

Properties of Solutions



Solutions

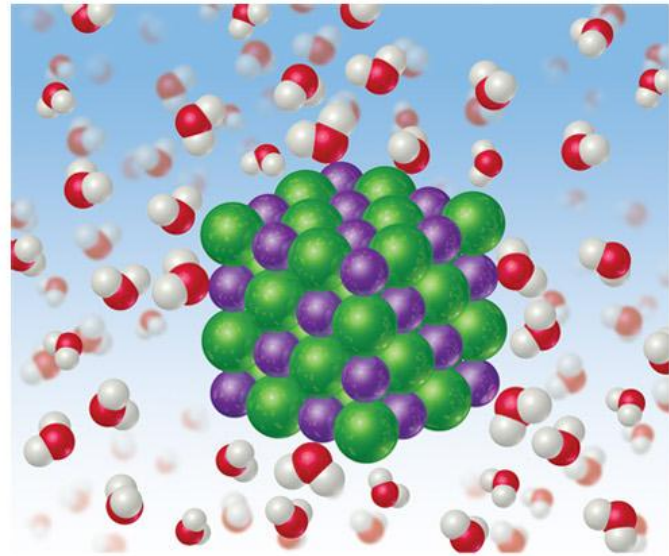
- Solutions are homogeneous mixtures of two or more pure substances.
- In a solution, the **solute** is dispersed uniformly throughout the **solvent**.

State of Solution	State of Solvent	State of Solute	Example
Gas	Gas	Gas	Air
Liquid	Liquid	Gas	Oxygen in water
Liquid	Liquid	Liquid	Alcohol in water
Liquid	Liquid	Solid	Salt in water
Solid	Solid	Gas	Hydrogen in palladium
Solid	Solid	Liquid	Mercury in silver
Solid	Solid	Solid	Silver in gold



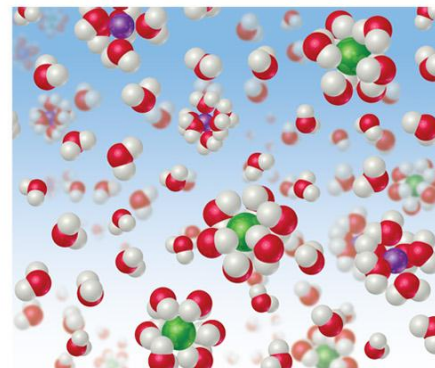
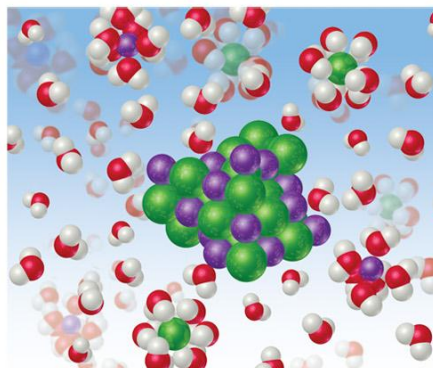
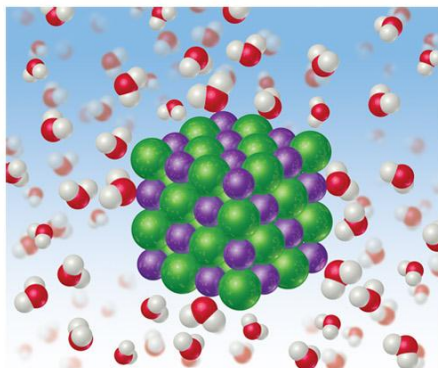
Solutions

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

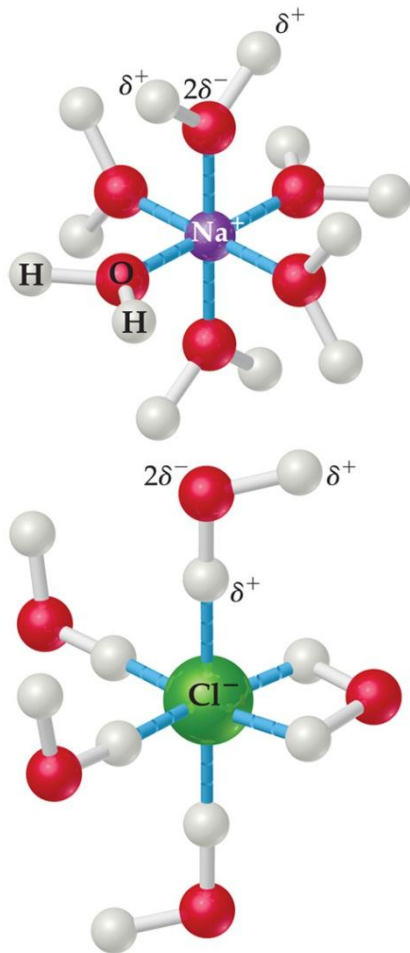


How Does a Solution Form?

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



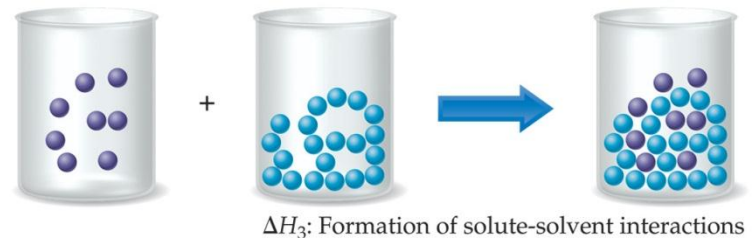
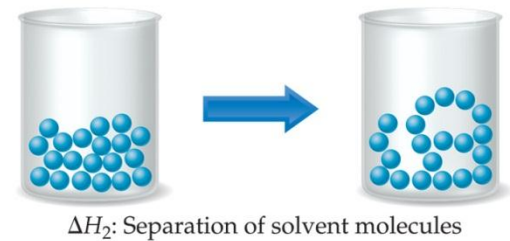
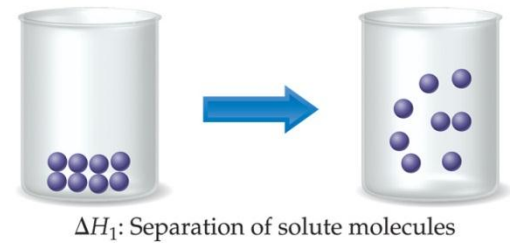
How Does a Solution Form



