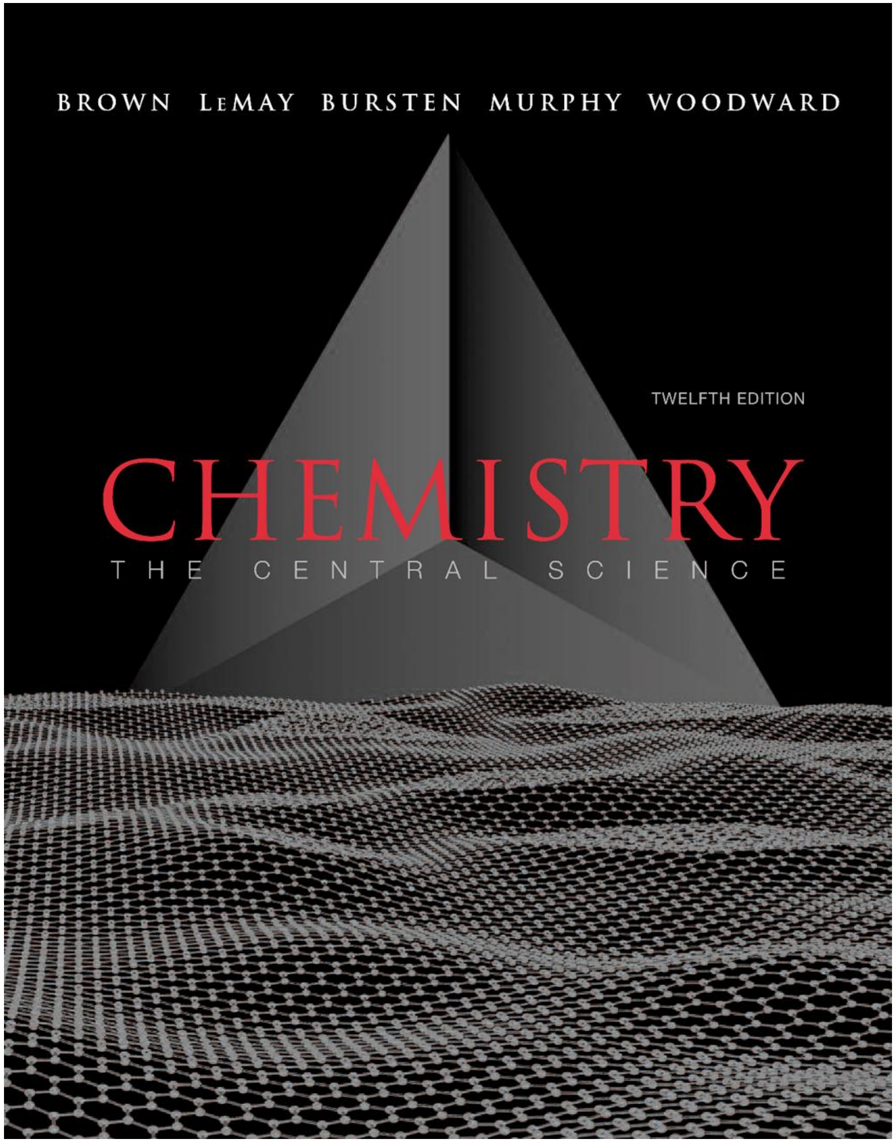


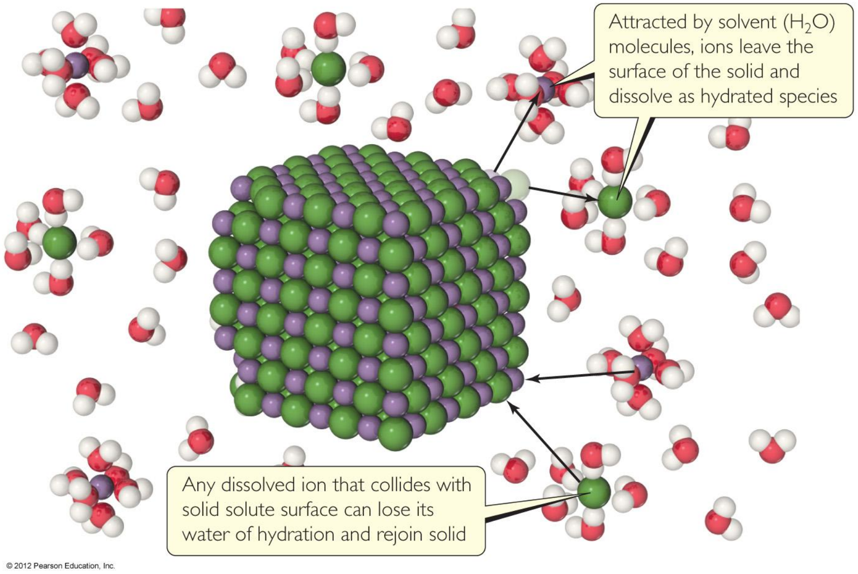
Lecture Presentation

Chapter 13

Properties of Solutions

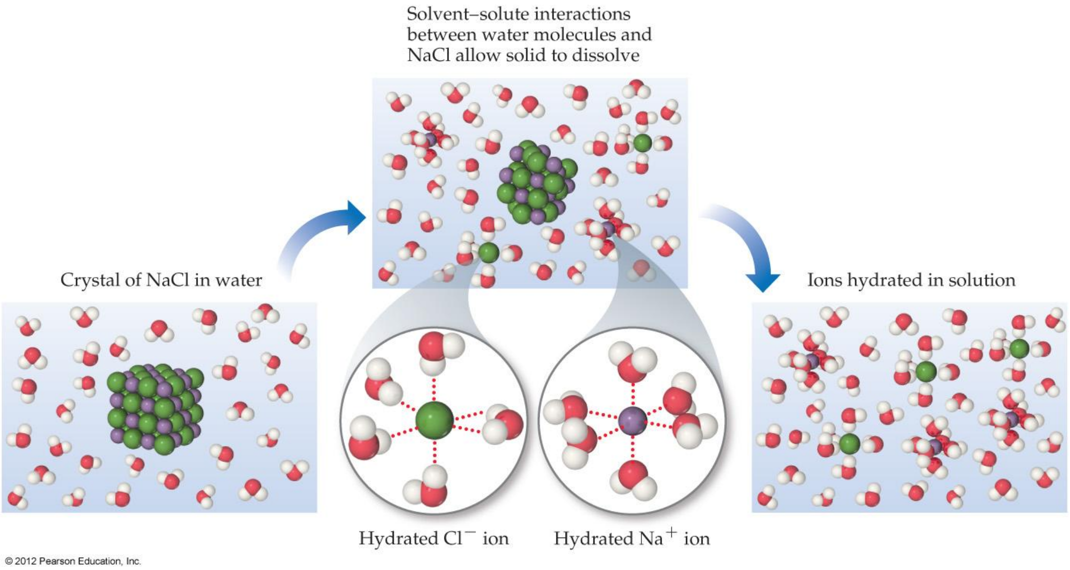
John D. Bookstaver
St. Charles Community College
Cottleville, MO

Solutions



- **Solutions** are homogeneous mixtures of two or more pure substances.
- In a solution, the **solute** is dispersed uniformly throughout the **solvent**.

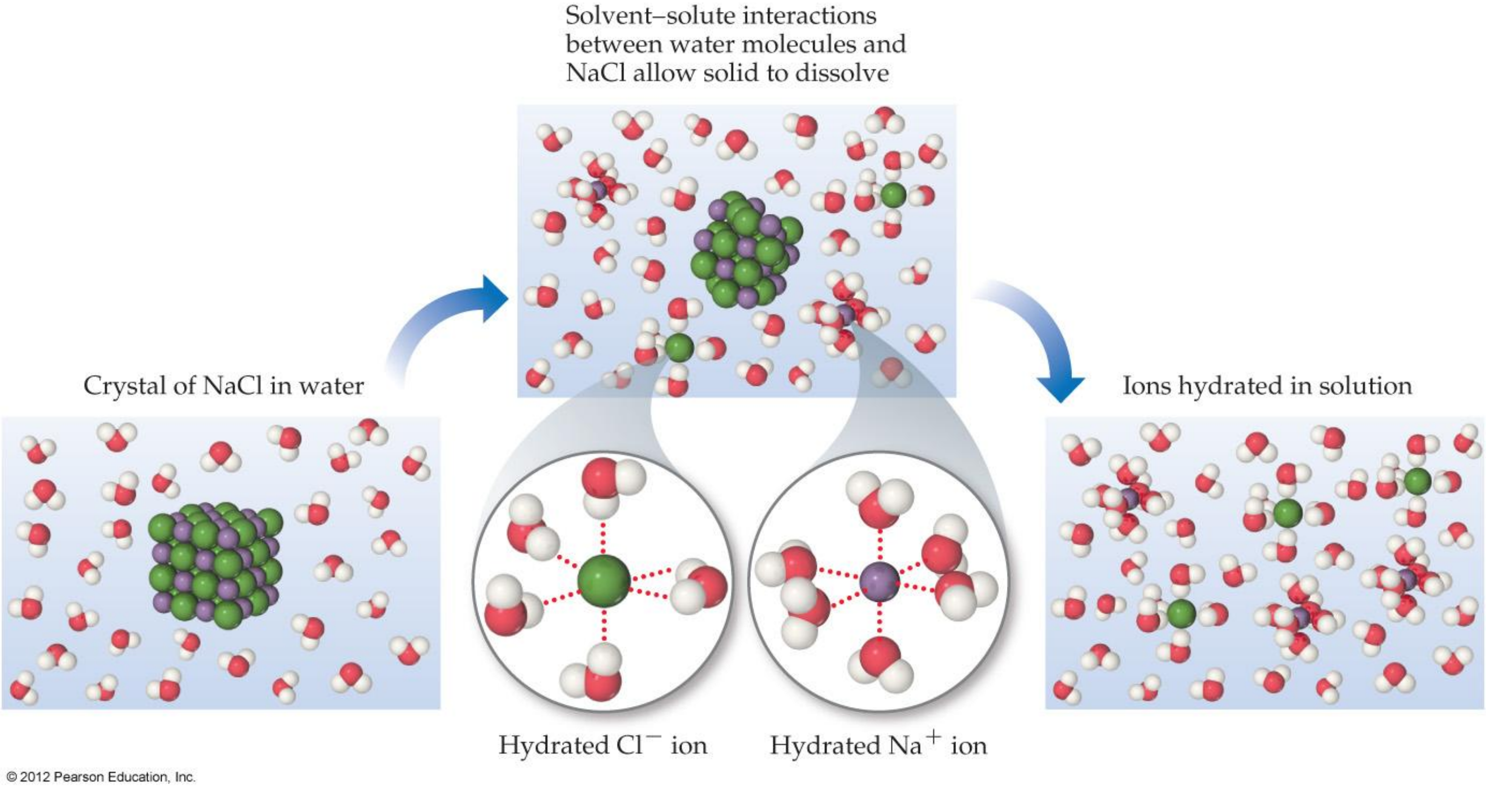
Solutions



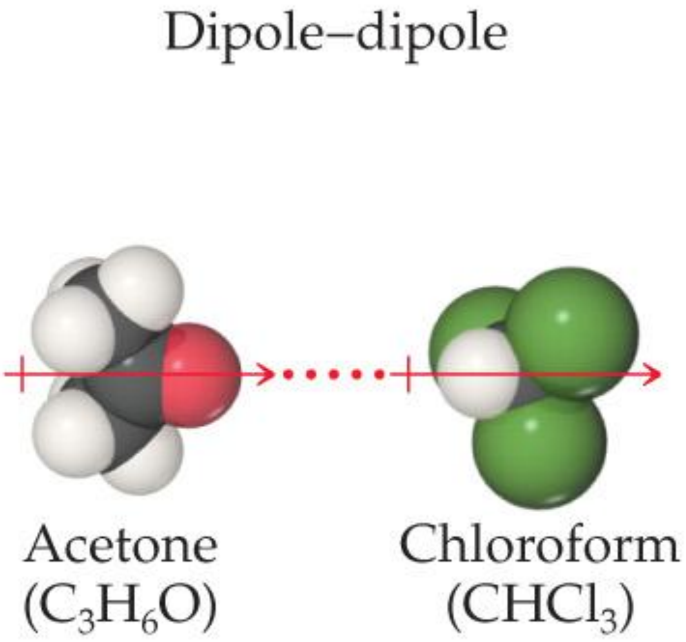
The intermolecular forces between solute and solvent particles must be strong enough to compete with those between solute particles and those between solvent particles.

