13.1 Why Solutions Form

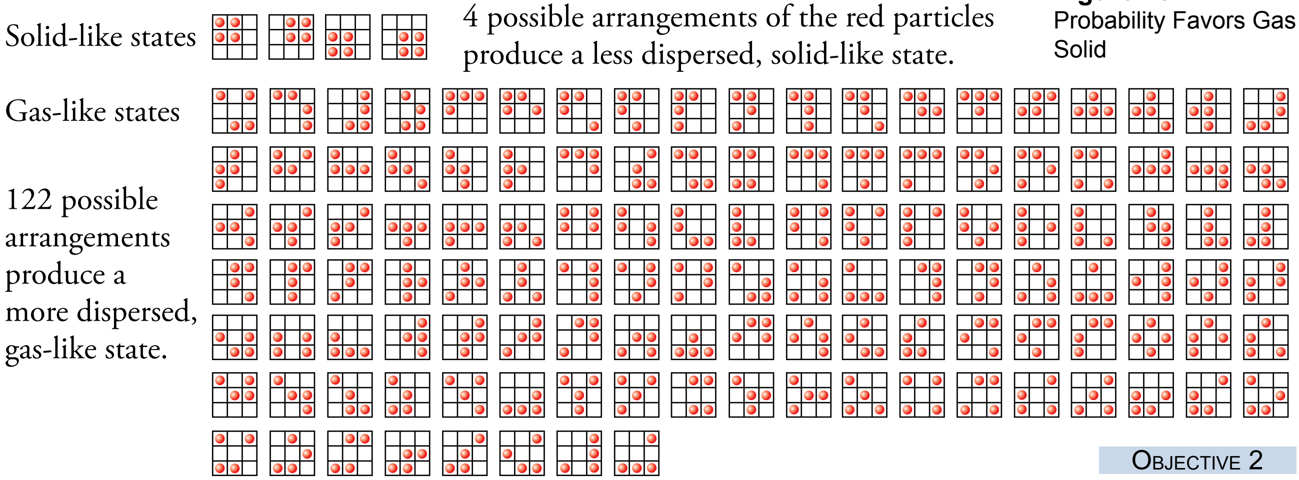
We start this stage of our exploration of the nature of solutions by looking at some of the reasons why certain substances mix to form solutions and why others do not. When you are finished reading this section, you will have the necessary tools for predicting the solubility of substances in liquids.

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 13.1 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 13.1 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 13.1 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 13.1
Probability Favors Gas over Solid



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.

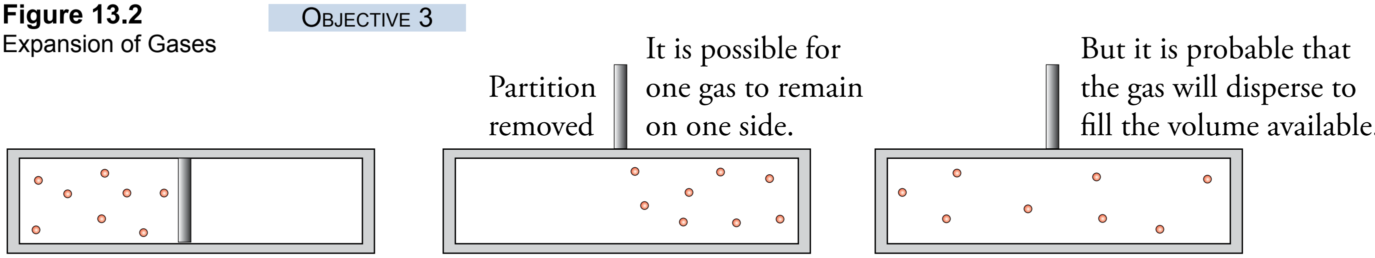
solid $\longrightarrow$	**gas**
Less dispersed	More dispersed
Fewer ways to arrange particles	More ways to arrange particles
Less probable	More probable

Objective 3

In general, **particles of matter tend to become more dispersed (spread out).** The simple system shown in Figure 13.2 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.

Figure 13.2
Expansion of Gases

Objective 3



(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.

