

Solutions

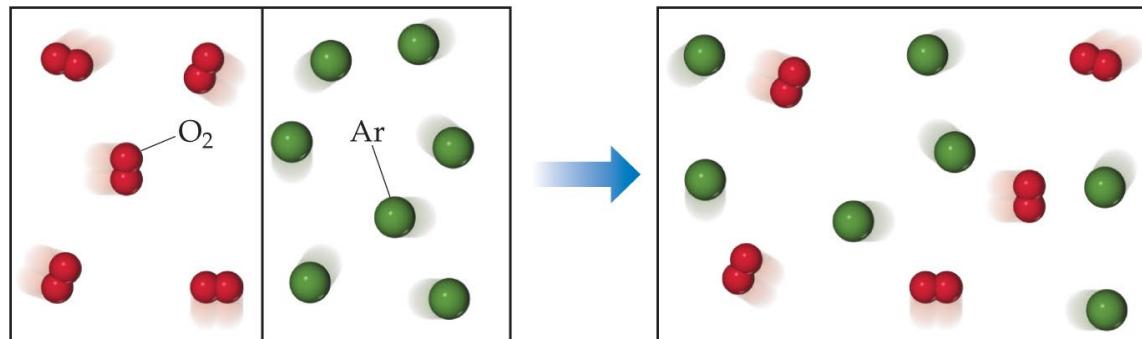
- **Solutions** are homogeneous mixtures of two or more pure substances.
- In a solution, the **solute** is dispersed uniformly throughout the **solvent**.
- The ability of substances to form solutions depends on
 - natural tendency toward mixing.
 - intermolecular forces.



Solutions

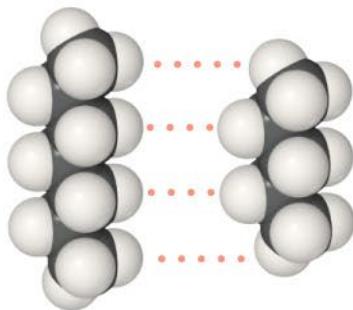
Natural Tendency toward Mixing

- Mixing of gases is a spontaneous process.
- Each gas acts as if it is alone to fill the container.
- Mixing causes more randomness in the position of the molecules, increasing a thermodynamic quantity called *entropy*.
- The formation of solutions is favored by the increase in entropy that accompanies mixing.



Intermolecular Forces of Attraction

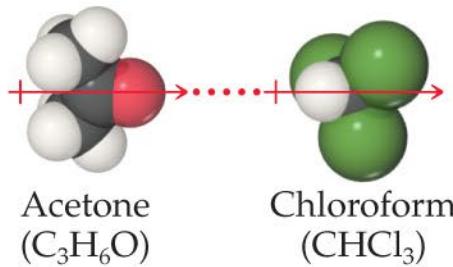
Dispersion



Heptane
(C_7H_{16})

Pentane
(C_5H_{12})

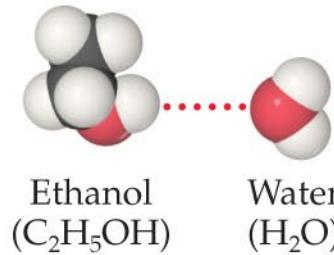
Dipole-dipole



Acetone
(C_3H_6O)

Chloroform
($CHCl_3$)

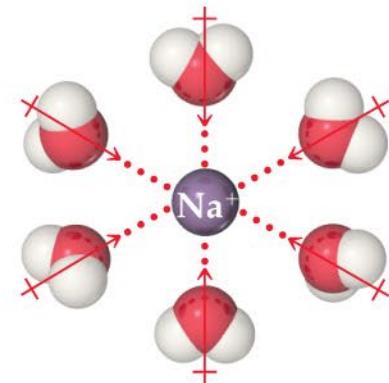
Hydrogen bond



Ethanol
(C_2H_5OH)

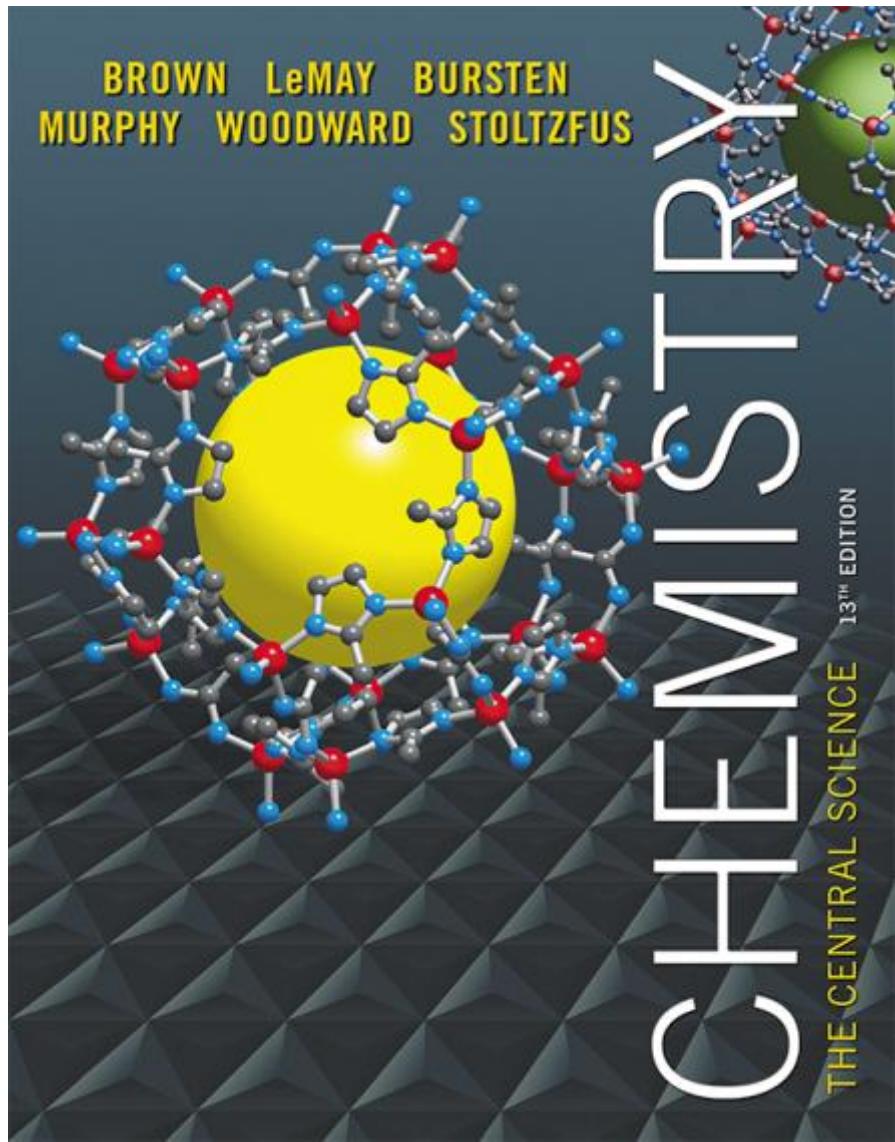
Water
(H_2O)

Ion-dipole



Any intermolecular force of attraction (Chapter 11) can be the attraction between solute and solvent molecules.