How Does a Solution Form?

As a solution forms, the solvent pulls solute particles apart and surrounds, or **solvates**, them.



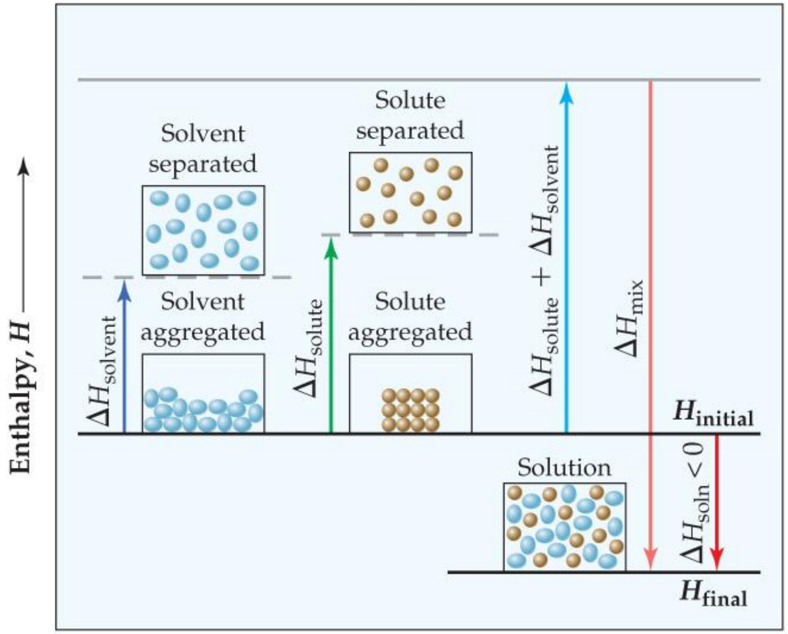
How Does a Solution Form?



If an ionic salt is soluble in water, it is because the ion–dipole interactions are strong enough to overcome the lattice energy of the salt crystal.

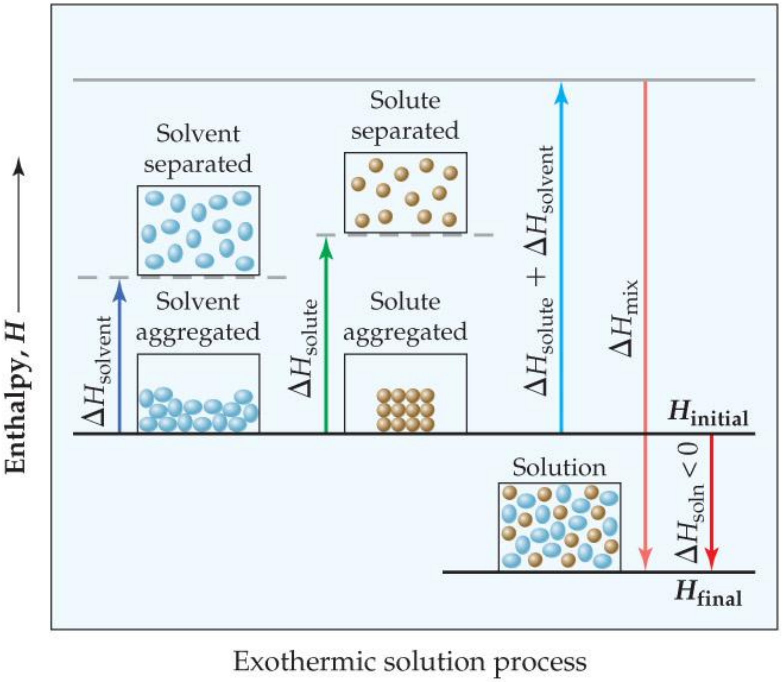
Energy Changes in Solution

- Simply put, three processes affect the energetics of solution:
  - Separation of solute particles,
  - Separation of solvent particles,
  - New interactions between solute and solvent.



Exothermic solution process

Energy Changes in Solution



Exothermic solution process

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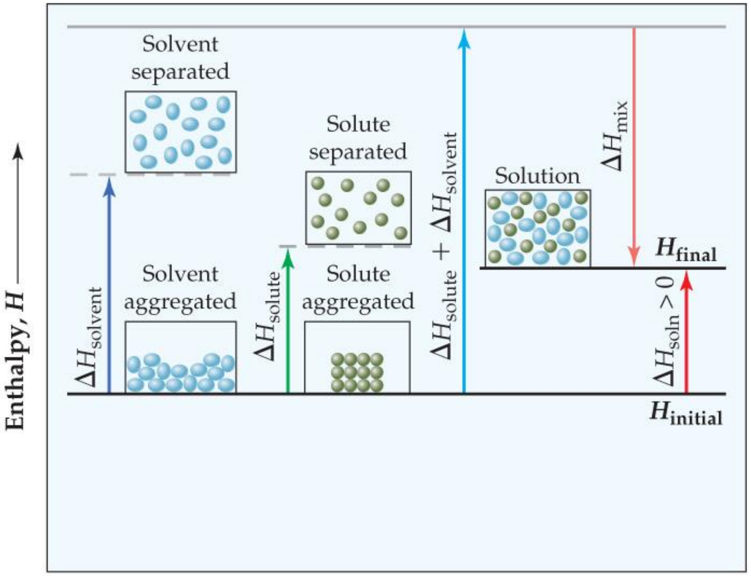
The enthalpy change of the overall process depends on Δ*H* for each of these steps.

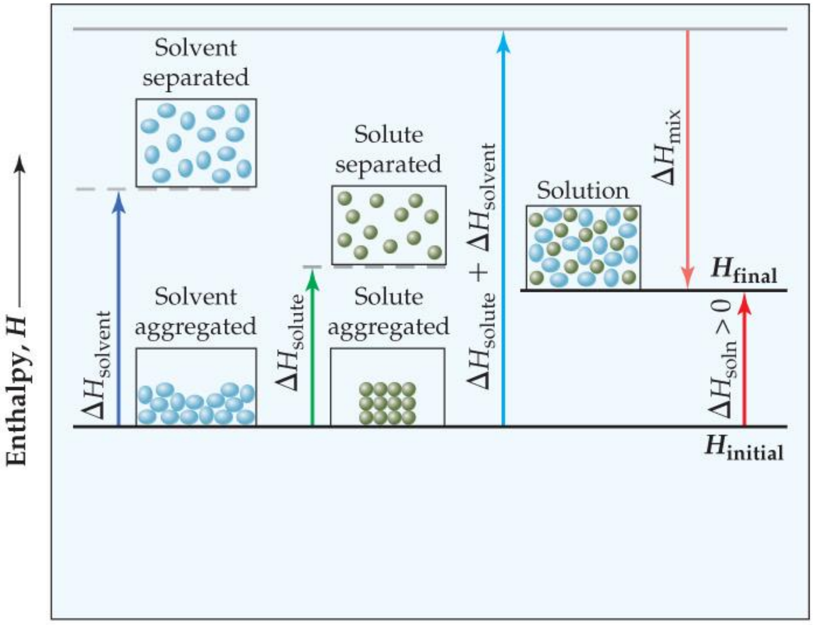
Why Do Endothermic Processes Occur?

Things do not tend to occur spontaneously (i.e., without outside intervention) unless the energy of the system is lowered.



Endothermic solution process

Why Do Endothermic Processes Occur?

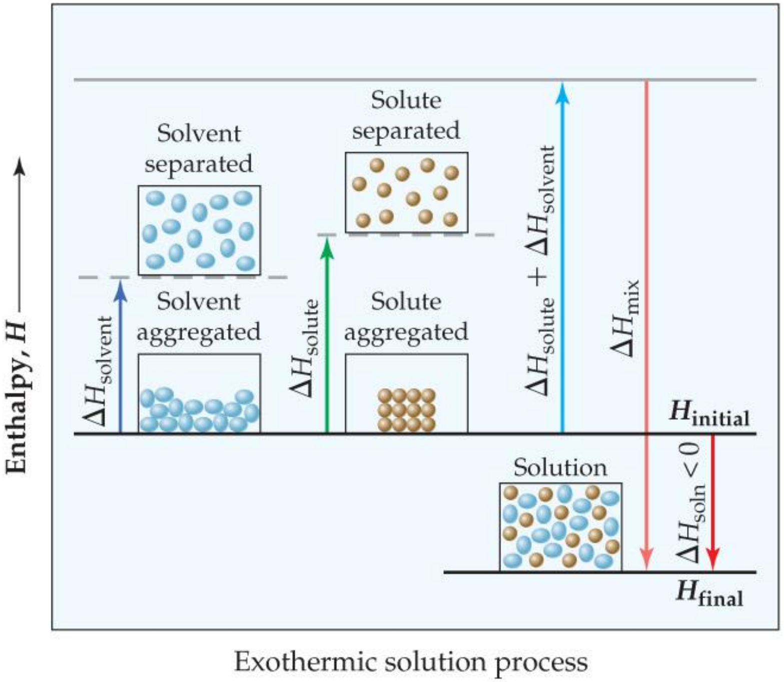


Endothermic solution process

Yet we know that in some processes, like the dissolution of NH_4NO_3 in water, heat is absorbed, not released.

