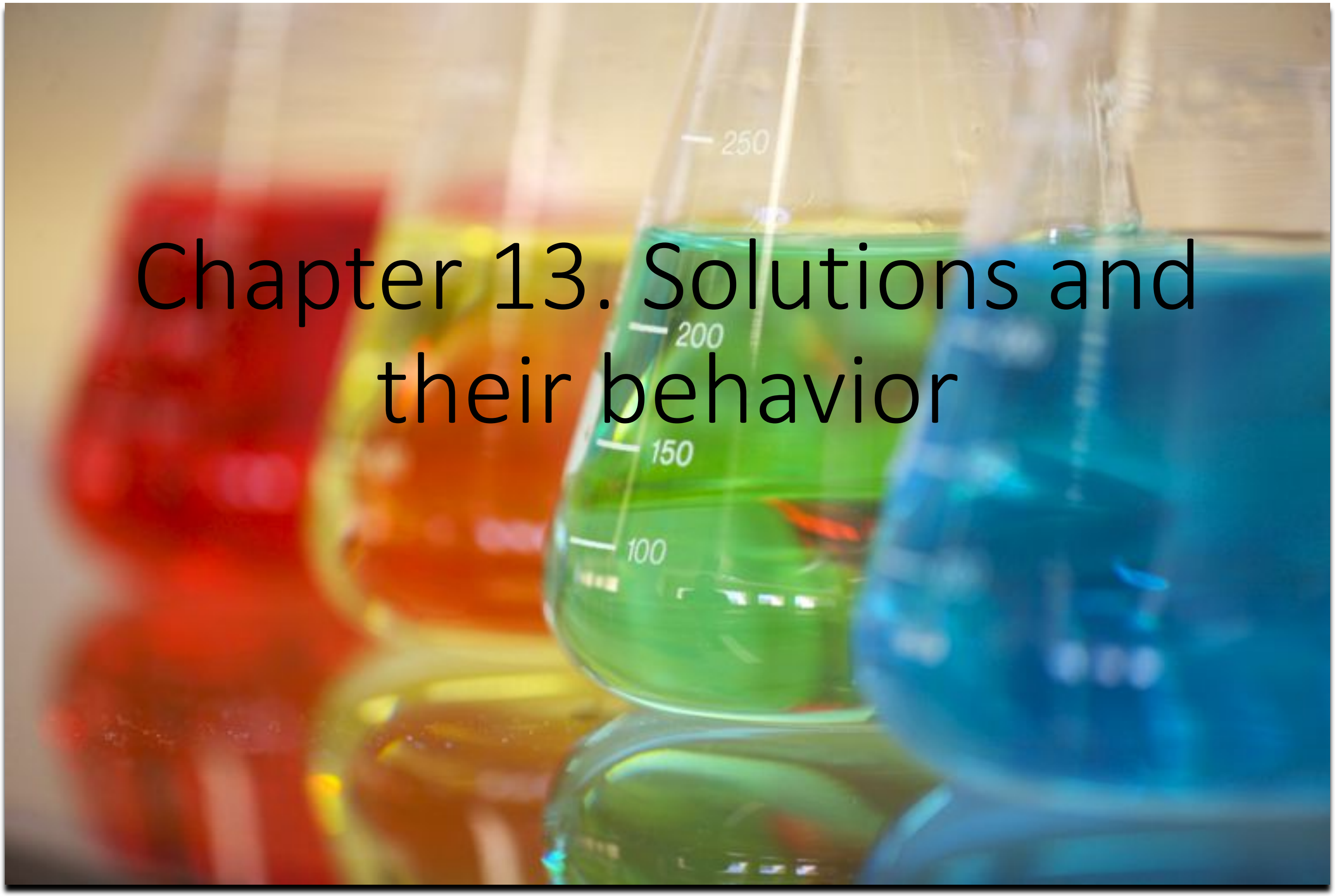


Chapter 13. Solutions and their behavior

Chapter outline

- Units of concentration
- The process of forming a solution
  - Enthalpy of solution
- Effects of P and T on solubility
  - Henry's law
- Colligative properties
  - Vapor pressure (Raoult's law)
  - Boiling point elevation
  - Freezing point depression
  - Osmotic pressure
- Colloids and surfactants

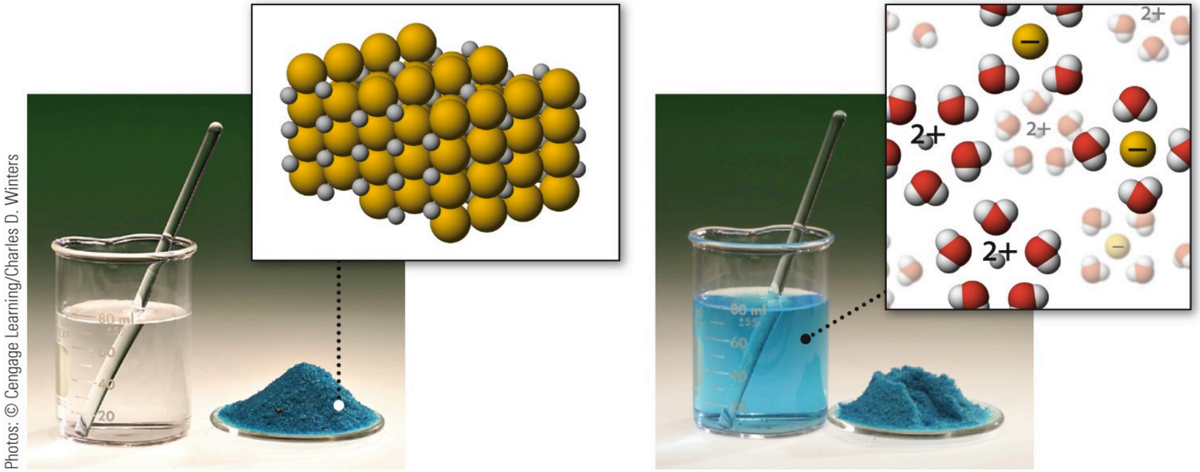
Solutions

Solution = ***solute*** + ***solvent***

That which dissolves (greater amount); H_2O for aqueous solutions

That which is dissolved (lesser amount)

Often solutes are solid (become aqueous upon dissolution in H_2O)



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(a) Copper(II) chloride, the solute, is added to water, the solvent.

(b) Interactions between water molecules and Cu^{2+} and Cl^- ions allow the solid to dissolve. The ions are now sheathed with water molecules.

Homogeneous mixtures

Units of concentration of solutions

- In a solution, we need to know the (amount of solute):(amount of solution) [or (amount of solute):(amount of solvent)] ratio
- We can do that by using suitable units of concentration
  - Molality (*m*)
  - Mole fraction (*X*)
  - Weight percent
  - Parts per million (ppm)

Molality, *m*

- Moles of solute per 1 kg of solvent
- $m = \dfrac{moles\ of\ solute}{1\ kg\ solvent}$

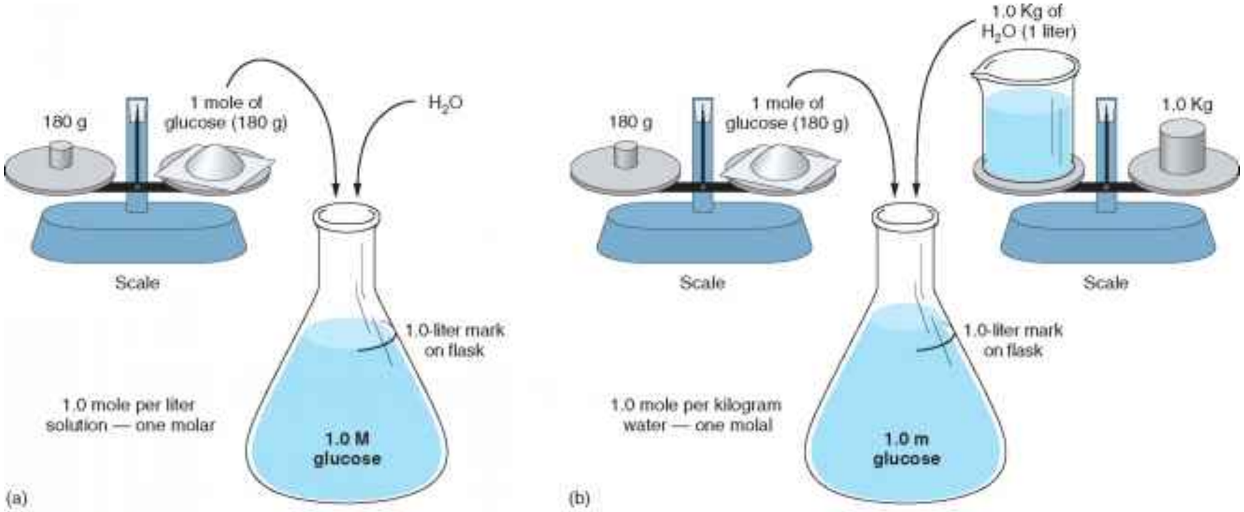


Figure 6.8 **Molar and molal solutions.** The diagrams illustrate the difference between (*a*) a one-molar (1.0 *M*) and (*b*) a one-molal (1.0 *m*) glucose

