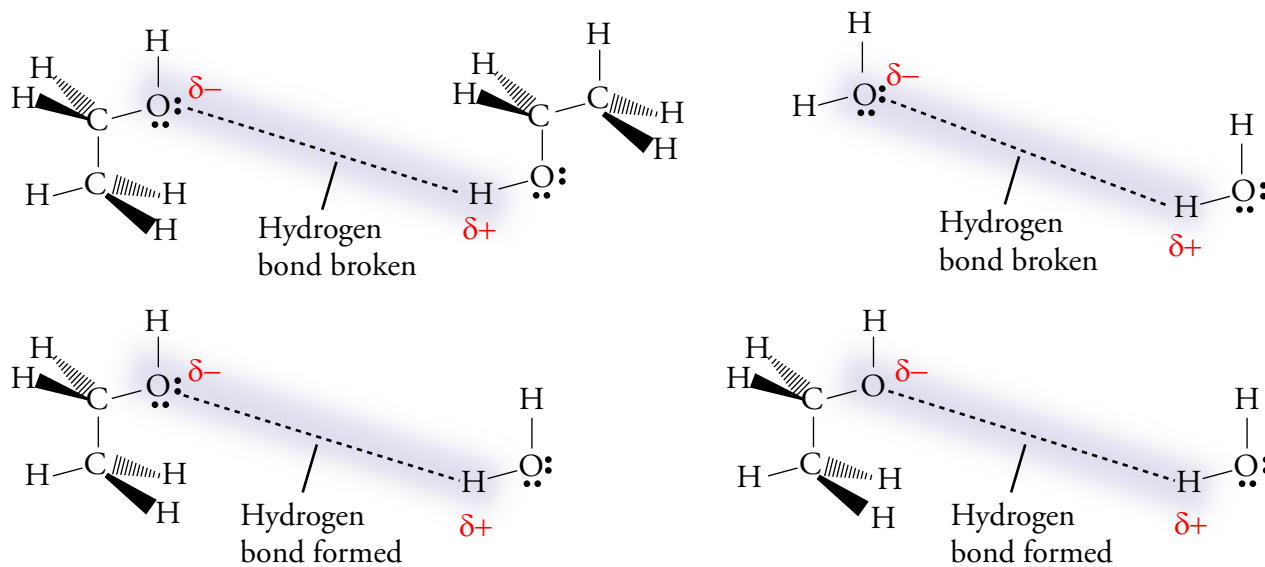
OBJECTIVE 4   Picture a layer of ethanol being carefully added to the top of some water (Figure 15.3). Because the particles of a liquid are moving constantly, some of the ethanol particles at the boundary between the two liquids will immediately move into the water, and some of the water molecules will move into the ethanol. In this process, water-water and ethanol-ethanol attractions are broken and ethanol-water attractions are formed. Because both the ethanol and the water are molecular substances with O−H bonds, the attractions broken between water molecules and the attractions broken between ethanol molecules are hydrogen bonds. The attractions that form between the ethanol and water molecules are also hydrogen bonds (Figure 15.4).

Because the attractions between the particles are so similar, the freedom of movement of the ethanol molecules in the water solution is about the same as their freedom of movement in the pure ethanol. The same can be said for the water. Because of this freedom of movement, both liquids will spread out to fill the total volume of the combined liquids. In this way, they will shift to the most probable, most dispersed state available, the state of being completely mixed. There are many more possible arrangements for this system when the ethanol and water molecules are dispersed throughout a solution than when they are restricted to separate layers. (Figure 15.3).

At the instant ethanol and water are mixed, the ethanol floats on top of the water.

Hydrogen bonds between ethanol molecules.

Because the attractions between their molecules are similar, the molecules mix freely, allowing each substance to disperse into the other.

Hydrogen bonds between water molecules

Hydrogen bonds between ethanol and water molecules

Ethanol and water mix

OBJECTIVE 4

Figure 15.3
Ethanol and Water Mixing

Hydrogen bond broken

Hydrogen bond broken

Hydrogen bond formed

Hydrogen bond formed

OBJECTIVE 4

Figure 15.4
The Attractions Broken and Formed When Ethanol Dissolves in Water

You will find an animation that illustrates the solution of ethanol in water at the textbook's Web site.

We can now explain why automobile radiator coolants dissolve in water. The coolants typically contain either ethylene glycol or propylene glycol, which, like ethanol and water, contain hydrogen-bonding O−H bonds.

Why do coolant and water mix?

ethylene glycol   propylene glycol
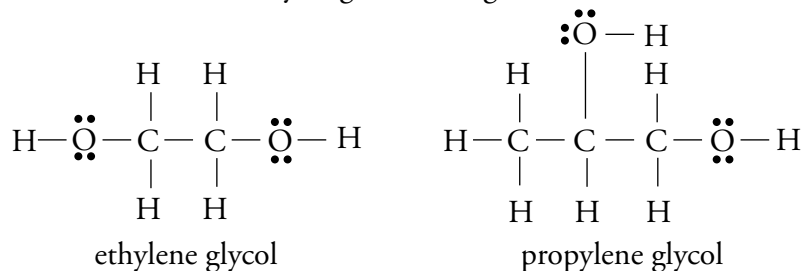
These substances mix easily with water for the same reason that ethanol mixes easily with water. The attractions broken on mixing are hydrogen bonds, and the attractions formed are also hydrogen bonds. There is no reason why the particles of each liquid cannot move somewhat freely from one liquid to another, and so they shift toward the most probable (most dispersed), mixed state.

Predicting Solubility

OBJECTIVE 5

The dividing line between what we call soluble and what we call insoluble is arbitrary, but the following are common criteria for describing substances as insoluble, soluble, or moderately soluble.

- If less than 1 gram of the substance will dissolve in 100 milliliters (or 100 g) of solvent, the substance is considered insoluble.
- If more than 10 grams of substance will dissolve in 100 milliliters (or 100 g) of solvent, the substance is considered soluble.
- If between 1 and 10 grams of a substance will dissolve in 100 milliliters (or 100 g) of solvent, the substance is considered moderately soluble.

Although it is difficult to determine specific solubilities without either finding them by experiment or referring to a table of solubilities, we do have guidelines that allow us to predict relative solubilities. Principal among these is

Like dissolves like.

For example, this guideline could be used to predict that ethanol, which is composed of *polar* molecules, would be soluble in water, which is also composed of *polar* molecules. Likewise, pentane (C_5H_{12}), which has *nonpolar* molecules, is miscible with hexane, which also has *nonpolar* molecules. We will use the *Like Dissolves Like* guideline to predict whether a substance is likely to be more soluble in water or in hexane. It can also be used to predict which of two substances is likely to be more soluble in water and which of two substances is likely to be more soluble in a nonpolar solvent, such as hexane:

OBJECTIVE 6
OBJECTIVE 7
OBJECTIVE 8

- Polar substances are likely to dissolve in polar solvents. For example, ionic compounds, which are very polar, are often soluble in the polar solvent water.
- Nonpolar substances are likely to dissolve in nonpolar solvents. For example, nonpolar molecular substances are likely to dissolve in hexane, a common nonpolar solvent.

Two additional guidelines are derived from these:

■ Nonpolar substances are not likely to dissolve to a significant degree in polar solvents. For example, nonpolar molecular substances, such as hydrocarbons, are likely to be insoluble in water.

■ Polar substances are not likely to dissolve to a significant degree in nonpolar solvents. For example, ionic compounds are insoluble in hexane.

It is more difficult to predict the solubility of polar molecular substances than to predict the solubility of ionic compounds and nonpolar molecular substances. Many polar molecular substances are soluble in both water and hexane. For example, ethanol is miscible with both water and hexane. The following generalization is helpful:

■ Substances composed of small polar molecules, such as acetone and ethanol, are usually soluble in water. (They are also often soluble in hexane.)
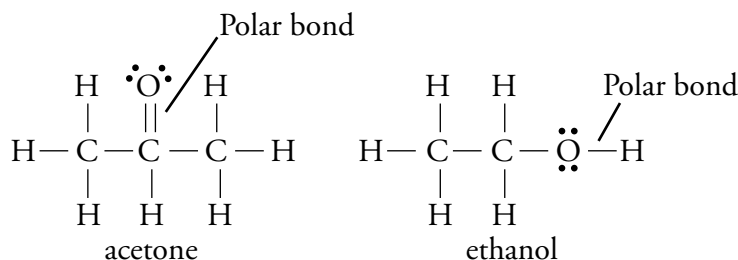
As the alcohol concentration of wine increases, the solvent's polarity decreases, and ionic compounds in the wine begin to precipitate.

The guidelines we have discussed are summarized in Table 15.1.

Table 15.1
Summary of Solubility Guidelines

| Type of substance	Soluble in water?	Soluble in hexane?
Ionic compounds	Often	No
Molecular compounds with nonpolar molecules	No	Yes
Molecular compounds with small polar molecules	Usually	Often

EXAMPLE 15.1 - Predicting Water Solubility

OBJECTIVE 6

Predict whether each compound is soluble in water or not.

   a. nickel(II) chloride, $NiCl_2$ (used in nickel plating)
   b. 2-propanol (isopropyl alcohol), $CH_3CH(OH)CH_3$ (in rubbing alcohol)
   c. 1-pentene, $CH_2CHCH_2CH_2CH_3$ (blending agent for high octane fuels)
   d. The nonpolar molecular compound carbon disulfide, CS_2 (used to make rayon and cellophane)
   e. The polar molecular compound propionic acid, $CH_3CH_2CO_2H$ (in the ionized form of propionate, acts as a mold inhibitor in bread)

Solution

   a. Although there are many exceptions, we expect ionic compounds, such as nickel(II) chloride, $NiCl_2$, to be **soluble in water**.
   b. Like all alcohols, 2-propanol, $CH_3CH(OH)CH_3$, is a polar molecular compound. Because this substance has relatively small polar molecules, we expect it to be **soluble in water**.
   c. Like all hydrocarbons, 1-pentene, $CH_2CHCH_2CH_2CH_3$, is a nonpolar molecular compound and therefore **insoluble in water**.
   d. We expect carbon disulfide, CS_2, like all nonpolar molecular compounds, to be **insoluble in water**.

$$\ddot{\underset{..}{S}}=C=\ddot{\underset{..}{S}}$$

   e. We expect polar molecular compounds with relatively small molecules, such as propionic acid, $CH_3CH_2CO_2H$, to be **soluble in water**.
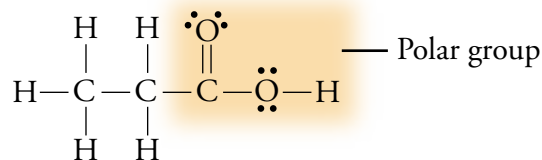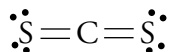
EXERCISE 15.1 - Predicting Water Solubility

OBJECTIVE 6

Predict whether each is soluble in water or not. (See Section 14.3 if you need to review the list of compounds that you are expected to recognize as composed of either polar or nonpolar molecules.)

   a. sodium fluoride, NaF (used to fluoridate water)
   b. acetic acid, CH_3CO_2H (added to foods for tartness)
   c. acetylene, C_2H_2 (used for welding and cutting torches)
   d. methanol, CH_3OH (a common solvent)

EXAMPLE 15.2 - Predicting Solubility in Hexane

Predict whether each is soluble in hexane, C_6H_{14}, or not.

   a. ethane, C_2H_6 (in natural gas)
   b. potassium sulfide (in depilatory preparations used for removing hair chemically)

Solution

a. Ethane, C_2H_6, like all hydrocarbons, is a nonpolar molecular compound, which are expected to be **soluble in hexane**.
b. Potassium sulfide, K_2S, is an ionic compound and therefore is expected to be **insoluble in hexane**.