Enthalpy Is Only Part of the Picture

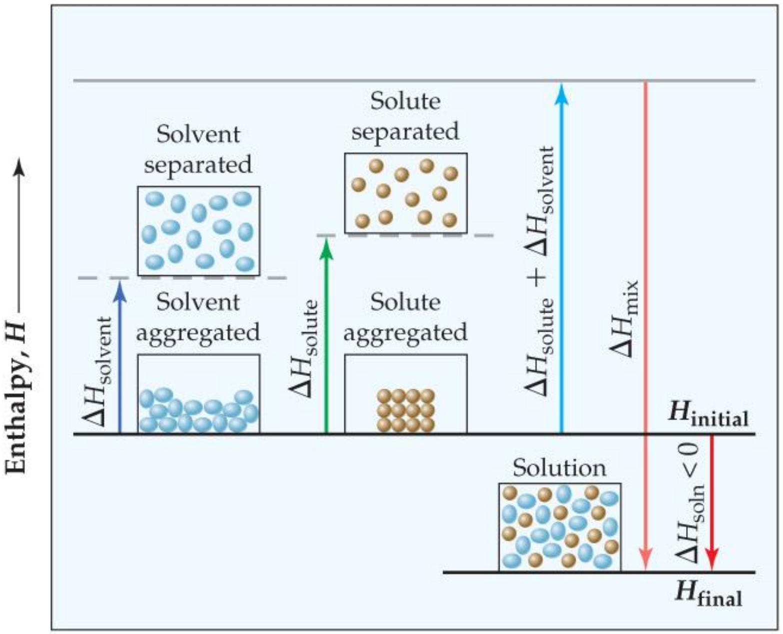
The reason is that increasing the disorder or randomness (known as **entropy**) of a system tends to lower the energy of the system.



Exothermic solution process

Enthalpy Is Only Part of the Picture

So even though enthalpy may increase, the overall energy of the system can still decrease if the system becomes more disordered.



Exothermic solution process

Student, Beware!

Nickel metal and hydrochloric acid

Nickel reacts with hydrochloric acid, forming $NiCl_2(aq)$ and $H_2(g)$. The solution is of $NiCl_2$, not Ni metal

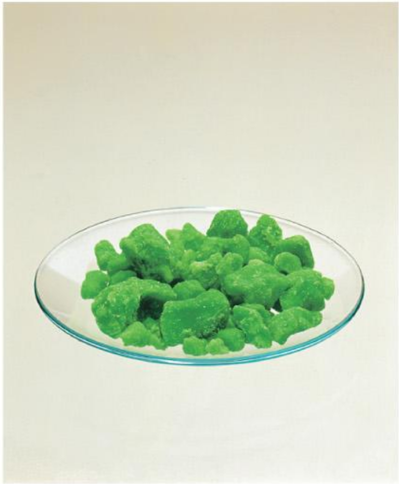
$NiCl_2 \cdot 6H_2O(s)$ remains when solvent evaporated

Just because a substance disappears when it comes in contact with a solvent, it doesn't mean the substance dissolved. It may have reacted.

Student, Beware!

Nickel metal and hydrochloric acid

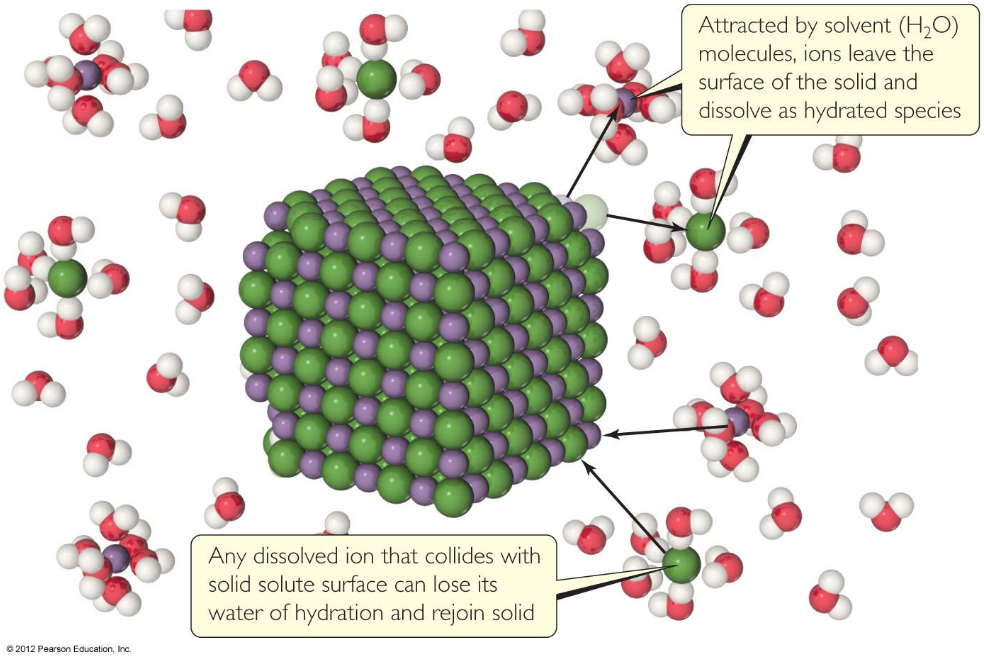
Nickel reacts with hydrochloric acid, forming $NiCl_2(aq)$ and $H_2(g)$. The solution is of $NiCl_2$, not Ni metal



$NiCl_2 \cdot 6H_2O(s)$ remains when solvent evaporated

- Dissolution is a physical change—you can get back the original solute by evaporating the solvent.
- If you can’t get it back, the substance didn’t dissolve, it reacted.

Types of Solutions

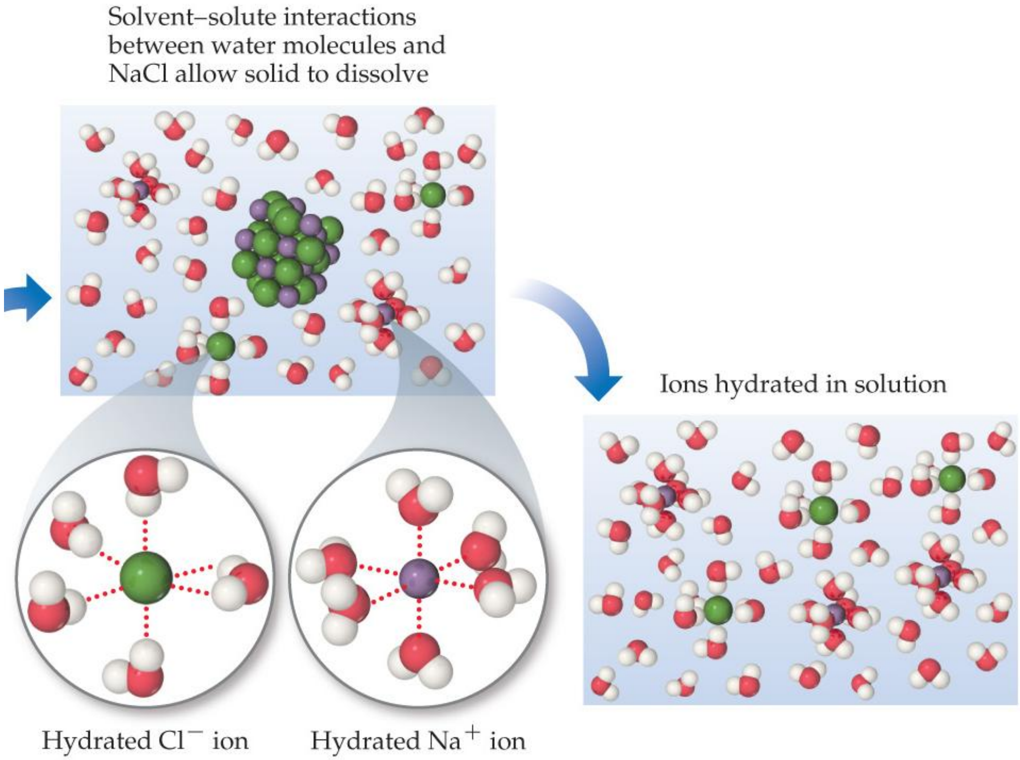

Attracted by solvent (H_2O) molecules, ions leave the surface of the solid and dissolve as hydrated species

Any dissolved ion that collides with solid solute surface can lose its water of hydration and rejoin solid

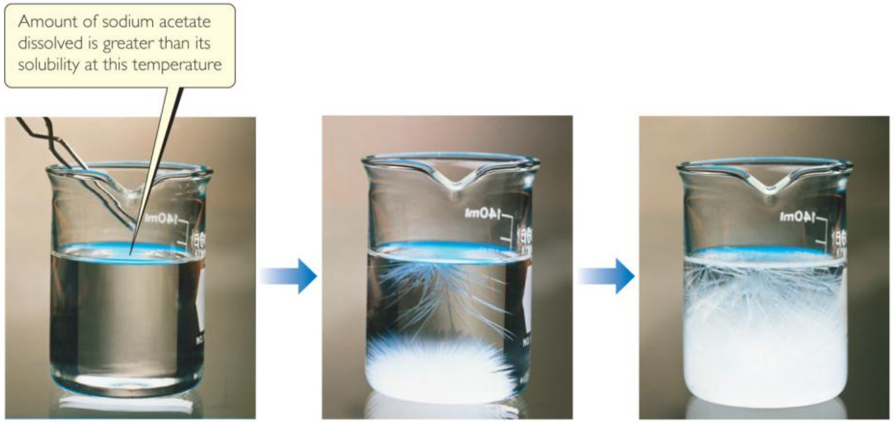
- Saturated
  - In a **saturated** solution, the solvent holds as much solute as is possible at that temperature.
  - Dissolved solute is in dynamic equilibrium with solid solute particles.

Types of Solutions

- Unsaturated
  - If a solution is **unsaturated**, less solute than can dissolve in the solvent at that temperature is dissolved in the solvent.



Types of Solutions



Seed crystal of sodium acetate added to supersaturated solution

Excess sodium acetate crystallizes from solution

Solution arrives at saturation

- Supersaturated
  - 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.

Factors Affecting Solubility

- Chemists use the axiom "like dissolves like."
  - Polar substances tend to dissolve in polar solvents.
  - Nonpolar substances tend to dissolve in nonpolar solvents.