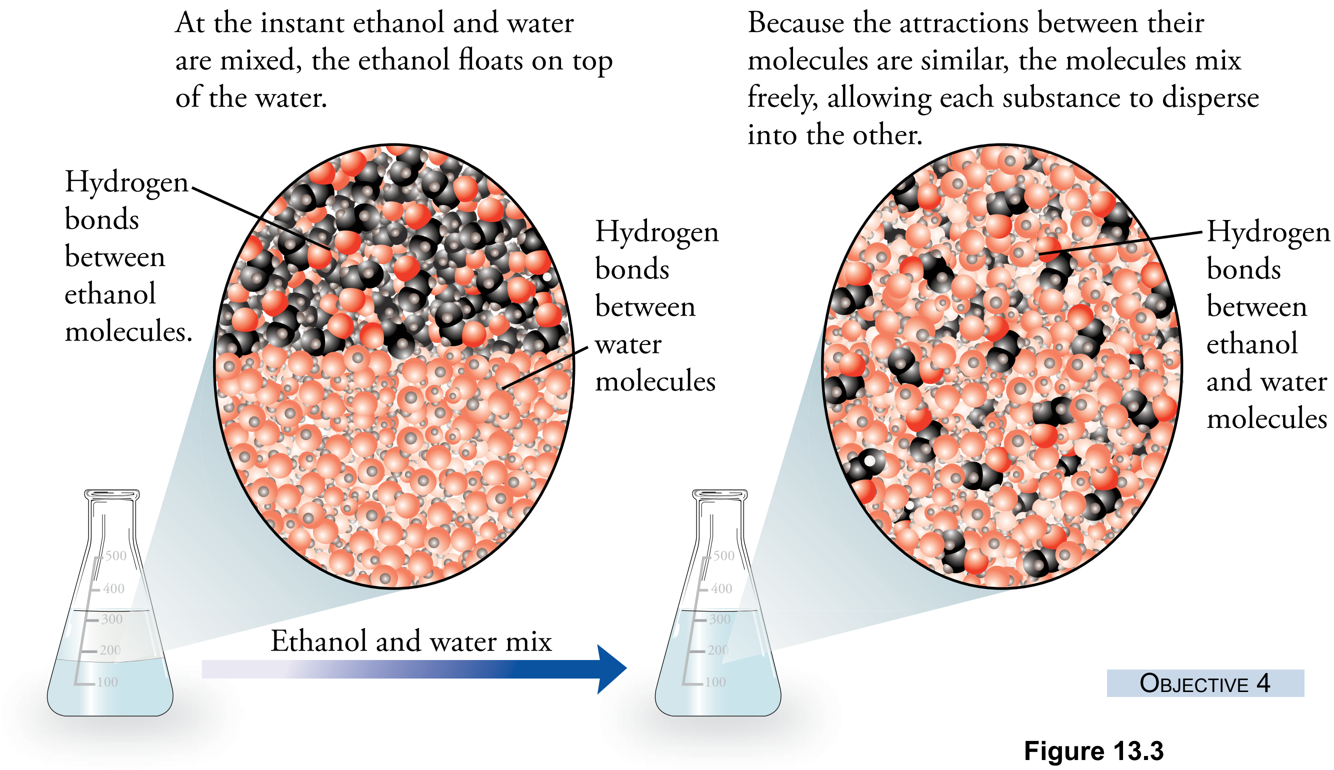
Why Do Solutions Form?

