

<b>Solution:</b>	homogeneous mixture
<b>Molarity (M)</b>	moles solute/liter solution
<b>Mass Percent</b>	mass solute/(mass solute + mass solvent) X 100
<b>Mole Fraction of A:</b>	moles A/total moles
<b>Molality (m):</b>	moles solute/kilograms solvent

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Problem: A solution is prepared by adding 5.84 g of formaldehyde,  $\text{H}_2\text{CO}$ , to 100.0 g of  $\text{H}_2\text{O}$ . The final volume of the solution was 104.0 mL. Calculate the molarity, molality, mass percent, and mole fraction.

$$5.84 \text{ g} \cdot \frac{1 \text{ mol}}{30.0 \text{ g}} = .195 \text{ mol}$$

$$M = \frac{\text{mol}}{L} = \frac{.195 \text{ mol}}{.104 \text{ L}} = 1.88 \text{ M}$$

$$m = \frac{\text{mol}}{\text{kg}} = \frac{.195 \text{ mol}}{.100 \text{ kg}} = 1.95 \text{ m}$$

$$\text{mass \%} = \frac{5.84 \text{ g}}{5.84 + 100.0} \times 100 = 5.52 \%$$

$$100.0 \text{ g H}_2\text{O} \cdot \frac{1 \text{ mol}}{18.0 \text{ g}} = 5.56 \text{ mol H}_2\text{O}$$

$$X_{\text{H}_2\text{CO}} = \frac{.195}{5.56 + .195} = .0339$$

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Chapter 11 problems 29, 33, and 35

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**Normality (N)** =  $\frac{\text{equivalents of solute}}{\text{liter of solution}}$

An equivalent is the mass of the solute that can furnish or accept one mole of protons ( $\text{H}^+$  in acid/base rxns) or one mole of electrons (in redox rxns)

e.g.  $\text{H}_3\text{PO}_4$ 3  $\text{H}^+$  equivalents/mol acid

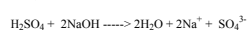
$$\text{equivalent weight} = \frac{98.0 \text{ g/mol}}{3 \text{ eq/mol}} = 32.7 \text{ g/eq}$$

e.g.  $\text{HCl}$ 1  $\text{H}^+$  equivalent/mole acid

$$\text{equivalent weight} = \frac{36.5 \text{ g/mol}}{1 \text{ eq/mol}} = 36.5 \text{ g/eq}$$

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Problem: Given the reaction,



If we have 28.42 g  $\text{H}_2\text{SO}_4$  in 800. mL of water, what are the normality and molarity of the solution?

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**HEAT OF SOLUTION**

"Like dissolves like"

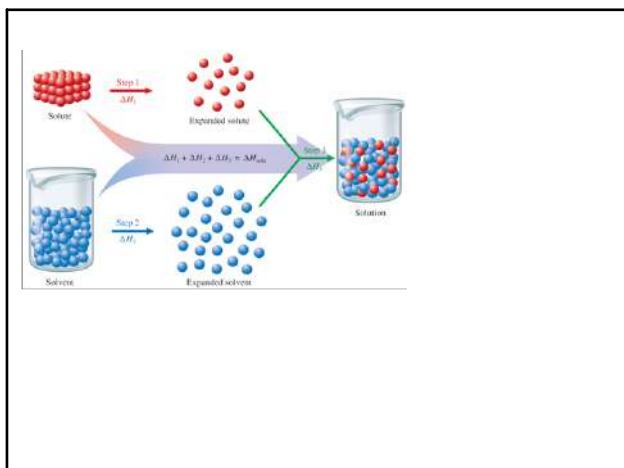
Solution formation occurs in three steps:

1. Expanding the solute (endothermic,  $\Delta H_1 = +$ )
2. Expanding the solvent (endothermic,  $\Delta H_2 = +$ )
3. Combining solute and solvent (exothermic,  $\Delta H_3 = -$ )

$$\Delta H_{\text{solution}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

Recall two factors driving reaction: **enthalpy and entropy must be considered.**

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Explain why oil and water do not mix using  $\Delta H_{\text{solution}}$  principles:

$\Delta H_1 = \text{very positive (strong LDFs)}$  - NP  
 $\Delta H_2 = \text{very positive (strong H-bonds)}$   
 $\Delta H_3 = 0$  - P  
 $\Delta H_{\text{soln}} = \text{very positive, unlikely}$

Explain why NaCl and water mix using  $\Delta H_{\text{solution}}$  principles:

$\Delta H_1$  very positive (ionic)  
 $\Delta H_2$  very positive (H-bonds)  
 $\Delta H_3$  slightly exo (+ ... - interactions occur)  
 $\Delta H_{\text{soln}}$  slightly pos or neg but entropy driven!