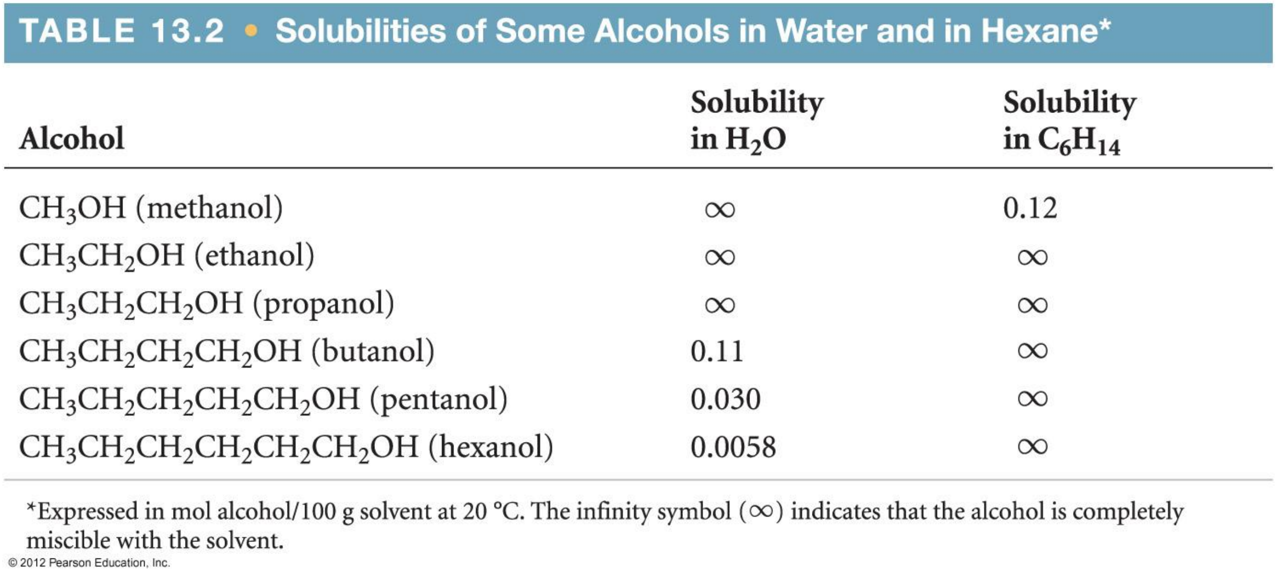
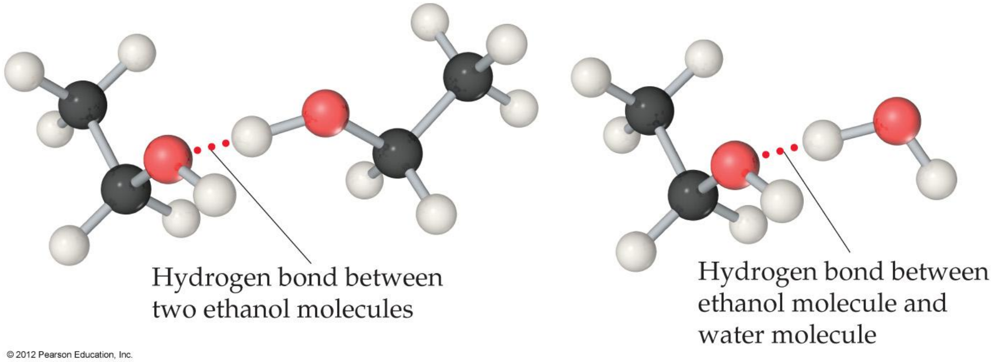


TABLE 13.2 • Solubilities of Some Alcohols in Water and in Hexane*

Alcohol	Solubility in H_2O	Solubility in C_6H_{14}
CH_3OH (methanol)	∞	0.12
CH_3CH_2OH (ethanol)	∞	∞
$CH_3CH_2CH_2OH$ (propanol)	∞	∞
$CH_3CH_2CH_2CH_2OH$ (butanol)	0.11	∞
$CH_3CH_2CH_2CH_2CH_2OH$ (pentanol)	0.030	∞
$CH_3CH_2CH_2CH_2CH_2CH_2OH$ (hexanol)	0.0058	∞

*Expressed in mol alcohol/100 g solvent at 20 °C. The infinity symbol (∞) indicates that the alcohol is completely miscible with the solvent.

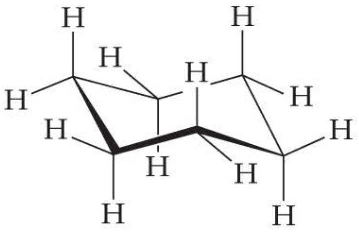
Factors Affecting Solubility



The more similar the intermolecular attractions, the more likely one substance is to be soluble in another.

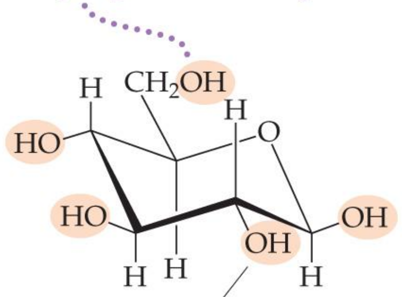
Factors Affecting Solubility

Glucose (which has hydrogen bonding) is very soluble in water, while cyclohexane (which only has dispersion forces) is not.



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.



Hydrogen-bonding sites

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

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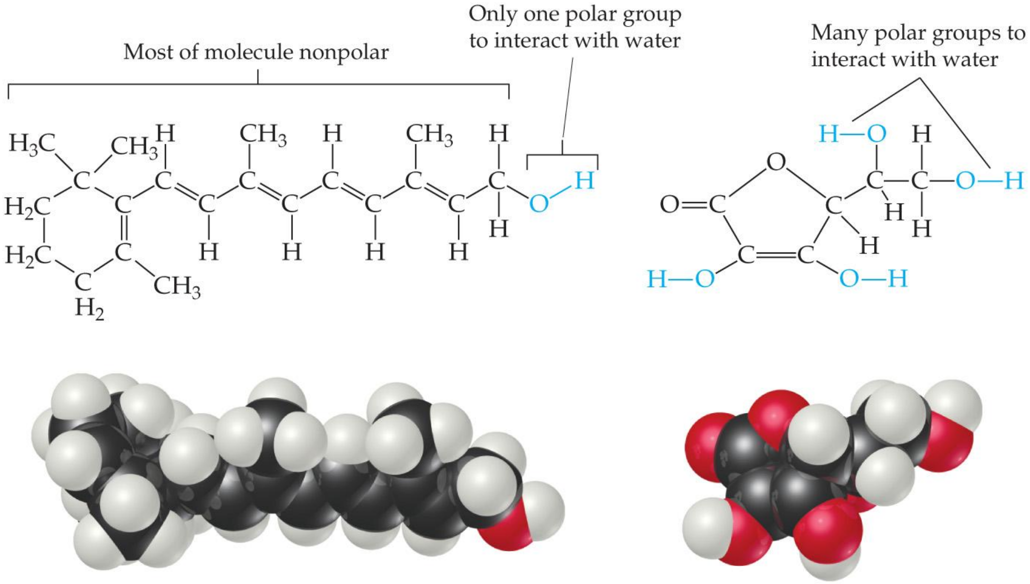
Factors Affecting Solubility

- Vitamin A is soluble in nonpolar compounds (like fats).
- Vitamin C is soluble in water.



Most of molecule nonpolar

Only one polar group to interact with water

Many polar groups to interact with water

Vitamin A

Vitamin C

Gases in Solution

- In general, the solubility of gases in water increases with increasing mass.
- Larger molecules have stronger dispersion forces.

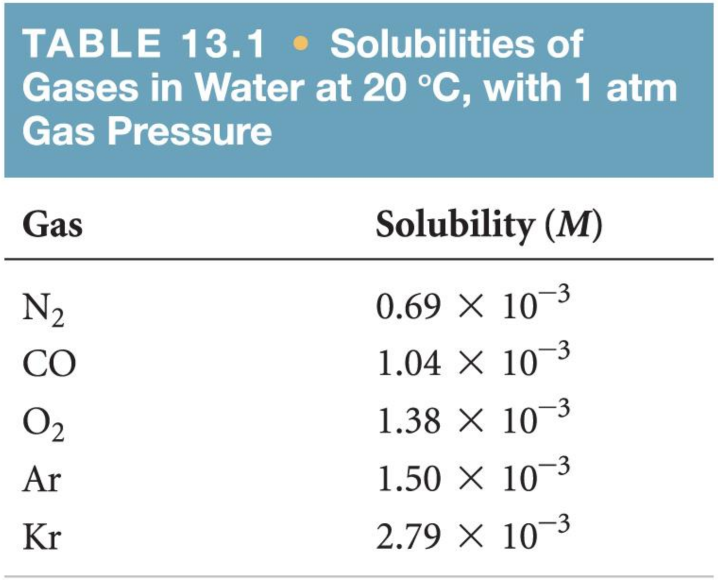
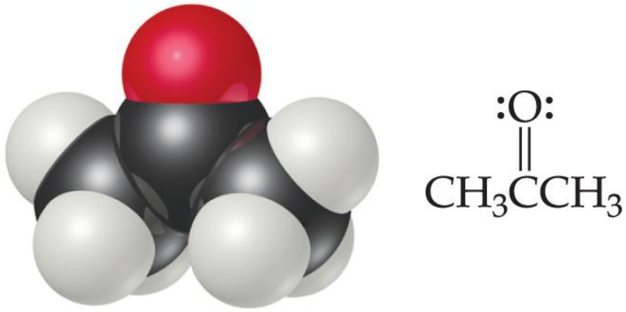


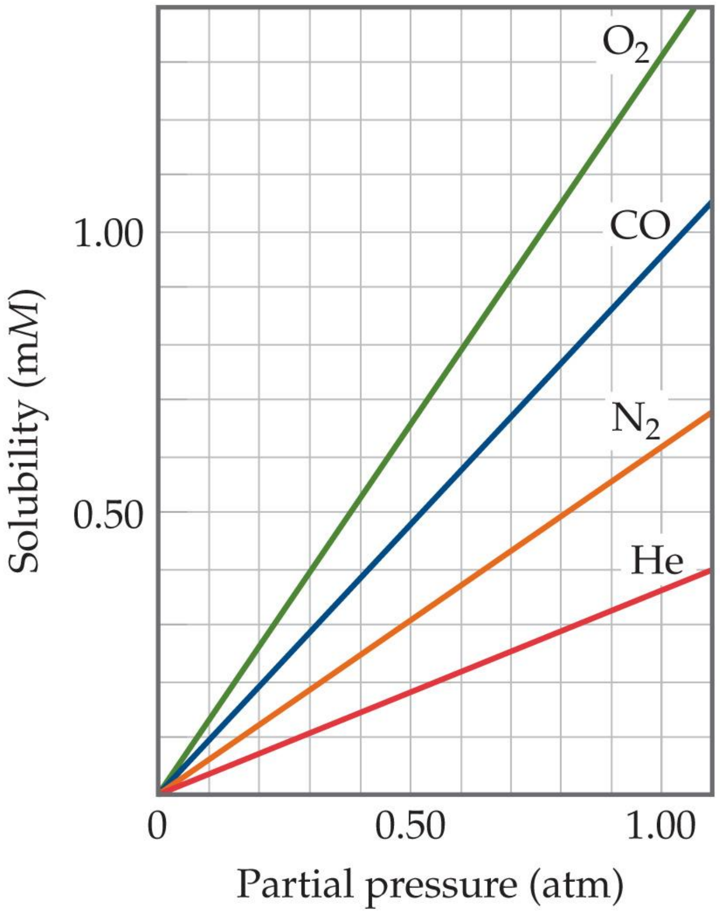
TABLE 13.1 • Solubilities of Gases in Water at 20 °C, with 1 atm Gas Pressure

Gas	Solubility (*M*)
N_2	0.69×10^{-3}
CO	1.04×10^{-3}
O_2	1.38×10^{-3}
Ar	1.50×10^{-3}
Kr	2.79×10^{-3}



Acetone

Gases in Solution



- The solubility of liquids and solids does not change appreciably with pressure.
- But the solubility of a gas in a liquid is directly proportional to its pressure.