EXERCISE 15.2 - Predicting Solubility in Hexane

Predict whether each is soluble in hexane, C_6H_{14}, or not.

   a. sodium perchlorate, $NaClO_4$ (used to make explosives)
   b. propylene, CH_3CHCH_2 (used to make polypropylene plastic for children's toys)

EXAMPLE 15.3 - Predicting Relative Solubility in Water and Hexane

Predict whether each is more soluble in water or hexane.

   a. pentane, C_5H_{12} (used in low temperature thermometers)
   b. strontium nitrate, $Sr(NO_3)_2$ (used in railroad flares)

Solution

a. Pentane, C_3H_8, like all hydrocarbons, is a nonpolar molecular compound that is expected to be **more soluble in hexane** than in water.
b. Strontium nitrate is an ionic compound, which is expected to be **more soluble in water** than hexane.

EXERCISE 15.3 - Predicting Relative Solubility in Water and Hexane

Predict whether each is more soluble in water or hexane.

   a. sodium iodate, $NaIO_3$ (used as a disinfectant)
   b. 2,2,4-trimethylpentane (sometimes called isooctane), $(CH_3)_3CCH_2CH(CH_3)_2$ (used as a standard in the octane rating of gasoline)

Hydrophobic and Hydrophilic Substances

OBJECTIVE 9

Organic compounds are often polar in one part of their structure and nonpolar in another part. The polar section, which is attracted to water, is called **hydrophilic** (literally, "water loving"), and the nonpolar part of the molecule, which is not expected to be attracted to water, is called **hydrophobic** ("water fearing"). If we need to predict the relative water solubility of two similar molecules, we can expect the one with the proportionally larger polar portion to have higher water solubility. We predict that the molecule with the proportionally larger nonpolar portion will be less soluble in water.

As an example, we can compare the structures of epinephrine (adrenaline) and amphetamine. Epinephrine is a natural stimulant that is released in the body in times of stress. Amphetamine (sold under the trade name Benzedrine) is an artificial stimulant that causes many of the same effects as epinephrine. The three −OH groups and the N−H bond in the epinephrine structure cause a greater percentage of that molecule to be polar, so we predict that epinephrine would be more soluble in water than amphetamine (Figure 15.5).

Figure 15.5
Molecular Line Drawings of Amphetamine and Epinephrine

amphetamine   epinephrine
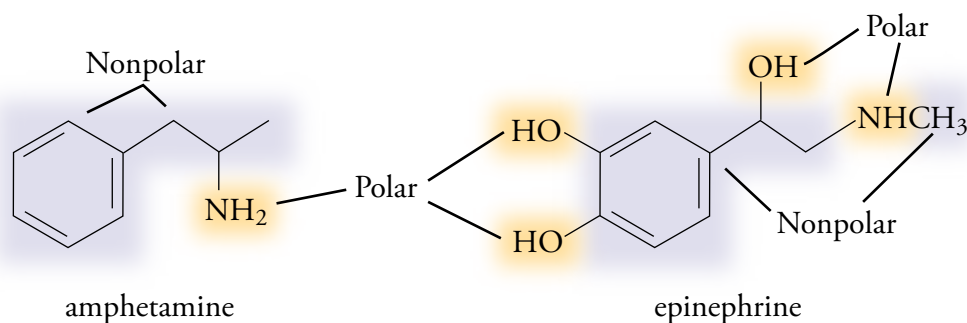
The molecular representations in Figure 15.5 are known as *line drawings*. The corners, where two lines meet, represent carbon atoms, and the end of any line that does not have a symbol attached also represents a carbon atom. We assume that each carbon has enough hydrogen atoms attached to yield four bonds total. Compare the line drawings in Figure 15.5 to the more complete Lewis structures in Figure 15.6.

Figure 15.6
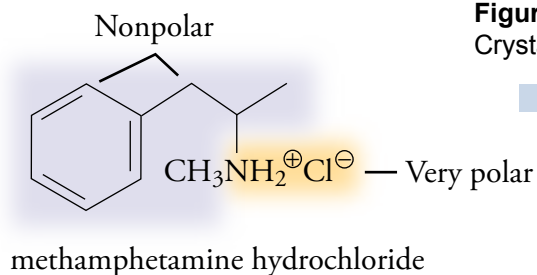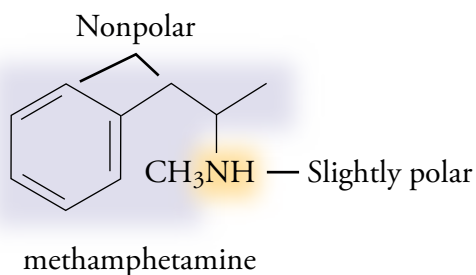Detailed Molecular Structures of Amphetamine and Epinephrine

OBJECTIVE 10
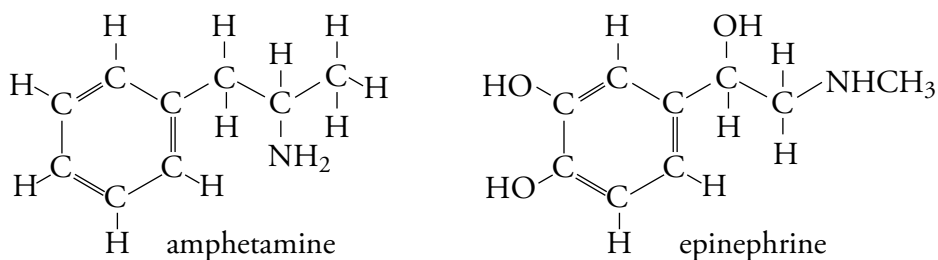
amphetamine   epinephrine

The difference in polarity between epinephrine and amphetamine has an important physiological consequence. The cell membranes that separate the blood stream from the inside of brain cells have a nonpolar interior and a polar exterior that tend to slow down the movement of polar substances in the blood into the brain tissue. Epinephrine is too polar to move quickly from the blood stream into the brain, but amphetamine is not. The rapid stimulant effects of amphetamine are in part due to its ability to pass

OBJECTIVE 11

more quickly through the blood brain barrier.

Methamphetamine is a stimulant that closely resembles amphetamine. With only

one polar N−H bond, it has very low water solubility, but it can be induced to dissolve in water when converted to the much more polar, ionic form called methamphetamine hydrochloride. On the street, the solid form of this illicit ionic compound is known as *crystal meth* (Figure 15.7).
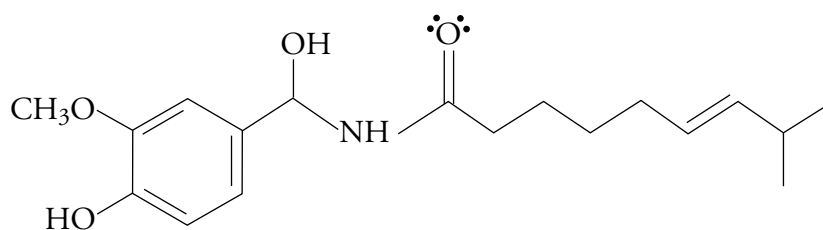
Nonpolar

Nonpolar

Figure 15.7
Crystal Meth

OBJECTIVE 11

CH_3NH — Slightly polar

$CH_3NH_2^{\oplus}Cl^{\ominus}$ — Very polar

methamphetamine

methamphetamine hydrochloride

If you get a bite of a spicy dish that has too much chili pepper, do you grab for a glass of water or a spoonful of sour cream to put out the flames? Capsaicin molecules, which are largely responsible for making green and red chili peppers hot, are mostly nonpolar. Therefore, the oil in the sour cream will more efficiently dissolve them, diluting them enough to minimize their effects. Because capsaicin is not water-soluble, the glass of water doesn't help much.

Chilis Drying in Rajasthan, India

EXAMPLE 15.4 - Predicting Relative Solubility in Water

OBJECTIVE 9

Butanoic acid is a foul smelling substance that contributes to body odor; however, it reacts with various alcohols to form esters that have very pleasant odors and that are often used in flavorings and perfumes. Stearic acid is a natural fatty acid that can be derived from beef fat. Which compound would you expect to be more soluble in water?

stearic acid
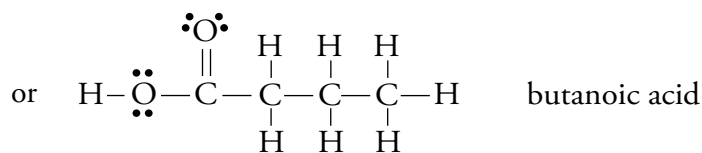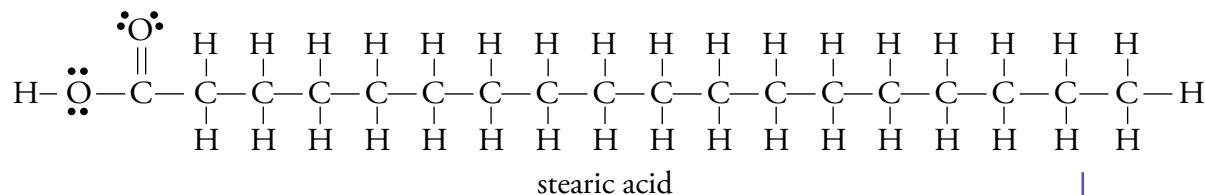
or   butanoic acid

Solution

Butanoic acid has a proportionally larger polar portion and is therefore **more soluble in water** than stearic acid is. In fact, butanoic acid is miscible with water (will mix with it in any proportion). The much higher proportion of the stearic acid structure that is nonpolar makes it almost insoluble in water.

EXERCISE 15.4 - Predicting Relative Solubility in Water

The compound to the left below, 2-methyl-2-propanol, often called t-butyl alcohol, is an octane booster for unleaded gasoline. The other compound, menthol, affects the cold receptors on the tongue so as to produce a "cool" taste when added to foods and medicines. Which of these two compounds would you expect to be more soluble in water?
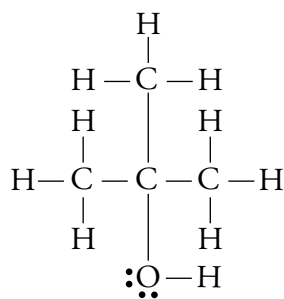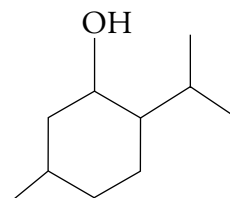
2-methyl-2-propanol   menthol

15.2 Fates, Oils, Soaps, and Detergents

Our understanding of solubility can be used to explain why soap and detergent help clean greasy dishes and oily clothes. As always, the properties of substances are a consequence of their chemical structures, so let's take a look at those structures.

Soap can be made from animal fats and vegetable oils, which in turn are composed of triacylglycerols, or triglycerides. (Although biochemists prefer the term *triacylglycerol*, we will use the more common term *triglyceride* for these compounds.) These are molecules that consist of long-chain hydrocarbon groups attached to a three-carbon backbone (Figure 15.8). In the general triglyceride structure shown below, R_1, R_2, and R_3 represent the hydrocarbon groups (groups that contain only carbon and hydrogen atoms).