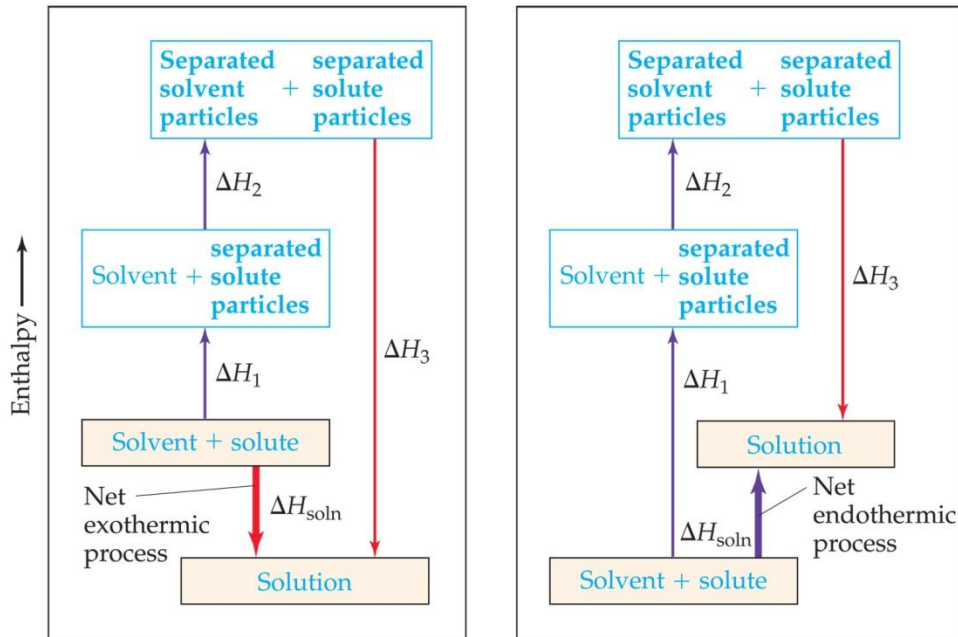
If an ionic salt is soluble in water, it is because the ion-dipole interactions are strong enough to overcome the lattice energy of the salt crystal.

Energy Changes in Solution

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



Energy Changes in Solution

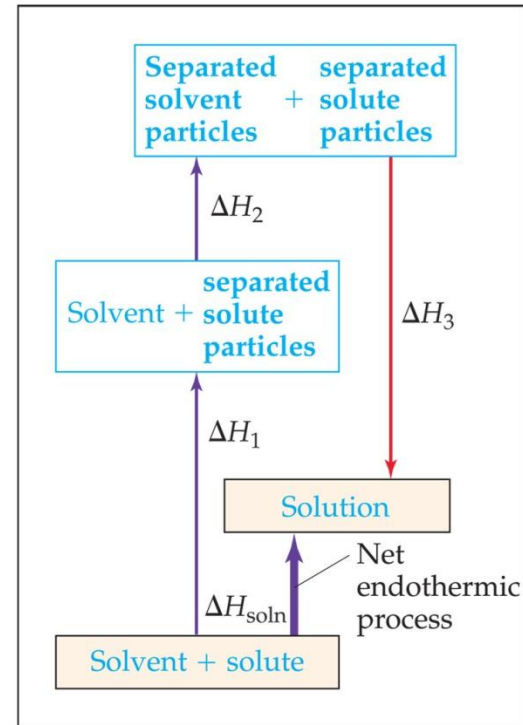


The enthalpy change of the overall process depends on ΔH for each of these steps.

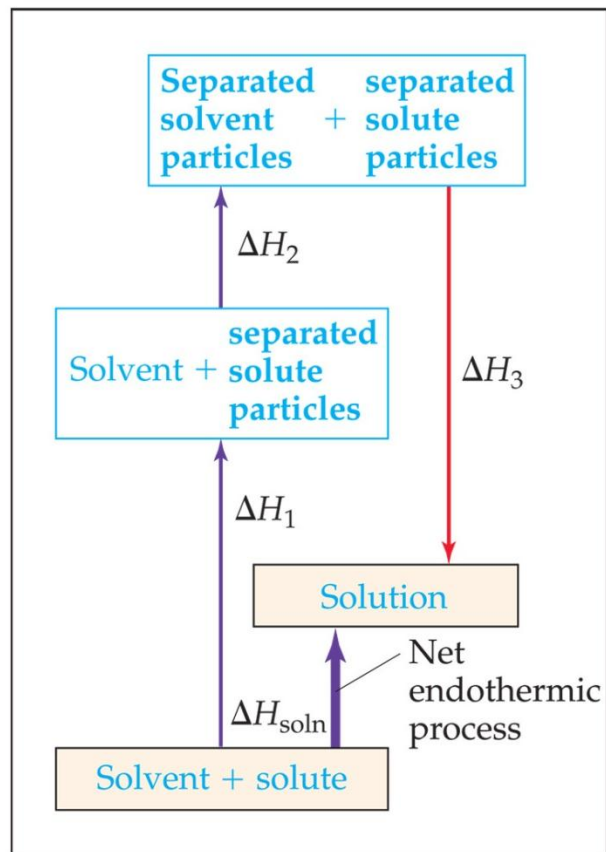


Why Do Endothermic Processes Occur?

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



Why Do Endothermic Processes Occur?

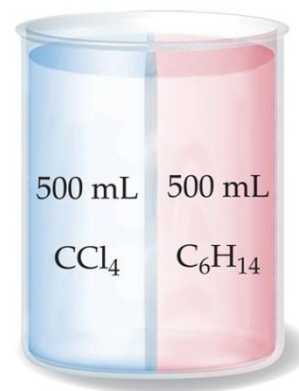


Yet we know that in some processes, like the dissolution of NH_4NO_3 in water, heat is absorbed, not released.

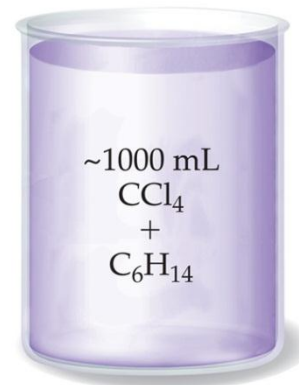


Enthalpy Is Only Part of the Picture

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



(a)

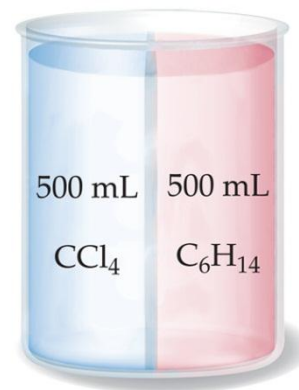


(b)

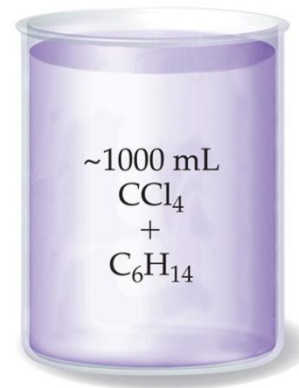


Enthalpy Is Only Part of the Picture

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



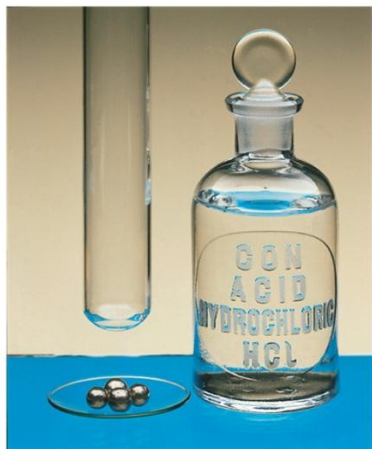
(a)



(b)



Student, Beware!