(note:  $\text{NH}_4^+$  salts in  $\text{H}_2\text{O}$  is endothermic)  
 $\text{CaCl}_2$  ... exothermic

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**Table 11.3 The Energy Terms for Various Types of Solutes and Solvents**

	$\Delta H_1$	$\Delta H_2$	$\Delta H_3$	$\Delta H_{\text{soln}}$	Outcome
Polar solute, polar solvent	Large	Large	Large, negative	Small	Solution forms
Nonpolar solute, polar solvent	Small	Large	Small	Large, positive	No solution forms
Nonpolar solute, nonpolar solvent	Small	Small	Small	Small	Solution forms
Polar solute, nonpolar solvent	Large	Small	Small	Large, positive	No solution forms

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**FACTORS AFFECTING SOLUBILITY**1. Structure Effects -nonpolar substances are hydrophobic (dislike water):

a hydrocarbon is considered to be nonpolar and hydrophobic

polar substances are hydrophilic (like water):

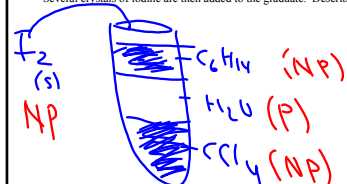
the most common polar groups are -OH and -NH; on a relatively small hydrocarbon these groups will make the molecular polar and hydrophilic

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Problem: 50 mL of each of the following are added to a test tube,

$\text{CCl}_4$        $D = 1.4 \text{ g/mL}$   
 $\text{H}_2\text{O}$          $D = 1.0 \text{ g/mL}$   
 $\text{C}_6\text{H}_{14}$        $D = 0.8 \text{ g/mL}$

Several crystals of iodine are then added to the graduate. Describe the appearance of the test tube.



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Chapter 11 problems 39-47 odd

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2. Pressure Effects -

The solubility of gases is, for the most part, independent of structure and is given by **Henry's Law**:

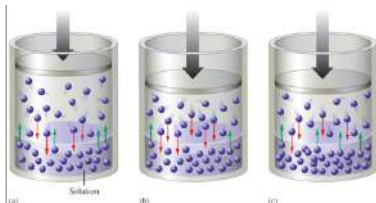
$$P = kC$$

$P$  = partial pressure of gaseous solute above soln (atm)

$C$  = concentration of dissolved gas (mol/L)

$k$  = temperature dependent constant for a particular reaction

Henry's Law applies for low gas concentrations and gases that do not react with the solution.



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Problem: The solubility of oxygen gas is  $2.2 \times 10^{-4}$  M at  $0^\circ\text{C}$  and 0.1 atm. Calculate the solubility of oxygen at  $0^\circ\text{C}$  and 0.35 atm.

$$\frac{.1}{2.2 \cdot 10^{-4}} = \frac{.35}{X}$$

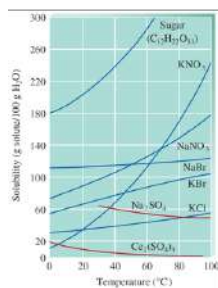
$$X = 7.84 \cdot 10^{-4} \text{ M}$$

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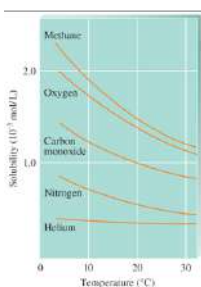
8. Temperature Effects -

The solubility of most, but not all, solids increases with temperature (review solubility curves).

The solubility of a gas in water typically decreases with increasing temperature.



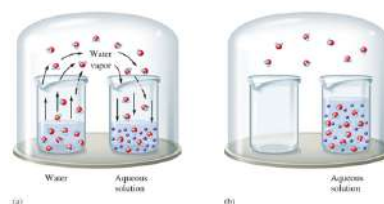
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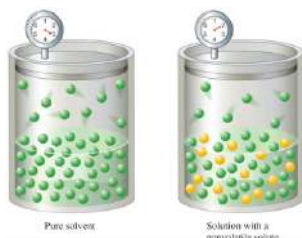
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Vapor Pressure of Solutions

Consider an experiment in which a sealed container encloses a beaker containing an aqueous sulfuric acid solution and a beaker containing pure water as illustrated on the next page. Gradually, the volume of the sulfuric acid solution increases and the volume of the pure water decreases. Why?