Solutions



Lecture Presentation

Chapter 13

Properties of Solutions

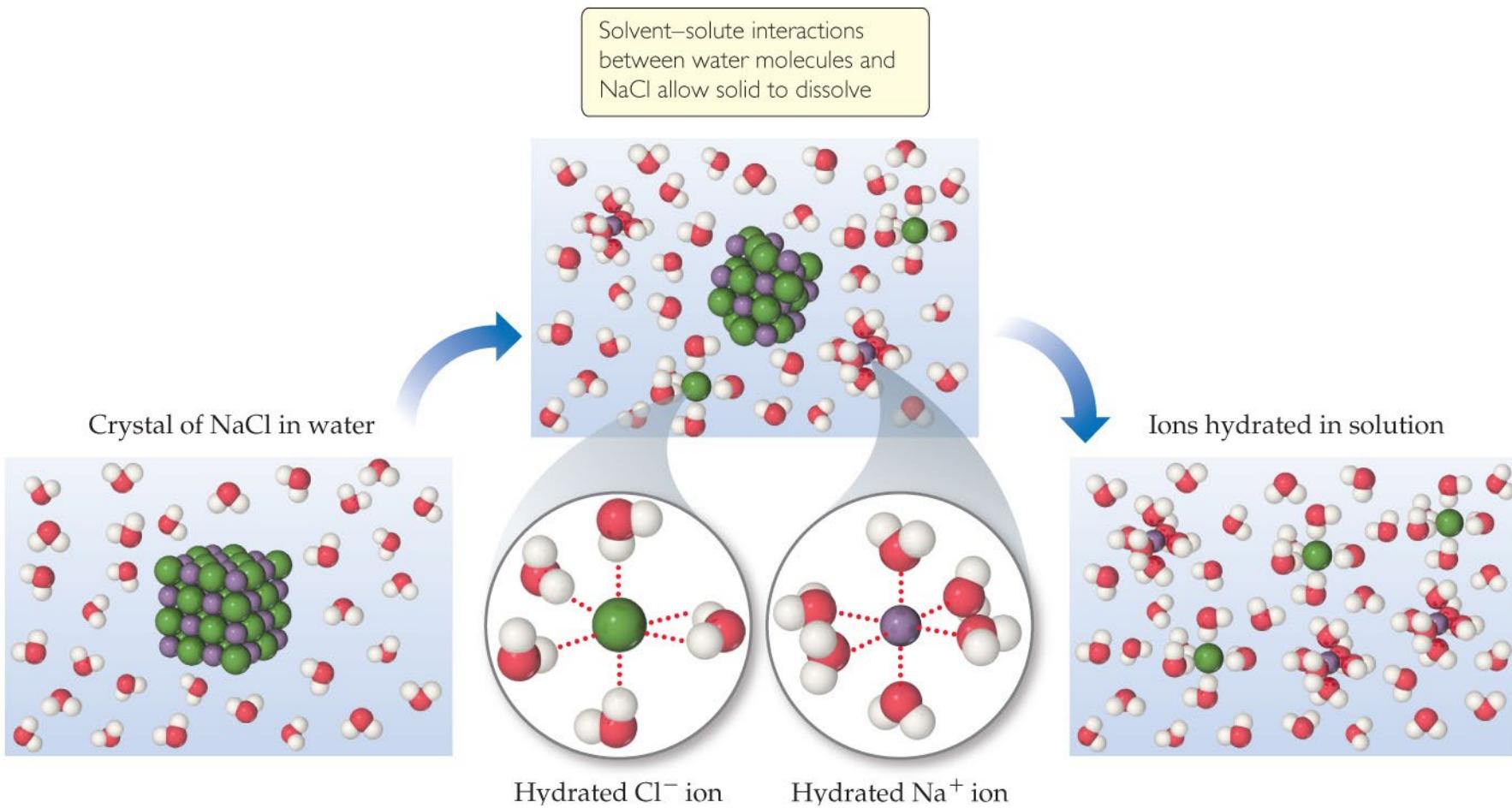
Solutions

Attractions Involved When Forming a Solution

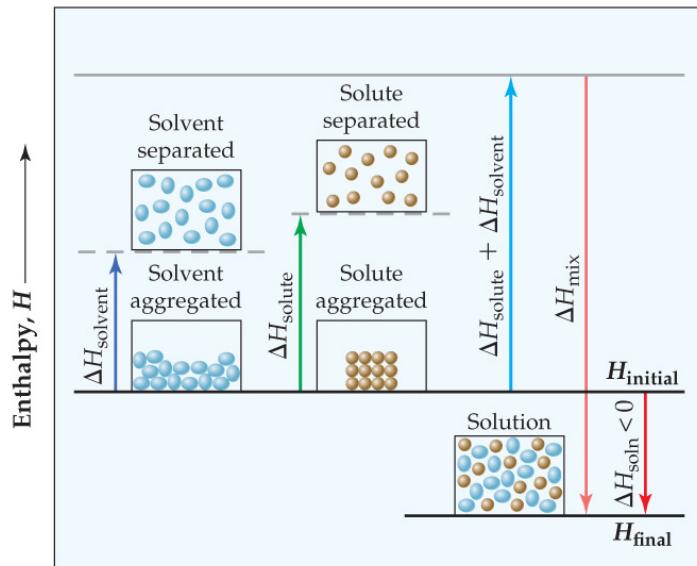
- *Solute–solute interactions* must be overcome to disperse these particles when making a solution.
- *Solvent–solvent interactions* must be overcome to make room for the solute.
- *Solvent–solute interactions* occur as the particles mix.