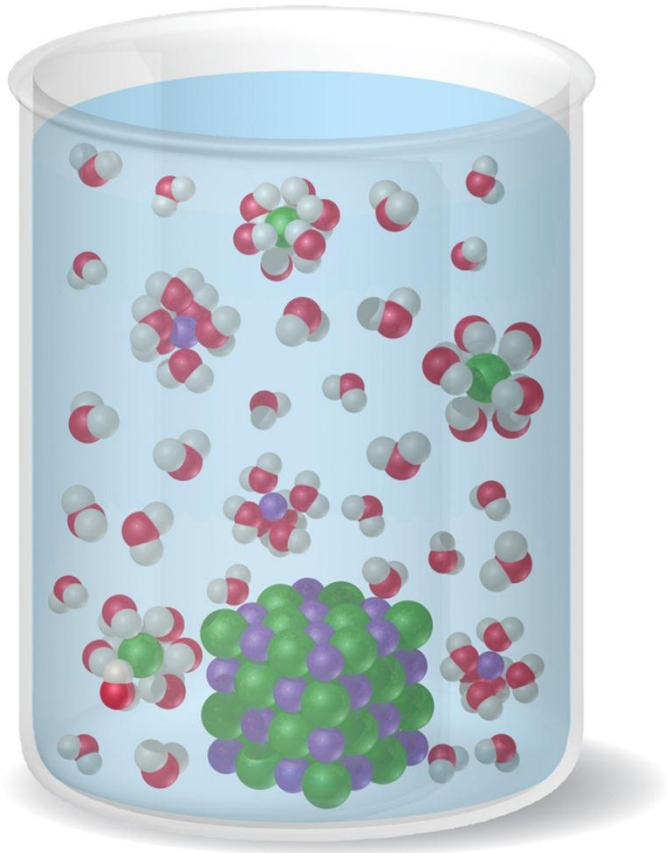
Just because a substance disappears when it comes in contact with a solvent, it doesn't mean the substance dissolved.

Student, Beware!



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

Types of Solutions

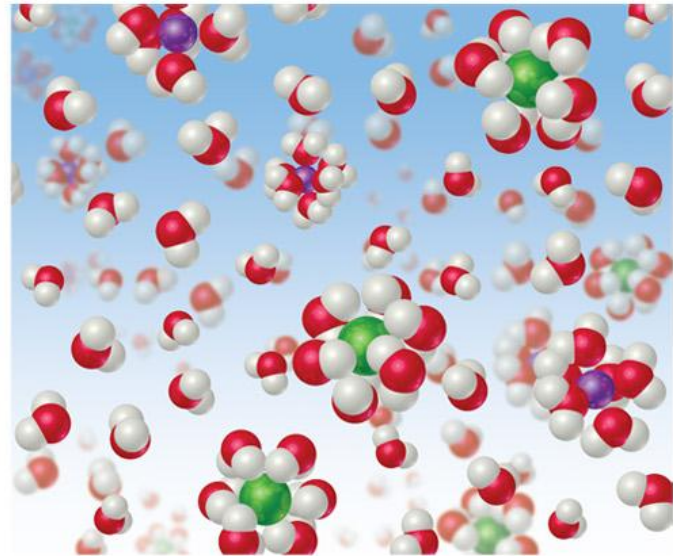


- Saturated
 - Solvent holds as much solute as is possible at that temperature.
 - Dissolved solute is in dynamic equilibrium with solid solute particles.



Types of Solutions

- Unsaturated
 - Less than the maximum amount of solute for that temperature is dissolved in the solvent.



Types of Solutions



- **Supersaturated**
 - 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.

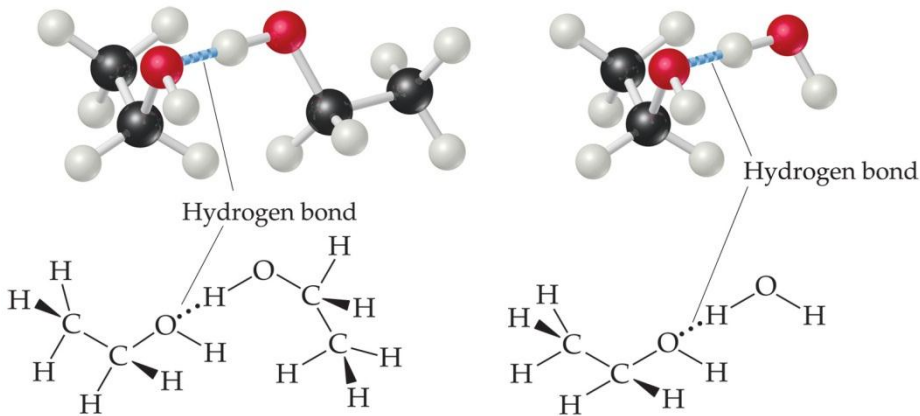
TABLE 13.3 Solubilities of Some Alcohols in Water and in Hexane*

Alcohol	Solubility in H ₂ O	Solubility in C ₆ H ₁₄
CH ₃ OH (methanol)	∞	0.12
CH ₃ CH ₂ OH (ethanol)	∞	∞
CH ₃ CH ₂ CH ₂ OH (propanol)	∞	∞
CH ₃ CH ₂ CH ₂ CH ₂ OH (butanol)	0.11	∞
CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ OH (pentanol)	0.030	∞
CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ OH (hexanol)	0.0058	∞
CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ OH (heptanol)	0.0008	∞