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1. Nonvolatile solutes: For nonvolatile solutes, behavior is described by **Raoult's Law**.

$$P_{\text{soln}} = X_{\text{solvent}} \cdot P_{\text{solvent}}^0$$

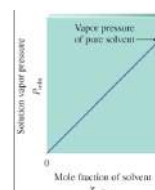
$P_{\text{soln}}$  = vapor pressure of the solution

$X_{\text{solvent}}$  = mole fraction of solvent

$P_{\text{solvent}}^0$  = vapor pressure of pure solvent

does not easily EVAPORATE

This equation says that the addition of a nonvolatile solute will cause the vapor pressure of the solution to fall in direct proportion to the mole fraction of the solute. For a solution that obeys Raoult's law, a plot of  $P_{\text{solution}}$  versus  $X_{\text{solvent}}$  gives a straight line.



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Problem: Glycerin,  $C_3H_8O_3$ , is a nonvolatile liquid that is also a nonelectrolyte. What is the vapor pressure of a solution made by adding 164 g of glycerin to 338 mL of  $H_2O$  at  $39.8^\circ C$ ? The vapor pressure of pure water at  $39.8^\circ C$  is 54.74 torr and its density is 0.992 g/mL.

$$164 \text{ g glycerin} \cdot \frac{1 \text{ mol}}{92.0 \text{ g}} = 1.78 \text{ mol glycerin}$$

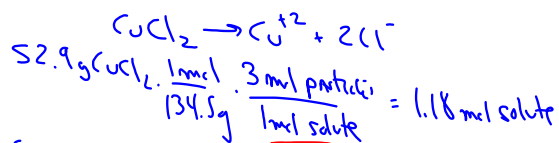
$$338 \text{ mL } H_2O \cdot \frac{0.992 \text{ g}}{1 \text{ mL}} \cdot \frac{1 \text{ mol}}{18.0 \text{ g}} = 18.6 \text{ mol } H_2O$$

$$P_{\text{soln}} = \left( \frac{18.6}{18.6 + 1.78} \right) (54.74 \text{ torr}) = 49.96 \text{ torr}$$

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Let's extend the concept further using a nonvolatile electrolyte that dissociates completely in water. When solving the problem, we are interested in moles of solute actually present in the solution (after dissociation), not moles added.

Problem: What is the vapor pressure of a solution made by adding 52.9 g of  $CuCl_2$ , a strong electrolyte, to 800.0 mL of water at  $52.0^\circ C$ ? The vapor pressure of water at  $52.0^\circ C$  = 102.1 torr and its density = 0.987 g/mL.



$$800.0 \text{ mL } H_2O \cdot \frac{0.987 \text{ g}}{1 \text{ mL}} \cdot \frac{1 \text{ mol}}{18.0 \text{ g}} = 43.9 \text{ mol } H_2O$$

$$P_{\text{soln}} = \left( \frac{43.9}{43.9 + 1.18} \right) (102.1 \text{ torr}) = 99.4 \text{ torr}$$

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#### Molecular Weight via Raoult's Law

Problem: At  $29.6^\circ C$  pure water has a vapor pressure of 31.1 torr. A solution is prepared by adding 86.7 g of "X", a nonvolatile nonelectrolyte to 350.0 g of water. The vapor pressure of the resulting solution is 28.6 torr. Calculate the molecular weight of X.

$$P_{\text{soln}} = X_{\text{solvent}} \cdot P_{\text{solvent}}^0$$

$$28.6 = X_{\text{solvent}} \cdot 31.1$$

$$350 \text{ g} \cdot \frac{1}{18} = 19.4 \text{ mol } H_2O$$

$$X_{\text{solvent}} = 0.920 = \frac{19.4}{19.4 + X}$$

$$X = 1.69 \text{ mol solute}$$

$$\therefore \text{molar mass} = \frac{86.7 \text{ g}}{1.69 \text{ mol}} = 51.3 \text{ g/mol}$$

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Chapter 11 problems 53, 54, and 55

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**Ideal Solutions** - one that obeys Raoult's Law. Nearly ideal behavior is often observed when the solute-solute, solvent-solvent, and solute-solvent interactions are very similar.

Strong solute-solvent interactions give a vapor pressure lower than that predicted by Raoult's Law. There will be a negative deviation from Raoult's Law. This occurs when the solute-solvent interaction has a large negative  $\Delta H$ .