Mole fraction, *X*

- Moles of one solute per moles of all the components of the solution (solvent and all the solutes)
- Recall using mole fraction for mixture of gases problems
- $X_A = \frac{n_A}{n_A + n_B + n_{C\ldots}}$

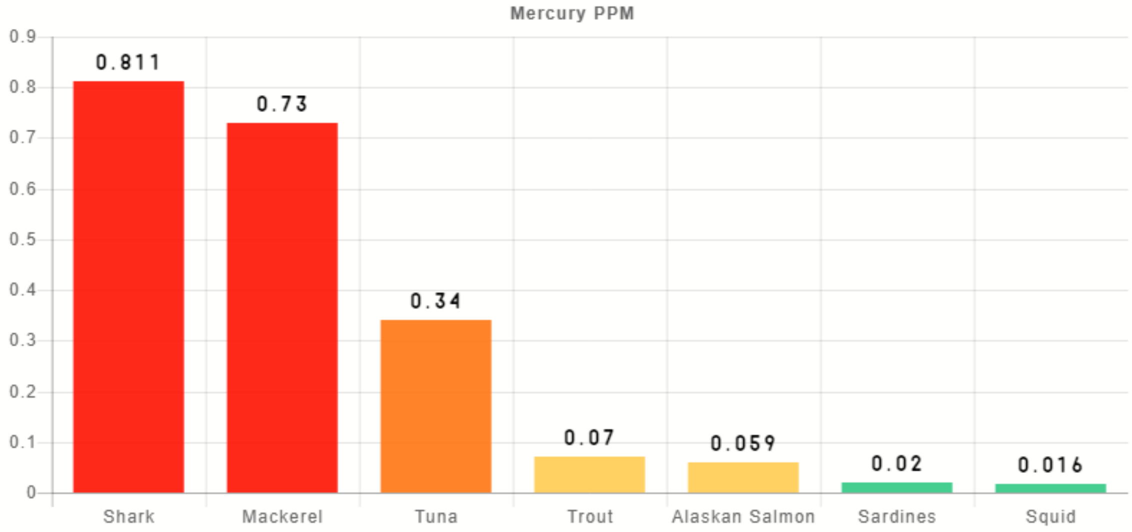
Weight percent

- Mass of solute per mass of solution
- Often used in everyday life
- $Weight\ \%\ A = \frac{mass_A}{mass_A + mass_B + mass_{C\ldots}} \times 100$

Active Ingredients:
Sodium Hypochlorite 6.0%
Other Ingredients: 94.0%
Total:..100%
(Yields 5.7% available chlorine)

Parts per million (ppm)

- Grams of solute (or any component) per 1,000,000 grams of solution (or any substance)
- Dilute aqueous solutions: mg/L (assuming solution density of 1 g/mL)



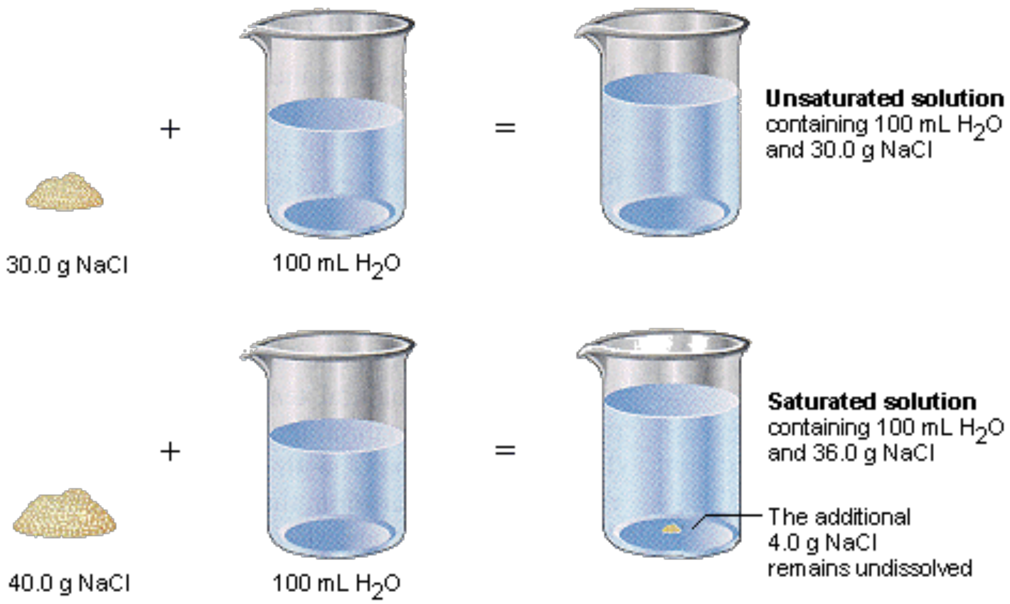
Sample problem

Suppose you add 1.2 kg of ethylene glycol, $HOCH_2CH_2OH$, as antifreeze to 4.0 kg of water in the radiator of your car. What are the mole fraction, molality and weight percent of ethylene glycol?

Forming a solution: saturated solutions

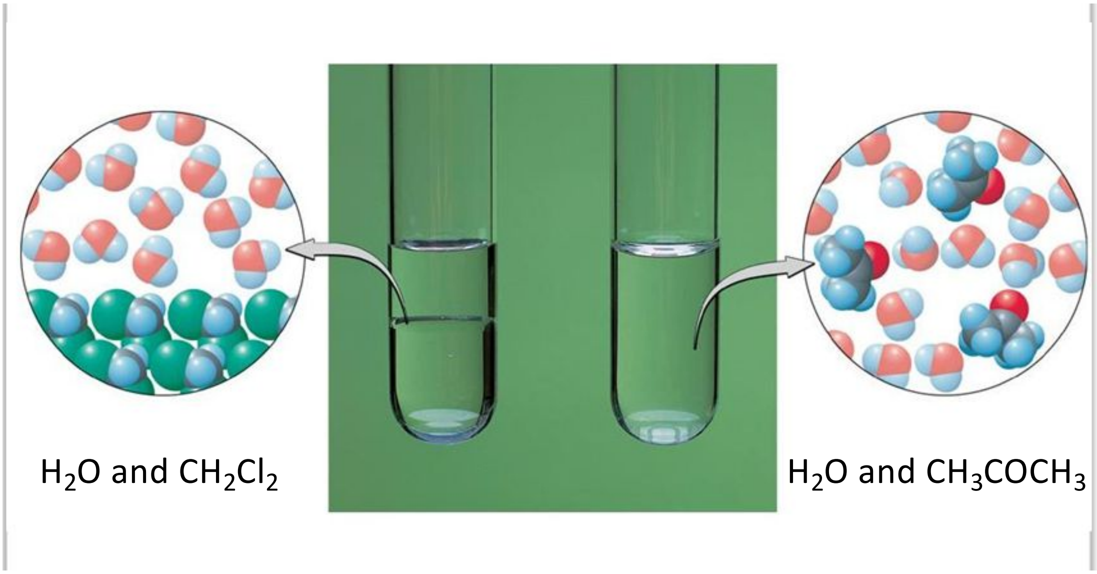
- When solutes dissolve in a solvent (e.g., NaCl in water): there’s a limit of how much solute will dissolve in an amount of solvent.
- When that limit is reached, the solution becomes **saturated**.
  - Adding any additional solute will not result in dissolving; instead, the solute will remain solid and precipitate