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



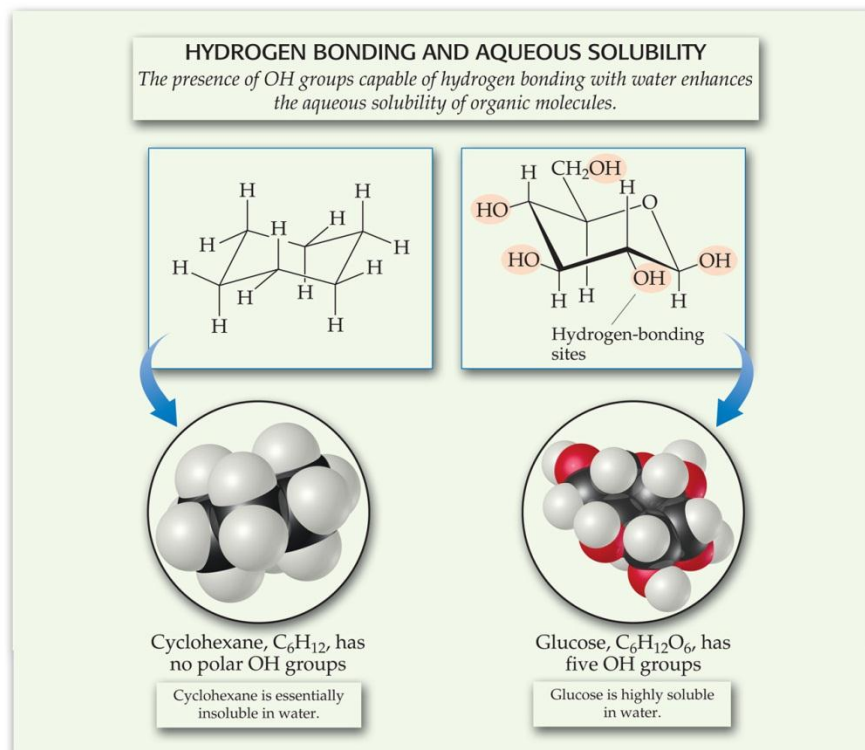
Factors Affecting Solubility



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

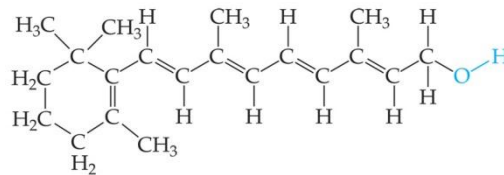
Factors Affecting Solubility

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



Factors Affecting Solubility

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



Vitamin A



Gases in Solution

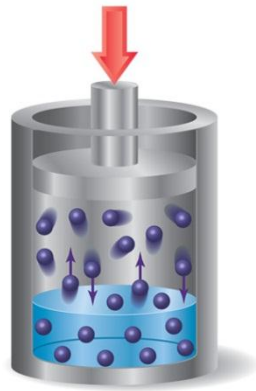
- In general, the solubility of gases in water increases with increasing mass.
- Larger molecules have stronger dispersion forces.

TABLE 13.2 Solubilities of Gases in Water at 20°C, with 1 atm Gas Pressure

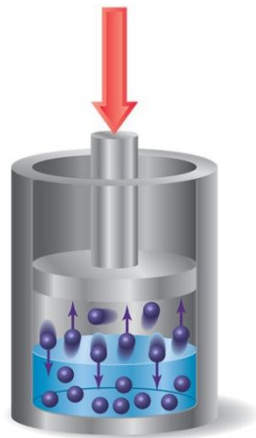
Gas	Solubility (<i>M</i>)
N ₂	0.69×10^{-3}
CO	1.04×10^{-3}
O ₂	1.38×10^{-3}
Ar	1.50×10^{-3}
Kr	2.79×10^{-3}



Gases in Solution



(a)



(b)

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

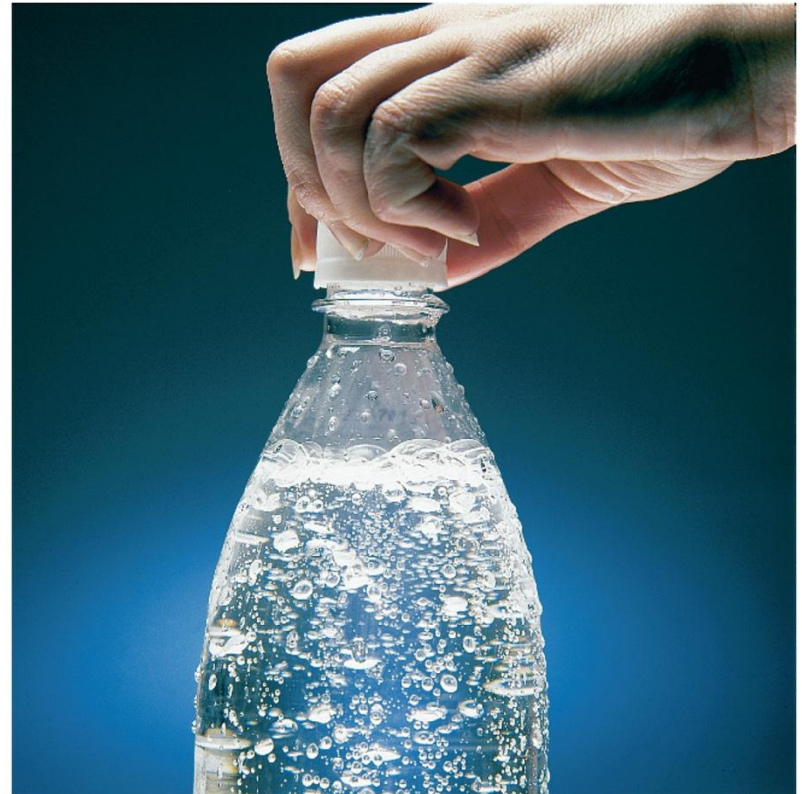


Henry's Law

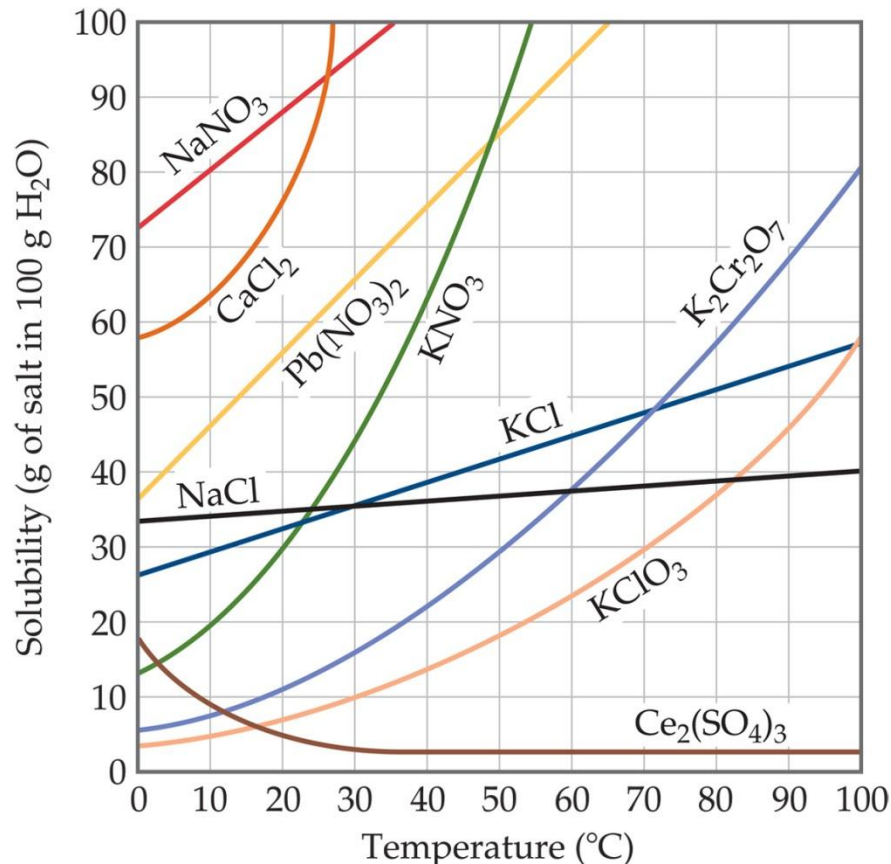
$$S_g = kP_g$$

where

- S_g is the solubility of the gas;
- k is the Henry's law constant for that gas in that solvent;
- P_g is the partial pressure of the gas above the liquid.