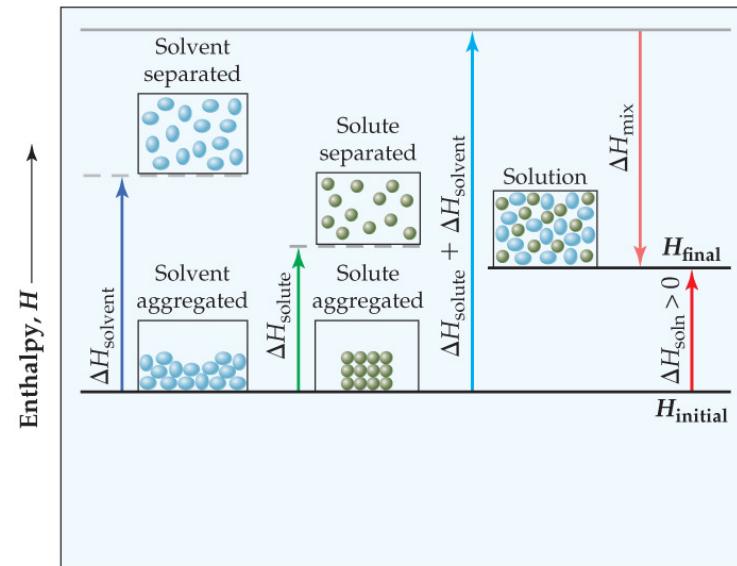
Energetics of Solution Formation



Exothermic or Endothermic



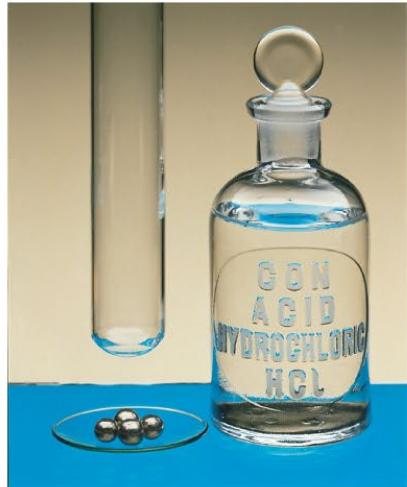
Exothermic solution process



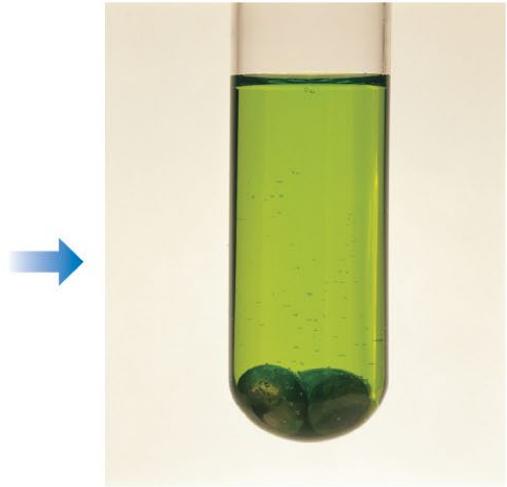
Endothermic solution process

- For a reaction to occur, ΔH_{mix} must be close to the sum of ΔH_{solute} and $\Delta H_{\text{solvent}}$.
- Remember that the randomness from entropy will affect the process, too.

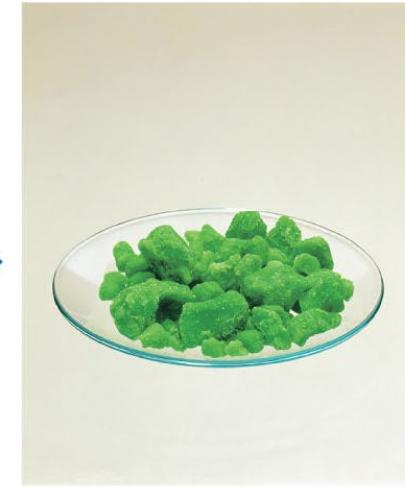
Aqueous Solution vs. Chemical Reaction



Nickel metal and hydrochloric acid



Nickel reacts with hydrochloric acid, forming $\text{NiCl}_2(aq)$ and $\text{H}_2(g)$. The solution is of NiCl_2 , not Ni metal



$\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}(s)$ remains when solvent evaporated

Just because a substance disappears when it comes in contact with a solvent, it does not mean the substance dissolved. It may have reacted, like nickel with hydrochloric acid.



Opposing Processes

- The solution-making process and **crystallization** are opposing processes.
- Solute + solvent $\xrightleftharpoons[\text{crystallize}]{\text{dissolve}}$ solution
- When the rate of the opposing processes is equal, additional solute will not dissolve unless some crystallizes from solution. This is a **saturated** solution.
- If we have not yet reached the amount that will result in crystallization, we have an **unsaturated** solution.

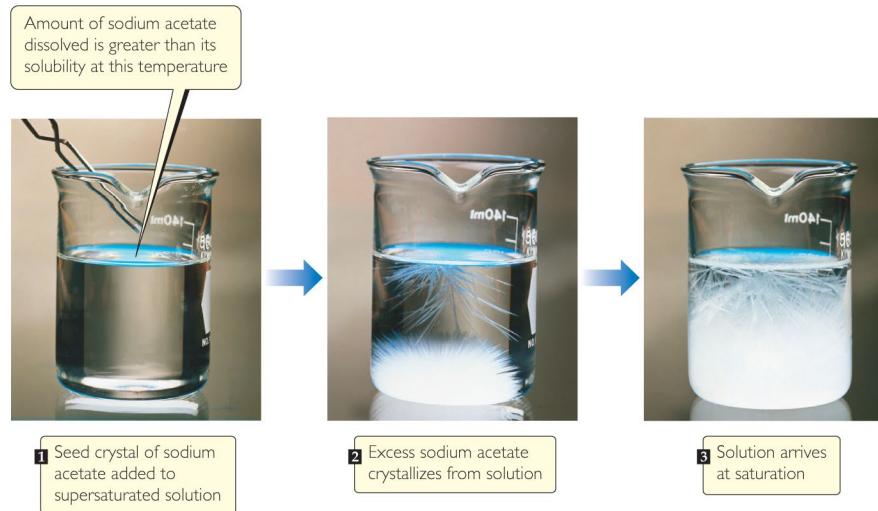


Solubility

- **Solubility** is the maximum amount of solute that can dissolve in a given amount of solvent at a given temperature.
- Saturated solutions have that amount of solute dissolved.
- Unsaturated solutions have any amount of solute *less* than the maximum amount dissolved in solution.
- Surprisingly, there is one more type of solution.



Supersaturated Solutions



- In **supersaturated** solutions, the solvent holds more solute than is normally possible at that temperature.
- These solutions are unstable; crystallization can usually be stimulated by adding a “seed crystal” or scratching the side of the flask.
- These are uncommon solutions.



Factors That Affect Solubility

- Solute–solvent Interactions
- Pressure (for gaseous solutes)
- Temperature



Solute–Solvent Interactions

- Simply put: “Like dissolves like.”
- That does not explain everything!
- The *stronger* the solute–solvent interaction, the *greater* the solubility of a solute in that solvent.
- The gases in the table only exhibit dispersion force. The larger the gas, the more soluble it will be in water.

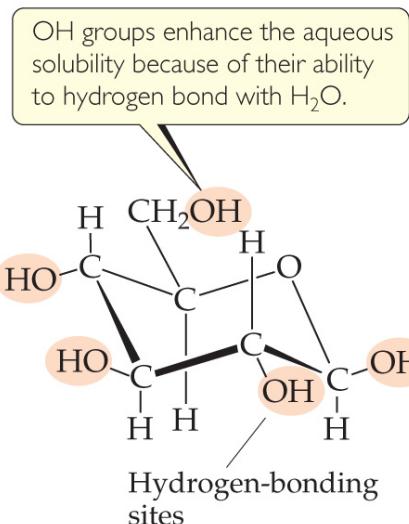
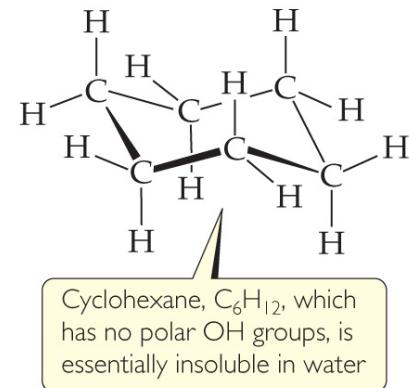
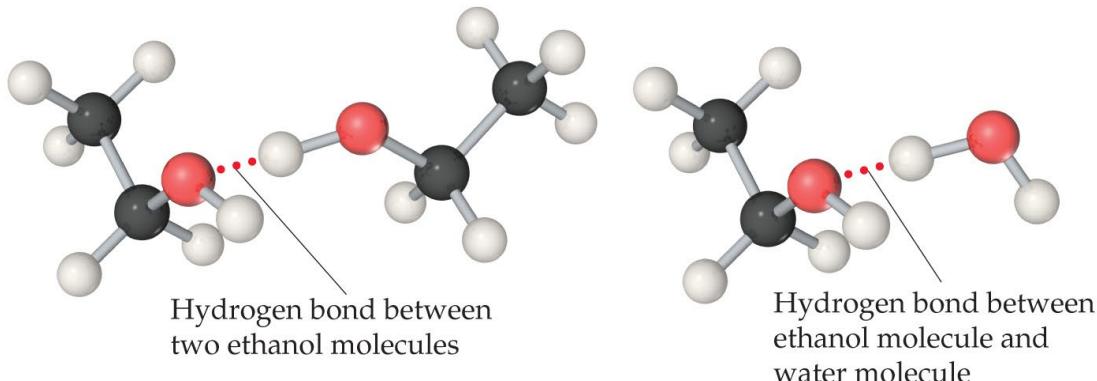
Table 13.1 Solubilities of Gases
in Water at 20 °C, with 1 atm Gas Pressure