Substance	Solubility in 1 L of H_2O at 20 ˚C
NaCl	360 g
KNO_3	242 g
$Ba(OH)_2$	39 g
$Ca(OH)_2$	1.73 g



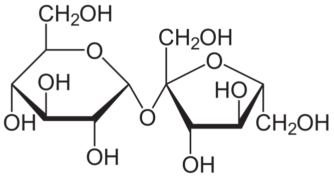
Dissolving liquids in liquids

- Some liquids can be mixed with other liquids at any proportion to form a homogeneous solution.
  - CH_3COCH_3 (acetone) and H_2O
  - Benzene (C_6H_6) and CH_2Cl_2
- Other liquids are immiscible with each other
  - H_2O and CH_2Cl_2
- **Like dissolves like!**
  - Polar liquids are miscible with other polar liquids (in general)
  - Nonpolar liquids are immiscible with polar liquids (in general)
  - It's relative



Like dissolves like

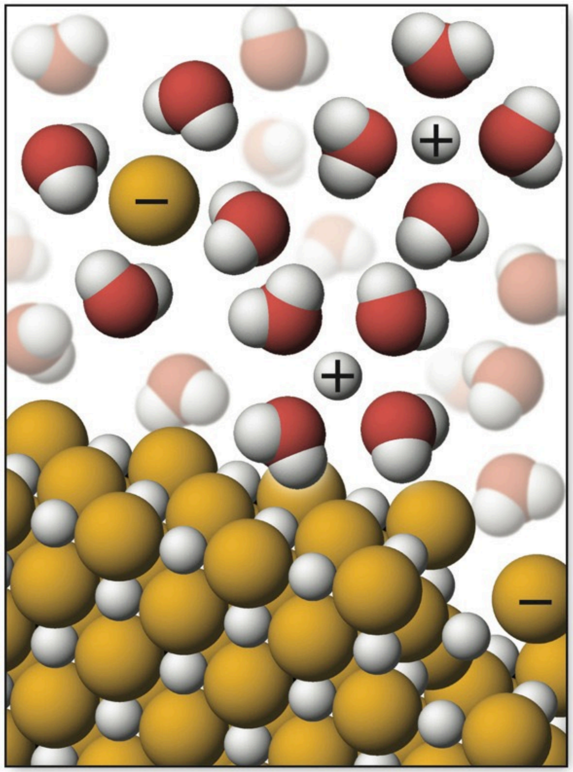
- Remember "solubility" is relative, not absolute
- Organic (less polar) substances dissolve better in organic solvents (CH_2Cl_2, acetone, CH_3CH_2OH…)
- More polar substances (especially soluble ionic salts) dissolve better in water
- Which of the following substances will dissolve well in water?
  - NaCl
  - Sucrose
  - I_2

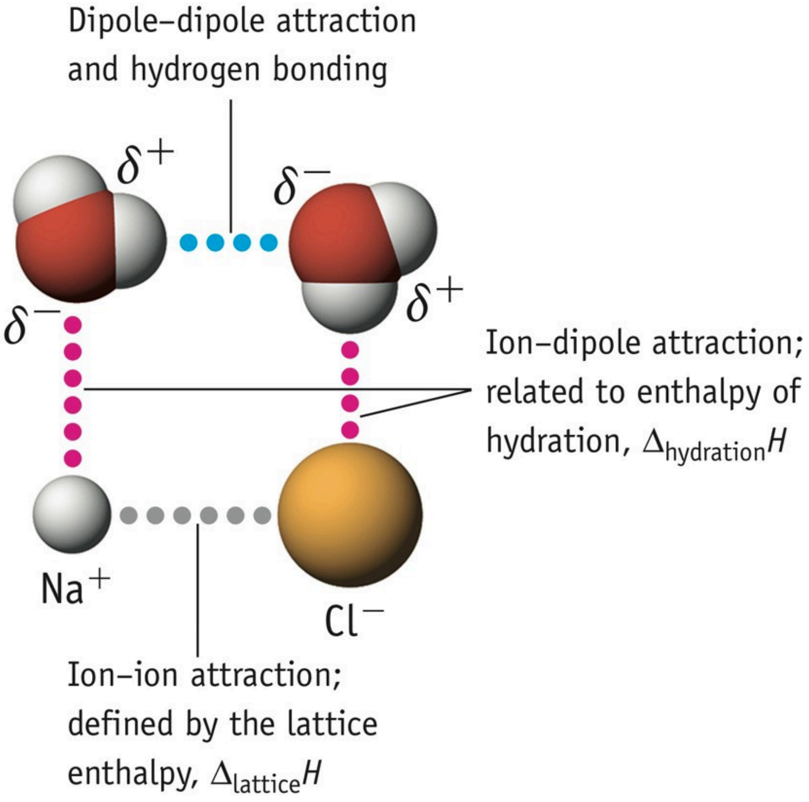


Enthalpy of solution

- Process of forming an aqueous solution of an ionic salt MX
  - MX (s) → MX (aq) $\Delta H_{solution}$
- First, ionic bonds between M^+ and X^- must be broken
  - (1) MX (s) → M^+ (g) + X^- (g) $-\Delta H_{lattice}$
  - Is this process exothermic or endothermic?
- Then, IMFs between M^+ and H_2O and X^- and H_2O must be formed
  - (2) M^+ (g) + X^- (g) → M^+ (aq) + X^- (aq) $\Delta H_{hydration}$
  - Is this process exothermic or endothermic?
- The magnitudes of (1) and (2) determine if dissolving a salt in water will cause a positive or negative ΔT.
  - $\Delta H_{solution}$ = (1) + (2)
- Many salts will dissolve even if $\Delta H_{solution} > 0$ because of entropy
  - Higher degree of disorder is created when particles of different substances are mixed