Temperature

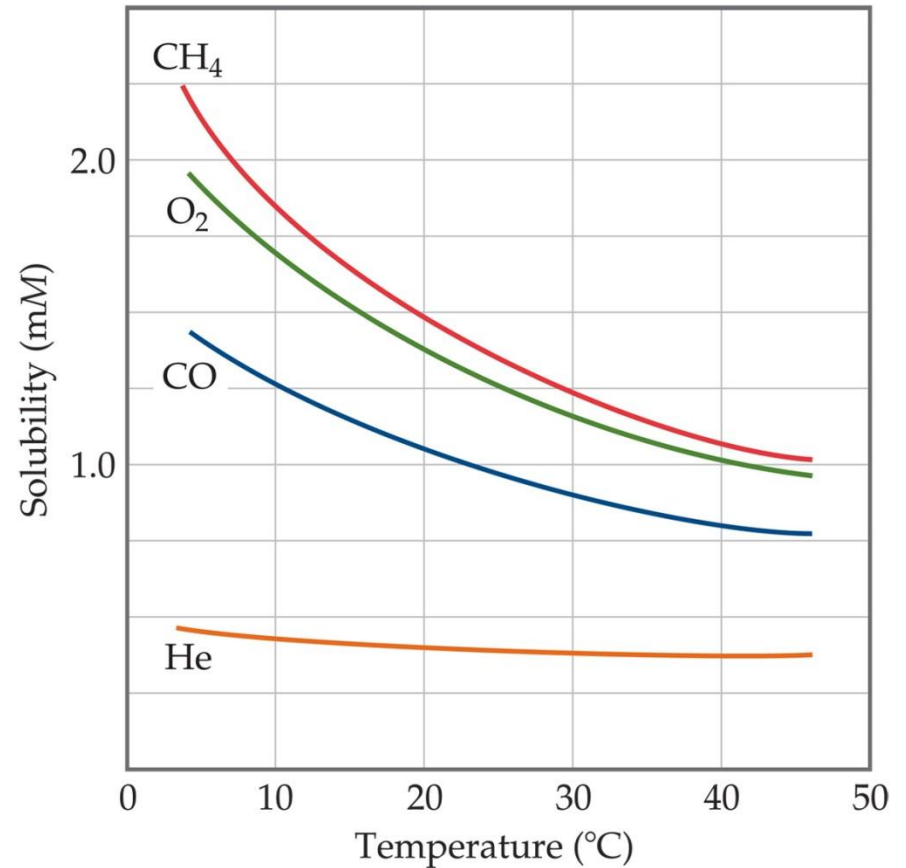


Generally, the solubility of solid solutes in liquid solvents increases with increasing temperature.



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

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



Parts per Million and Parts per Billion

Parts per Million (ppm)

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

Parts per Billion (ppb)

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



Mole Fraction (X)

$$X_A = \frac{\text{moles of A}}{\text{total moles in solution}}$$

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



Molarity (M)

$$M = \frac{\text{mol of solute}}{\text{L of solution}}$$

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



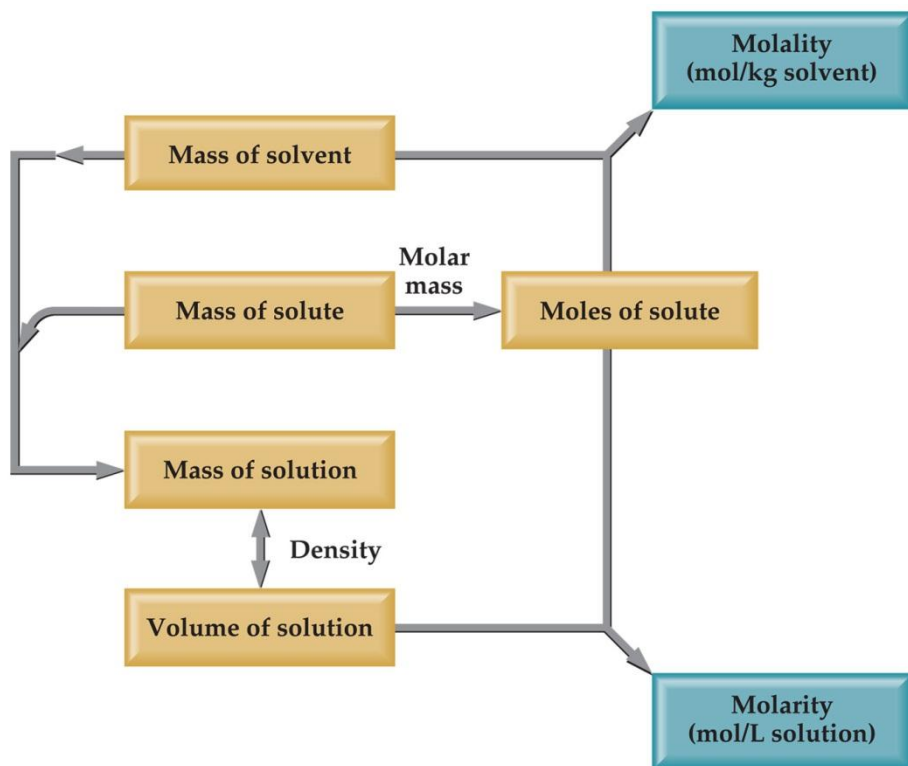
Molality (m)

$$m = \frac{\text{mol of solute}}{\text{kg of solvent}}$$

Because 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.

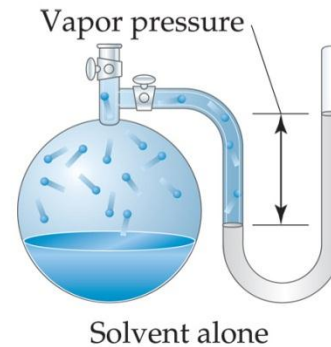
Colligative Properties

- 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

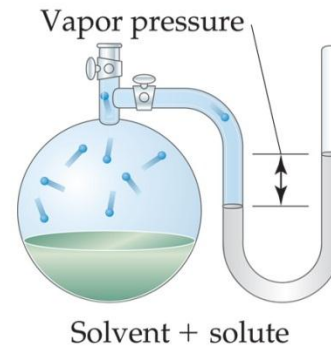


Vapor Pressure

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



(a)



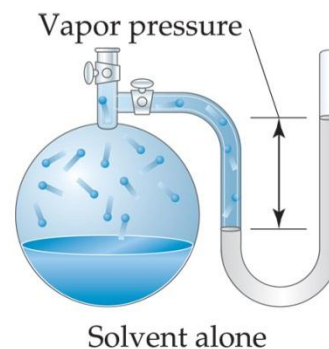
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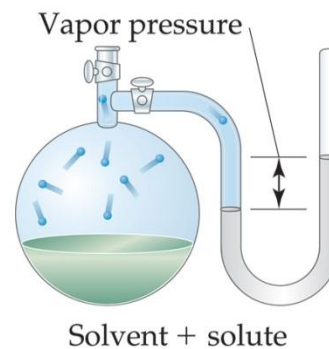
Solutions