Gas	Molar Mass (g/mol)	Solubility (M)
N ₂	28.0	0.69×10^{-3}
O ₂	32.0	1.38×10^{-3}
Ar	39.9	1.50×10^{-3}
Kr	83.8	2.79×10^{-3}

Solutions

Organic Molecules in Water

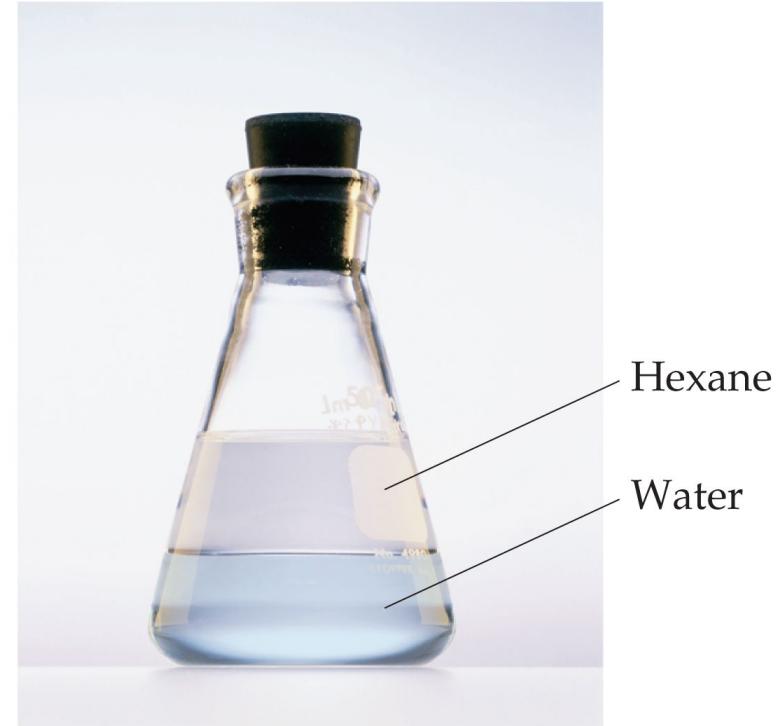
- Polar organic molecules dissolve in water better than nonpolar organic molecules.
- Hydrogen bonding increases solubility, since C–C and C–H bonds are not very polar.



Solutions

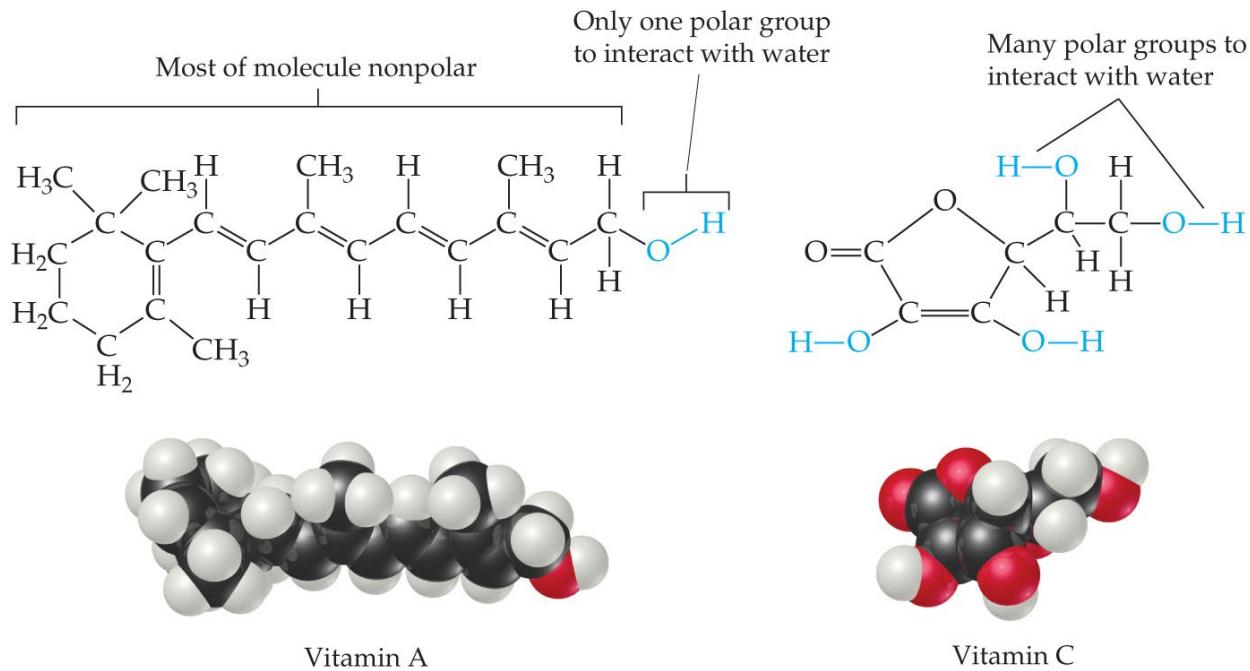
Liquid/Liquid Solubility

- Liquids that mix in all proportions are **miscible**.
- Liquids that do *not* mix in one another are **immiscible**.
- Because hexane is nonpolar and water is polar, they are immiscible.



Solubility and Biological Importance

- Fat-soluble vitamins (like vitamin A) are nonpolar; they are readily stored in fatty tissue in the body.
- Water-soluble vitamins (like vitamin C) need to be included in the daily diet.