Figure 15.8
Triglycerides
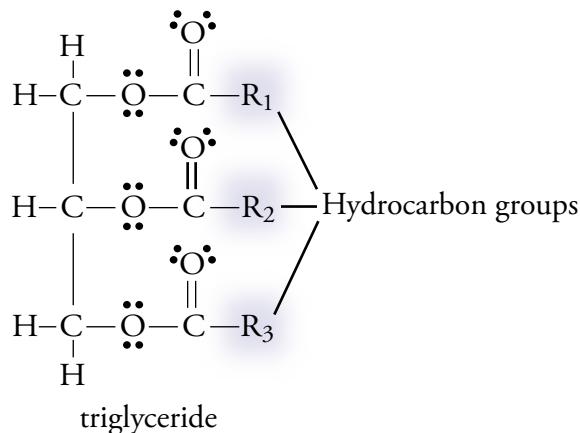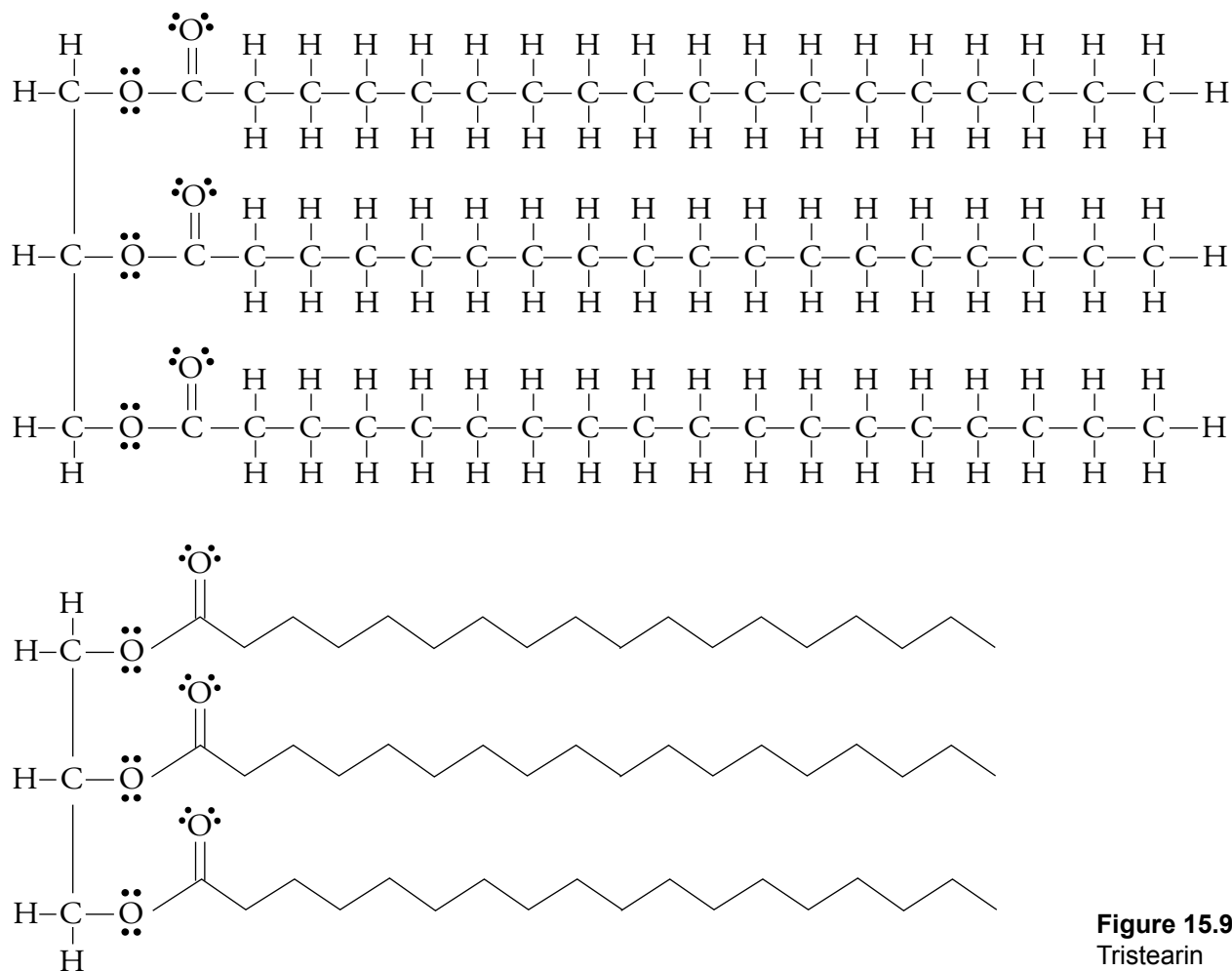The marbling in a steak is composed of triglycerides.

triglyceride

Photo Courtesy of Bill Schutz

An example of a triglyceride is tristearin, a typical fat molecule found in beef fat. The Lewis structure and line drawing for tristearin are shown in Figure 15.9.

Figure 15.9
Tristearin

Most triglyceride molecules differ from tristearin in that three different hydrocarbon groups are attached to the carbon backbone. (In tristearin, those three hydrocarbon groups are all alike.) The hydrocarbon groups can differ in the length of the carbon chain and in the number of double bonds between carbon atoms. A higher number of carbon-carbon double bonds in its molecules causes a triglyceride to be liquid at room temperature. The triglycerides in vegetable oils, for example, have enough carbon-carbon double bonds to remain liquid (Figure 15.10). The triglycerides in animal fats have fewer carbon-carbon double bonds and tend to form a solid.
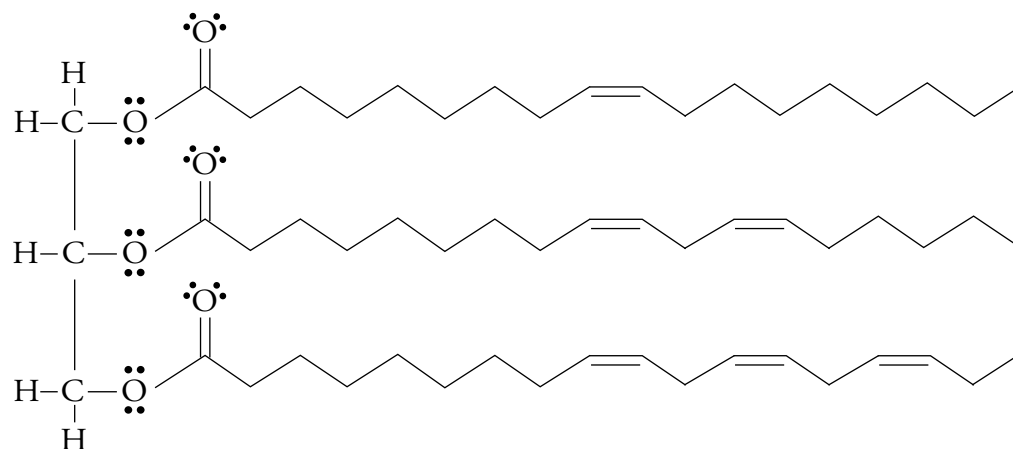
OBJECTIVE 12

Figure 15.10
Typical Liquid Triglyceride
Liquid triglycerides are rich in carbon-carbon double bonds.

OBJECTIVE 14

OBJECTIVE 13

A soap is an ionic compound composed of a cation (usually sodium or potassium) and an anion with the general form RCO_2^-, in which R represents a long chain hydrocarbon group. Because the hydrocarbon chains in fats and oils differ, soaps are mixtures of various similar structures (Figure 15.11). They are produced in the reaction of triglyceride and sodium hydroxide, with glycerol as a byproduct. Old fashioned lye soap was made by heating fats and oils, collected from cooking, with lye, which is sodium hydroxide.

Figure 15.11
Formation of Soap

triglyceride in fat or oil

3NaOH

glycerol   soap
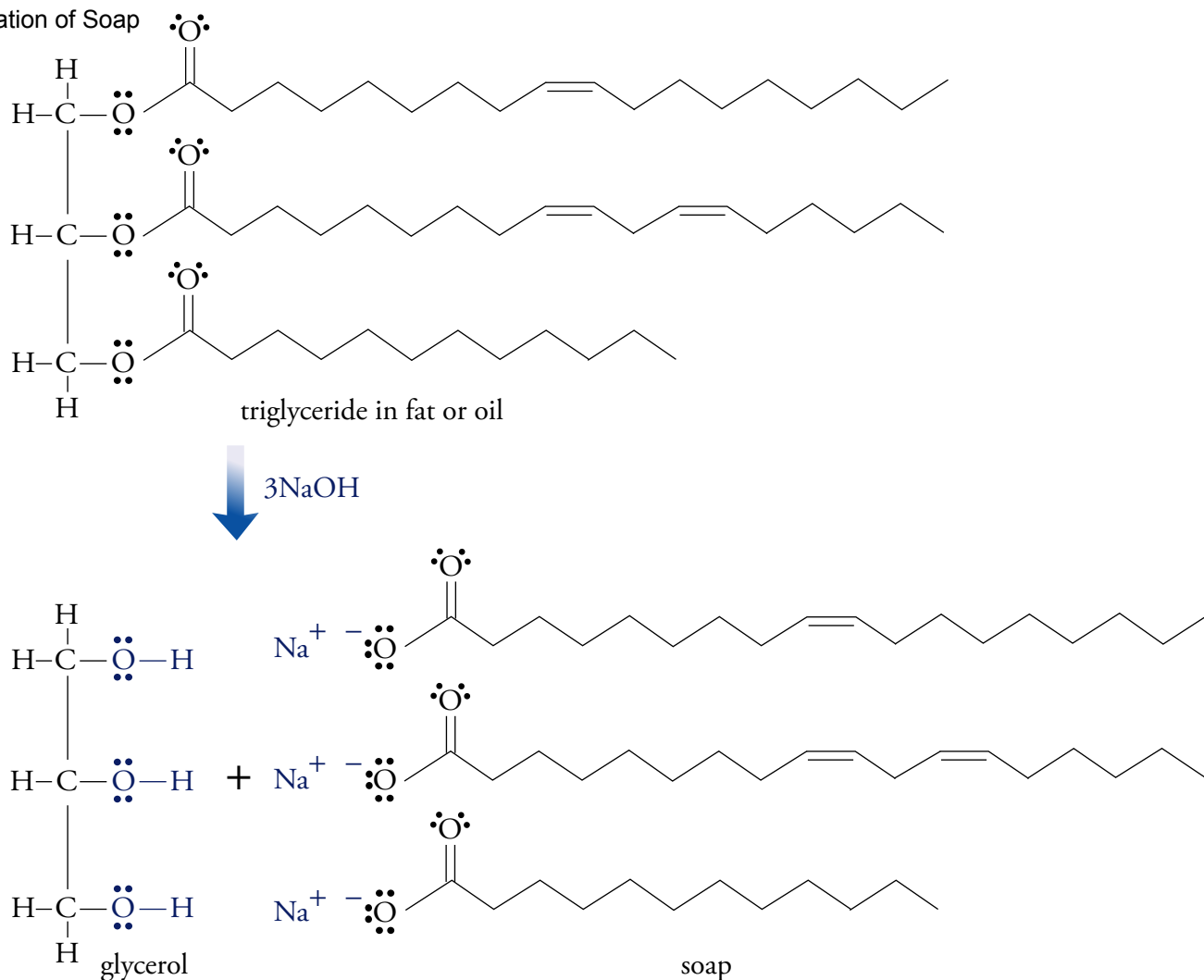
OBJECTIVE 14

The hydrophobic, nonpolar hydrocarbon portion of each soap anion does not mix easily with water, but the hydrophilic, negatively charged end of each anion does form attractions to water molecules, and these attractions are strong enough to keep the anion in solution.

OBJECTIVE 15

Now let's picture the events taking place at the molecular level in a tub of soapy water and greasy dishes. To clean a greasy dish, we first scrub its surface and agitate the water to break up the grease into smaller droplets, but without soap (or detergent) in the water, the oil droplets would quickly regroup and return to the dish's surface. If soap anions are in the solution, however, the agitation helps their nonpolar hydrocarbon ends to enter the nonpolar triglyceride droplets, while their anionic ends remain sticking out into the water. Soon every drop of fat or oil is surrounded by an outer coating of soap.

When two droplets approach each other, the negative ends of the soap anions cause the droplets to repel each other, preventing the triglyceride droplets from recombining and redepositing on the object being cleaned (Figure 15.12). The droplets stay suspended in the solution and are washed down the drain with the dishwater (Figure 15.13).

Hydrophobic ends of soap or detergent enter droplet.

Hydrophilic ends of soap or detergent stick out into the water.

Coated with negative charges, droplets repel each other.