Vapor Pressure

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



(a)



(b)



Raoult's Law

$$P_A = X_A P_A^\circ$$

where

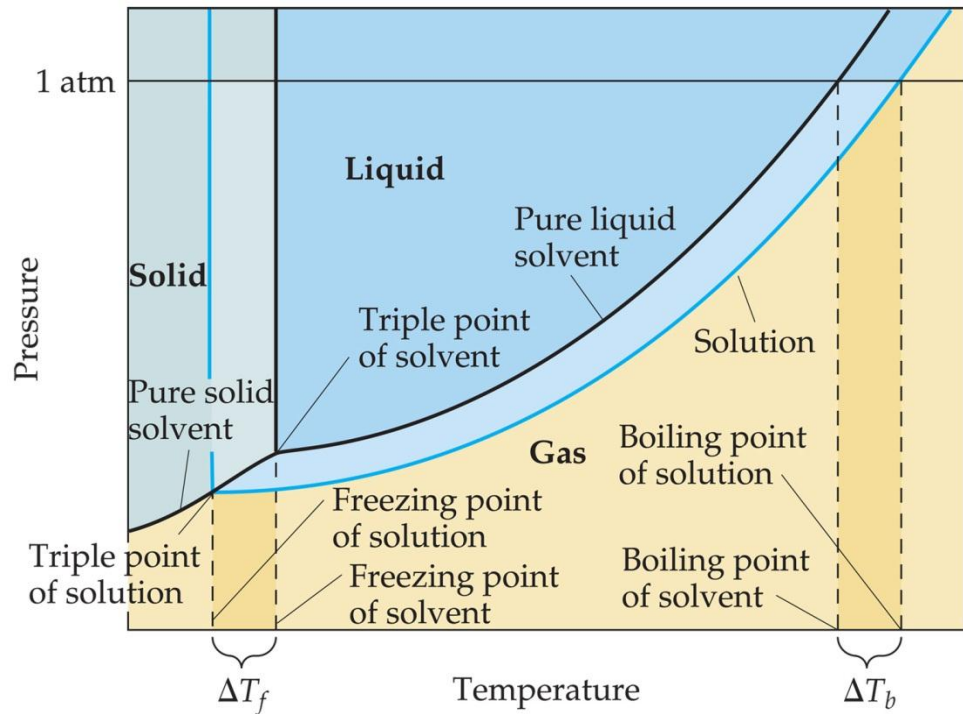
- X_A is the mole fraction of compound A
- P_A° is the normal vapor pressure of A at that temperature

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.

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

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	1.2	-114.6	.99
Carbon tetrachloride, CCl ₄	76.8	5.02	-22.3	29.8
Chloroform, CHCl ₃	61.2	3.6	-63.5	.68



Freezing Point Depression

- The change in freezing point can be found similarly:

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

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
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Chloroform, CHCl ₃	61.2	3.6	-63.5	.68

- 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*.

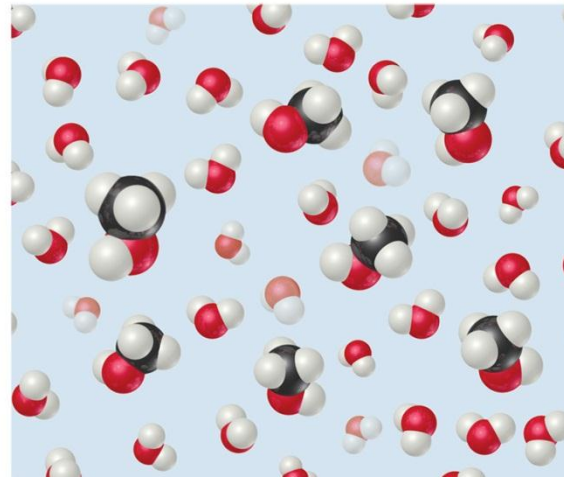
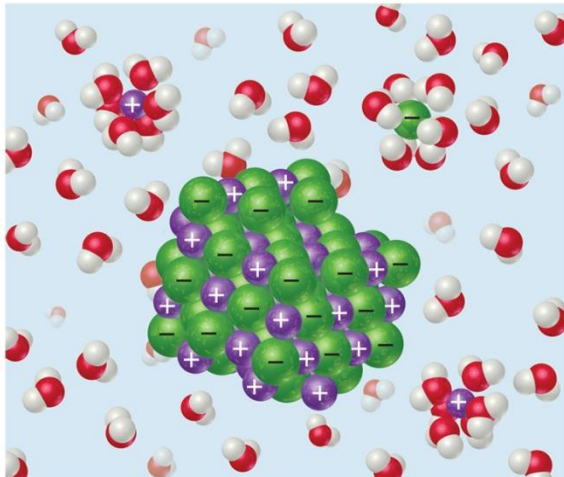
$$\Delta T_b = K_b \cdot m$$

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



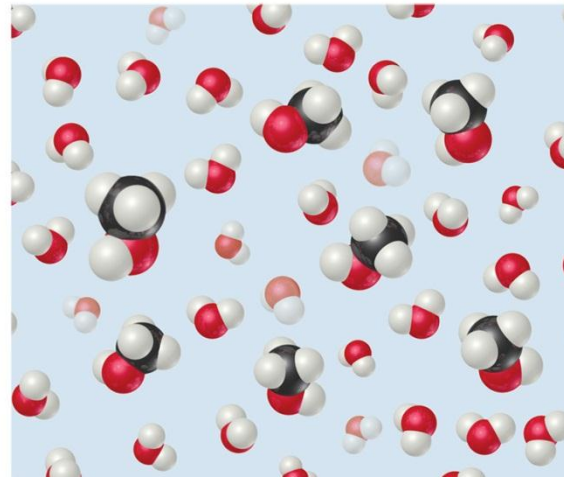
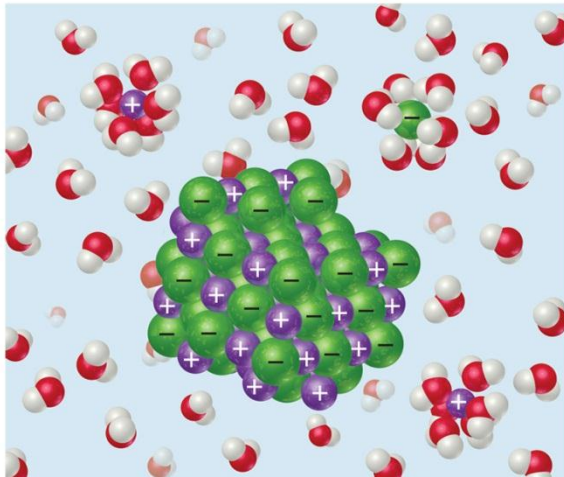
Colligative Properties of Electrolytes