Henry’s Law

$$S_g = kP_g$$

where

- S_g is the solubility of the gas,
- k is the Henry’s Law constant for that gas in that solvent, and
- P_g is the partial pressure of the gas above the liquid.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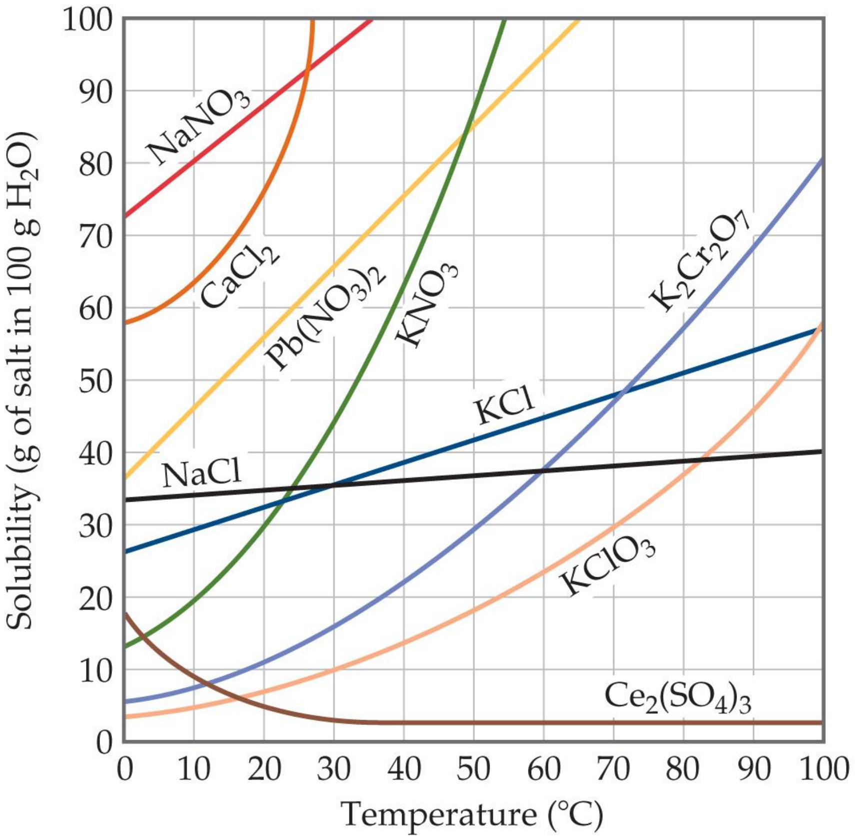
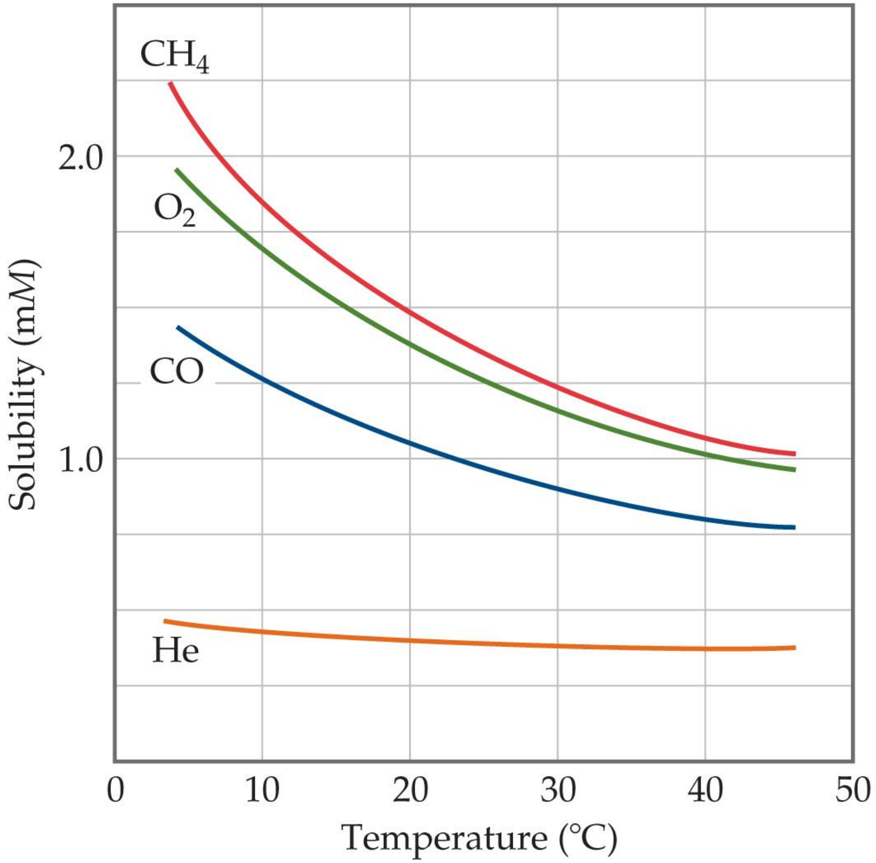
Temperature



Generally, the solubility of solid solutes in liquid solvents increases with increasing temperature.

Temperature

- The opposite is true of gases.
  - Carbonated soft drinks are more “bubbly” if stored in the refrigerator.
  - Warm lakes have less O_2 dissolved in them than cool lakes.



Ways of Expressing Concentrations of Solutions

Mass Percentage

$$\text{Mass \% of } A = \frac{\text{mass of } A \text{ in solution}}{\text{total mass of solution}} \times 100$$

Parts per Million and Parts per Billion

Parts per million (ppm)

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

Parts per billion (ppb)

$$\text{ppb} = \frac{\text{mass of } A \text{ in solution}}{\text{total mass of solution}} \times 10^9$$

Mole Fraction (*X*)

$$X_A = \frac{\text{moles of } A}{\text{total moles of all components}}$$

- In some applications, one needs the mole fraction of *solvent*, not solute—make sure you find the quantity you need!

Molarity (M)

$$M = \frac{\text{moles of solute}}{\text{liters of solution}}$$

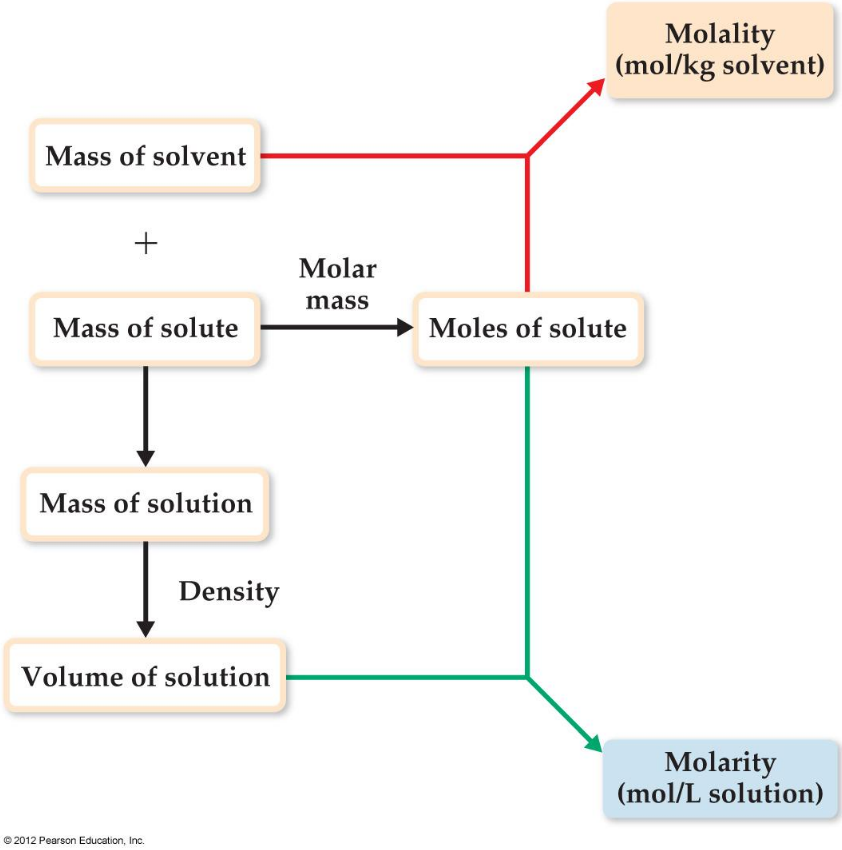
- You will recall this concentration measure from Chapter 4.
- Since volume is temperature-dependent, molarity can change with temperature.

Molality (*m*)

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

Since both moles and mass do not change with temperature, molality (unlike molarity) is *not* temperature-dependent.

Changing Molarity to Molality

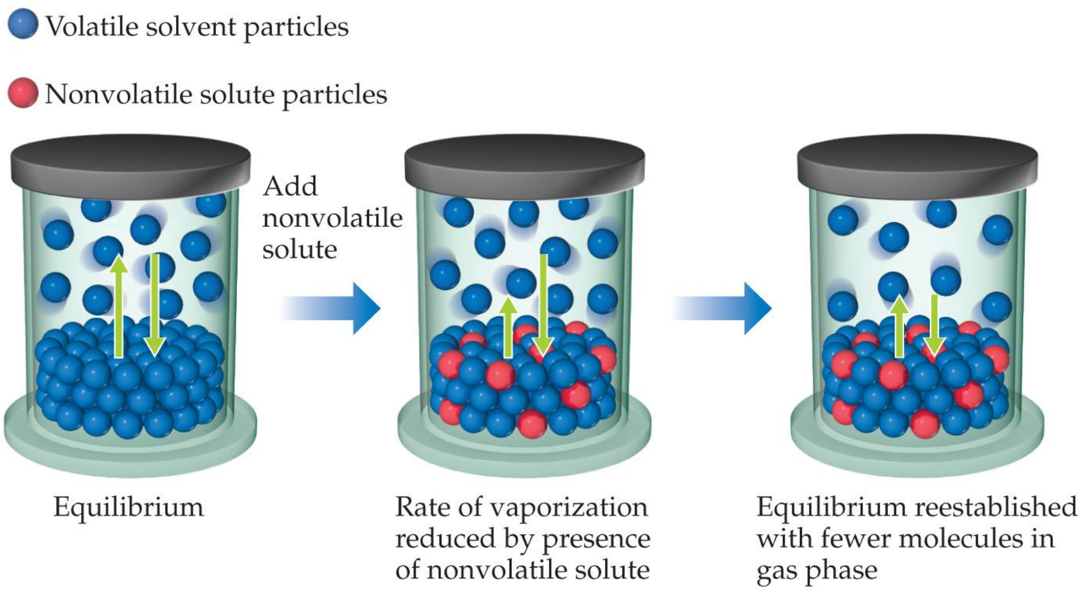


If we know the density of the solution, we can calculate the molality from the molarity, and vice versa.