Enthalpy of solution



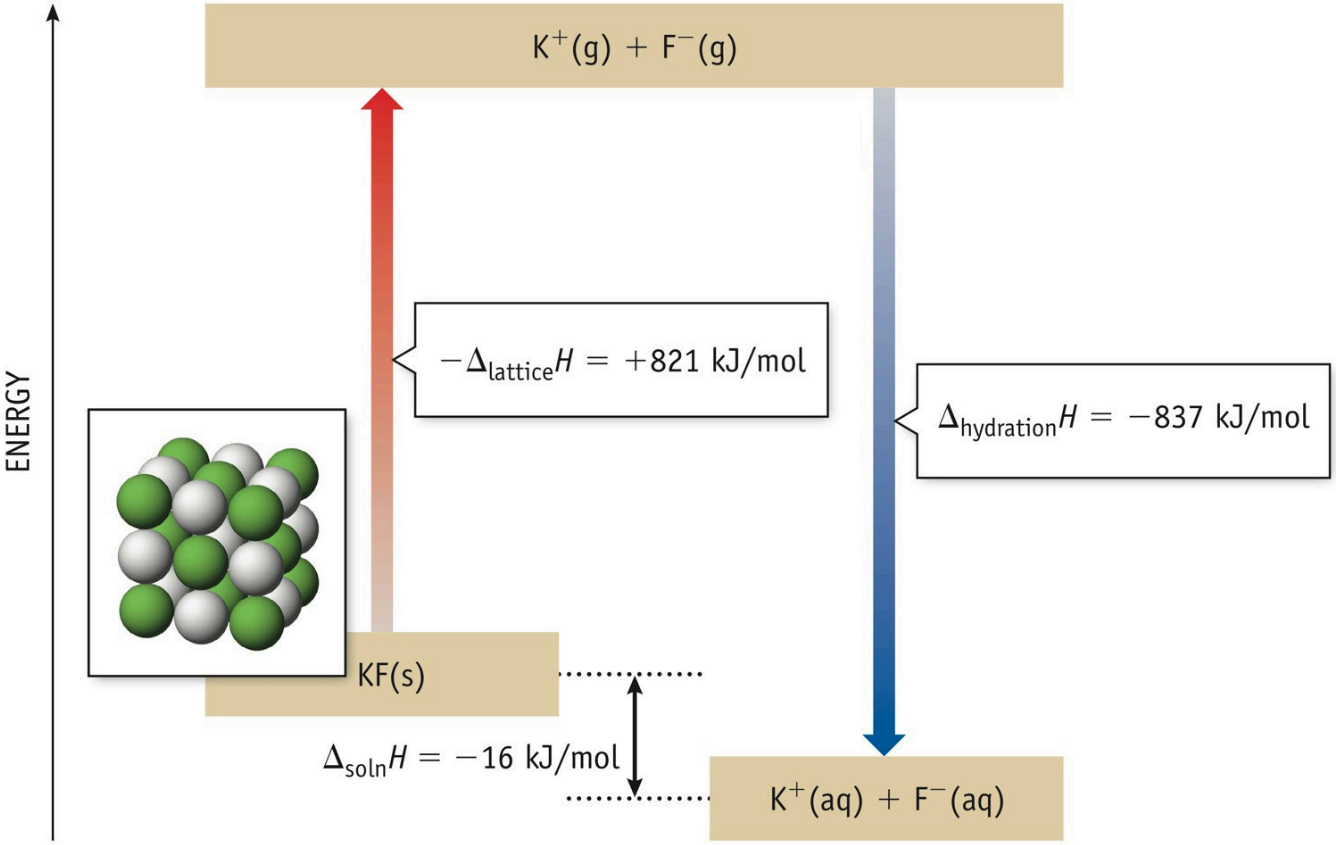


Dipole–dipole attraction and hydrogen bonding

Ion–dipole attraction; related to enthalpy of hydration, $\Delta_{hydration}H$

Ion–ion attraction; defined by the lattice enthalpy, $\Delta_{lattice}H$

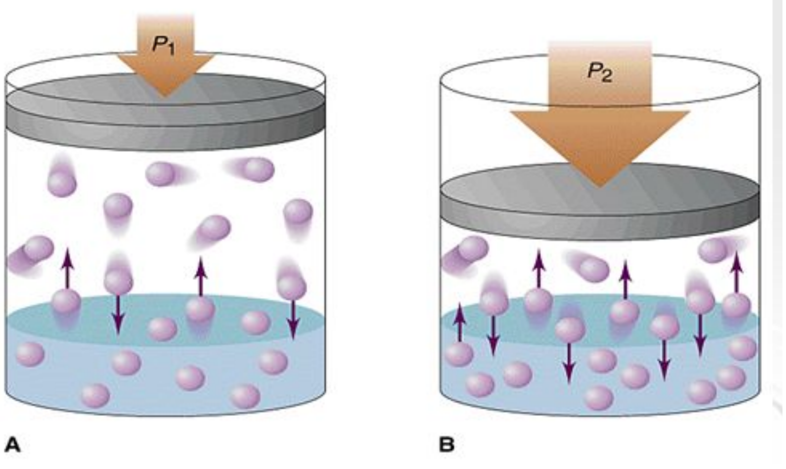
Enthalpy of solution



Enthalpy of solution from ΔH_f data

- Another way to calculate enthalpy of solution
- Consider the process of dissolving NaCl (s) in water
- $NaCl\ (s) \rightarrow NaCl\ (aq)$ $\Delta H_{solution}$
- $Na\ (s) + ½\ Cl_2\ (g) \rightarrow NaCl\ (s)$ $\Delta H_f = -411.1$ kJ
- $Na\ (s) + ½\ Cl_2\ (g) \rightarrow NaCl\ (aq)$ $\Delta H_f = -407.3$ kJ

Dissolving gases in liquids



- Increasing gas pressure will increase the solubility of a gas in a liquid
- **Henry's law**
- $S_g = k_H P_g$
  - S_g = solubility of gas (concentration units)
  - k_H = Henry's constant unique for each gas (concentration/P units); temperature dependent (usually listed for 25 ˚C)
  - P_g = pressure of gas (P units)

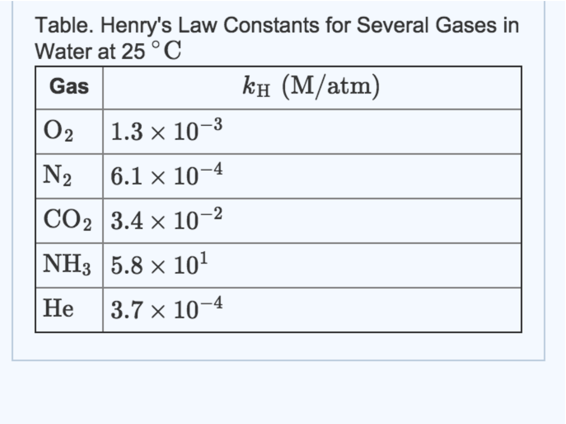


Table. Henry's Law Constants for Several Gases in Water at 25 °C

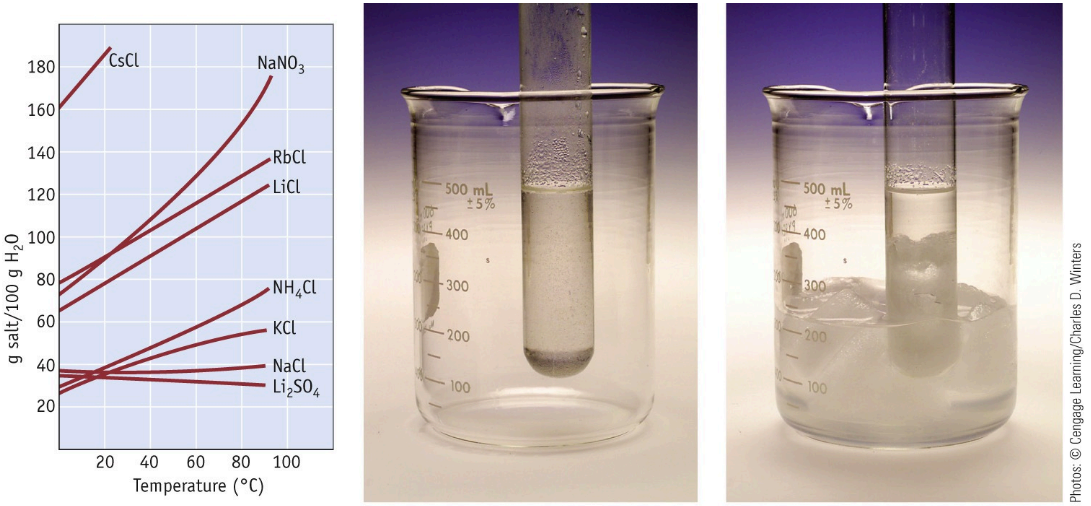
Gas	k_H (M/atm)
O_2	1.3×10^{-3}
N_2	6.1×10^{-4}
CO_2	3.4×10^{-2}
NH_3	5.8×10^{1}
He	3.7×10^{-4}

Sample problem

What is the concentration of O_2 (in g O_2 per kg of water) in a freshwater stream in equilibrium with air at 25 ˚C and at a pressure of 1.0 bar? The mole fraction of O_2 in air is 0.21.

Effect of temperature on solubility

- Increasing T causes gas solubility to decrease
  - Gas particles have more kinetic energy at higher T's – can escape solution more readily
- Increasing T usually causes solid solubility to increase



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(a) Temperature dependence of the solubility of some ionic compounds.

(b) NH_4Cl dissolved in water.