OBJECTIVE 15

Figure 15.12
Oil Droplets and Soaps or Detergents

Oil

Agitation

Oil breaks into droplets.

Without soap or detergent, droplets recombine.

Soap or detergent anions keep droplets suspended.

OBJECTIVE 15

Figure 15.13
Cleaning Greasy Dishes
Why do soaps and detergents help clean grease away?

For soap to work, its anions must stay in solution. Unfortunately, they tend to precipitate from solution when the water is "hard." Hard water is water that contains dissolved calcium ions, Ca^{2+}, magnesium ions, Mg^{2+}, and often iron ions, Fe^{2+} or Fe^{3+}. These ions bind strongly to soap anions, causing the soap to precipitate from hard water solutions.

OBJECTIVE 16

Detergents have been developed to avoid this problem of soap in hard water. Their structures are similar to (although more varied than) that of soap, but they are less likely to form insoluble compounds with hard water ions. Some detergents are ionic like soap, and some are molecular. For example, in sodium dodecyl sulfate (SDS), a typical ionic detergent, the $-CO_2^-$ portion of the conventional soap structure is replaced by an $-OSO_3^-$ group, which is less likely to link with hard water cations and precipitate from the solution:

OBJECTIVE 17

SDS, a typical ionic detergent
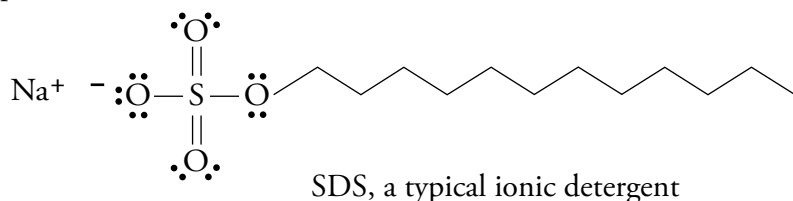
15.3 Saturated Solutions and Dynamic Equilibrium

Why is there a limit to the amount of salt that will dissolve in water? Why does it take longer for a sugar cube to dissolve than for the same amount of granular sugar, and why can you speed things up by stirring? Why does sugar dissolve so much faster in hot coffee than in iced tea? To answer these questions, we need to know more about the rate at which solutes go into solution and the rate at which they return to the undissolved form.

Two Opposing Rates of Change

When a solid is added to a liquid, a competition begins between two opposing rates of change. On the one hand, particles leave the surface of the solid and move into solution, and on the other hand, particles leave the solution and return to the solid form.
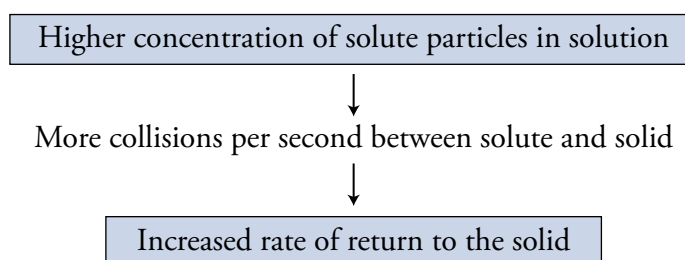
OBJECTIVE 18

To examine these changes at the molecular or ionic level, let's picture what happens when table salt dissolves in water. (You might want to review Section 4.2, which describes this process in detail.) Imagine the NaCl solid sitting on the bottom of the container. The sodium and chloride ions at the solid's surface are constantly moving out into the water and then being pulled back by their attractions to the other ions still on the surface of the solid. Sometimes when an ion moves out into the water, a water molecule collides with it and pushes it farther out into the solution. Other water molecules move into the gap between the ion and the solid and shield the ion from being recaptured by the solid (Figure 4.2). The ion, now in solution, is kept stable by attractions between its charge and the charges of the polar water molecules that surround it. If the ion is a cation, it is surrounded by the negative oxygen atoms of the water molecules; if it is an anion, it is surrounded by their positive hydrogen ends.

OBJECTIVE 18

OBJECTIVE 19

Once the ions dissolve, they travel throughout the solution like any other particle in a liquid. Eventually they collide with the surface of the remaining solid. When this happens, they are recaptured by the attractions that hold the particles of the solid together, and they are likely to return to the solid form. One of the most important factors that determine the rate at which solute particles return to solid form is the concentration of the solute in the solution. The more particles of solute per liter of solution, the more collisions between solute particles and the solid. A higher rate of collisions results in a greater rate of return of solute particles from the solution to the solid (Figures 15.14 and 15.15).

Figure 15.14
Solute Concentration and Rate of Return to Solid Form

OBJECTIVE 19

Higher concentration of solute particles in solution

↓

More collisions per second between solute and solid

↓

Increased rate of return to the solid

The concentration of solute in the solution is low, so the rate of return is low.

The concentration of solute in the solution is higher, so the rate of return is higher.
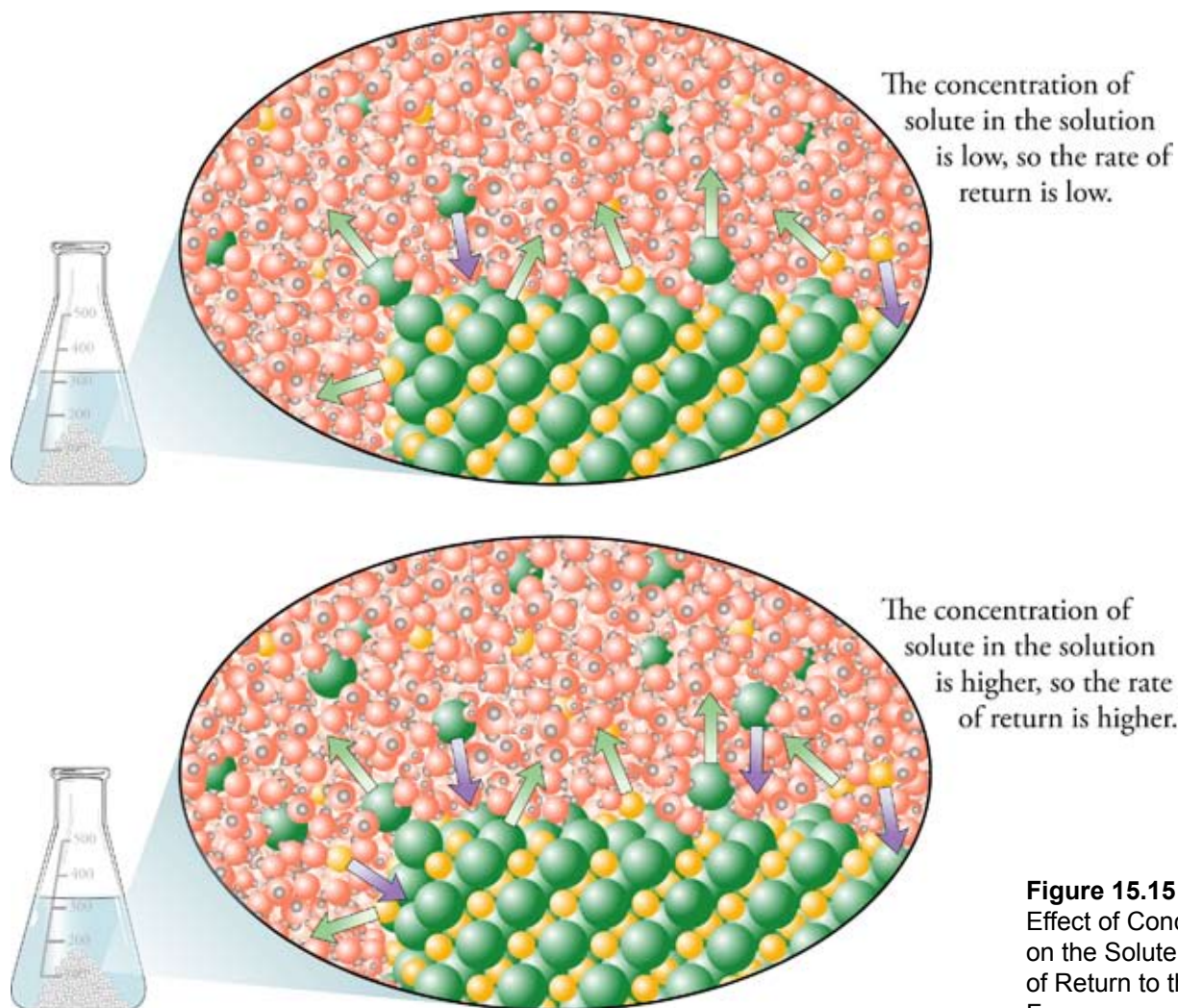
Figure 15.15
Effect of Concentration on the Solute's Rate of Return to the Solid Form

Net Rate of Solution

When a solid is first added to a liquid, there are more particles leaving its surface and moving into solution than there are particles returning from the solution to the solid form. As long as the rate of solution is greater than the rate of return, there will be a net shift of particles into solution.

The net rate of change in the number of particles in solution is equal to the number of particles that move from solid to solution per second minus the number of solute particles that return to the solid per second. This net rate of solution depends on three factors:

OBJECTIVE 20

OBJECTIVE 21

- ■ Surface area of the solute

- ■ Degree of agitation or stirring

- ■ Temperature

To understand why surface area affects the rate of solution, picture a lump of sugar added to water. There are a certain number of particles at the surface of the sugar cube, and these are the only particles that have a possibility of escaping into the solution. The particles in the center of the cube cannot dissolve until the particles between
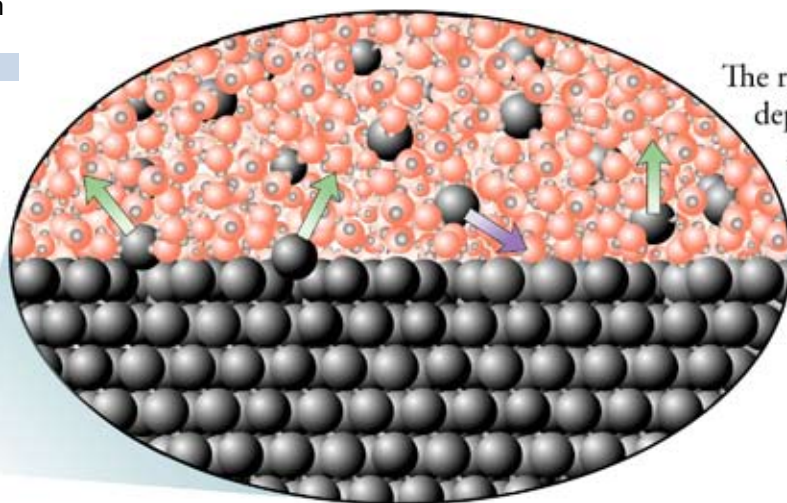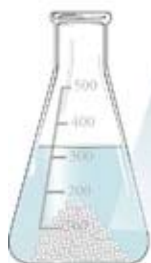
OBJECTIVE 22

Why does powdered sugar dissolve faster than granular sugar?

them and the surface have escaped. If the sugar cube is split in half, however, and the two halves are separated, two new surfaces are exposed. Some particles that used to be in the center of the cube, and unable to escape, are now at the surface and can dissolve. The cutting of the cube has therefore increased the rate of solution (Figure 15.16). When bakers want to dissolve sugar, they do not want to wait too long, so they add very finely powdered sugar. This sugar dissolves much more rapidly than granular sugar or sugar cubes, because it has a much greater total surface area.