Pressure Effects

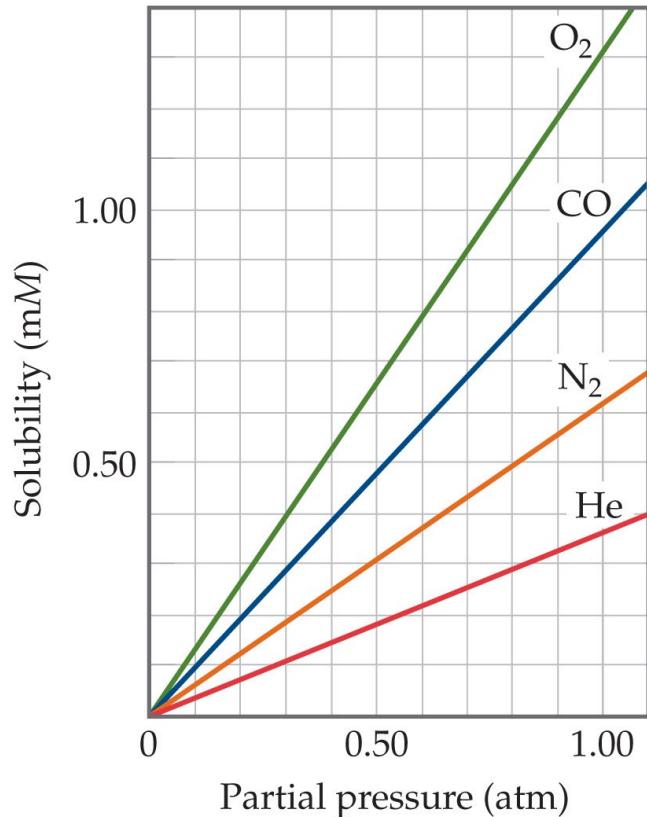
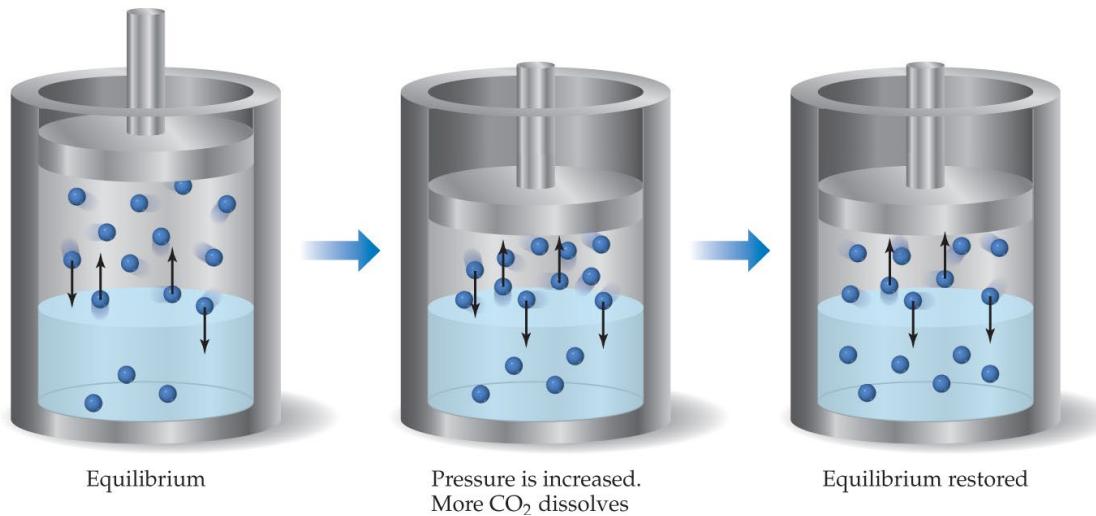
- The solubility of solids and liquids are *not* appreciably affected by pressure.
- Gas solubility is affected by pressure.



Solutions

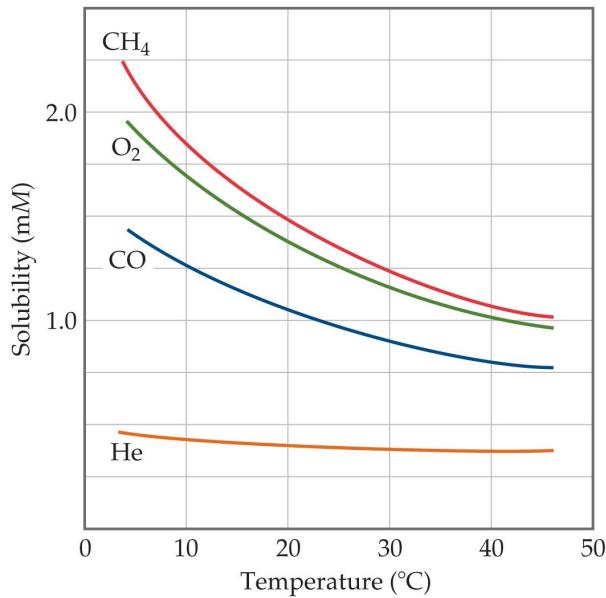
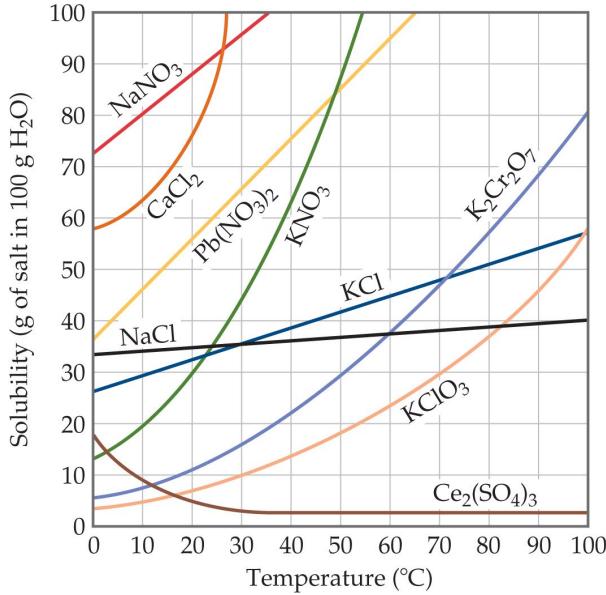
Henry's Law

- The solubility of a gas is proportional to the partial pressure of the gas above the solution.
- $S_g = kP_g$



Temperature Effects

- For most solids, as temperature increases, solubility increases. However, clearly this is not always true—some increase greatly, some remain relatively constant, and others decrease.
- For *all* gases, as temperature increases, solubility decreases. Cold rivers have higher oxygen content than warm rivers.



Solution Concentration

- We have discussed solubility and solutions qualitatively: saturated (which is quantitative), unsaturated, and supersaturated.
- Now we will give specific amounts to solutions.



Units of Concentration

- 1) Mass percentage
- 2) Parts per million (ppm)
- 3) Parts per billion (ppb)
- 4) Mole fraction
- 5) Molarity
- 6) Molality



1) Mass Percentage

- Percent means “out of 100.”
- Take the ratio of the mass of the solute to the total solution mass.
- Multiply by 100 to make it a percent.

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



- 2) Parts per Million (ppm)
- 3) Parts per Billion (ppb)

- still relating mass of a solute to the total mass of the solution
- Since percent is out of 100, we multiplied by 100.
- ppm is per million, so we multiply by 10^6 .

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

- ppb is per billion, so we multiply by 10^9 .

Solutions

(4) Mole Fraction (χ)

- Mole fraction is the ratio of moles of a substance to the total number of moles in a solution.
- It does not matter if it is for a solute or for a solvent.

$$\text{Mole fraction of component} = \frac{\text{moles of component}}{\text{total moles of all components}}$$

Solutions

(5) Molarity (M)

(6) Molality (m)

- Be careful of your penmanship!
- Molarity was discussed in Chapter 4 as moles of solute per liter of solution.

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

- Molality is moles of solute per kilogram of solvent.

$$\text{Molality} = \frac{\text{moles of solute}}{\text{kilograms of solvent}}$$



Molarity vs. Molality

- When water is the solvent, dilute solutions have similar molarity and molality.
- Molality does not vary with temperature (mass does not change).
- Molarity varies with temperature (volume changes).



Converting Units

- Follow dimensional analysis techniques from Chapter 1.
- To convert between molality and molarity, the density of the *solution* must be used.