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

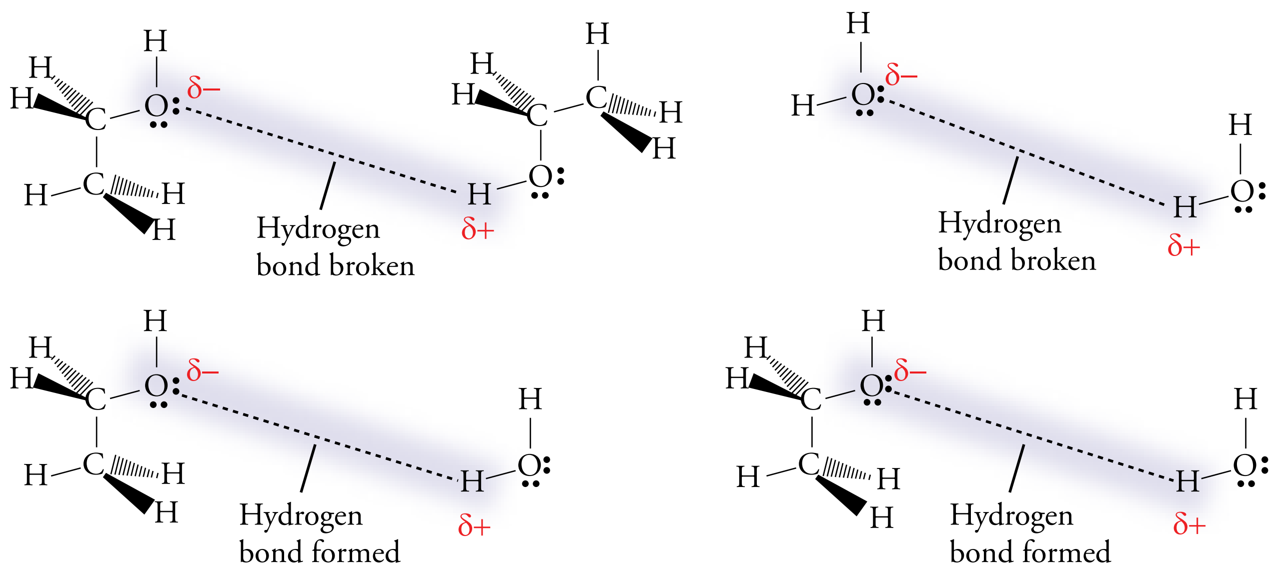
Picture a layer of ethanol being carefully added to the top of some water (Figure 13.3). Because the particles of a liquid are moving constantly, some of the ethanol particles at the boundary between the two liquids will immediately move into the water, and some of the water molecules will move into 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 13.4).

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 13.3).



Objective 4

Figure 13.3
Ethanol and Water Mixing



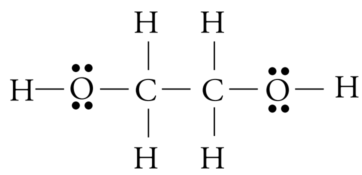
Objective 4

Figure 13.4
The Attractions Broken and Formed When Ethanol Dissolves in Water

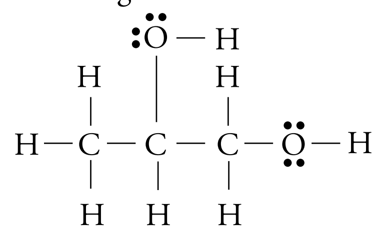
You will find an animation that illustrates the solution of ethanol in water at the textbook's Web site.

Why do coolant and water mix?

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.



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:

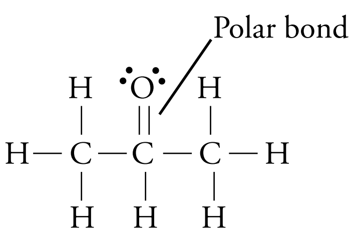
OBJECTIVE 6
OBJECTIVE 7
OBJECTIVE 8

- 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.

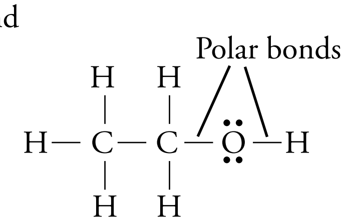
As the alcohol concentration of wine increases, the solvent's polarity decreases, and ionic compounds in the wine begin to precipitate.

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.)



acetone



ethanol

The guidelines we have discussed are summarized in Table 13.1.

Table 13.1
Summary of Solubility Guidelines

OBJECTIVE 6
OBJECTIVE 7
OBJECTIVE 8

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 13.1 - Predicting Water Solubility

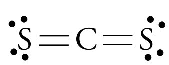
Objective 6

Predict whether each compound is soluble in water or not.