Figure 15.16
Surface Area and
Rate of Solution

OBJECTIVE 22

The rate of solution depends on the number of particles at the solid's surface.
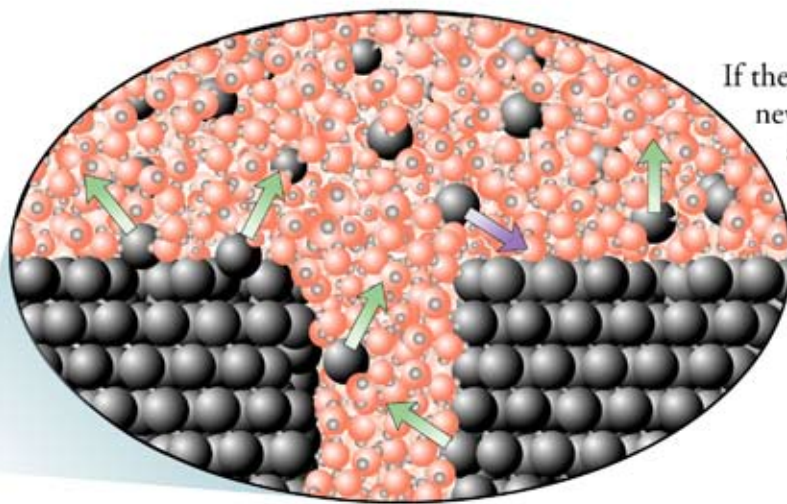
If the solid is fragmented, new surfaces are exposed, allowing more particles to escape into solution.

OBJECTIVE 23   Near the solid, close to where particles are leaving the solid surface and entering solution, the concentrations of dissolved solute are higher than in more remote parts of the liquid. As we observed earlier, a higher concentration of solute leads to a higher rate of return to the solid form. This higher rate of return leads to a lower overall net rate

of solution. However, if we stir or in some way agitate the solution, the solute particles near the solid are quickly carried away, and the relatively high local concentrations of solute are decreased. This diminishes the rate of return and increases the net rate of solution, which explains why stirring your coffee dissolves the sugar in the coffee more rapidly (Figures 15.17 and 15.18).
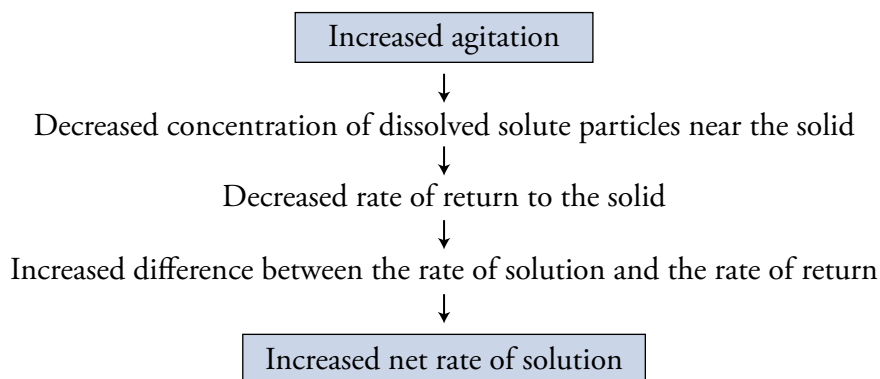
Figure 15.17
Agitation and Rate of Solution

OBJECTIVE 23

| Increased agitation |
↓
Decreased concentration of dissolved solute particles near the solid
↓
Decreased rate of return to the solid
↓
Increased difference between the rate of solution and the rate of return
↓
| Increased net rate of solution |

Figure 15.18
Agitation and Rate of Solution

Without stirring

More particles near the solid leads to a higher rate of return.

Lower net rate of solution

OBJECTIVE 23

With stirring

Fewer particles near the solid leads to a lower rate of return.

Higher net rate of solution

Finally, increasing the temperature of the system increases the average velocity of the solute and solvent particles. More rapidly moving particles in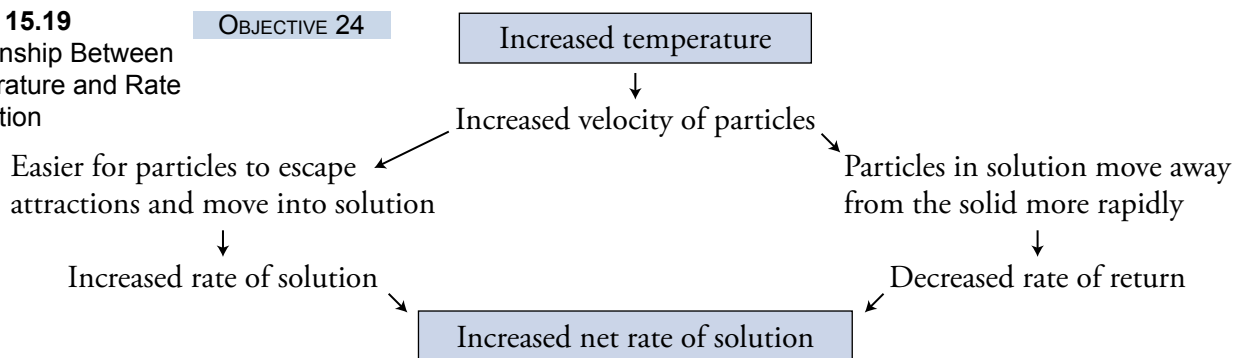 the solid escape more easily into the solution, increasing the rate of solution. Increased temperature also leads to a situation that is similar to agitation. The higher-velocity solute particles move away from the surface of the solid more quickly, minimizing the concentration of dissolved solute in the solid's vicinity (Figure 15.19). This decreases the rate of return of particles to the solid, increasing the net rate of solution, which explains why hot coffee will dissolve sugar more rapidly than cold iced tea.

Figure 15.19
Relationship Between Temperature and Rate of Solution

OBJECTIVE 24

Increased temperature
↓
Increased velocity of particles

Easier for particles to escape attractions and move into solution
↓
Increased rate of solution

Particles in solution move away from the solid more rapidly
↓
Decreased rate of return

Increased net rate of solution

Saturated Solutions

If you keep adding sugar to your coffee, eventually you reach a point where the maximum amount has dissolved, and adding more sugar leaves solid sugar on the bottom of the cup. At this point, you have reached the solubility limit of sugar in your coffee solution. Let's try to visualize what this means at the molecular level.
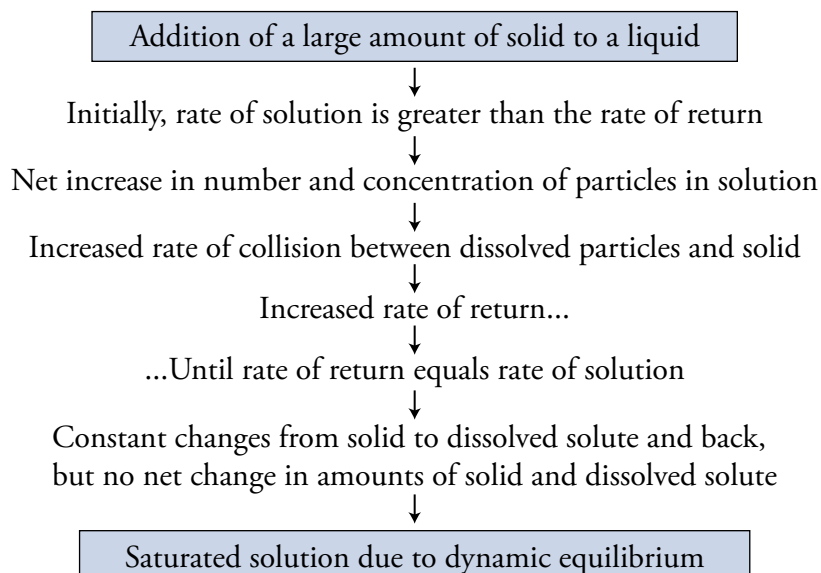
OBJECTIVE 25

If the surface area, temperature, and degree of agitation remain essentially the same, the rate at which the particles move into the solution remains close to constant. Meanwhile, the rate at which the particles return to the solid will depend on the concentration of solute particles in solution. As long as the rate of solution is greater than the rate of return, there will be a net movement of particles into solution, but as the concentration of dissolved solute increases, the rate of return will increase as well.

If there is enough solid in the solution, the rate of return will eventually become equal to the rate of solution, and the system will reach a dynamic equilibrium. (If too little solid has been added, it will all dissolve before equilibrium is reached.) At that point, for every particle that leaves the solid and moves into solution, a particle somewhere else in the system is returning from the dissolved to the solid form. There is a constant movement of particles from the solid to the dissolved state and back again, but there is no net change in the amounts of solid and solute in the system. The solution has reached its solubility limit. When enough solute has been added to the solution to reach that limit, we call the solution **saturated**. (Figures 15.20 and 15.21). Table 15.2 lists water solubilities of some common substances. If a solution has less solute dissolved than is predicted by the solubility limit, it is **unsaturated**.

OBJECTIVE 26

A saturated solution need not be accompanied by excess solid in its container, although if it does, there will be a dynamic equilibrium between the rate of solution and the rate of return. A saturated solution without excess solid can be made by first adding solid to a solvent until no more will dissolve, and then filtering out the excess solid.

Addition of a large amount of solid to a liquid

↓

Initially, rate of solution is greater than the rate of return

↓

Net increase in number and concentration of particles in solution

↓

Increased rate of collision between dissolved particles and solid

↓

Increased rate of return...

↓

...Until rate of return equals rate of solution

↓

Constant changes from solid to dissolved solute and back,
but no net change in amounts of solid and dissolved solute

↓

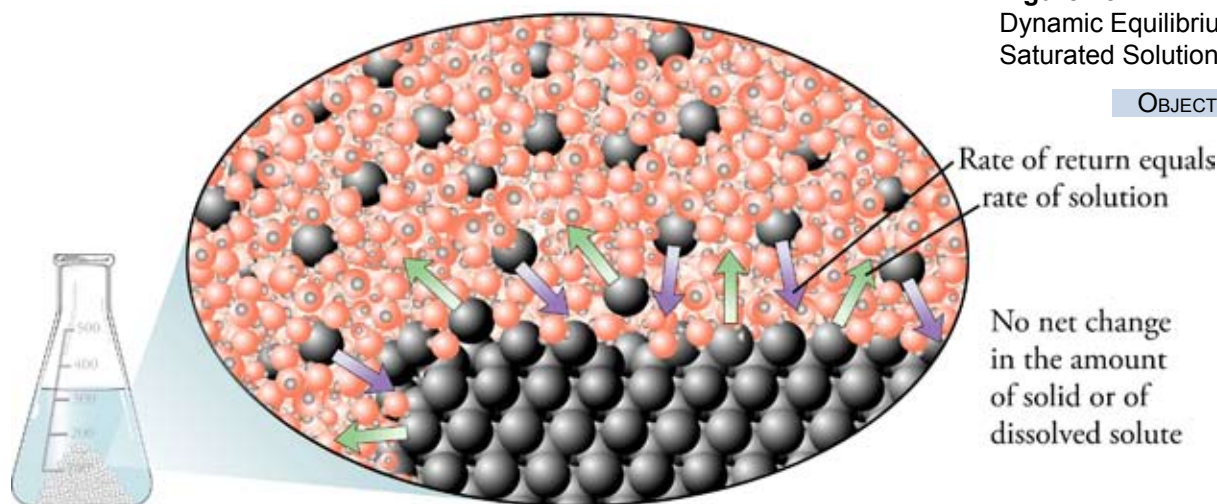Saturated solution due to dynamic equilibrium

Figure 15.20
Dynamic Equilibrium and
Saturated Solutions

OBJECTIVE 25

You can visit
the textbook's
Web site to see
a description of
supersaturated
solutions and how
they are made.