Colligative Properties

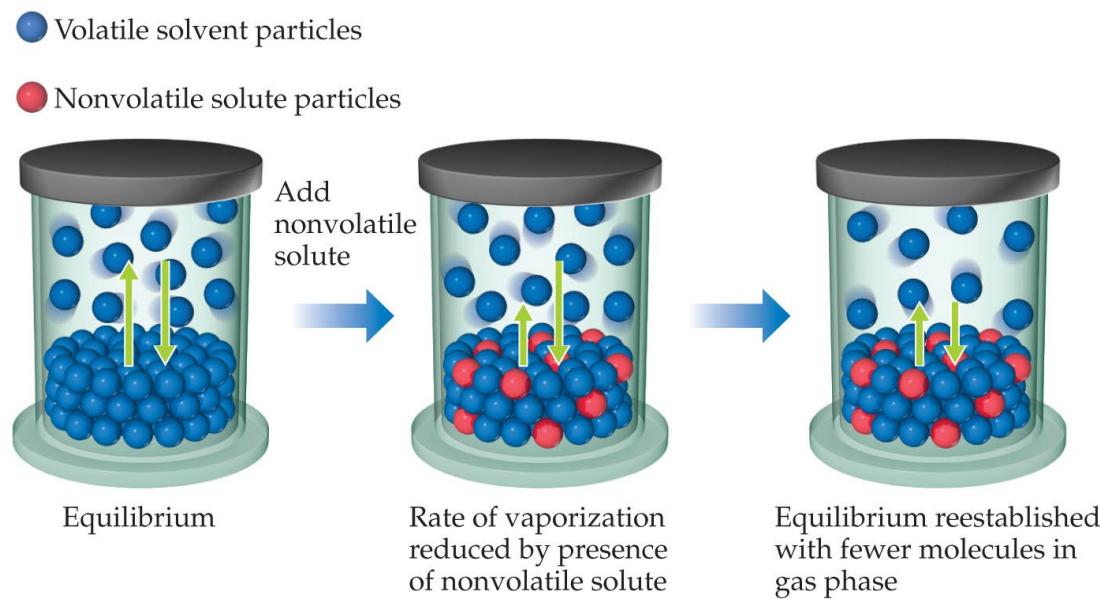
- **Colligative properties** depend only on the *quantity*, not on the *identity* of the solute particles.
- Among colligative properties are:
 - Vapor-pressure lowering
 - Boiling-point elevation
 - Freezing-point depression
 - Osmotic pressure



Solutions

Vapor Pressure

Because of solute–solvent intermolecular attraction, higher concentrations of nonvolatile solutes make it harder for solvent to escape to the vapor phase. Therefore, the vapor pressure of a solution is lower than that of the pure solvent.



Raoult's Law

- The vapor pressure of a volatile solvent over the solution is the product of the mole fraction of the solvent times the vapor pressure of the pure solvent.

$$P_{\text{solution}} = X_{\text{solvent}} P_{\text{solvent}}^{\circ}$$

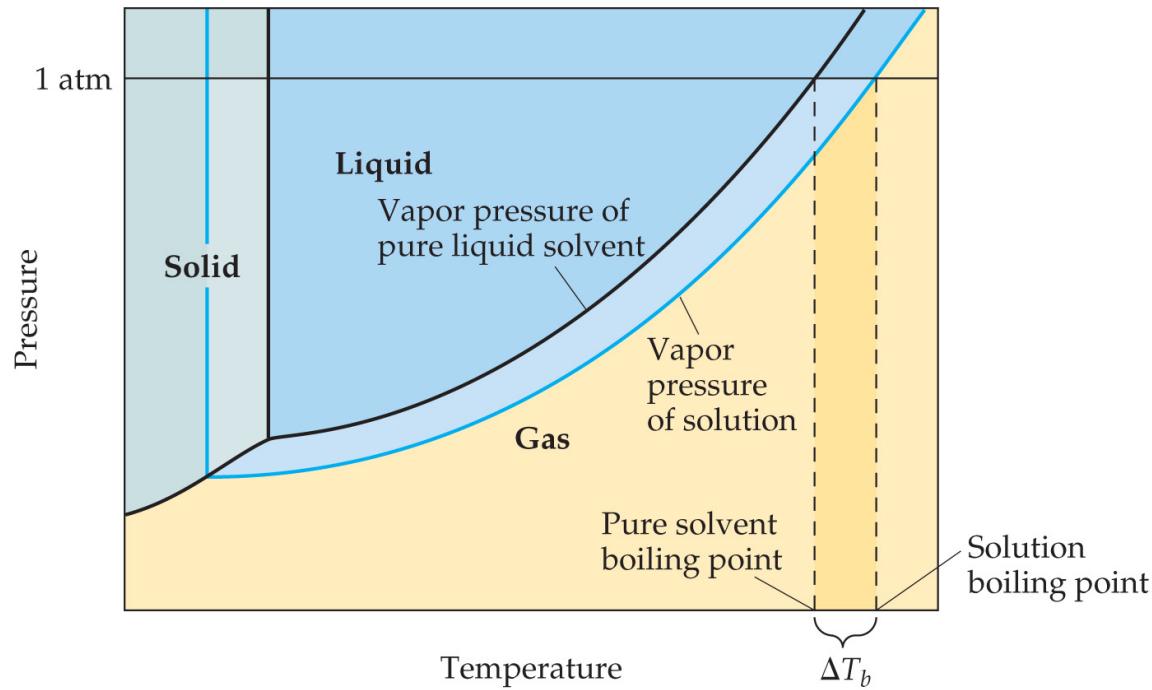
- In ideal solutions, it is assumed that each substance will follow Raoult's Law.