I. Volatile Solutes - contribute to the vapor pressure such that:

$$P_{\text{total}} = P_{\text{solute}} + P_{\text{solvent}}$$

The vapor pressure of each component can be expressed by Raoult's Law:

$$P_{\text{solute}} = X_{\text{solute}} \cdot P_{\text{solute}}^0$$

$$P_{\text{solvent}} = X_{\text{solvent}} \cdot P_{\text{solvent}}^0$$

therefore,

$$P_{\text{total}} = (X_{\text{solute}} \cdot P_{\text{solute}}^0) + (X_{\text{solvent}} \cdot P_{\text{solvent}}^0)$$

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$C_6H_6$

Problem: The vapor pressure of pure hexane ( $C_6H_{14}$ ) at  $60.0^\circ C$  is 573 torr. That of pure benzene is 391 torr. What is the expected vapor pressure of a solution prepared by mixing 58.9 g of hexane with 44.0 g of benzene (assuming ideal solution)?

$58.9 \text{ g hex} \cdot \frac{1 \text{ mol}}{86.09} = .685 \text{ mol hex}$   
 $44.0 \text{ g b.} \cdot \frac{1 \text{ mol}}{78.09} = .564 \text{ mol ben}$   
 $X_{\text{hex}} = \frac{.685}{.685 + .564} = .548 \therefore X_{\text{ben}} = .452$   
 $P_{\text{soln}} = X_{\text{hex}} P_{\text{hex}}^{\circ} + X_{\text{ben}} P_{\text{ben}}^{\circ}$   
 $= (.548)(573) + (.452)(391)$   
 $= 314 + 177 = 491 \text{ torr}$

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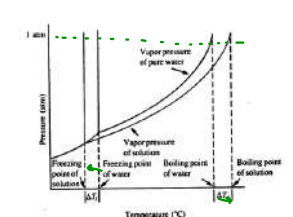
Chapter 11 problems 57, 59, and 63

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**COLLIGATIVE PROPERTIES**

Colligative properties of a solution are properties that depend only on the number, and not on the identity, of the solute particles.

1. **Vapor Pressure Depression** - adding solute particles to a solvent decreases the number of solvent particles on the surface and thus lowers the vapor pressure. Solute-solvent particle interactions are also important and contribute to a decrease in pressure.



Note the overall effect of adding a nonvolatile solute to a liquid is to **extend the range of the solvent**.

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2. **Boiling Point Elevation** - the increase in boiling point of a liquid due to the addition of a nonvolatile solute is directly proportional to the molality of the resulting solution:

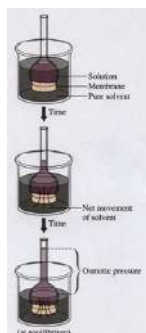
$$\Delta T_b = K_b \cdot m \quad \text{for } H_2O, K_b = 0.51^\circ C/m \text{ of nonelectrolyte}$$

3. **Freezing Point Depression** - the decrease in freezing point of a liquid due to the addition of a nonvolatile solute is directly proportional to the molality of the resulting solution:

$$\Delta T_f = K_f \cdot m \quad \text{for } H_2O, K_f = 1.86^\circ C/m \text{ of nonelectrolyte}$$

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4. **Osmotic Pressure** - the pressure that just stops osmosis. **Osmosis** is the flow of a solvent into a solution through a semipermeable membrane. Osmotic pressure is a colligative property because its value depends on the concentration of the solute, not its nature. Osmotic pressure is especially useful for determining molecular weights experimentally because **small solute concentrations produce large osmotic pressures**.



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The relationship between osmotic pressure and solution concentration is given by:

$$\pi = MRT$$

$\pi$  = osmotic pressure (atm)  
 $M$  = molarity of soln (mol/L)  
 $R = 0.08206 \text{ (L}\cdot\text{atm/mol}\cdot\text{K)}$   
 $T$  = Kelvin temperature

Note: for dilute solutions,  $M \approx m$ .