Figure 15.21
Dynamic Equilibrium and
Saturated Solutions

OBJECTIVE 26

Rate of return equals
rate of solution

No net change
in the amount
of solid or of
dissolved solute

Table 15.2 Water Solubilities of Common Substances at Room Temperature

Substance	Approximate Solubility at Room Temperature (g substance/100 mL H$_2$O)
Ethanol, C_2H_5OH (in alcoholic beverages)	Miscible (infinite)
Acetic acid, $HC_2H_3O_2$ (in vinegar)	Miscible (infinite)
Sucrose, $C_{12}H_{22}O_{11}$ (white table sugar)	200
Hydrogen chloride, HCl	69
Sodium chloride, NaCl (table salt)	36
Carbon dioxide, CO_2	0.17
Methane, CH_4	0.0069
Oxygen, O_2	0.0045
Calcium carbonate, $CaCO_3$ (in limestone)	0.0014

15.4 Solutions of Gases in Liquids

Why do scuba divers get drowsy and disoriented when they dive too deeply? Why do divers get the bends if they rush to the surface too quickly? Why is moving to the surface too quickly like opening a soft drink can? As we study the properties of solutions of gases in liquids, we will discover the answers to these questions.

Imagine a system consisting of a gas above a liquid in a closed container (Figure 15.22). The gas particles move rapidly, colliding with each other, with the walls of their container, and with the surface of the liquid. When such a particle collides with the liquid surface, its momentum takes it into the liquid at least a short way, and it forms attractions to the liquid particles. As this happens, the gas becomes a solute in the liquid.

The dissolved gas particle moves throughout the liquid like any other particle in the liquid. It eventually makes its way back to the surface, and if it has enough energy to break the attractions that hold it in the liquid form, it can escape from the surface back into the gas phase above the liquid. Therefore, in a system with a gas above a liquid, there are two opposing rates of change: the rate of solution and the rate of escape.

Gas Solubility

The gas's rate of solution is dependent on the number of collisions with the surface of the liquid per second. The gas's rate of escape is dependent on the number of solute particles at the surface, on the strengths of attractions between the gas and liquid particles, and on the temperature of the system. The overall solubility of the gas in the liquid is dependent on the relative rates of solution and escape.

Objective 27   Let's take a closer look at the changes that take place in this system. At the instant that a gas is placed over a pure liquid in a closed container, there are no particles of that gas in solution, so the rate of escape is zero. Immediately, however, the particles begin to collide with the surface of the liquid, so gas particles begin to move into solution right away. As long as the rate of solution is greater than the rate of escape, the concentration of dissolved gas particles will increase. This increase in solute concentration leads to an increase in the number of solute particles at the surface of the liquid and to an increase in the rate of escape. Eventually, a dynamic equilibrium will be reached where the rate of solution and the rate of escape are equal. At that point, there is no net change in the amount of gas above the liquid or in the concentration of dissolved gas in the solution. The solubility limit has been reached (Figures 15.22 and 15.23).
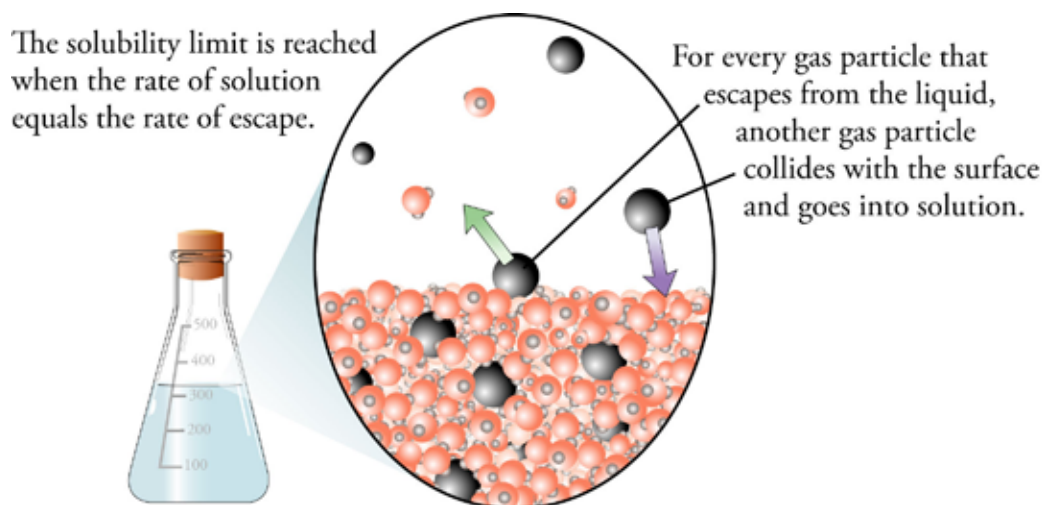
Figure 15.22
Dynamic Equilibrium for a Solution of a Gas in a Liquid

OBJECTIVE 27

The solubility limit is reached when the rate of solution equals the rate of escape.

For every gas particle that escapes from the liquid, another gas particle collides with the surface and goes into solution.

Figure 15.23
Gas Solubility

OBJECTIVE 27

Add a gas above a liquid in a closed container

Initially, the rate of solution is greater than the rate of escape → Net shift of particles into solution

Increased rate of escape... ← Increased concentration of dissolved gas

...Until the rate of escape equals rate of solution ⟶ Constant changes between dissolved and undissolved gas, but no net change in amount of either

Dynamic equilibrium (solubility limit)

Partial Pressure and Gas Solubility

If the partial pressure of a gas over a liquid is increased, the solubility of that gas is increased. To understand why, picture a system consisting of a gas above a liquid in a closed container. Assume that a dynamic equilibrium has formed between the rate of solution and the rate of escape. If more gas is pumped into the space above the liquid, the concentration of gas and therefore the partial pressure of the gas above the liquid increases. This leads to an increased rate of collision between the gas particles and the surface of the liquid and an increase in the rate of solution. At this stage, the rate of solution is greater than the rate of escape, and there is a net movement of particles into solution. Eventually, however, the concentration of solute in solution will be high enough to create a new dynamic equilibrium, with a higher rate of escape equal to the higher rate of solution. Figure 15.24 summarizes these events.

OBJECTIVE 28

Figure 15.24
Partial Pressure and Gas Solubility

Increased partial pressure of a gas over a liquid in a system initially at dynamic equilibrium (Rate of solution = Rate of escape)

Increased rate of collision between gas particles and liquid ⟶ Increased rate of solution

Net movement of gas particles into solution ← Rate of solution greater than rate of escape

Increased concentration of solute in solution ⟶ Increased rate of escape until it equals the higher rate of solution

Greater solubility

Gas Solubility and Breathing

When air is drawn into your lungs, it enters 300 million tiny air sacs called alveoli. Through the very thin, two-cell-width walls of the alveoli, an exchange of gases takes place between your blood and the inhaled air. The huge number of alveoli provide a very high surface area of about 60-80 m^2, which allows large amounts of gases to be

SPECIAL TOPIC 15.1 Gas Solubility, Scuba Diving, and Soft Drinks

When scuba divers descend into the ocean, the external pressure they experience is the sum of the atmospheric pressure on the top of the water and the pressure due to the weight of the water above them. Unless a diver is completely sealed in a diving capsule, the pressure of the air taken into the lungs is equal to this external pressure, which increases by one atmosphere, or 101 kPa, for each ten meters that the diver descends.

As the total pressure of the air taken into the lungs increases, the partial pressure of the oxygen in the air increases, and the concentration of the oxygen in the blood goes up. If too much oxygen is taken into the blood, the excess oxygen can begin to oxidize enzymes and other chemicals and cause damage to the nervous system. In the extreme, it can lead to coma and death. For this reason, deep sea divers commonly use mixtures of gases whose percentage of oxygen is lower than the amount in normal air.

There are other problems encountered by scuba divers as a result of the higher gas pressures of the air they breathe. The higher partial pressure of nitrogen that enters the lungs at greater depths leads to a higher concentration of nitrogen in the blood. This can cause a condition called nitrogen narcosis, or rapture of the deep. Its disorientation, drowsiness, and other symptoms similar to alcohol intoxication can lead to serious consequences.

As long as the diver remains deep below the surface, bubbles of significant size do not form, because the external pressure is greater than their potential pressure, but when the diver begins to rise, the situation changes. If the diver rises slowly, the gases in the blood are expelled from the lungs at a rapid enough rate to keep the potential pressure of the bubbles lower than the external pressure, and no bubbles form. If the diver rises too rapidly (perhaps because he has become disoriented by nitrogen narcosis), the gases do not leave the blood stream fast enough to keep the potential pressure of the bubbles below the diminishing external pressure. Bubbles then remain in the blood stream, blocking the smooth flow of blood through the smaller vessels.

Because this causes severe muscle and joint pain as well as more serious damage, it is called the *bends*.

One way of avoiding the bends is to substitute a less soluble gas such as helium for the nitrogen gas in the air tank. Less gas will enter the blood as a result, leading to lower potential pressures of gas bubbles and less likelihood of experiencing the bends.

The formation of bubbles when a soft drink bottle is opened is very similar to the formation of bubbles in the blood stream of someone with the bends. Soft drinks are bottled under about 4 atm of carbon dioxide, whereas the usual partial pressure of CO_2 in dry air is about 0.00035. The much higher CO_2 pressure in the soft drink container leads to a much higher solubility of CO_2 in the water solution in the can. The higher concentration of dissolved carbon dioxide leads in turn to a much higher potential pressure for the bubbles in the liquid. In the closed container, the 4 atm of pressure exerted on the liquid is enough to keep the bubbles from forming. When the soft drink container is opened, the external pressure immediately drops to about 1 atm, which is less than the potential pressure of the bubbles, and the bubbles form.

Why do bubbles form when a soft drink is opened, and how is this similar to the bubbles that form in a diver's blood if she goes to the surface too quickly?

exchanged very rapidly. Even so, this system never reaches equilibrium—but it still provides us with an example of the effect of partial pressures of gases on solubility.

In dry air, about 21% of the particles are oxygen molecules. Because the overall atmospheric pressure changes with altitude, the partial pressure of oxygen in the air is different in different places. For example, in Mexico City, the site of the 1968 Olympics, the total atmospheric pressure is about 75 kPa compared to 101 kPa at sea level. Thus the partial pressure of oxygen in Mexico City is about 16 kPa compared to about 21 kPa at sea level. This lower partial pressure of oxygen gas leads to a lower rate of solution of O_2 into the blood and lower concentrations of oxygen in the blood. Because of the need for a steady supply of oxygen to the muscles to maintain peak athletic performance, this was an important issue for Olympic athletes.

Lower partial pressures of oxygen at high altitudes mean that less oxygen enters the lungs of a runner's blood.

You can visit the textbook's Web site to see a description of how changes in temperature affect solid and gas solubility.

SPECIAL TOPIC 15.2   Global Warming, Oceans, and CO_2 Torpedoes

Real world situations are more complicated than the simple systems described in this chapter, but you can use what you have learned here to understand them better. For example, what you have learned about the solution of gases can be used to understand more about the solution of carbon dioxide in the ocean and its effect on global warming.

Greenhouse gases were defined in Special Topic 10.1: *Big Problems Require Bold Solutions—Global Warming and Limiting Reactants*. They are gases in the atmosphere that trap some of the infrared energy released by the earth as it cools. We have seen that carbon dioxide is a greenhouse gas and that scientists are searching for ways to reduce its concentration in the atmosphere.

As we saw in Special Topic 10.1, a large amount of carbon dioxide from the atmosphere eventually enters the ocean. The first step in this process can be understood in terms of the model used in this chapter to describe how gas dissolves in a liquid. The collisions between the CO_2 gas particles and the surface of the ocean lead to the movement of about 9.2×10^{13} kg of CO_2 into the oceans per year. There is a competing rate

of CO_2 escape from the ocean—about 9.0×10^{13} kg CO_2 per year. Thus the net rate of movement of CO_2 into the ocean is about 2×10^{12} kg per year.

Several plans have been proposed for reducing the release of greenhouse gases into the atmosphere. One is to collect the carbon dioxide produced by fossil fuel-burning power plants and place it directly into the ocean. This idea is controversial, however, because when carbon dioxide dissolves in water, it forms carbonic acid, H_2CO_3. Dissolving large quantities of CO_2 from power plants in ocean water could lead to significant changes in the acidity of the water and major biological changes.