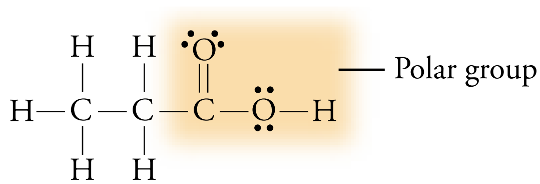
a. nickel(II) chloride, $NiCl_2$ (used in nickel plating)
b. 2-propanol (isopropyl alcohol), $CH_3CH(OH)CH_3$ (in rubbing alcohol)
c. 1-pentene, $CH_2CHCH_2CH_2CH_3$ (blending agent for high octane fuels)
d. The nonpolar molecular compound carbon disulfide, CS_2 (used to make rayon and cellophane)
e. 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**.

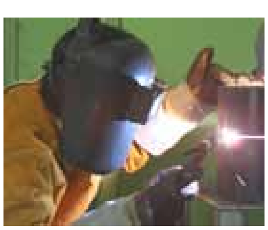


e. We expect polar molecular compounds with relatively small molecules, such as propionic acid, $CH_3CH_2CO_2H$, to be **soluble in water**.



Exercise 13.1 - Predicting Water Solubility

Objective 6



Predict whether each is soluble in water or not. (See Section 12.3 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 13.2 - Predicting Solubility in Hexane

Objective 7

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 13.2 - Predicting Solubility in Hexane

Objective 7

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

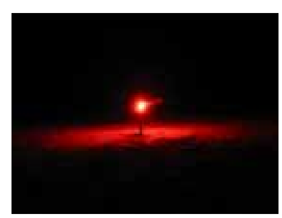
a. sodium perchlorate, $NaClO_4$ (used to make explosives)
b. propylene, CH_3CHCH_2 (used to make polypropylene plastic for children's toys)

Example 13.3 - Predicting Relative Solubility in Water and Hexane

Objective 8

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 13.3 - Predicting Relative Solubility in Water and Hexane

Objective 8

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)

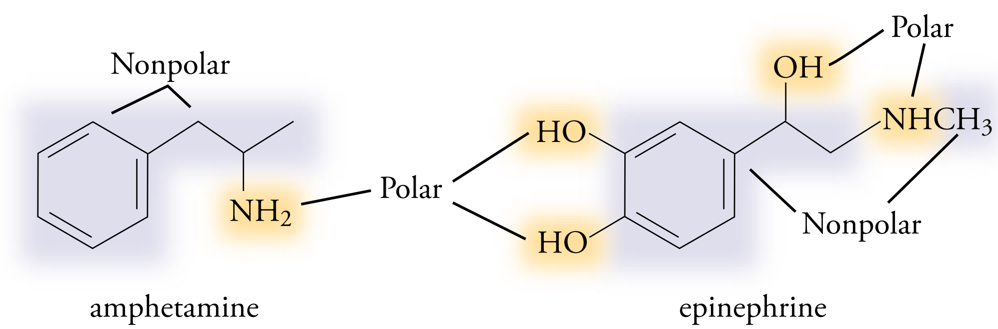
Hydrophobic and Hydrophilic Substances

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 13.5).

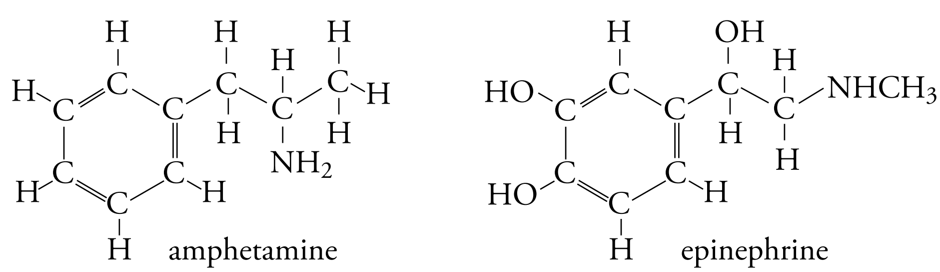
Figure 13.5
Molecular Line Drawings of Amphetamine and Epinephrine



The molecular representations in Figure 13.5 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 13.5 to the more complete Lewis structures in Figure 13.6.