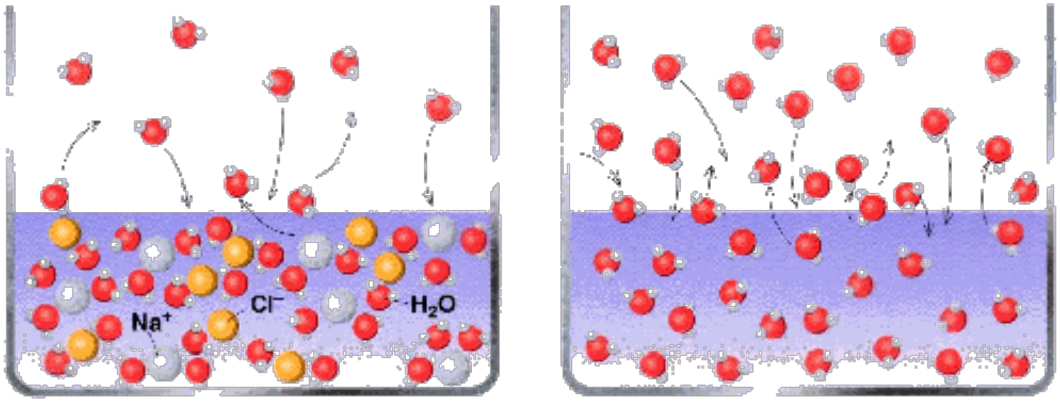
(c) NH_4Cl precipitates when the solution is cooled in ice.

Colligative properties

- Depend on **number of particles in solution**, NOT the identity of particles
- Vapor pressure
- Boiling point elevation
- Freezing point depression
- Osmotic pressure

Vapor pressure and Raoult’s Law

- When a non-volatile solute dissolves in a liquid solvent to form an ideal solution (e.g., NaCl in H_2O), **the vapor pressure of the solvent is lowered**
- Raoult’s Law: $\mathbf{P_{solvent} = x_{solvent}P^{\circ}_{solvent}}$
- Ideal solution: A-B IMFs ~ A-A IMFs/B-B IMFs



(a) Sea water

(b) Pure water

Sample problem

You dissolve 651 g of ethylene glycol, $HOCH_2CH_2OH$, in 1.50 kg of water. What is the vapor pressure of the water over the solution at 90 ˚C? Assume ideal behavior for the solution. The vapor pressure of pure water at 90 ˚C is 525.8 torr.

Sample problem

Glycerin ($C_3H_8O_3$) is a nonvolatile nonelectrolyte with a density of 1.26 g/mL at 25 ˚C. Calculate the vapor pressure at 25 ˚C of a solution made by adding 50.0 mL of glycerin to 500.0 mL of water. The vapor pressure of pure water at 25 ˚C is 23.8 torr and its density is 1.00 g/mL.

Sample problem (2 volatile components)

The vapor pressure of pure benzene (C_6H_6) and pure toluene ($C_6H_5CH_3$) at 25 ˚C are 95.1 torr and 28.4 torr, respectively. A solution is prepared in which the mole fractions of both benzene and toluene are 0.500.

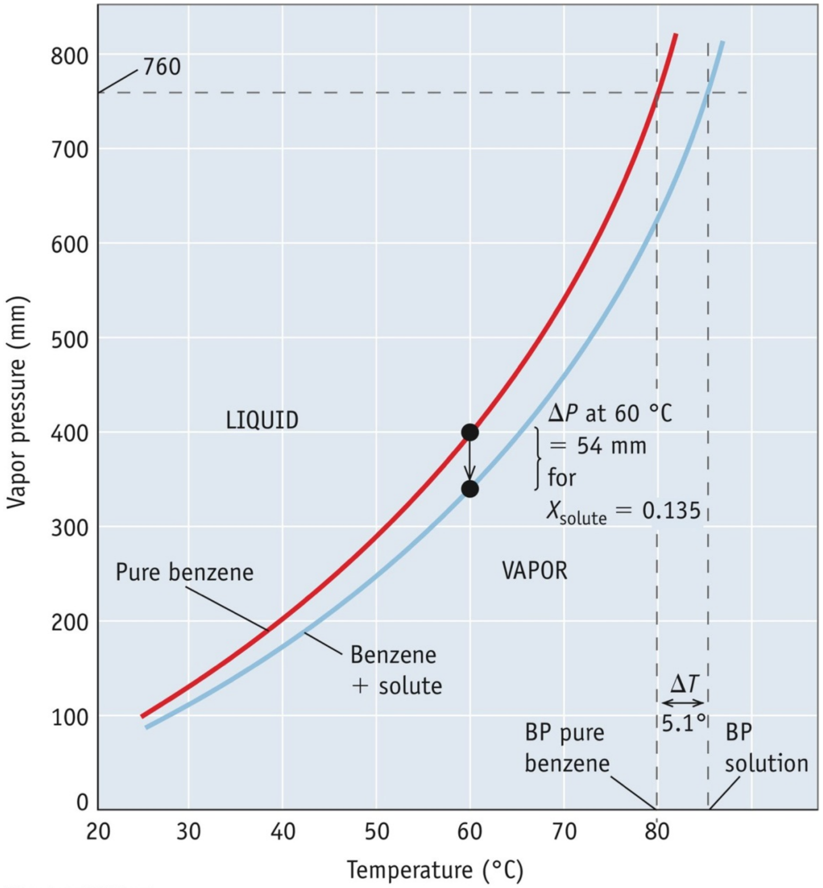
a) What are the partial pressures of benzene and toluene above the solution? What is the total vapor pressure?

b) What are the mole fractions of benzene and toluene in the vapor phase?

Boiling point elevation

- Raoult's Law: $P_{solvent}$ is lowered when non-volatile solute particles are added to it
- Remember that for a liquid to boil, its vapor pressure need to equal atmospheric pressure
- As a result, **adding non-volatile solute particles to a solvent causes boiling point elevation**
  - As long as the solution is still ideal
  - The more concentrated a solution becomes, the less ideal it is

Example: vapor pressure of a benzene solution with a concentration 2.00 *m* in nonvolatile solute



Boiling point elevation

- **$\Delta T_{bp} = K_{bp}mi$**
  - K_{bp} = molal boiling point elevation constant (˚C/*m*); unique for each solvent
  - *m* = molality of solution
  - *i* = van’t Hoff factor
- *i* = 1 for nonelectrolytes
- *i* = (number of ions/electrolyte formula unit) for dilute solutions of strong electrolytes (e.g., ionic salts) assuming complete dissociation
  - Recall, colligative properties depend on the total number of dissolved particles in solution
  - e.g., $CaCl_2 \rightarrow i = 3$

Freezing point depression

- Similar effect as boiling point elevation
- **$\Delta T_{fp} = K_{fp}mi$**

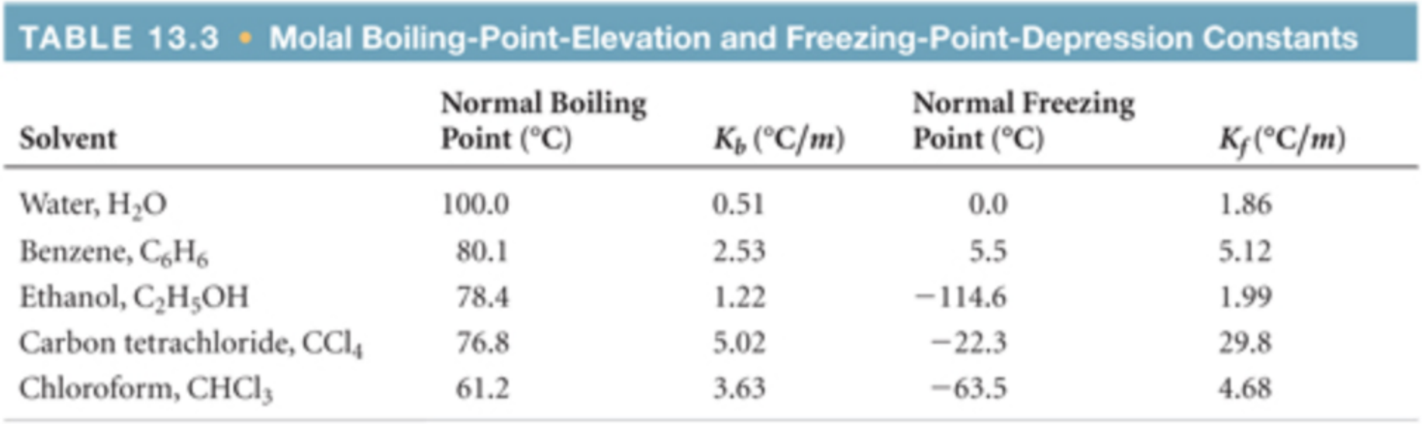


TABLE 13.3 • Molal Boiling-Point-Elevation and Freezing-Point-Depression Constants