Colligative Properties

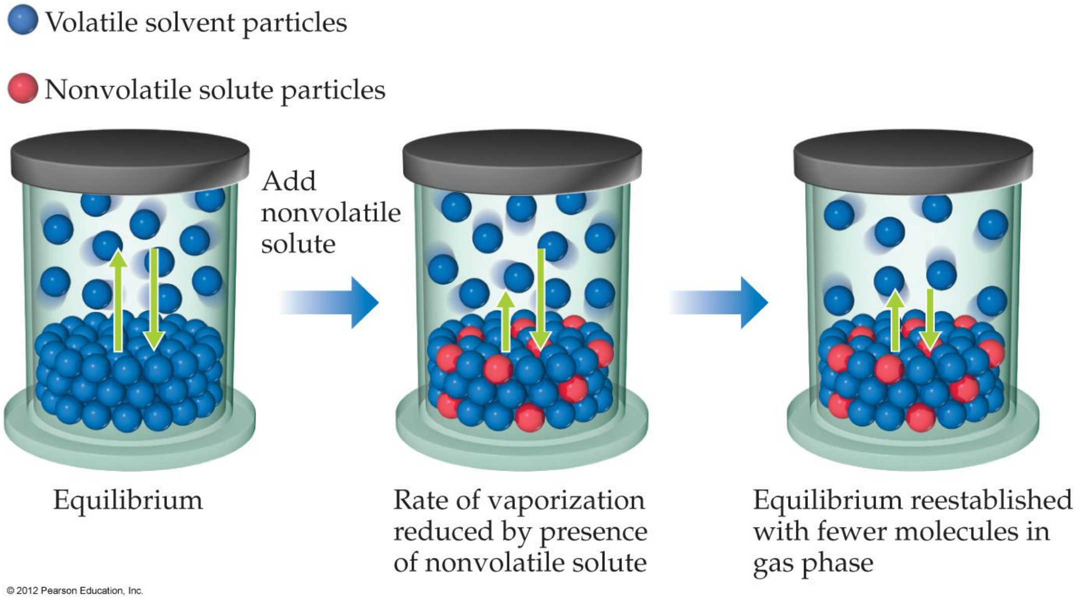
- Changes in **colligative properties** depend only on the *number* of solute particles present, not on the *identity* of the solute particles.
- Among colligative properties are
  - Vapor-pressure lowering
  - Boiling-point elevation
  - Melting-point depression
  - Osmotic pressure

Vapor Pressure



Because of solute–solvent intermolecular attraction, higher concentrations of nonvolatile solutes make it harder for solvent to escape to the vapor phase.

Vapor Pressure



Therefore, the vapor pressure of a solution is lower than that of the pure solvent.

Raoult's Law

$$P_A = X_A P^\circ_A$$

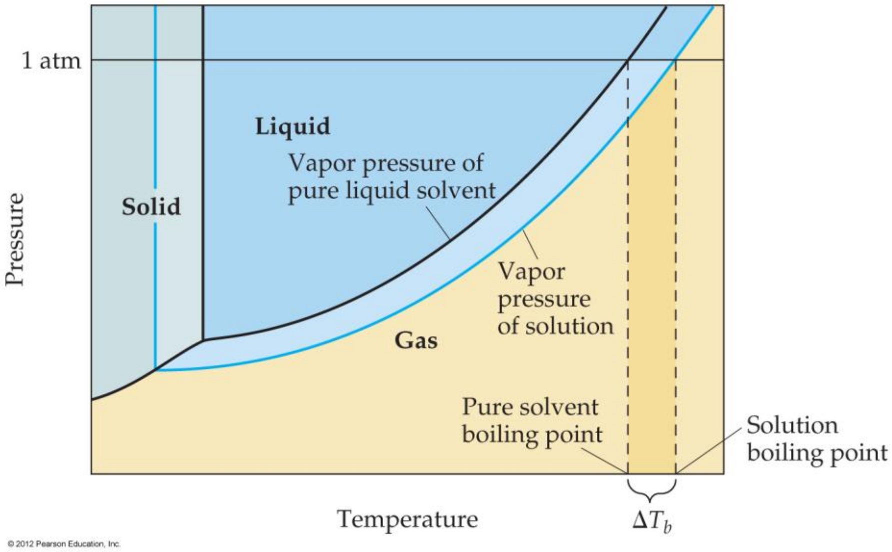
where

- X_A is the mole fraction of compound *A*, and
- P°_A is the normal vapor pressure of *A* at that temperature.

Note: This is one of those times when you want to make sure you have the vapor pressure of the *solvent*.

Boiling-Point Elevation and Freezing-Point Depression

Nonvolatile solute–solvent interactions also cause solutions to have higher boiling points and lower freezing points than the pure solvent.



Boiling-Point Elevation

- The change in boiling point is proportional to the molality of the solution:

$$\Delta T_b = K_b \cdot m$$

where K_b is the molal boiling-point elevation constant, a property of the solvent.

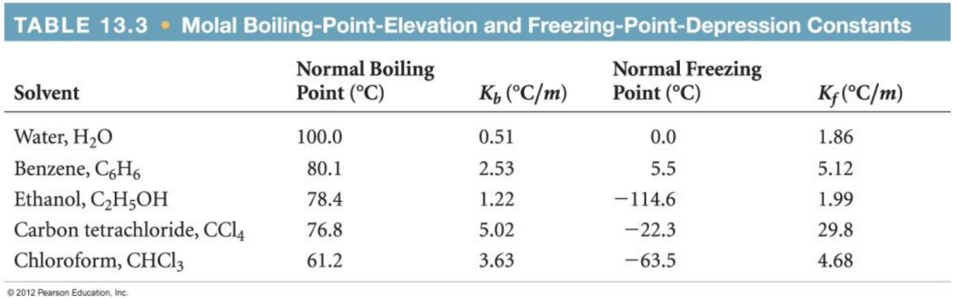
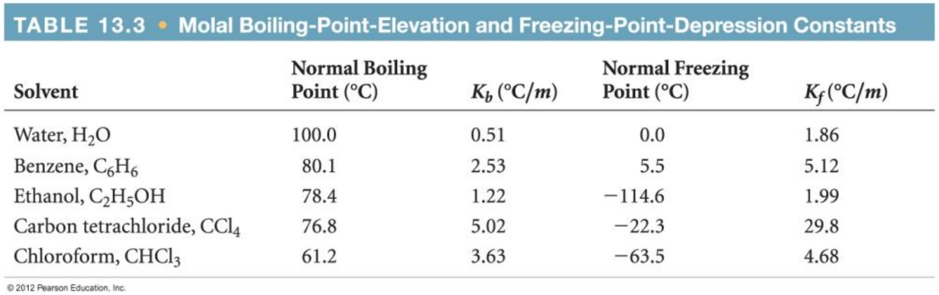


TABLE 13.3 • Molal Boiling-Point-Elevation and Freezing-Point-Depression Constants

Solvent	Normal Boiling Point (°C)	K_b (°C/m)	Normal Freezing Point (°C)	K_f (°C/m)
Water, H_2O	100.0	0.51	0.0	1.86
Benzene, C_6H_6	80.1	2.53	5.5	5.12
Ethanol, C_2H_5OH	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

ΔT_b is *added to* the normal boiling point of the solvent.

Boiling-Point Elevation



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Benzene, C_6H_6	80.1	2.53	5.5	5.12
Ethanol, C_2H_5OH	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

- The change in freezing point can be found similarly:

$$\Delta T_f = K_f \cdot m$$

- Here K_f is the molal freezing-point depression constant of the solvent.

ΔT_f is *subtracted from* the normal freezing point of the solvent.

Boiling-Point Elevation and Freezing-Point Depression

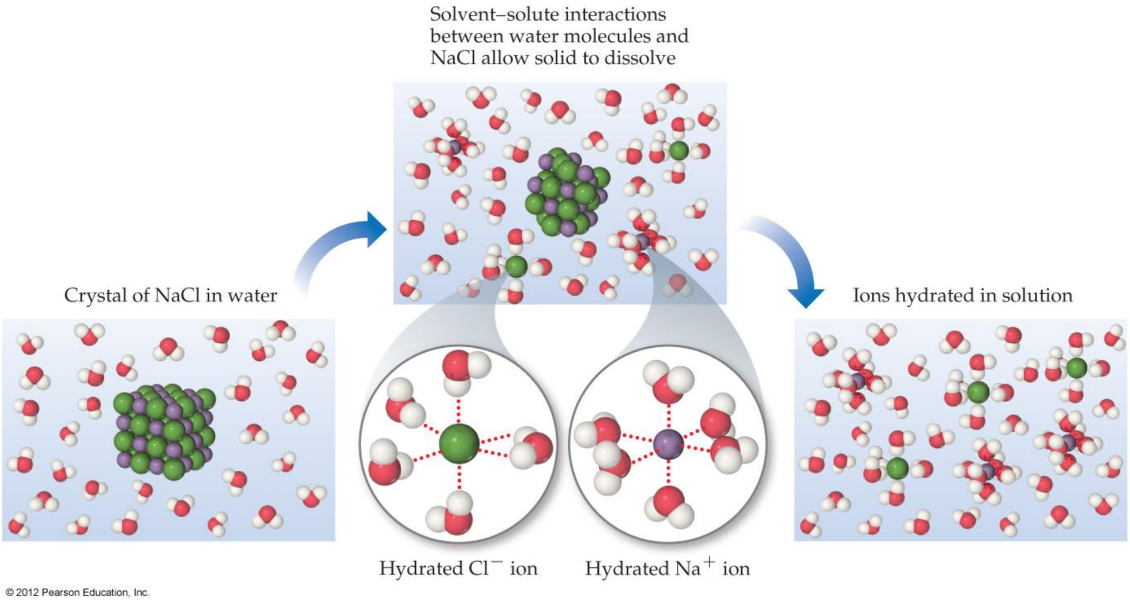
Note that in both equations, ΔT does not depend on *what the solute is*, but only on *how many particles* are dissolved.

$$\Delta T_b = K_b \bullet m$$

$$\Delta T_f = K_f \bullet m$$

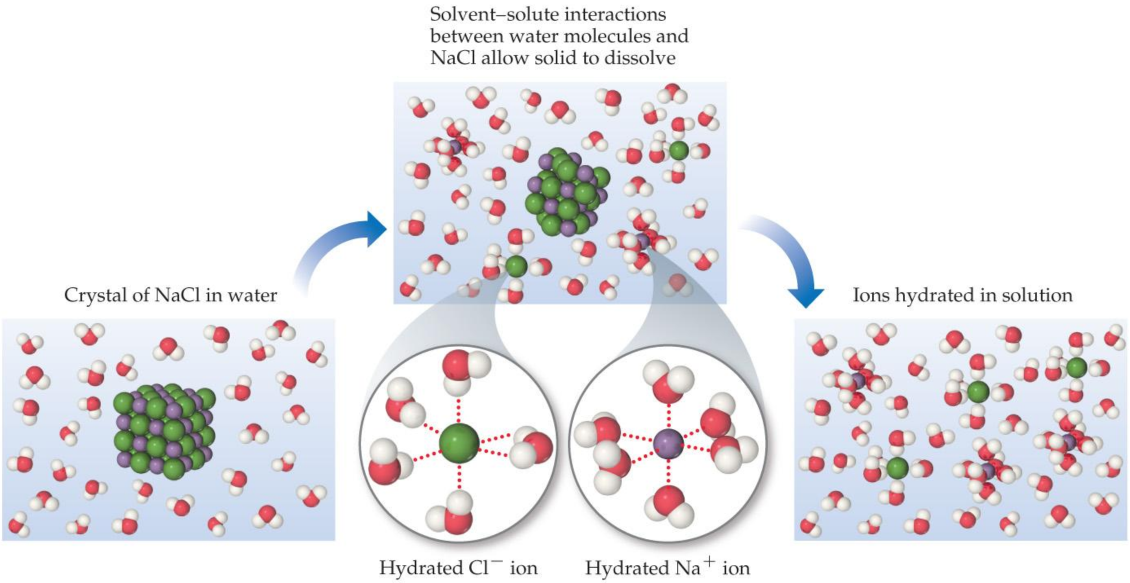
Colligative Properties of Electrolytes

Since the colligative properties of electrolytes depend on the number of particles dissolved, solutions of electrolytes (which dissociate in solution) should show greater changes than those of nonelectrolytes.

