

## PROPERTIES OF SOLUTION

The content in this topic is the basis for mastering Learning Objectives 2.1, 2.7, 2.8, 2.9, 2.10, 2.14, 2.15, and 6.24 as found in the Curriculum Framework.

When you finish reviewing this topic, be sure you are able to:

- Describe and interpret the interactive forces between solute and solvent ions and molecules
- Construct visual representations of solute and solvent particles in solution
- Apply energy principles to explain the factors that affect solubility of solutes
- Explain solubility data of ionic substances in water and justify with considerations of energy and entropy
- Use chemical formulas to predict the solubilities of compounds in water and other solvents
- Calculate molarity and construct visual models to demonstrate different molar concentrations
- Explain how the technique of chromatography uses intermolecular attractions to separate mixtures

### The Solution Process

#### Section 13.1

A **solution** is a homogeneous mixture of one or more solutes dispersed uniformly throughout a solvent, normally the substance in greatest amount. The concentration of the solute(s) and the intermolecular forces among the components determine the physical properties of a solution.

**Entropy** is a state of randomness or disorder of a system. An increase in entropy is associated with the mixing that occurs when a solution forms. The driving force of most solution processes is the natural tendency for systems to increase in entropy. (A more detailed discussion of entropy appears in Section 19.2.)

Energetically, the solution process involves three kinds of intermolecular interactions. Recall that bond breaking (or separating attracted particles) is endothermic and bond making (or attracting particles) is exothermic.

When a solute dissolves in a solution:

**Solute-solute interactions** between solute particles **break** (endothermic).

**Solvent-solvent interactions** between solvent molecules **break** (endothermic).

**Solvent-solute interactions form** (exothermic).

A solution process is exothermic when solvent-solute interactions release more energy than is required to break both the solvent-solvent and solute-solute forces.

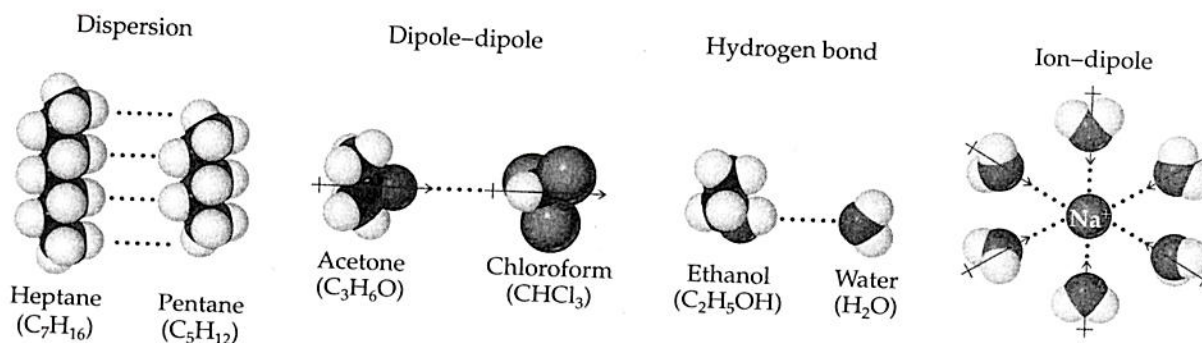
Recall that solvent-solute and solvent-solvent interactions are the intermolecular attractive forces discussed in Topic 11:

**Dispersion forces** act between particles of a nonpolar solvent and a nonpolar solute.

**Dipole-dipole forces**, including **hydrogen bonding**, act between particles of a polar solvent and a polar solute.

**Ion-dipole forces** act between a polar solute and ions in solution.

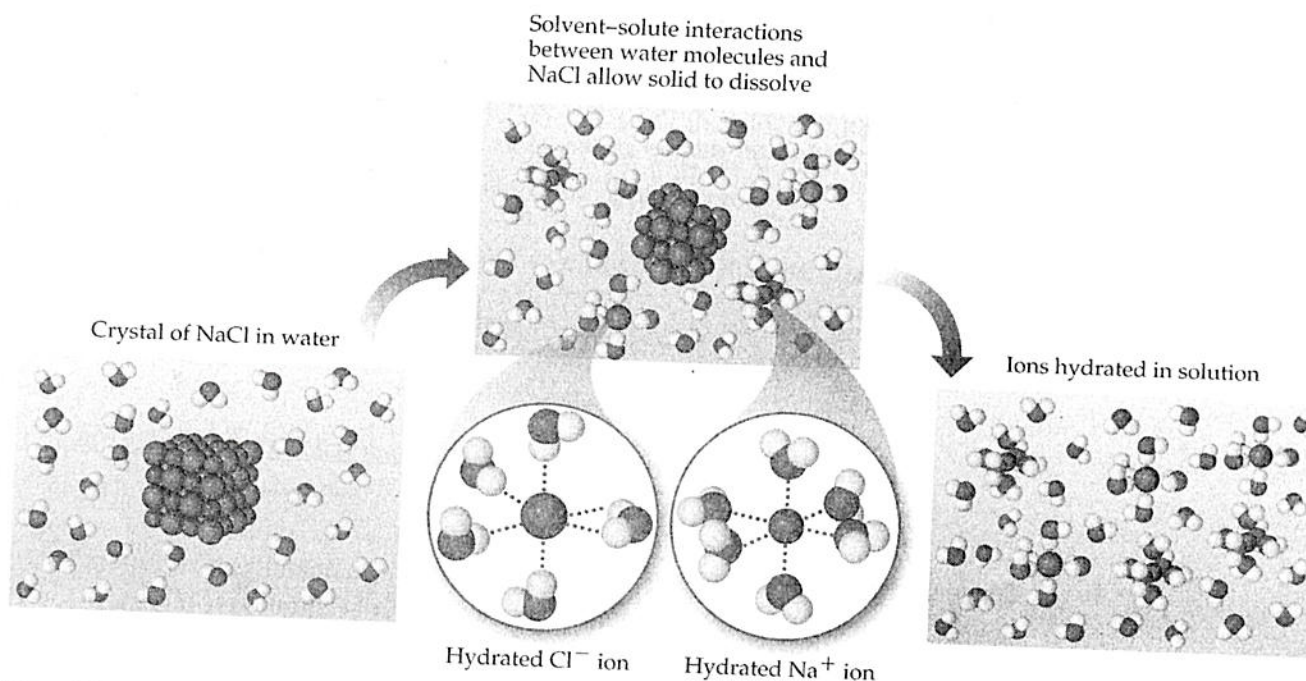
Figure 13.1 illustrates examples of solvent-solute forces in solution.



**Figure 13.1** Intermolecular interactions involved in solutions.

Figure 13.2 illustrates what happens when sodium chloride dissolves in water. Solute-solute forces (ionic bonds) between sodium ions and chloride ions in the ionic solid break. Solvent-solvent forces between the water molecules break. Ion-dipole forces between the ions and water form. The positive ends of water dipoles attract anions while cations are attracted to the negative ends of water dipoles.

**Hydrated ions** are ions attracted to water molecules by ion-dipole intermolecular forces.



**Figure 13.2** Hydrated  $\text{Na}^+$  and  $\text{Cl}^-$  ions form ion-dipole interactions with water molecules when sodium chloride dissolves.

The solute-solute forces in ionic solids are ionic bonds. Solubility of ionic solids in water depends, in part, on the strength of the ionic bonds.

**Hydration** forces are a measure of the strength of the ion-dipole forces that keep dissociated ions hydrated minus the forces required to overcome the solute-solute interactions.

When the ion-dipole forces are **greater than** the ionic bonds, the ionic compound **dissolves exothermically**, with the release of heat to the solution.

Most ionic compounds **dissolve endothermically** because the energy required to break the ionic bonds is usually greater than the energy released when the ion-dipole interactions are formed in the solution. The heat required for the process comes from the solution as it cools. The driving force of an endothermic dissolving process is the increase in entropy of the system.

A few ionic compounds dissolve exothermically when the ion-dipole forces formed in the solution are greater than the forces required to overcome the ionic bonds of the solid and the attractions between solvent particles. Exothermic processes tend to be thermodynamically favored. The amount of released heat is essentially the difference in the energies.



## Your Turn 13.1

Calcium chloride dissolves in water with an increase in temperature of the water. Is this process endothermic or exothermic? Use intermolecular forces and ionic bonding to explain. Write your answer in the space provided.

**Concentration** is the quantity of solute present in a given quantity of solvent or solution. In chemistry, the most common way to express concentration is molarity.