Another suggestion is to drop 100- to 1000-ton torpedo shaped blocks of solid carbon dioxide (dry ice) into the ocean. If these CO_2 torpedoes could be encased in an insulating layer of solid water (regular ice), it is believed that they would survive the plunge to the bottom of the ocean and embed themselves about 10 m into the sediments on the ocean floor. The CO_2 would then combine with water to form structures that would trap the gas permanently, thus preventing it from changing the ocean's acidity.

Chapter Glossary

Miscible   Can be mixed in any proportion without any limit to solubility.

Hydrophilic ("water loving")   A polar molecule or ion (or a portion of a molecule or polyatomic ion) that is attracted to water.

Hydrophobic ("water fearing")   A nonpolar molecule (or a portion of a molecule or polyatomic ion) that is not expected to mix with water.

Saturated solution   A solution that has enough solute dissolved to reach the solubility limit.

Unsaturated solution   A solution that has less solute dissolved than is predicted by the solubility limit.

You can test yourself on the glossary terms at the textbook's Web site.

Chapter Objectives

The goal of this chapter is to teach you to do the following.

1. Define all of the terms in the Chapter Glossary.

Section 15.1 Why Solutions Form

2. Using the shift from solid to gas as an example, explain why particles change from less dispersed states to more dispersed states.
3. Using the expansion of gas as an example, explain why particles tend to become dispersed.
4. Explain why water and compounds that are like water (that is composed of relatively small polar molecules with hydrogen bonds that link them) mix to form solutions.
5. Given the solubility of a substance in grams of substance that will dissolve in 100 g (or 100 mL) of solvent, classify the substance as soluble, insoluble, or moderately soluble in the solvent.
6. Given a description of a compound as either ionic, polar molecular, or nonpolar molecular (or enough information to determine this), predict whether it would be soluble or insoluble in water.
7. Given a description of a compound as either ionic, polar molecular, or nonpolar molecular (or enough information to determine this), predict whether it would be soluble or insoluble in hexane.
8. Given a description of a compound as either ionic, polar molecular, or nonpolar molecular (or enough information to determine this), predict whether it would be expected to be more soluble in water or hexane.
9. Given descriptions of two compounds that differ in the percentages of their structures that are polar and nonpolar (hydrophilic and hydrophobic), predict their relative solubilities in water and in hexane.
10. Explain why amphetamine can pass through the blood brain barrier more easily than epinephrine.
11. Explain why methamphetamine is often converted to methamphetamine hydrochloride.

Section 15.2 Fats, Oils, Soaps, and Detergents

12. Write or identify a description of the general structure of a triglyceride molecule.

13. Given the chemical formula for a triglyceride, write the chemical formulas for the products of its reaction with sodium hydroxide.

14. Describe the structure of a typical soap, identifying the hydrophilic and hydrophobic portions of its structure.

15. Explain how soap and detergent help the cleaning process.

16. Describe hard water, and explain why soap does not work as well in hard water as it does in soft water.

17. Describe the difference in structure of a typical anionic detergent and a typical soap, and explain why detergent works better in hard water.

Section 15.3 Saturated Solutions and Dynamic Equilibrium

18. Describe the reversible change that takes place when an ionic compound, such as sodium chloride, is dissolved in water.

19. Explain why an increase in the concentration of solute particles in a solution containing undissolved solid leads to an increase in the rate of return of the solute to the solid form.

20. Describe the difference between a rate of solution and a *net* rate of solution.

21. List three factors that determine net rates of solution.

22. Explain why increased surface area of a solid solute leads to an increase in the rate of solution of the solid.

23. Explain why agitation or stirring leads to an increase in the rate of solution of a solid.

24. Explain why increased temperature leads to an increase in the rate of solution of a solid.

25. Explain why the addition of a relatively large amount of solid to a liquid leads to a dynamic equilibrium system with no net change in the amount of undissolved solid and dissolved solute.

26. Describe the changes that take place in a system that contains undissolved solid in equilibrium with dissolved solute.

Section 15.4 Solutions of Gases in Liquids

27. Describe the reversible change that takes place when a closed container holds a liquid with a space above it that contains a gas that dissolves in the liquid. Explain why this system comes to a dynamic equilibrium with no net change in the amount of gas above the liquid or the amount of gas dissolved in the liquid.

28. Explain why an increase in the partial pressure of a gaseous substance over a liquid leads to an increase in the solubility of the substance in the liquid.

29. With reference to the relationship between the partial pressure of substances and their solubility, explain why the concentration of oxygen in the blood decreases as you move to higher elevations.

Review Questions

1. In the past, sodium bromide was used medically as a sedative. Describe the process by which this ionic compound dissolves in water, including the nature of the particles in solution and the attractions between the particles in the solution. Identify the solute and solvent in this solution.

2. Draw a reasonable Lewis structure and a geometric sketch for each of the following molecules. Identify each compound as polar or nonpolar.

   a. C_2H_6 c. CH_3CO_2H
   b. CH_3CH_2OH

3. For each of the following substances, write the name for the type of particle viewed as forming the structure of its solid, liquid, or gas, and write the name of the type of attraction holding these particles in the solid and liquid form.

   a. heptane, C_7H_{16} d. methanol, CH_3OH
   b. formic acid, HCO_2H e. iodine, I_2
   c. copper(II) sulfate, $CuSO_4$ f. carbon dioxide, CO_2

4. When liquid propane is pumped into an empty tank, some of the liquid evaporates, after which both liquid and gaseous propane are present in the tank. Explain why the system adjusts so that there is a constant amount of liquid and gas in the container. With reference to the constant changes that take place inside the container, explain why this system can be described as a dynamic equilibrium.

Key Ideas

Complete the following statements by writing one of these words or phrases in each blank.

10	moderately
any proportion	net
attracted	nonpolar
cation	nonpolar solvents
degree of agitation or stirring	not
dispersed	oils
fats	polar solvents
gas	polar substances
hard	precipitate
hard-water	probability
hydrophilic	simplified
hydrophobic	small
insoluble	solid
larger	solubility
liquid	surface area of the solute
long-chain	temperature

5. It is common for scientists to develop and explain their ideas by considering _____ systems first.

6. In real systems, which provide a huge number of possible positions for particles, there is an extremely high probability that substances will shift from the less dispersed, _____ form, which has fewer ways of arranging the particles, to the more dispersed, _____ form, which has more ways of arranging particles.

7. We can apply the conclusions derived from the consideration of simplified systems to _____ systems.

8. Particles of matter tend to become more _____ (spread out).

9. Because there are more possible arrangements for gas particles when they are dispersed throughout a container than when they are concentrated in one corner of it, _____ suggests that they will spread out to fill the total volume available to them.

10. Miscible liquids can be mixed in _____ without any limit to their solubility.

11. If less than 1 gram of the substance will dissolve in 100 milliliters (or 100 g) of solvent, the substance is considered _____.

12. If more than _____ grams of substance will dissolve in 100 milliliters (or 100 g) of solvent, the substance is considered soluble.

13. If between 1 and 10 grams of a substance will dissolve in 100 milliliters (or 100 g) of solvent, the substance is considered _____ soluble.

14. Polar substances are likely to dissolve in _____.

15. Nonpolar substances are likely to dissolve in _____.

16. Nonpolar substances are _____ likely to dissolve to a significant degree in polar solvents.

17. _____ are not likely to dissolve to a significant degree in nonpolar solvents.

18. Substances composed of _____ polar molecules are usually soluble in water.

19. A polar section of a molecule, which is _____ to water, is called hydrophilic (literally, "water loving"), and a(n) _____ part of the molecule, which is not expected to be attracted to water, is called hydrophobic ("water fearing").

20. If we need to predict the relative water solubility of two similar molecules, we can expect the one with the proportionally _____ polar portion to have higher water solubility.

21. Soap can be made from animal _____ and vegetable _____, which in turn are composed of triglycerides.

22. A higher number of carbon-carbon double bonds in a triglyceride's molecules causes it to be _____ at room temperature.

23. A soap is an ionic compound composed of a(n) _____ (usually sodium or potassium) and an anion with the general form RCO_2^-, in which R represents a(n) _____ hydrocarbon group.

24. The _____, nonpolar hydrocarbon portion of each soap anion does not mix easily with water, but the _____, negatively charged end of each anion does form attractions to water molecules, and these attractions are strong enough to keep the anion in solution.

25. _____ water is water that contains dissolved calcium ions, Ca^{2+}, magnesium ions, Mg^{2+}, and often iron ions, Fe^{2+} or Fe^{3+}. These ions bind strongly to soap anions, causing the soap to _____ from hard-water solutions.

26. Detergent structures are similar to (although more varied than) that of soap, but they are less likely to form insoluble compounds with _____ ions.

27. The net rate of solution depends on three factors: _____, _____, and _____.

28. If we stir or in some way agitate a solution containing a solid, the solute particles near the solid are quickly carried away, and the relatively high local concentrations of solute are decreased. This diminishes the rate of return and increases the _____ rate of solution.

29. If the partial pressure of a gas over a liquid is increased, the _____ of that gas is increased.

Chapter Problems

OBJECTIVE 2

OBJECTIVE 3

Section 15.1 Why Solutions Form

30. Dry ice is often used to keep ice cream cold at picnics. As the day goes on, the dry ice disappears as the solid sublimes (goes directly from solid to gas). Explain why this change takes place.

31. The container in (a) shown below consists of two chambers separated by an partition. One side contains a gas, and the other side is empty. When the partition between the two chambers is removed, the gas moves between the chambers until it is evenly distributed. Explain why this happens. Your explanation should compare the relative degree of dispersal of the particles and the number of ways to arrange the particles in the system.

(a)   (b)
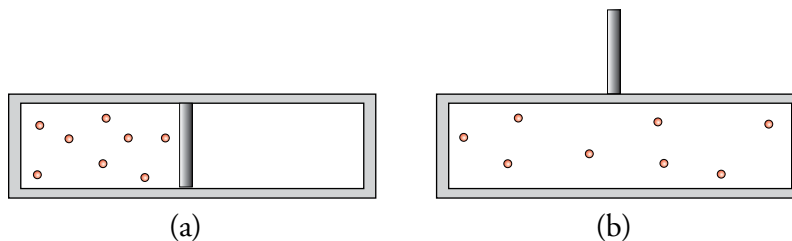
32. Acetone is commonly used to clean laboratory glassware when soap and water cannot do the job. Acetone works well because it dissolves certain substances that are not soluble in water. It is also a good choice because, being miscible with water, it can easily be rinsed from the cleaned glassware with water. Explain what it means when we say acetone is miscible with water.