Solutions

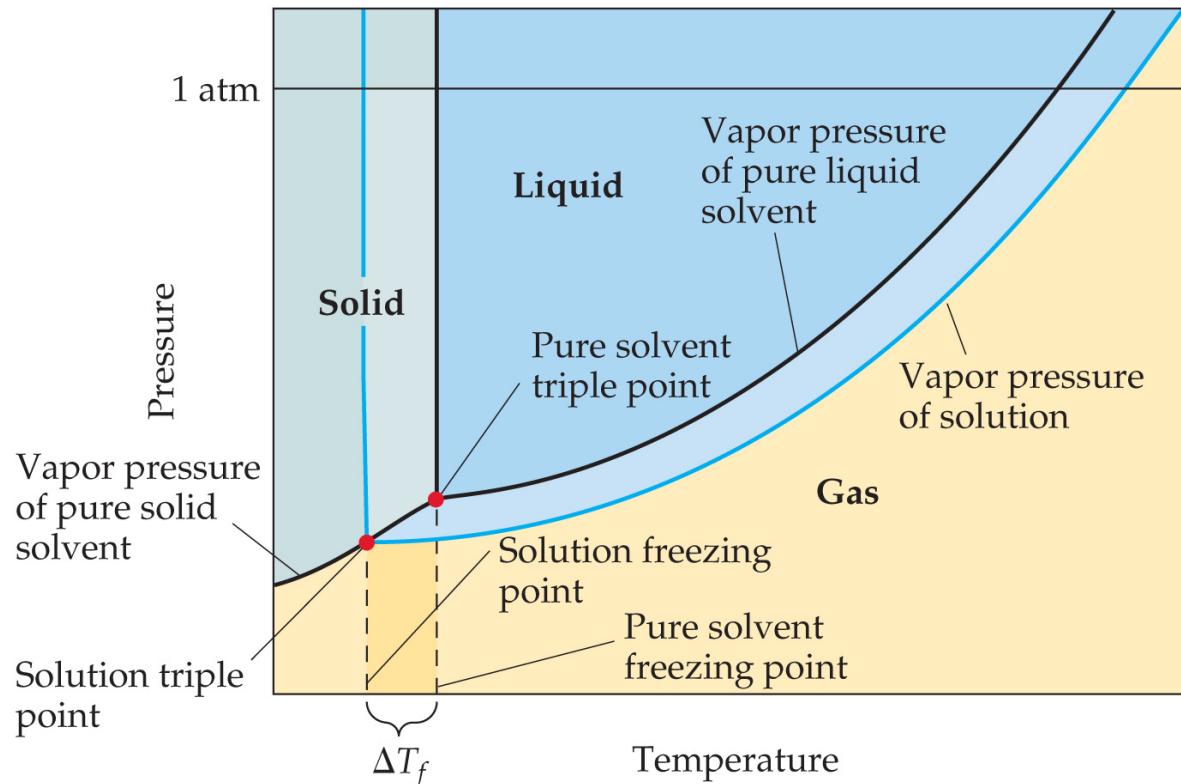
Boiling-Point Elevation

Since vapor pressures are lowered for solutions, it requires a higher temperature to reach atmospheric pressure. Hence, boiling point is raised.



Freezing-Point Depression

The construction of the phase diagram for a solution demonstrates that the freezing point is lowered while the boiling point is raised.



Boiling-Point Elevation and Freezing-Point Depression

- The change in temperature is directly proportional to molality (using the van't Hoff factor: i).

$$\Delta T_b = T_b(\text{solution}) - T_b(\text{solvent}) = iK_b m$$

$$\Delta T_f = T_f(\text{solution}) - T_f(\text{solvent}) = -iK_f m$$

Table 13.3 Molal Boiling-Point-Elevation and Freezing-Point-Depression Constants

Solvent	Normal Boiling Point (°C)	K_b (°C/m)	Normal Freezing Point (°C)	K_f (°C/m)
Water, H ₂ O	100.0	0.51	0.0	1.86
Benzene, C ₆ H ₆	80.1	2.53	5.5	5.12
Ethanol, C ₂ H ₅ OH	78.4	1.22	-114.6	1.99
Carbon tetrachloride, CCl ₄	76.8	5.02	-22.3	29.8
Chloroform, CHCl ₃	61.2	3.63	-63.5	4.68

Solutions

The van't Hoff Factor (*i*)

- What is the van't Hoff factor?
- It takes into account dissociation in solution!
- Theoretically, we get 2 particles when NaCl dissociates. So, $i = 2$.
- In fact, the amount that particles remain together is dependent on the concentration of the solution.

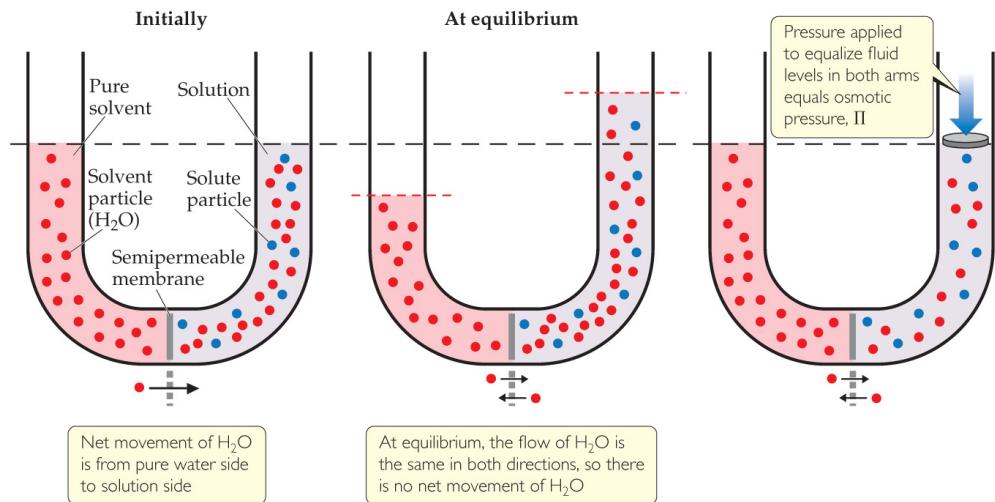
Table 13.4 Measured and Expected van't Hoff Factors for Several Substances at 25 °C

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



Osmosis

- Some substances form **semipermeable membranes**, allowing some smaller particles to pass through, but blocking larger particles.
- The net movement of solvent molecules from solution of low to high concentration across a semipermeable membrane is **osmosis**. The applied pressure to stop it is **osmotic pressure**.



Osmotic Pressure

- Osmotic pressure is a colligative property.

$$\Pi = i \left(\frac{n}{V} \right) RT = iMRT$$

- If two solutions separated by a semipermeable membrane have the *same* osmotic pressure, no osmosis will occur.



Types of Solutions & Osmosis

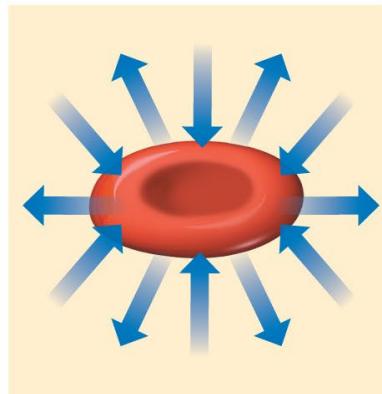
- 1) Isotonic solutions: Same osmotic pressure; solvent passes the membrane at the same rate both ways.
- 2) Hypotonic solution: Lower osmotic pressure; solvent will leave this solution at a higher rate than it enters with.
- 3) Hypertonic solution: Higher osmotic pressure; solvent will enter this solution at a higher rate than it leaves with.



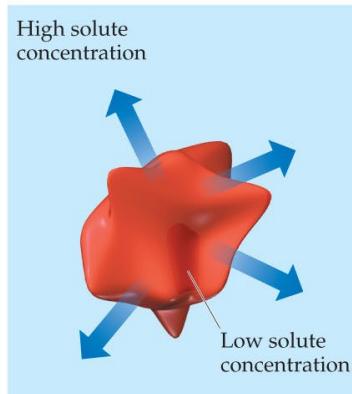
Osmosis and Blood Cells

- Red blood cells have semipermeable membranes.
- If stored in a hypertonic solution, they will shrivel as water leaves the cell; this is called **crenation**.
- If stored in a hypotonic solution, they will grow until they burst; this is called **hemolysis**.

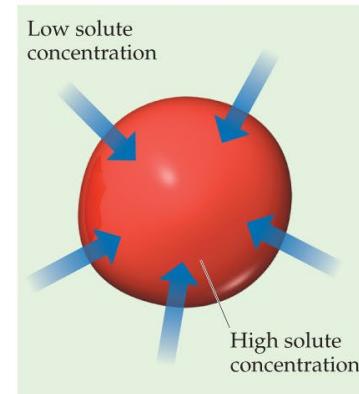
The arrows represent the net movement of water molecules.