The **molarity** of a solute in a solution is the number of moles of solute per liter of solution:  $\text{molarity} = M = \frac{\text{mol solute}}{\text{L soln}}$

**Examples:**

Calculate the molarity of a solution made by dissolving 25.0 g of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in a total volume of 500.0 mL.

**Solution:**

$$\begin{aligned} x \text{ mol/L} &= (25.0 \text{ g CuSO}_4 \cdot 5\text{H}_2\text{O} / 0.5000 \text{ L}) \\ &\quad (1 \text{ mol} / 249.5 \text{ g}) \\ &= 0.200 \text{ M} \end{aligned}$$

## Your Turn 13.2

Copper sulfate pentahydrate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , is a light blue ionic solid that readily dissolves in water to form a blue solution.

- Would 500.0 mL that contains 12.5 g of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  be darker or lighter than one of the same volume that contains 25.0 g of solute? Explain.
- Draw representations of the two solutions in Part a. Use a small  $x$  to represent each 0.01 M of solution.

# Saturated Solutions and Solubility

## Section 13.2

As a solute dissolves in a solvent, its concentration increases. This increases the chance that dissolved solute particles will collide with the surface of the solid and recrystallize. Dissolving and crystallization are opposite processes.

**Dynamic equilibrium** is the condition in which two opposite processes occur at the same rate.

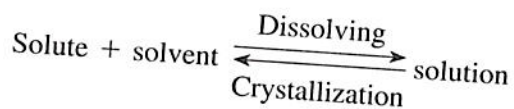
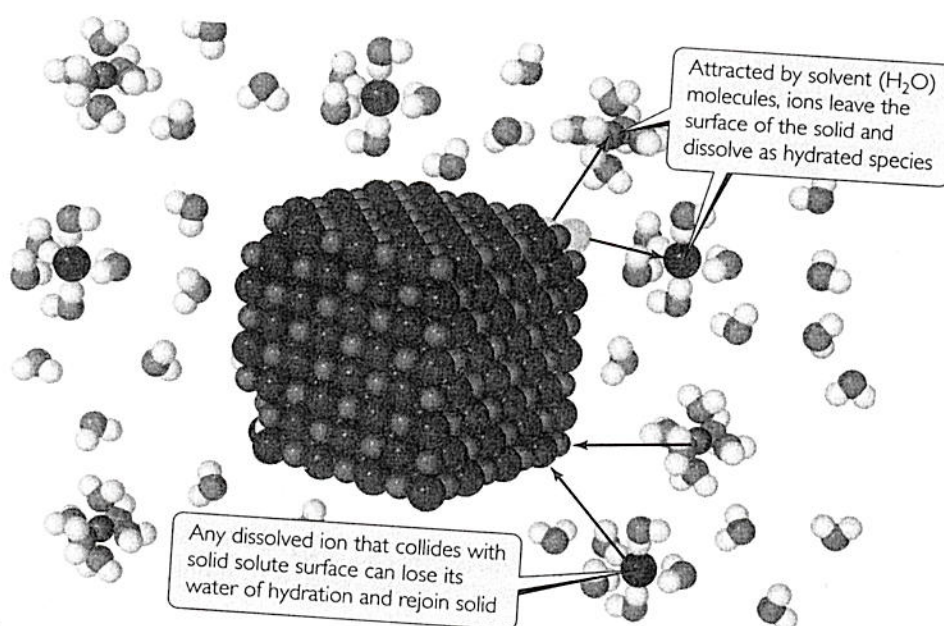


Figure 13.3 shows an example of a dynamic equilibrium.



**Figure 13.3** Dynamic equilibrium in a saturated solution with excess ionic solute.

A **saturated solution** is one in which dissolved solute is in dynamic equilibrium with undissolved solute.

**Solubility** is the amount of solute needed to form a saturated solution in a given amount of solvent. The units of solubility for an aqueous solution are usually grams of solute per 100 mL of water, g solute/100 mL water.

An **unsaturated solution** contains less solute than a saturated solution.

A **supersaturated solution** contains more solute than a saturated solution. Supersaturation can be achieved because many substances are more soluble at high temperatures than they are at low temperatures. If a hot, saturated solution is slowly cooled, an unstable supersaturated solution often forms.