33. The primary components of vinegar are acetic acid and water, both of which are composed of polar molecules with hydrogen bonds that link them. These two liquids will mix in any proportion. Explain why acetic acid and water are miscible.
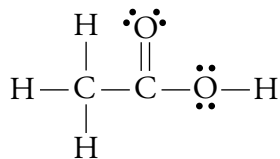
Acetic acid

34. The solubilities in water of several substances are listed below. Classify each of these substances as soluble, insoluble, or moderately soluble, based on the criteria presented in the chapter.

   a. Camphor, $C_{10}H_{16}O$ (a topical anti-infective): 0.1 g per 100 mL H_2O at 25 °C
   b. Sodium formate, $NaHCO_2$ (used in dyeing and printing fabrics): 97.2 g per 100 g H_2O at 20 °C
   c. Cobalt(II) fluoride, CoF_2 (a catalyst in organic reactions): 1.5 g per 100 g H_2O at 25 °C

35. What is meant by *like* in the solubility guideline *like dissolves like*?

36. Would the following combinations be expected to be soluble or insoluble?
   a. polar solute and polar solvent
   b. nonpolar solute and polar solvent
   c. ionic solute and water
   d. molecular solute with small molecules and hexane
   e. hydrocarbon solute and water

37. Would the following combinations be expected to be soluble or insoluble?
   a. polar solute and nonpolar solvent
   b. nonpolar solute and nonpolar solvent
   c. ionic solute and hexane
   d. molecular solute with small molecules and water
   e. hydrocarbon solute and hexane

38. Write the chemical formula for the primary solute in each of the following solutions. Explain how the solubility guideline *like dissolves like* leads to the prediction that these substances would be soluble in water.
   a. vinegar
   b. household ammonia

39. Write the chemical formula for the primary solute in each of the following solutions. Explain how the solubility guideline *like dissolves like* leads to the prediction that these substances would be soluble in water.
   a. hydrochloric acid
   b. vodka

OBJECTIVE 6

40. Predict whether each of the following is soluble in water or not.
   a. the polar molecular compound 1-propanol, $CH_3CH_2CH_2OH$ (a solvent for waxes and vegetable oils)
   b. cis-2-pentene, $CH_3CHCHCH_2CH_3$ (a polymerization inhibitor)
   c. the polar molecular compound formic acid, HCO_2H (transmitted in ant bites)
   d. strontium chlorate, $Sr(ClO_3)_2$ (used in tracer bullets)

OBJECTIVE 6

41. Predict whether each of the following is soluble in water or not.
   a. potassium hydrogen sulfate, $KHSO_4$ (used in wine making)
   b. the polar molecular compound propylene glycol, $CH_3CH(OH)CH_2OH$ (used in some antifreezes)
   c. benzene, C_6H_6 (use to produce many organic compounds)

OBJECTIVE 7

42. Predict whether each of the following is soluble in hexane, C_6H_{14}, or not.
   a. butane, C_4H_{10} (fuel for cigarette lighters)
   b. potassium hydrogen oxalate, KHC_2O_4 (used to remove stains)

OBJECTIVE 7

43. Predict whether each of the following is soluble in hexane, C_6H_{14}, or not.
   a. lithium chromate, Li_2CrO_4 (a corrosion inhibitor in alcohol-based antifreezes and water-cooled reactors)
   b. ethylene, CH_2CH_2 (in orchard sprays to accelerate fruit ripening)

OBJECTIVE 8

44. Predict whether each of the following would be more soluble in water or hexane.
   a. toluene, $C_6H_5CH_3$ (in aviation fuels)
   b. lithium perchlorate, $LiClO_4$ (in solid rocket fuels)

OBJECTIVE 8

45. Predict whether each of the following would be more soluble in water or hexane.
   a. magnesium nitrate, $Mg(NO_3)_2$ (in fireworks)
   b. heptane, C_7H_{16} (a standard for gasoline octane rating)

46. Chlorine, Cl_2, helps to keep swimming pools clean, but it has to be constantly either added to the water or formed in the water from other substances. With reference to the solubility of chlorine in water, explain why this is necessary.

OBJECTIVE 9

47. Would you expect acetone, CH_3COCH_3 (in some nail polish removers) or 2-hexanone, $CH_3COCH_2CH_2CH_2CH_3$ (a solvent) to be more soluble in water? Why?

OBJECTIVE 9

48. Would you expect lactic acid, $CH_3CH(OH)CO_2H$ (in sour milk) or myristic acid, $CH_3(CH_2)_{12}CO_2H$ (used to make cosmetics) to be more soluble in water? Why?

OBJECTIVE 7

49. Would you expect ethane, C_2H_6 (in natural gas) or strontium perchlorate, $Sr(ClO_4)_2$, (in fireworks) to be more soluble in hexane, C_6H_{14}? Why?

OBJECTIVE 7

50. Would you expect potassium phosphate, K_3PO_4, (used to make liquid soaps) or ethyl propionate, $CH_3CH_2CO_2CH_2CH_3$ (due to its pineapple smell, used in fruit essences), to be more soluble in hexane, C_6H_{14}? Why?

OBJECTIVE 10

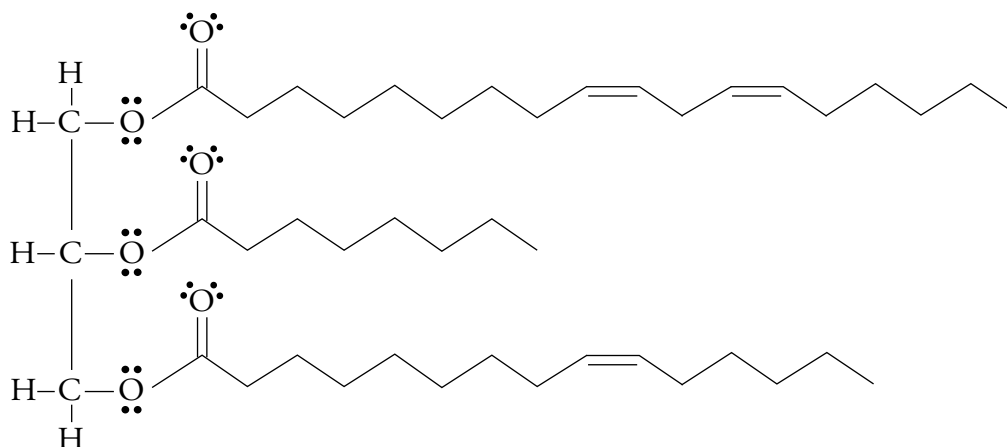51. Explain why amphetamine can pass through the blood-brain barrier more easily than epinephrine.

OBJECTIVE 11

52. Explain why methamphetamine is often converted to methamphetamine hydrochloride.
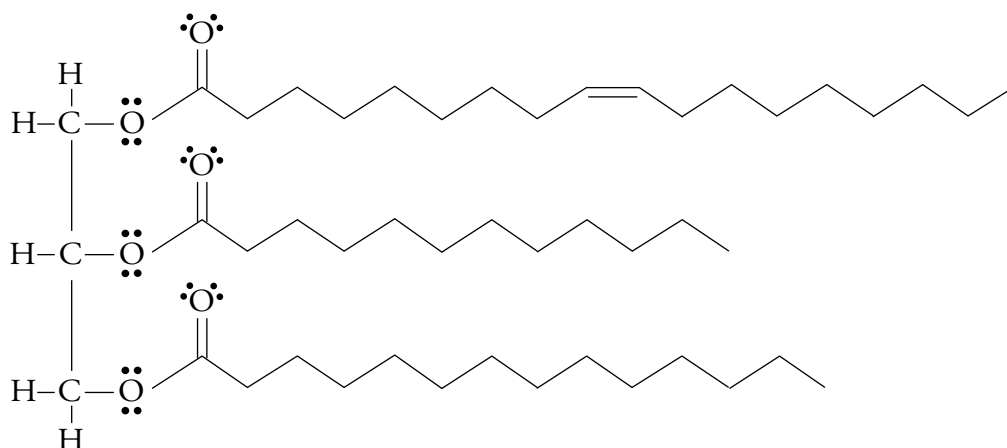
Section 15.2 Fats, Oils, Soaps, and Detergents

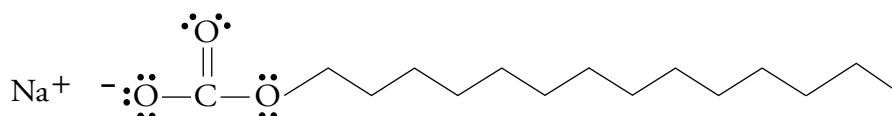**53.** What are the products of the reaction between the following triglyceride and sodium hydroxide?

54. What are the products of the reaction between the following triglyceride and sodium hydroxide?

55. What part of the following soap structure is hydrophilic and what portion is hydrophobic?

56. You throw a backyard party that resembles your idea of a big Texas barbecue. The guests get more food than they could possibly eat, including a big juicy steak in the center of each plate. Describe how soap or detergent can help you clean the greasy plates you're left with when your guests go home, referring to the interactions between particles and the corresponding changes that take place on the submicroscopic level.

57. If you live in an area that has very hard water, detergents are a better choice of cleaning agents than soap. Describe the difference in structure between a typical anionic detergent and a typical soap. Describe what makes water hard, and explain why detergents work better in hard water than soap.

Section 15.3 Saturated Solutions and Dynamic Equilibrium

58. List three ways to increase the rate at which salt dissolves in water.

59. Epsom salts, a common name for magnesium sulfate heptahydrate, $MgSO_4 \cdot 7H_2O$, can be used to help reduce swelling caused by injury. For example, if you want to reduce the swelling of a sprained ankle, you can soak the ankle in a saturated solution of magnesium sulfate prepared by adding an excess of Epsom salts to water and waiting until the greatest possible amount of solid dissolves.

OBJECTIVE 18

    a. Describe the reversible change that takes place as the $MgSO_4$ dissolves. (You do not need to mention the water of hydration that is attached to the magnesium sulfate.)

OBJECTIVE 19

    b. Explain why an increase in the concentration of solute particles in this solution containing undissolved solid leads to an increase in the rate of return of the solute to the solid form.

OBJECTIVE 23

    c. Why does the magnesium sulfate dissolve faster if the solution is stirred?

    d. When the maximum amount of magnesium sulfate has dissolved, does the solid stop dissolving? Explain.

60. A person who has trouble swallowing tablets can dissolve aspirin in water and drink the solution. The fastest way to dissolve the aspirin is to grind it to a powder and then dissolve it in hot water.

OBJECTIVE 22

    a. Why does powdered aspirin dissolve faster than an aspirin tablet?

OBJECTIVE 24

    b. Why does aspirin dissolve faster in hot water than in cold water?

61. If you wanted to make sugar dissolve as quickly as possible, would you use

    a. room temperature water or hot water. Why?

    b. powdered sugar or granular sugar. Why?

62. Some of the minerals found in rocks dissolve in water as it flows over the rocks. Would these minerals dissolve more quickly

    a. at the bottom of a waterfall or in a still pond? Why?

    b. in a cold mountain stream or in the warmer water downstream? Why?

    c. over large rocks or over sand composed of the same material? Why?

OBJECTIVE 26

63. What does it mean to say a solution is saturated? Describe the changes that take place at the particle level in a saturated solution of sodium chloride that contains an excess of solid NaCl. Is the NaCl still dissolving?

64. Solutions are called dilute when the concentration of the solute in solution is relatively low and concentrated when the concentration is relatively high. Can a solution be both dilute and saturated? Explain your answer.

65. Can a solution be both concentrated (with a relatively high concentration of solute) and unsaturated? Explain your answer.

Section 15.4 Solutions of Gases in Liquids

66. The soft drinks sold at county fairs are often dispensed from large pressurized containers that contain carbon dioxide gas above the liquid at a partial pressure of about 4 atm, compared to carbon dioxide's normal partial pressure of 0.00035 atm in the air at sea level.

    a. Describe the reversible change that takes place inside one of these soft drink containers when the pressure of CO_2 above the liquid is first brought from 0.00035 atm to 4 atm. Explain why this system comes to a dynamic equilibrium in which there is no net change in the amount of gas above the liquid or the amount of gas dissolved in the liquid.

    OBJECTIVE 27

    b. Explain why an increase in the partial pressure of CO_2 over a liquid leads to an increase in the solubility of the gas in the liquid.

    OBJECTIVE 28

67. Consider a soft drink bottle with a screw cap. When the cap is removed, the excess CO_2 in the space above the soft drink escapes into the room, leaving normal air above the liquid. Explain why the soft drink will lose its carbonation more quickly if the cap is left off than if the cap is immediately put back on tightly.

68. You visit a dude ranch located in a beautiful mountain valley at an altitude of 6000 feet. The day you arrive, you decide to take your usual evening run. On this evening, however, you don't run as far as usual, because you feel winded and tired much sooner than at home by the beach. Why does this happen?

    OBJECTIVE 29

Discussion Question

69. The particles of air inside a typical classroom number about 10^{28}. Is it possible for all of these particles to be found in one corner of the room? Would you change your answer if there were only five air particles in the room?