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

Sample problem

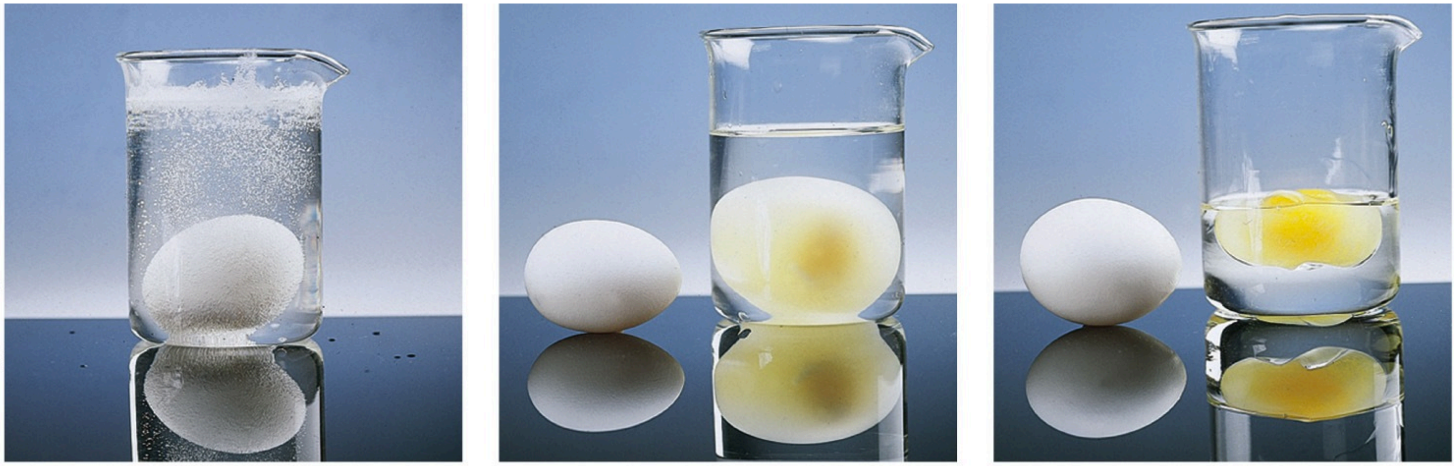
Eugenol, a compound found in nutmeg and cloves, has the formula $C_{10}H_{12}O_2$. What is the boiling point of a solution containing 0.144 g of this compound dissolved in 10.0 g of benzene?

Sample problem

If 52.5 g of LiF is dissolved in 306 g of water, what is the expected freezing point of this solution?

Osmotic pressure

- Osmosis = movement of solvent molecules from region of low C to region of high C
  - Solvent will move in an attempt to equalize concentration
  - Semipermeable membrane: allows solvent, but not solute, molecules to pass through
- Equilibrium is reached when the pressure on both sides of the membranes is the same
  - Osmotic pressure, Π



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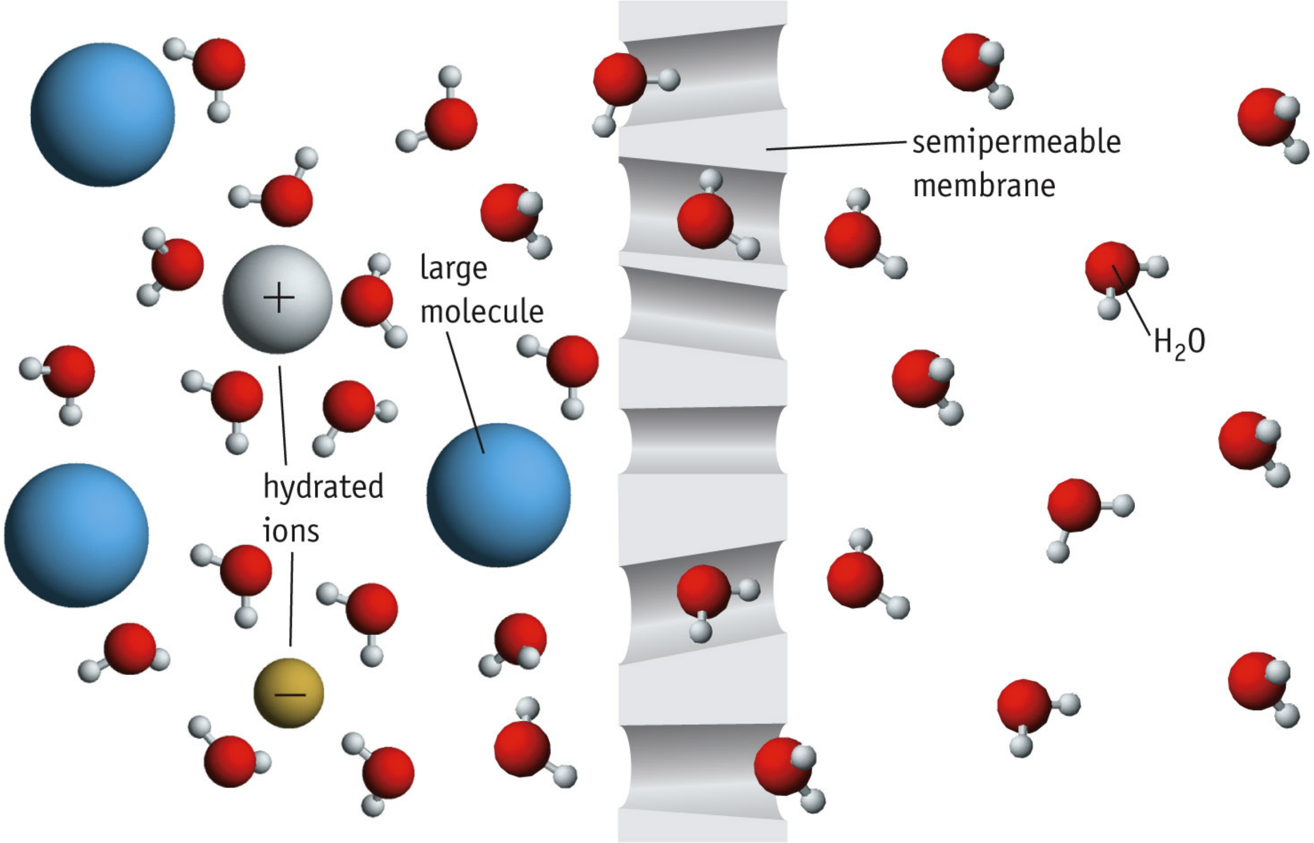
(a) A fresh egg is placed in dilute acetic acid. The acid reacts with the $CaCO_3$ of the shell but leaves the egg membrane intact.