## Section 13.3

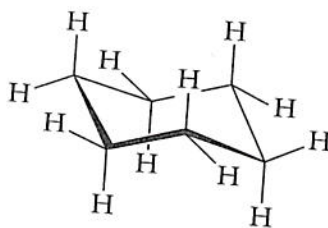
**Factors Affecting Solubility**

Solubility increases with increasing strength of attractions between solvent and solute particles.

Substances with similar intermolecular attractive forces tend to be soluble in one another. An easily remembered adage is, **"Like dissolves like."**

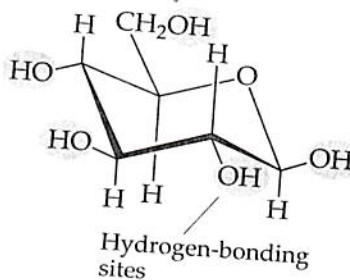
Polar solutes tend to dissolve in polar solvents. Nonpolar solutes tend to dissolve in nonpolar solvents. Polar substances do not dissolve in nonpolar substances. Polar solvents, because of their relatively strong dipole-dipole forces, tend to exclude nonpolar substances with their relatively weak dispersion forces.

Figure 13.4 shows the chemical structures of cyclohexane and glucose. Glucose is soluble in water because it contains many polar OH groups that can hydrogen bond with water. Cyclohexane is soluble in gasoline because it is nonpolar like gasoline and it has weak dispersion forces similar to gasoline.



Cyclohexane,  $C_6H_{12}$ , which has no polar OH groups, is essentially insoluble in water

OH groups enhance the aqueous solubility because of their ability to hydrogen bond with  $H_2O$ .



Glucose,  $C_6H_{12}O_6$ , has five OH groups and is highly soluble in water

**Figure 13.4** Structure and solubility.



**Miscible liquids** are pairs of liquids that dissolve in all proportions. They do so because their attractive forces are similar, either both polar or both nonpolar. Ethanol,  $\text{CH}_3\text{CH}_2\text{OH}$ , and water,  $\text{HOH}$ , are completely miscible because they both strongly hydrogen bond. Hexane and benzene are also completely miscible because both molecules have only weak London dispersion forces.

**Immiscible liquids** are those that do not dissolve in each other. Their attractive forces are dissimilar, one is polar and the other is nonpolar.

Table 13.1 shows the solubilities of several alcohols in water and in hexane.

**Table 13.1** Solubilities of some alcohols in water and in hexane.\*

Alcohol	Solubility in $\text{H}_2\text{O}$	Solubility in $\text{C}_6\text{H}_{14}$
$\text{CH}_3\text{OH}$ (methanol)	$\infty$	0.12
$\text{CH}_3\text{CH}_2\text{OH}$ (ethanol)	$\infty$	$\infty$
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ (propanol)	$\infty$	$\infty$
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ (butanol)	0.11	$\infty$
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ (pentanol)	0.030	$\infty$
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ (hexanol)	0.0058	$\infty$

\*Expressed in mol alcohol/160 g solvents at  $20^\circ\text{C}$ . The infinity symbol ( $\infty$ ) indicates that the alcohol is completely miscible with the solvent.

Notice that all alcohols have OH groups that can hydrogen bond with water. However, only the alcohols with short carbon-carbon chains are readily soluble in water and only those with longer C—C chains are readily soluble in the hydrocarbon, hexane. As the number of nonpolar C—C bonds increases, the OH group becomes a smaller part of the molecule and the molecule behaves like a nonpolar hydrocarbon. As a result, the short-chain alcohols dissolve in water while the long-chain molecules dissolve more readily in hydrocarbons.

Explain using intermolecular forces why gasoline and water do not mix. Write your answer in the space provided.

**Your Turn 13.3**

Gases tend to be more soluble in liquids at higher pressure and at lower temperature. The solubility of a gas increases in direct proportion to its partial pressure above the solution.

### Your Turn 13.4

Why do bubbles appear in a plastic soda bottle when the cap is removed? Justify your answer by discussing the intermolecular forces that interact between the solute and the solvent.

Write your answer in the space provided.

### Chromatography

**Chromatography** is a versatile and powerful method used extensively in chemistry to separate and purify substances. In the three common types of chromatography—gas, liquid, and paper—a mobile solution phase carries a mixture of compounds over a stationary insoluble phase. As the mixture moves, the compounds separate because they bind differently through weak intermolecular forces with the stationary phase.