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van't Hoff Factor ( $i$ ) - for electrolyte solutions:

$i$  = moles of particles in soln/moles of solute dissolved

The expected value for  $i$  is not always the real value because of ion pairing - at a given instant a small number of ions are paired and thus counted as a single particle. Ion pairing is important in concentrated solutions and where ions have multiple charges. Note that for nonelectrolytes will be 1

$$\Delta T = iK_m$$

$$\pi = iMRT$$

Problem: A solution is prepared by adding 31.65 g of sodium chloride to 220.0 mL of water at 34.0°C (density = 0.994 g/mL,  $k_b$  for water = 0.52°C/m). Calculate the boiling point of the solution, assuming complete dissociation of NaCl in solution.

$$\Delta T_b = K_b \cdot m \cdot i \quad i = 2$$

$$31.65 \text{ g NaCl} \cdot \frac{1 \text{ mol}}{58.5 \text{ g}} = .5410 \text{ mol NaCl}$$

$$220.0 \text{ mL} \cdot \frac{0.994 \text{ g}}{1 \text{ mL}} \cdot \frac{1}{1000} = .219 \text{ kg H}_2\text{O}$$

$$\Delta T_b = \left( \frac{.5410 \text{ mol}}{.219 \text{ kg}} \right) (0.52^\circ\text{C/m}) (2)$$

$$= 2.6^\circ\text{C}$$

$$\therefore T_b = 100 + 2.6 = 102.6^\circ\text{C}$$

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Problem: How many grams of glycerin,  $\text{C}_3\text{H}_8\text{O}_3$ , must be added to 350.0 g of water in order to lower the freezing point to  $-3.84^\circ\text{C}$ ? The  $k_f$  for water =  $1.86^\circ\text{C/m}$ .

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

$$3.84^\circ\text{C} = 1.86^\circ\text{C} \cdot m \cdot 1$$

$$m = 2.06 = \frac{\text{X mol solute}}{.350 \text{ kg}}$$

$$X = .722 \text{ mol} \cdot \frac{92.0 \text{ g}}{1 \text{ mol}} = 66.4 \text{ g glycerin}$$

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Problem: The osmotic pressure of a solution containing 26.5 mg of aspartame (a nonelectrolyte) per liter is 1.70 torr at 30.0°C. Calculate the molecular weight of aspartame.

$$\pi = MRTi \quad \frac{1.70 \text{ torr} \cdot 1 \text{ atm}}{760 \text{ torr}} =$$

$$.00224 = M (.0821) (303 \text{ K}) (1) \cdot .00224 \text{ atm}$$

$$M = 9.00 \cdot 10^{-5} = \frac{\text{X mol}}{1 \text{ Liter}}$$

$$X = 9.00 \cdot 10^{-5} \text{ mol}$$

$$\therefore \text{molecular weight} = \frac{.0265 \text{ g}}{9.00 \cdot 10^{-5} \text{ mol}}$$

$$= 294 \text{ g/mol}$$

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Problem: Calculate the freezing point and expected osmotic pressure of a 0.05m  $\text{FeCl}_3$  solution at 25.0°C ( $i = 3.4$ ). Assume the density of the final solution = 1.0 g/mL and the liquid volume is unchanged by the addition of the ferric chloride.

$$\pi = MRTi \quad M \approx m$$

$$= (.05) (.0821) (298) (3.4)$$

$$= 4.16 \text{ atm} = 4.2 \text{ atm}$$

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

$$= (.05) (1.86^\circ\text{C/m}) (3.4)$$

$$= .32^\circ\text{C}$$

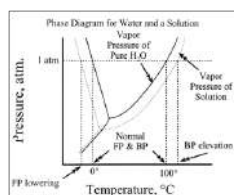
$$\therefore T_f = 0 - .32 - .32^\circ\text{C}$$

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Chapter 11 problems 67, 69, 71, 73, and 77

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Let's consider a **phase diagram for an aqueous solution**:



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**Dialysis:** a phenomenon in which a semipermeable membrane allows transfer of both solvent molecules and small solute molecules and ions.

**Isotonic Solutions:** solutions that have identical osmotic pressures.

**Hypertonic Solutions:** solutions having an osmotic pressure higher than that of cell fluids - cells shrink because of net transfer of water out (crenation).

**Hypotonic Solutions:** solutions with an osmotic pressure lower than that of the cell fluids - water flows into the cell (lysis).

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#### Reverse Osmosis - Desalination

If a solution in contact with pure solvent across a semipermeable membrane is subjected to an external pressure, reverse osmosis occurs. The pressure will cause a net flow from the solution to the solvent. In reverse osmosis the semipermeable membrane acts as a "molecular filter" to remove solute particles - application is desalination.

**Colloids:** A colloid is a suspension of particles in a dispersing medium. It appears that electrostatic repulsions help stabilize a colloid.

**Tyndall Effect:** the scattering of light by particles in suspensions; used to distinguish between a suspension and a true solution.

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