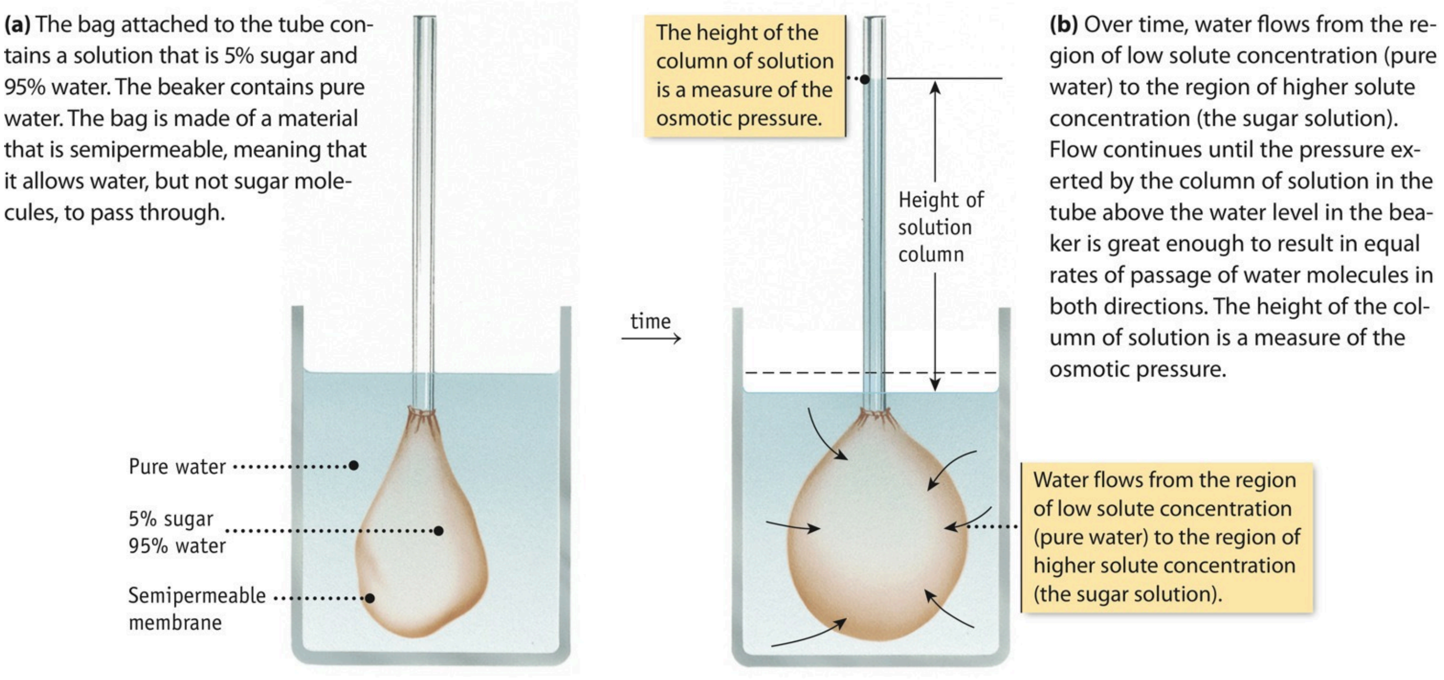
(b) If the egg, with its shell removed, is placed in pure water, the egg swells.

(c) If the egg, with its shell removed, is placed in a concentrated sugar solution, the egg shrivels.

Osmosis at the particle level



Osmotic pressure



(a) The bag attached to the tube contains a solution that is 5% sugar and 95% water. The beaker contains pure water. The bag is made of a material that is semipermeable, meaning that it allows water, but not sugar molecules, to pass through.

The height of the column of solution is a measure of the osmotic pressure.

(b) Over time, water flows from the region of low solute concentration (pure water) to the region of higher solute concentration (the sugar solution). Flow continues until the pressure exerted by the column of solution in the tube above the water level in the beaker is great enough to result in equal rates of passage of water molecules in both directions. The height of the column of solution is a measure of the osmotic pressure.

Water flows from the region of low solute concentration (pure water) to the region of higher solute concentration (the sugar solution).

Same Π on both sides of the membrane = **isotonic** solutions

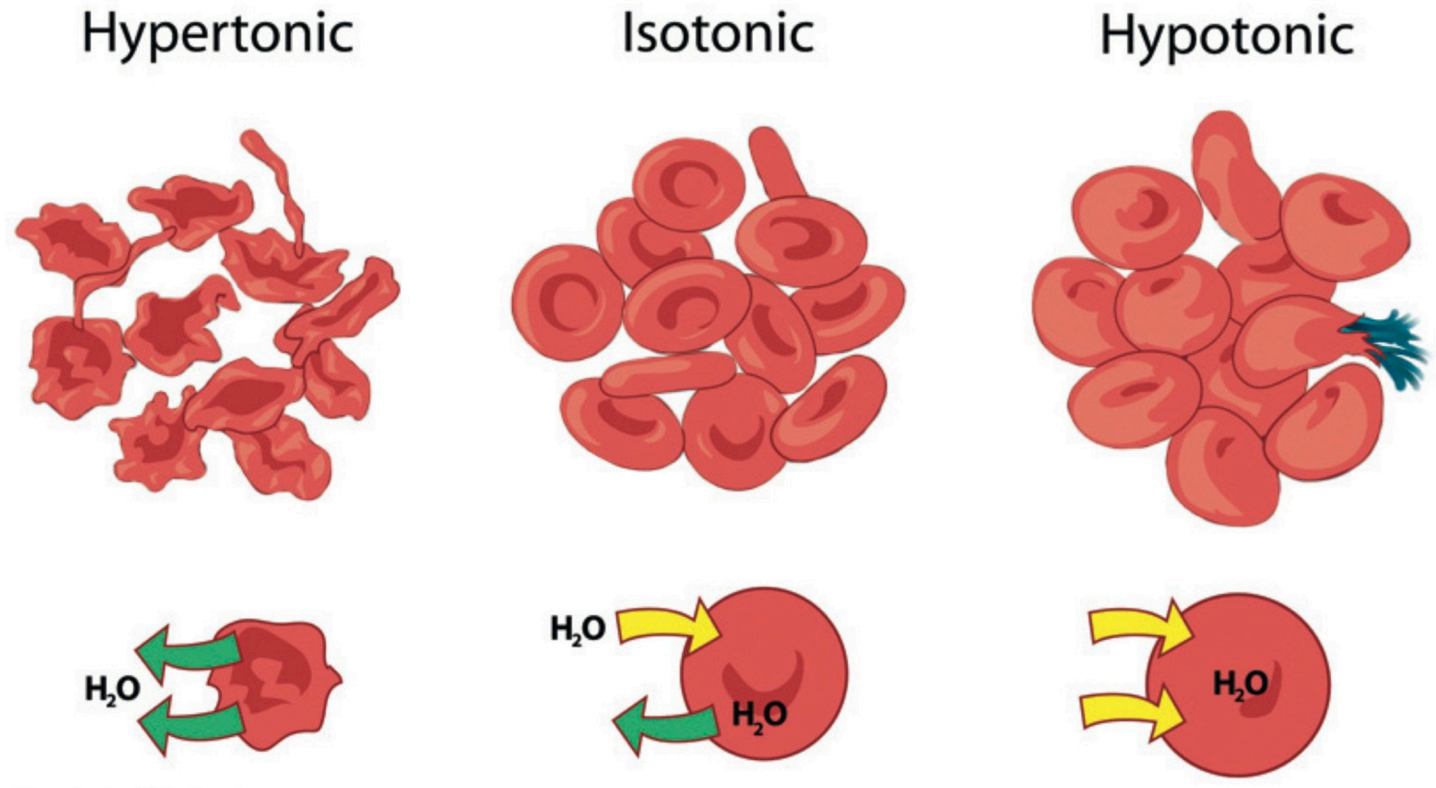
Osmotic pressure

- **Π = cRT** (analogous to PV = nRT)
  - c = concentration of particles (how many particles are there per 1 mol of $NaNO_3$?)
  - R = ideal gas constant
- Even very dilute solutions exert significant Π
  - 0.001 M aqueous solution will exert Π = 18.5 torr (can be measured accurately)
  - 0.001 *m* aqueous solution will lower FP of solvent by 0.002 ˚C (hard to measure accurately)
  - As a result, measuring osmotic pressure is a great technique to determine molar mass (e.g., of large biomolecules like proteins)

Sample problem

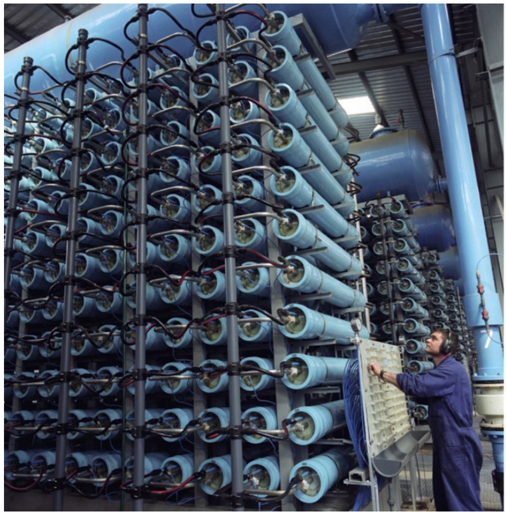
Beta-carotene is the most important of the A vitamins. Calculate the molar mass of β-carotene if 10.0 mL of a solution containing 7.68 mg of β-carotene has an osmotic pressure of 26.57 torr at 25.0 ˚C.