Figure 13.6
Detailed Molecular Structures of Amphetamine and Epinephrine

Objective 10



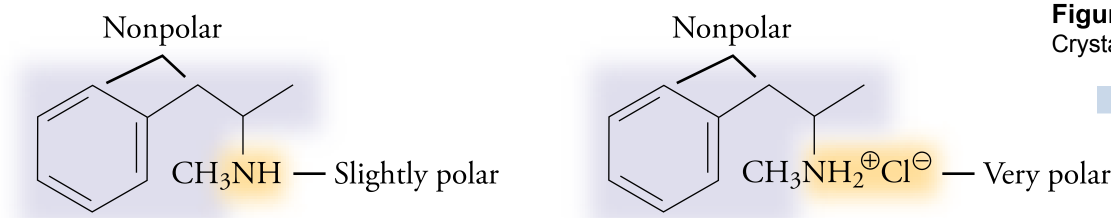
The difference in polarity between epinephrine and amphetamine has an important physiological consequence. The cell membranes that separate the blood stream from the inside of brain cells have a nonpolar interior and a polar exterior that tend to slow down the movement of polar substances in the blood 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 more quickly through the blood brain barrier.

Objective 11

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 13.7).

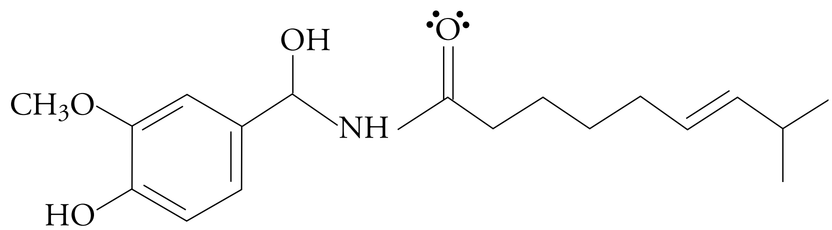
Figure 13.7
Crystal Meth

OBJECTIVE 11



methamphetamine   methamphetamine hydrochloride

Chilis Drying in Rajasthan, India

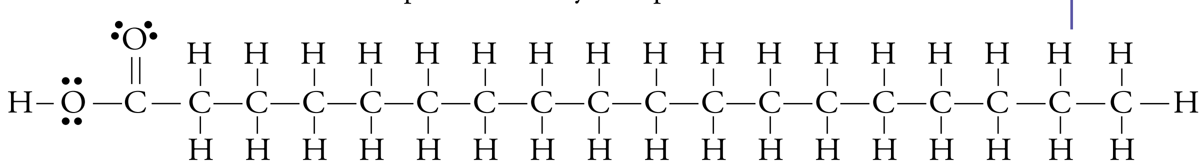


If you get a bite of a spicy dish that has too much chili pepper, do you grab for a glass of water or a spoonful of sour cream to put out the flames? Capsaicin molecules, which are largely responsible for making green and red chili peppers hot, are mostly nonpolar. Therefore, the oil in the sour cream 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.

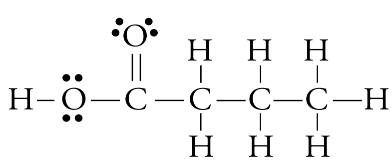
EXAMPLE 13.4 - Predicting Relative Solubility in Water

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

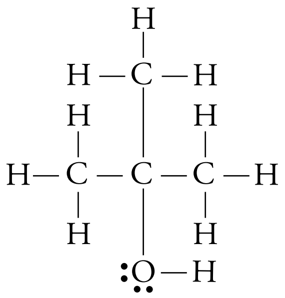
Solution

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.

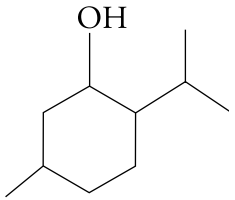
Exercise 13.4 - Predicting Relative Solubility in Water

Objective 9

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