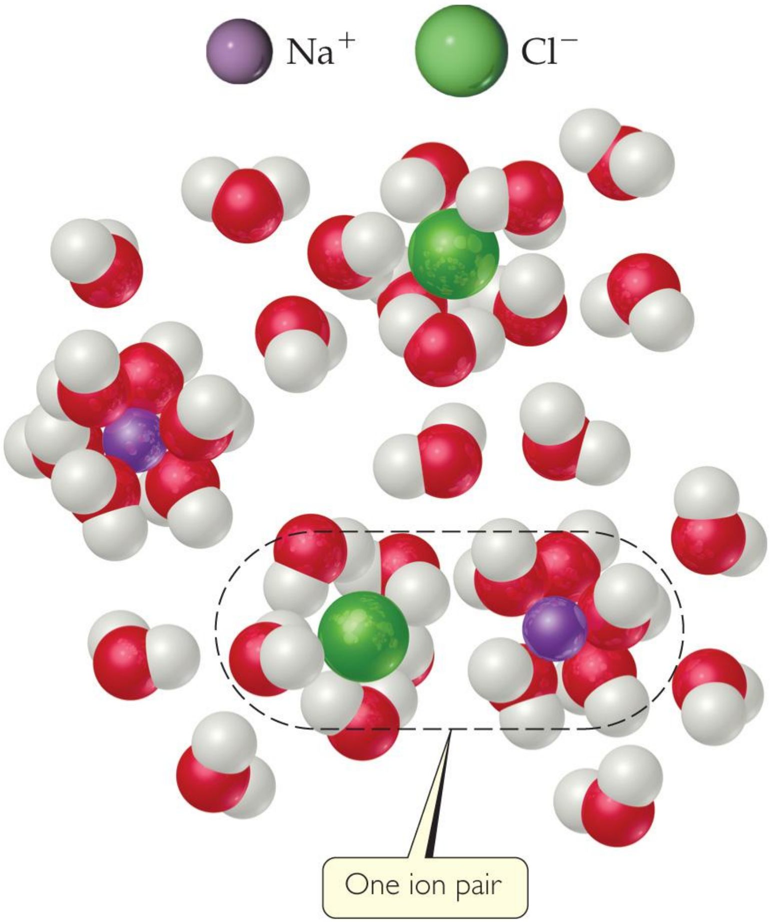


Colligative Properties of Electrolytes

However, a 1*M* solution of NaCl does not show twice the change in freezing point that a 1*M* solution of methanol does.

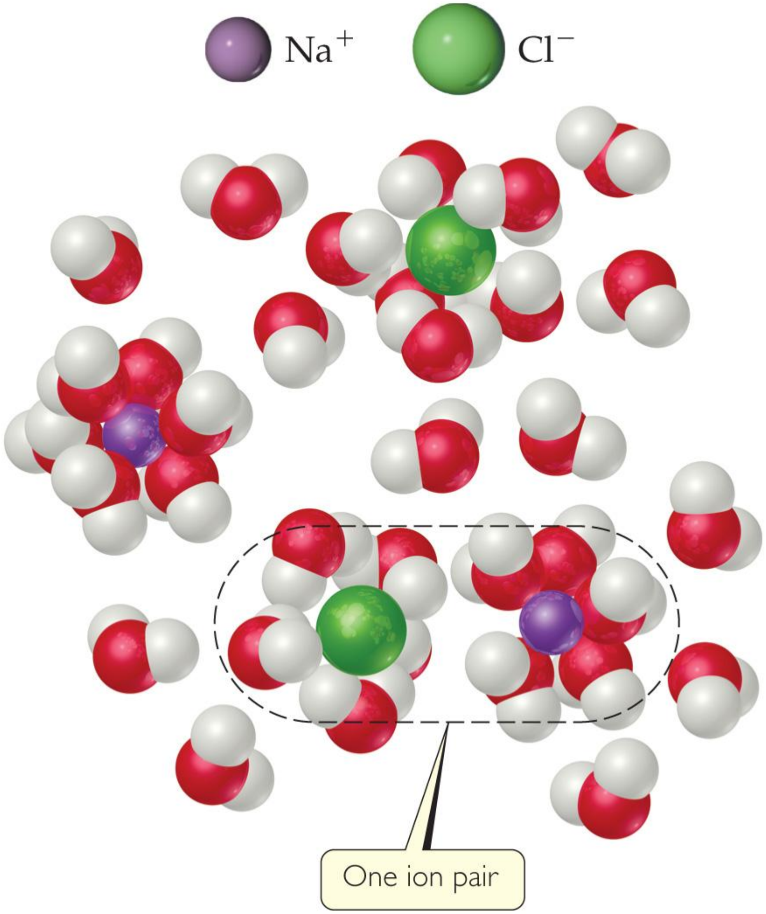


van’t Hoff Factor



One mole of NaCl in water does not really give rise to two moles of ions.

van’t Hoff Factor



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Some Na^+ and Cl^- reassociate for a short time, so the true concentration of particles is somewhat less than two times the concentration of NaCl.

van’t Hoff Factor

- Reassociation is more likely at higher concentration.
- Therefore, the number of particles present is concentration-dependent.

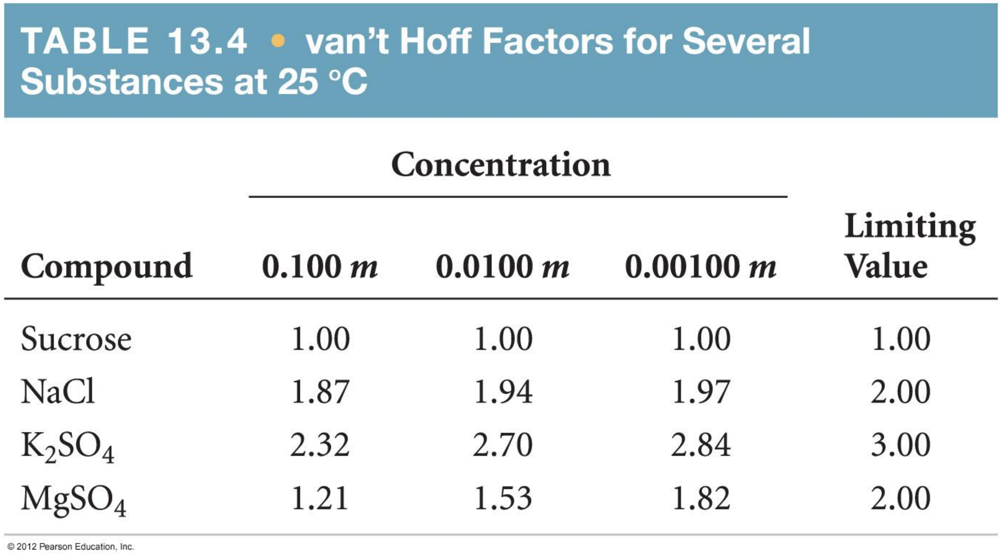


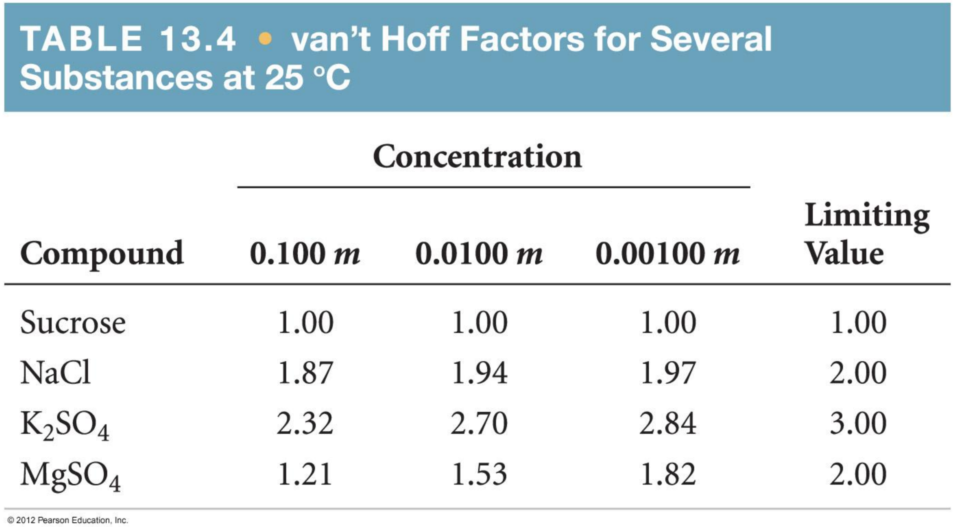
TABLE 13.4 • van’t Hoff Factors for Several Substances at 25 °C