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

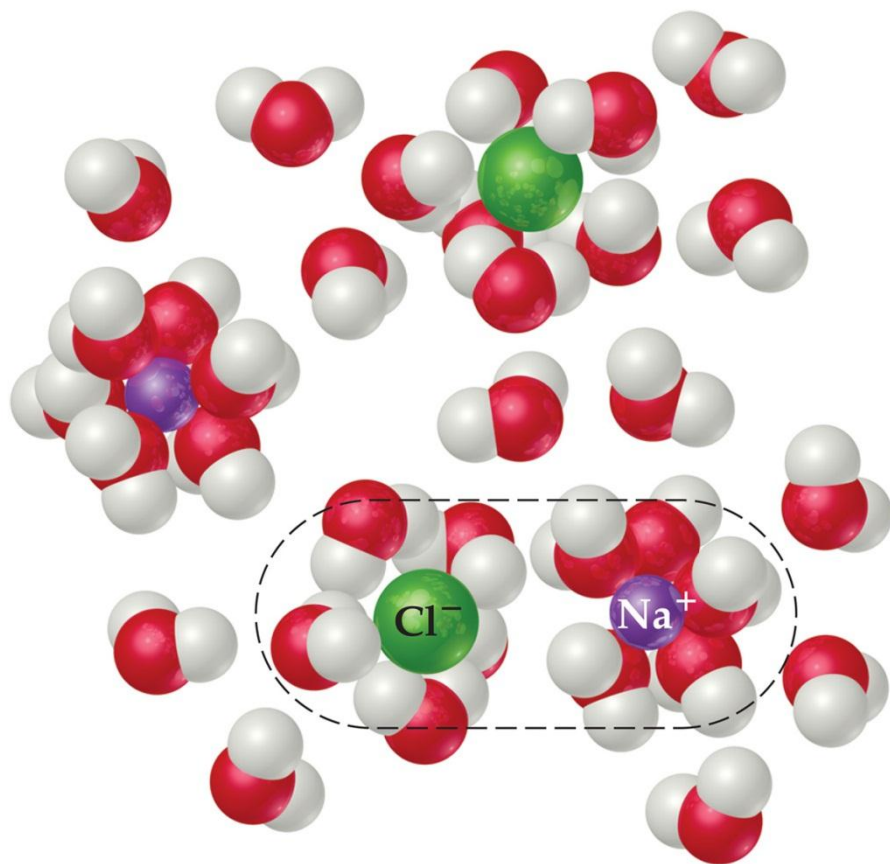


Colligative Properties of Electrolytes

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

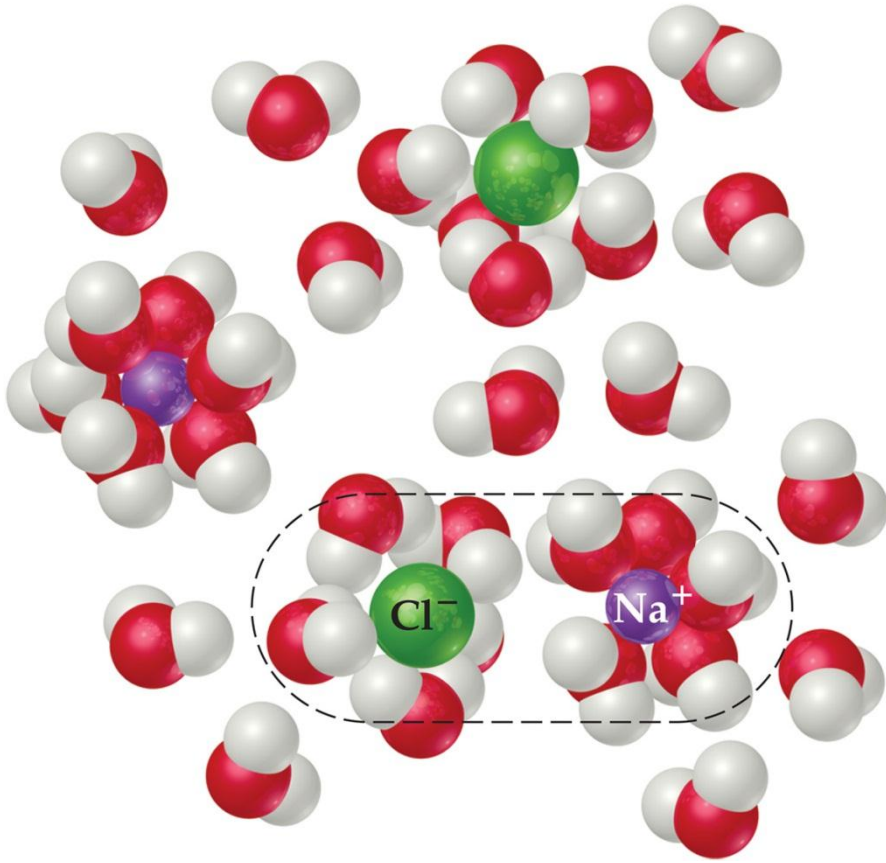


van't Hoff Factor



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

van't Hoff Factor



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 .

The van't Hoff Factor

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

Compound	Concentration			Limiting Value
	0.100 <i>m</i>	0.0100 <i>m</i>	0.00100 <i>m</i>	
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



The van't Hoff Factor

We modify the previous equations by multiplying by the van't Hoff factor, i

Compound	Concentration			Limiting 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