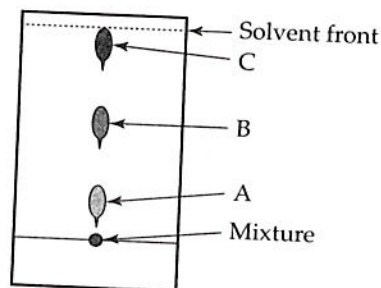
In **gas chromatography**, the mobile phase is a gas and the stationary phase is a liquid bound to a solid support. Both **liquid** and **paper chromatography** employ a liquid mobile phase and a solid stationary phase.

The rates of movement of the compounds in the mixture depend on their relative strengths of attraction for the mobile phase and the stationary phase. For example, if the mobile phase is less polar than the stationary phase, polar groups of the stationary phase strongly attract polar compounds in the mobile phase and slow their movement. Nonpolar compounds, which are not as strongly attracted to the stationary phase, move more quickly. If the stationary phase is less polar than the mobile phase, then the less polar compounds will move more slowly.

The differential rate of movement of the compounds due to their relative attractions to the stationary phase is the basis for their separation. Chromatography is versatile because a chemist can vary the phases to match the compounds she wishes to separate.



A typical separation of food dyes by paper chromatography illustrates the technique. Figure 13.5 shows a paper chromatogram of a mixture of three food dyes. A liquid mixture of three dyes, A, B, and C, is applied near the bottom of the paper and the paper is placed in a solvent. As the solvent (mobile phase) climbs the paper (stationary phase) by capillary action, the three dyes separate. Just before the solvent front reaches the top, the paper is removed and dried. The result is a chromatogram shown in Figure 13.5.



**Figure 13.5** A paper chromatogram of a mixture of three food dyes.

The three dyes separate because they each have different affinities for a relatively nonpolar solvent and the polar paper. The differences in polarity cause each dye to bind differently to the solvent and to the paper. Dye A is the most polar and relatively strong intermolecular forces of attraction bind Dye A to the paper and slow its rate of ascent. Dye C is the least polar, so it spends the most time in the nonpolar solvent and moves quickly up the paper. Dye B is of intermediate polarity. The different rates at which each dye ascends effect a clean separation.

**Common misconception:** Most sources commonly misidentify the stationary phase in paper chromatography as only the paper. In reality, the stationary phase consists of an intimate relationship between the cellulose of the paper and water molecules hydrogen bonded to the cellulose. Experiments show that under the same conditions, papers of different water content produce very different separations.



**Multiple Choice Questions**

1. *The aqueous solution of which salt will have the strongest cation–dipole interactions?*
  - A)  $\text{NaCl}$
  - B)  $\text{MgCl}_2$
  - C)  $\text{K}_2\text{SO}_4$
  - D)  $\text{Cr}(\text{NO}_3)_3$
  - E)  $\text{CaSO}_4$
2. *Enough water is added to 11.5 g of ethanol to make 2.00 L of solution. What is the molarity of the ethanol?*
  - A) 0.125
  - B) 0.250
  - C) 0.500
  - D) 5.75
  - E) 0.333
3. *Which pairs of substances will dissolve in each other:*
  - I.  $\text{CH}_3\text{OH}$
  - II.  $\text{C}_6\text{H}_6$
  - III.  $\text{CH}_3\text{CH}_3$
  - A) I and II only
  - B) II and III only
  - C) I and III only
  - D) I and II, II and III
  - E) I and II, I and III, II and III
4. *All the following substances will dissolve in water EXCEPT:*
  - A)  $\text{CH}_3\text{CH}_2\text{OH}$
  - B)  $\text{AlCl}_3$
  - C)  $\text{Ca}(\text{NO}_3)_2$
  - D)  $\text{C}_6\text{H}_6$
  - E)  $\text{CH}_2\text{OHCH}_2\text{OH}$

Use the structures of cyclohexane and glucose in Figure 13.4 and pentane and acetone in Figure 13.1 to answer Questions 5–7.