	Concentration			
Compound	**0.100 *m***	**0.0100 *m***	**0.00100 *m***	**Limiting Value**
Sucrose	1.00	1.00	1.00	1.00
NaCl	1.87	1.94	1.97	2.00
K_2SO_4	2.32	2.70	2.84	3.00
$MgSO_4$	1.21	1.53	1.82	2.00

van’t Hoff Factor

- We modify the previous equations by multiplying by the van’t Hoff factor, *i:*

$$\Delta T_f = K_f \cdot m \cdot i$$



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	Concentration			
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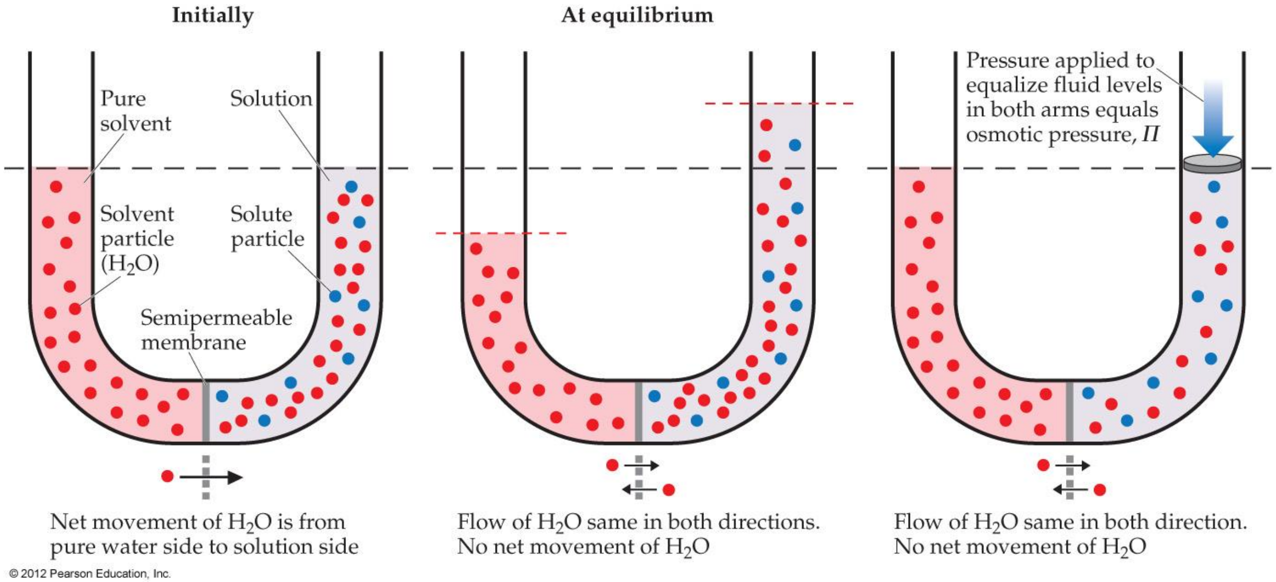
NaCl	1.87	1.94	1.97	2.00
K_2SO_4	2.32	2.70	2.84	3.00
$MgSO_4$	1.21	1.53	1.82	2.00

Osmosis

- Some substances form **semipermeable membranes**, allowing some smaller particles to pass through, but blocking other larger particles.
- In biological systems, most semipermeable membranes allow water to pass through, but solutes are not free to do so.

Osmosis



Net movement of H_2O is from pure water side to solution side

Flow of H_2O same in both directions. No net movement of H_2O

Flow of H_2O same in both direction. No net movement of H_2O

In osmosis, there is net movement of solvent from the area of **higher solvent concentration** (*lower solute concentration*) to the area of **lower solvent concentration** (*higher solute concentration*).

Osmotic Pressure

The pressure required to stop osmosis, known as **osmotic pressure**, π, is

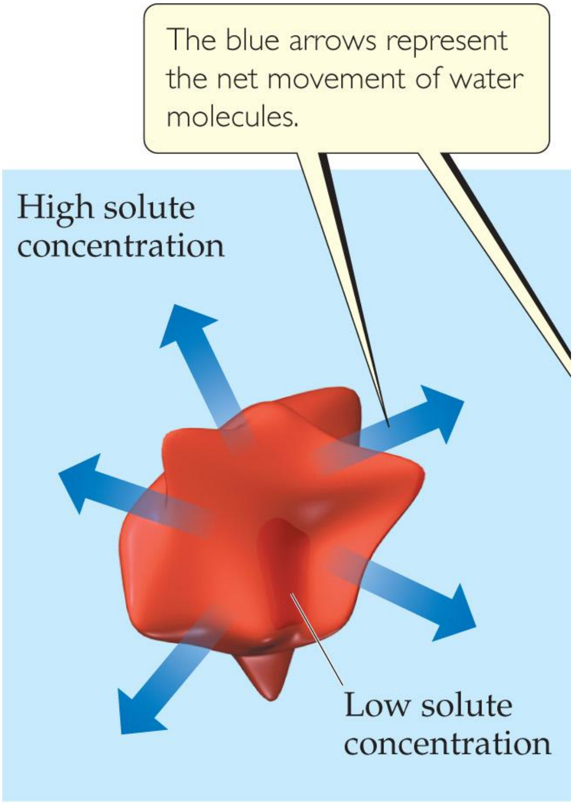
$$\pi = \left(\frac{n}{V}\right)RT = MRT$$

where M is the molarity of the solution.

If the osmotic pressure is the same on both sides of a membrane (i.e., the concentrations are the same), the solutions are **isotonic**.

Osmosis in Blood Cells

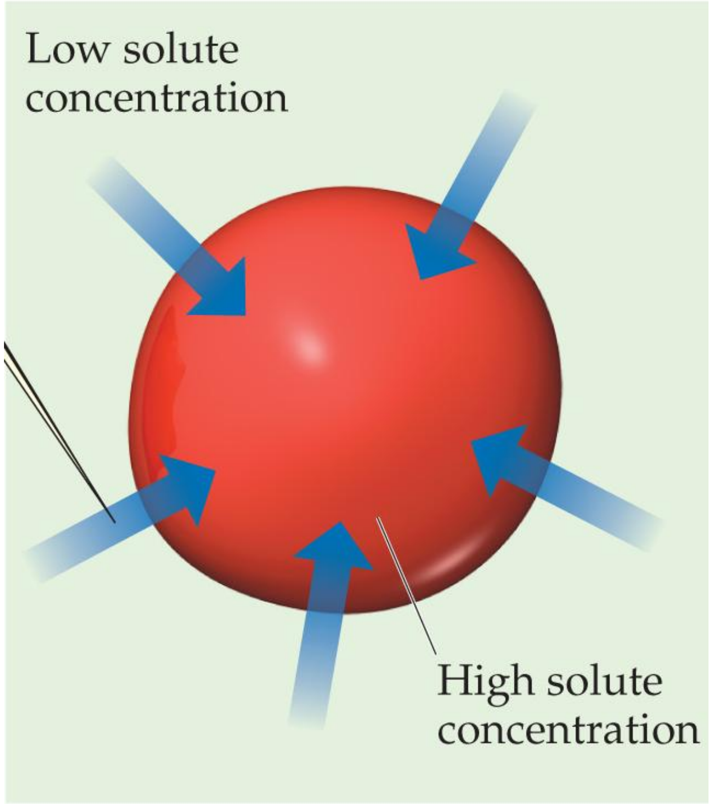
- If the solute concentration outside the cell is greater than that inside the cell, the solution is **hypertonic**.
- Water will flow out of the cell, and **crenation** results.



Crenation of red blood cell placed in hypertonic environment

Osmosis in Cells

- If the solute concentration outside the cell is less than that inside the cell, the solution is **hypotonic**.
- Water will flow into the cell, and **hemolysis** results.



Hemolysis of red blood cell placed in hypotonic environment

Colloids

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

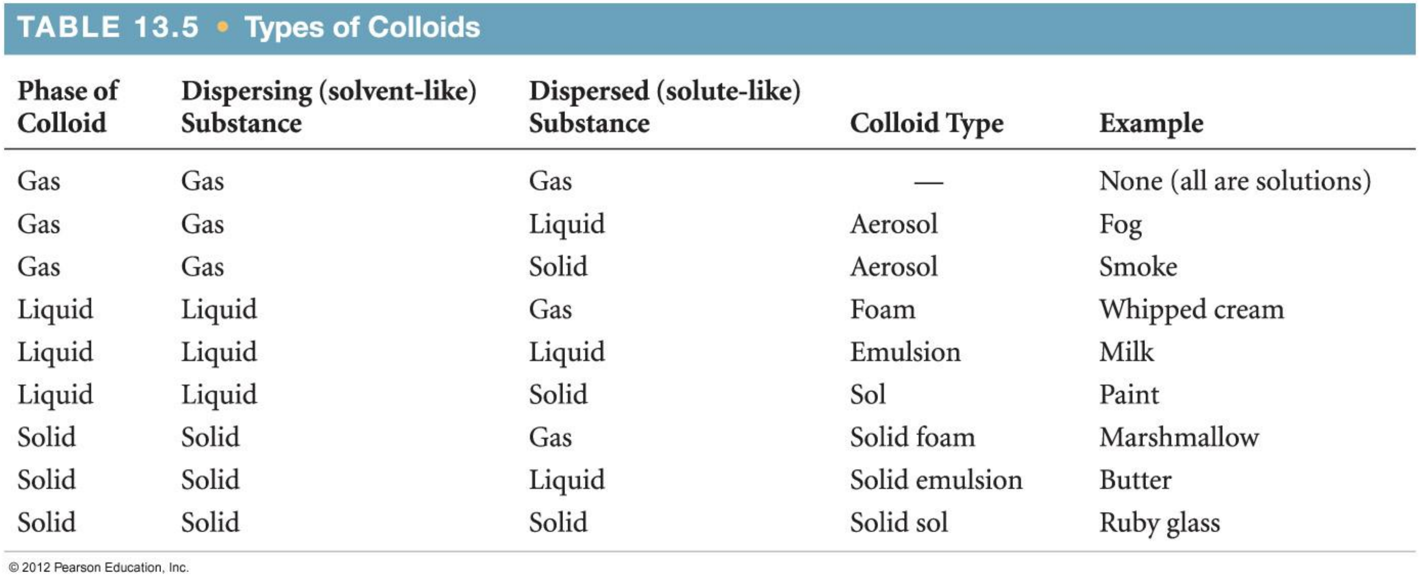


TABLE 13.5 • Types of Colloids

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

Tyndall Effect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- Colloidal suspensions can scatter rays of light.
- This phenomenon is known as the **Tyndall effect**.


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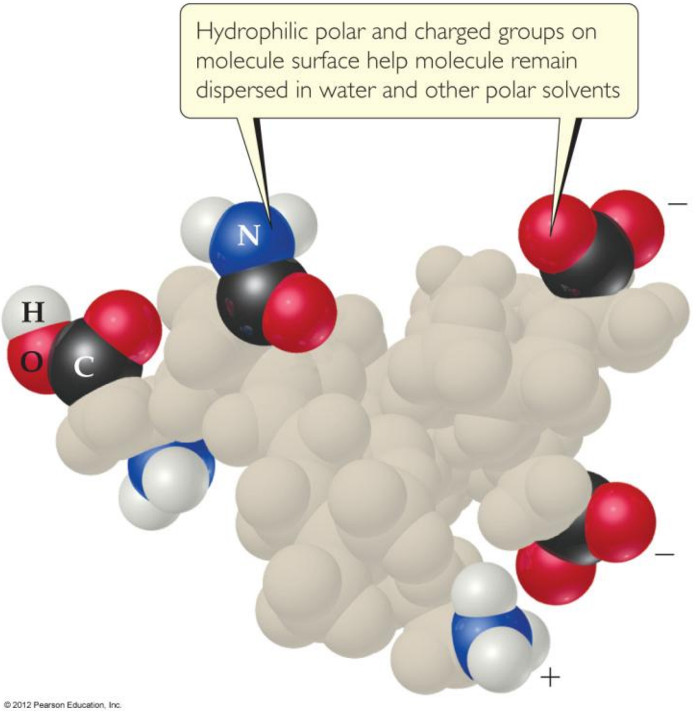
Colloids in Biological Systems

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


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

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Colloids in Biological Systems

These molecules can aid in the emulsification of fats and oils in aqueous solutions.