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

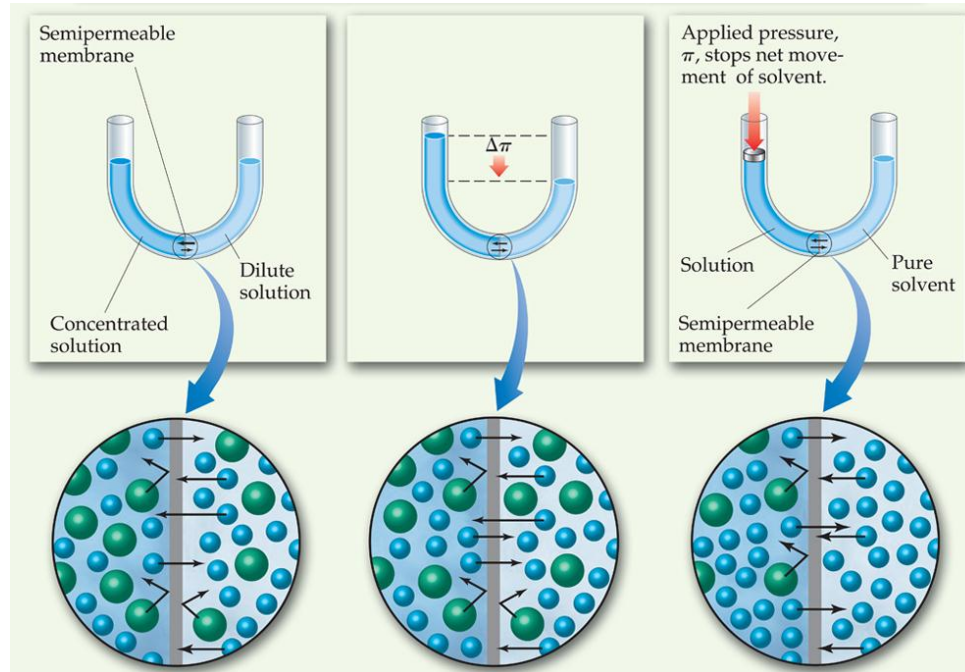


Osmosis

- 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



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

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

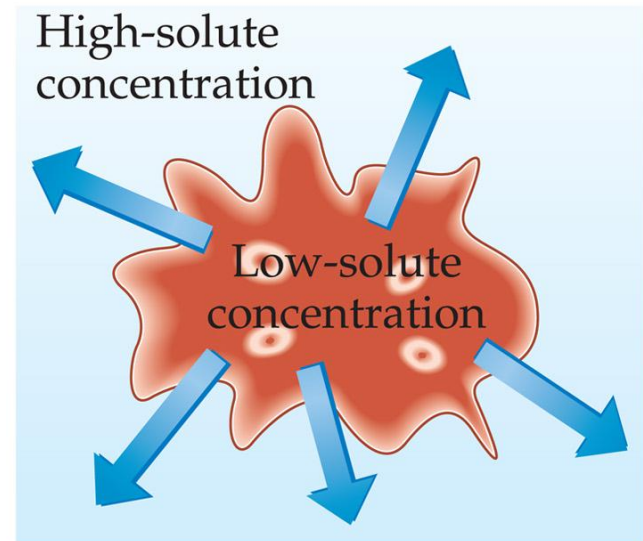
where M is the molarity of the solution

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



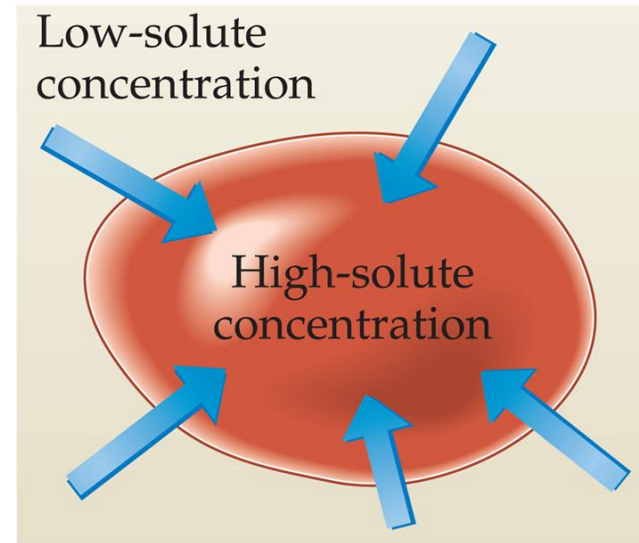
Osmosis in Blood Cells

- 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.



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.



Molar Mass from Colligative Properties



125 mg of an alkaline earth metal chloride (XCl_2) dissolved in enough water to make 50.0 mL of solution at 298°C has an osmotic pressure of 1.16 atm. Identify the alkaline earth metal.

Use the measured osmotic pressure to determine the molar concentration of dissolved particles.

Use the molarity of dissolved particles, and knowledge of the compound formula, to determine the molarity of the *compound*.

Use the molarity of the compound and the volume of solution to determine the number of moles of compound in solution.

Use the number of moles of compound and the number of grams of compound in solution to determine molar mass.

Knowing molar mass, determine the identity of the alkaline earth chloride.

We can use the effects of a colligative property such as osmotic pressure to determine the molar mass of a compound.



Colloids:

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

Phase of Colloid	Dispersing (solventlike) Substance	Dispersed (solutelike) 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

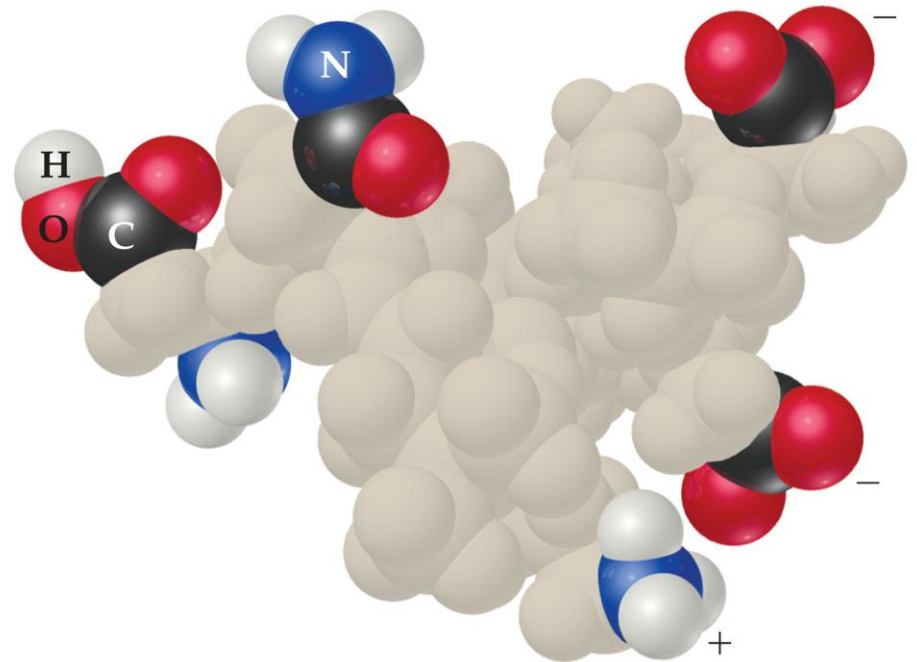


- Colloidal suspensions can scatter rays of light.
- This phenomenon is known as the Tyndall effect.

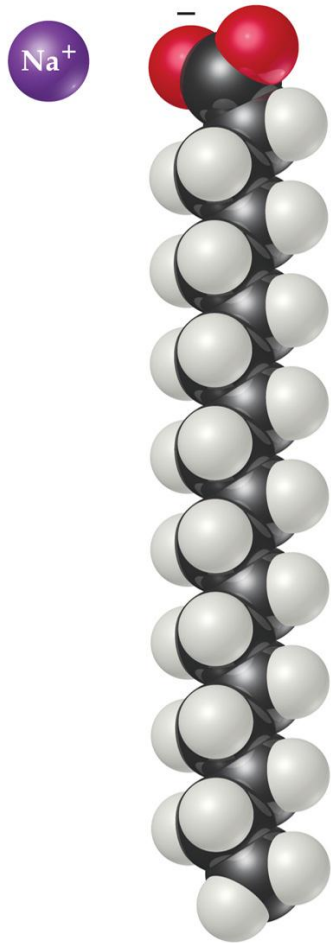


Colloids in Biological Systems

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



Colloids in Biological Systems



Sodium stearate
is one example
of such a
molecule.

Colloids in Biological Systems

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