5. Pentane is most soluble in
  - A) glucose only.
  - B) glucose and acetone.
  - C) glucose, acetone, and cyclohexane.
  - D) cyclohexane only.
  - E) cyclohexane and glucose.
6. When glucose dissolves in water, the strongest intermolecular forces in the solution are
  - A) dispersions.
  - B) ion–dipoles.
  - C) hydrogen bonds.
  - D) ionic.
  - E) covalent.
7. Which of these molecules will not dissolve in water?
  - A) acetone
  - B) cyclohexane
  - C) pentane
  - D) acetone and cyclohexane
  - E) cyclohexane and pentane

### Free Response Questions

1. Answer the following questions about these laboratory observations.  
 Solid ammonium chloride dissolves in water with a marked decrease in temperature. Solid calcium chloride dissolves in water with a marked increase in temperature. Little or no temperature change is observed when solid sodium chloride dissolves in water.
  - a. Write an equation that describes the dissolving process of ammonium chloride.
  - b. Is the dissolving of calcium chloride endothermic or exothermic? Explain.
  - c. Describe the opposing forces of attraction that are at work in the dissolution of calcium chloride. Which are greater? Why?



d. What can be said about opposing forces of attraction when sodium chloride dissolves in water? Why?

e. Use the observation for ammonium chloride to discuss these seemingly contradictory statements:

*Exothermic processes tend to be thermodynamically favored.*

*Most processes are thermodynamically favored when there is an increase in entropy.*

2. Two important vitamins are shown in Figure 13.6.

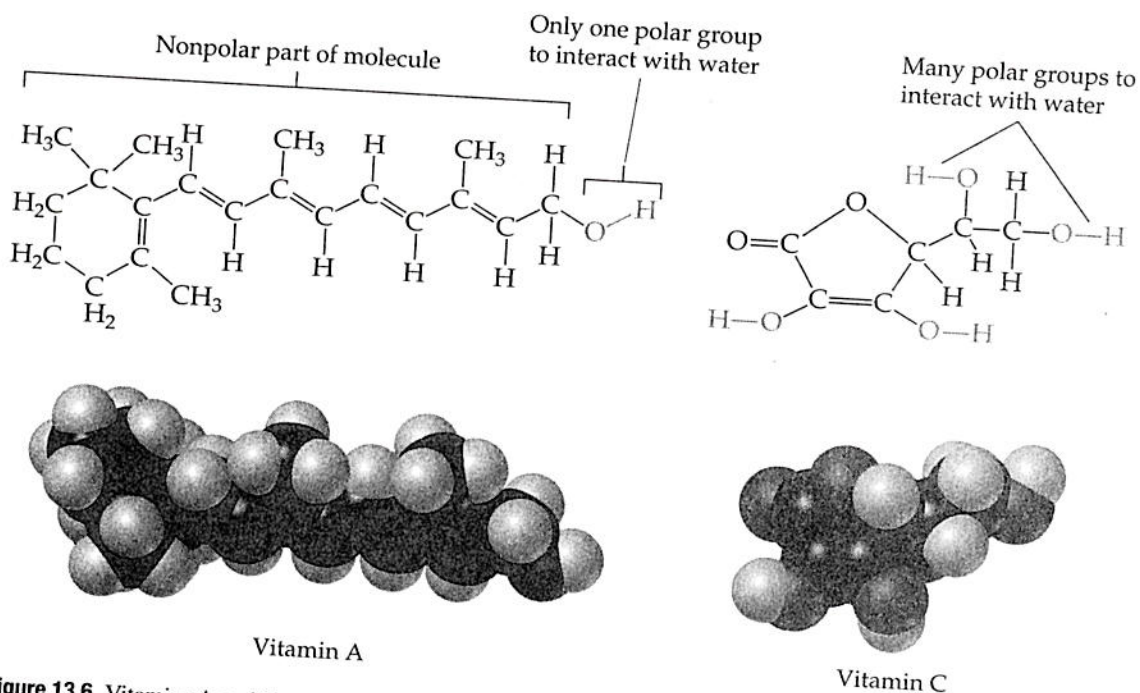


Figure 13.6 Vitamins A and C.

- Tell whether each vitamin is more likely to be water soluble or fat soluble. Justify your reasoning.
- What is the principle intermolecular force acting when a nonpolar substance dissolves in a nonpolar solvent?
- Describe the principle intermolecular force(s) acting when a water-soluble vitamin dissolves in water?
- Identify one aspect that the space-filling models in the figure represent accurately and one aspect that limits their usefulness.
- Identify one aspect that the structural formulas represent accurately and one aspect that limits their usefulness.