Red blood cell in isotonic medium
neither swells nor shrinks.



Crenation of red blood cell placed
in hypertonic environment



Hemolysis of red blood cell placed
in hypotonic environment

Solutions

Colloids

Suspensions of particles larger than individual ions or molecules, but too small to be settled out by gravity, are called **colloids**.

Table 13.5 Types of Colloids

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

Solutions

Tyndall Effect



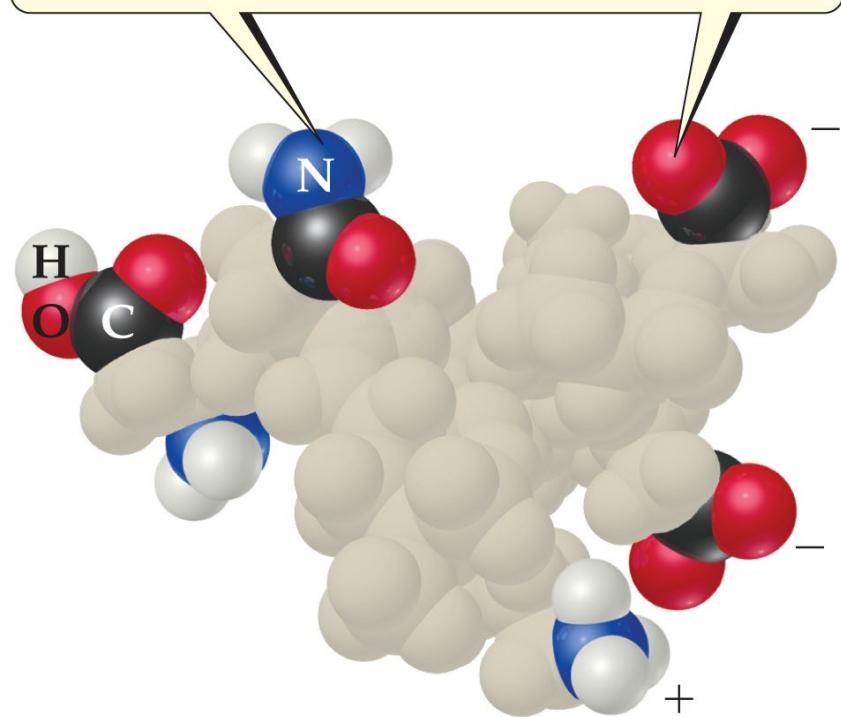
- Colloidal suspensions can scatter rays of light. (Solutions do not.)
- This phenomenon is known as the **Tyndall effect**.



Colloids and Biomolecules

Some molecules have a polar, **hydrophilic** (*water-loving*) end and a nonpolar, **hydrophobic** (*water-fearing*) end.

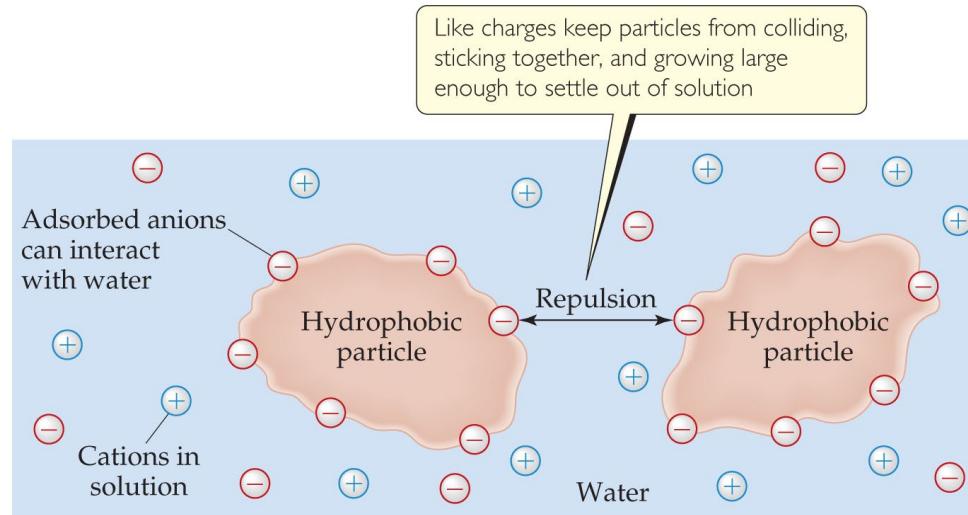
Hydrophilic polar and charged groups on molecule surface help molecule remain dispersed in water and other polar solvents



Solutions

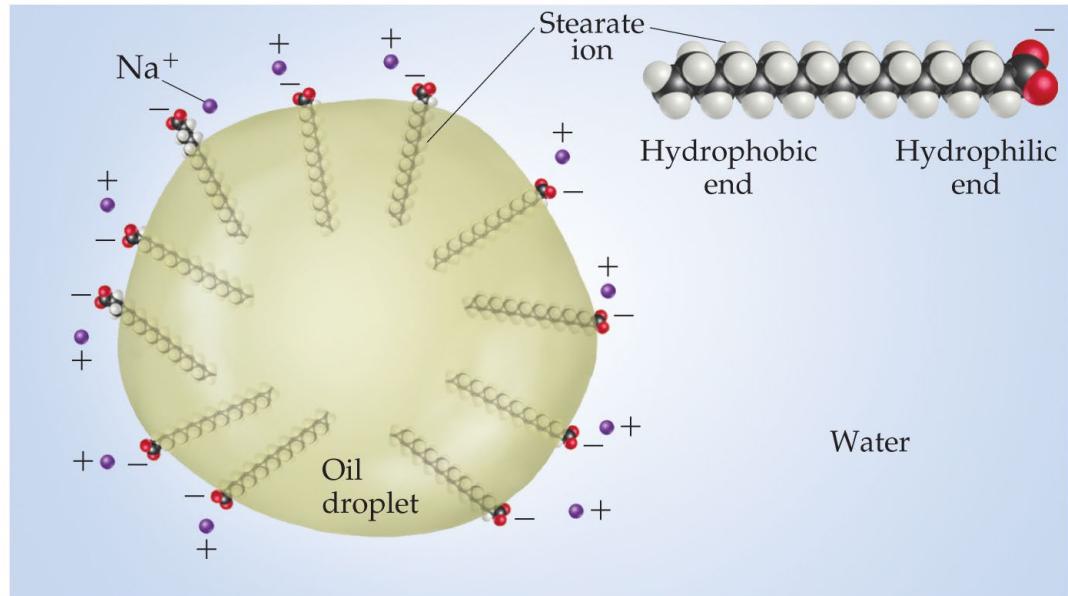
Stabilizing Colloids by Adsorption

- Ions can adhere to the surface of an otherwise hydrophobic colloid.
- This allows it to interact with aqueous solution.



Colloids in Biological Systems

- Colloids can aid in the emulsification of fats and oils in aqueous solutions.
- An emulsifier causes something that normally does *not* dissolve in a solvent to do so.



Brownian Motion

Motion of colloids due to numerous collisions with the much smaller solvent.

Table 13.6 Calculated Mean Free Path, after One Hour, for Uncharged Colloidal Spheres in Water at 20 °C

Radius of sphere, nm	Mean Free Path, mm
1	1.23
10	0.390
100	0.123
1000	0.039

Solutions