Osmotic pressure and living cells



Purifying seawater by reverse osmosis

- P greater than osmotic pressure is applied to seawater to purify it



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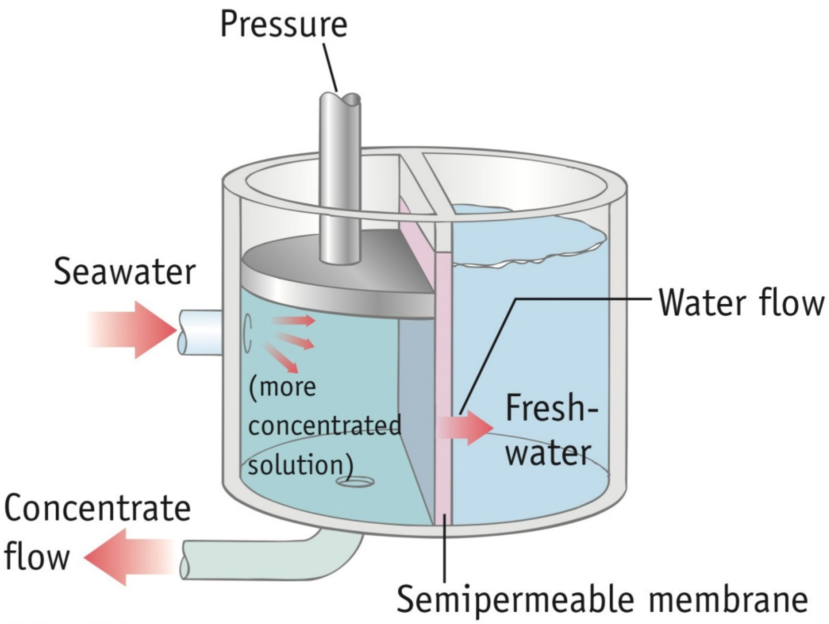
Water desalination plant



Colloids

- (Homogeneous) solutions = particles do not settle down (precipitate) from the solvent over time
- Colloids = relatively large (1-1000 nm) particles dispersed in some medium
  - Take longer to settle down than suspensions
- Colloids exhibit Tyndall effect (scattering of light by the dispersed particles)

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Colloid types

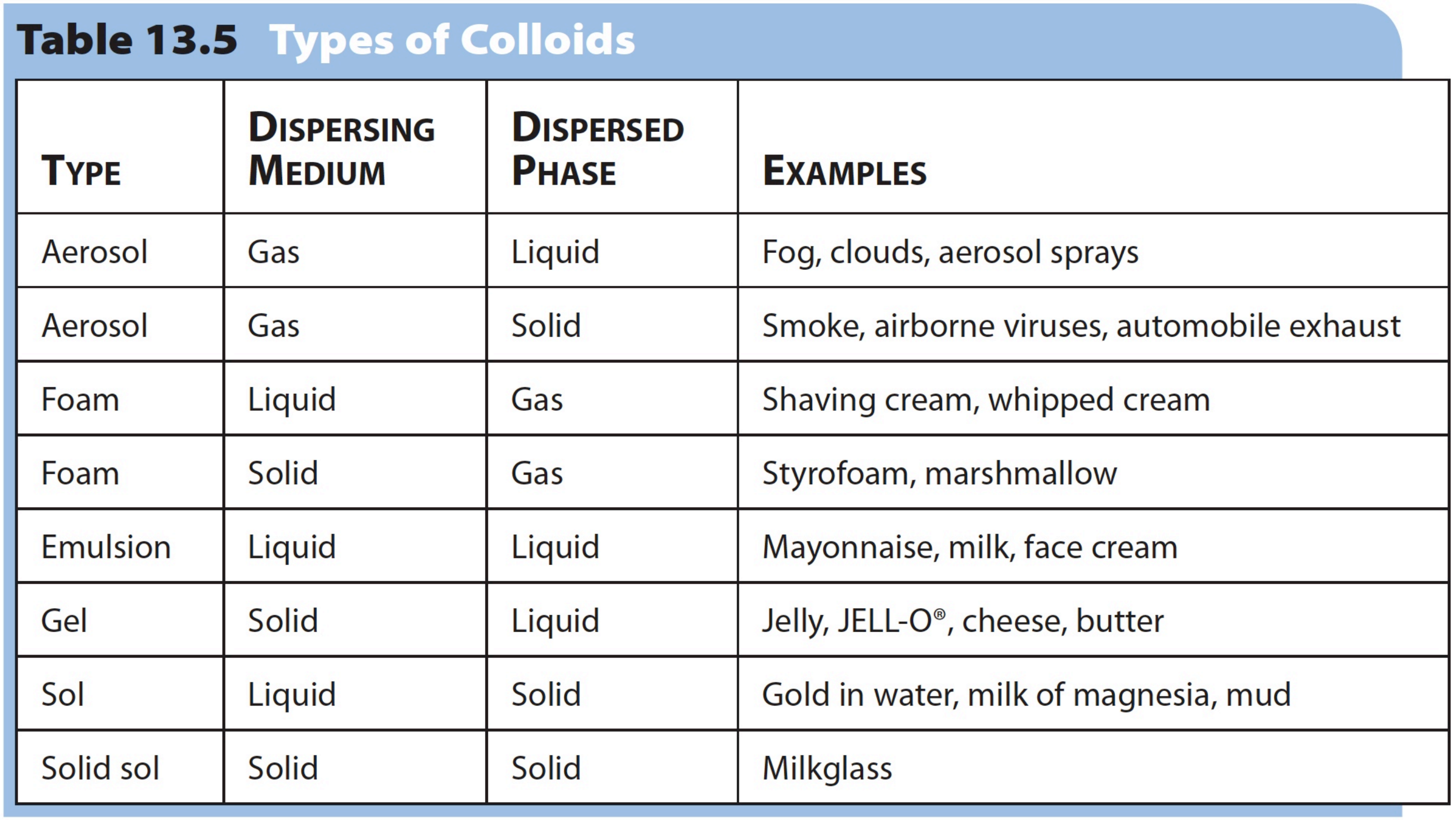
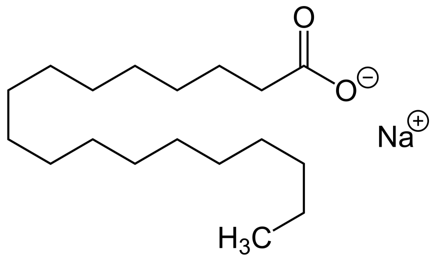


Table 13.5 **Types of Colloids**

TYPE	DISPERSING MEDIUM	DISPERSED PHASE	EXAMPLES
Aerosol	Gas	Liquid	Fog, clouds, aerosol sprays
Aerosol	Gas	Solid	Smoke, airborne viruses, automobile exhaust
Foam	Liquid	Gas	Shaving cream, whipped cream
Foam	Solid	Gas	Styrofoam, marshmallow
Emulsion	Liquid	Liquid	Mayonnaise, milk, face cream
Gel	Solid	Liquid	Jelly, JELL-O®, cheese, butter
Sol	Liquid	Solid	Gold in water, milk of magnesia, mud
Solid sol	Solid	Solid	Milkglass

Surfactants (soaps)

- Soaps
  - Heat KOH or NaOH with fat
  - This produces salts of fatty acids
- Soap particles have hydrophobic and hydrophilic parts
  - Hydrophilic (charged) parts allow soaps to interact with water
  - Hydrophobic (long CH chains) parts allow soaps to interact with oil



Sodium stearate, a soap