

Chapter 12 Physical Properties of Solutions

Problems - Page 535 – 541 **Set 1:**16, 22, 24, 29, 31; **Set 2:** 34, 38, 45, 52, 60; **Set 3:** 62, 66, 74, 90, 93; **Set 4:** 94, 96, 101, 107, 108, 114 **Set 5:** 120, 123, 128, 134.

I. SOLUTIONS

- A. A solution is a homogeneous mixture of two or more substances. The particles in a true solution are molecules, atoms, or ions that will pass easily through the pores of filter paper. Solutions cannot be separated into their components by filtration.
- B. There are two parts to a solution ; the solvent and the solute
1. Solute is the substance being dissolved
 2. Solvent is doing the dissolving and is the more abundant substance. Most common solvent is water.
- C. The dissolving process - dissolving mechanism
1. Solution process is spontaneous (for solids in liquids)
 2. Solid particles are separated from the solid mass (as a solid changing phase to a liquid) - if the solid is ionic this is called dissociation. This requires energy. Endothermic
 3. Solvent particles move apart to allow solute particles to enter liquid phase; this requires energy. Endothermic
 4. Solute particles are attracted to the solvent particles and surround them. This is called solvation unless the solvent is water then its called hydration. This gives off energy. Exothermic
 5. If the net change is endothermic, the temperature of the solution decreases as the solid dissolves - most common - temperature increase will increase the solubility
 6. If the net change is exothermic, the temperature of the solution increases - temperature increase will decrease solubility
 7. For a spontaneous dissolving to occur higher entropy must be favored over lower energy (refresh - tendencies in nature). The particles in a solution are in a greater state of entropy
 8. When ions are separated from solid they act as if they are independent
 9. “Likes dissolve likes” referring to polarity. Polars dissolve polars. Nonpolars dissolve nonpolars. Exception - nonpolar solid in nonpolar liquid - depends on melting point and heat of fusion. Why ? Solids with low melting points and low heats of fusion will be more soluble because of the weak intermolecular forces.
- D. Factors that affect the dissolving process
1. Stirring speeds up the particles diffusion, allows more solvent to come into contact with more solute
 2. Powdering the solute (solid) solution process only occurs on the surface of solid thus powdering increases the surface.
 3. Heating the solution increases the molecular activity particles come in contact with each other more quickly. Works for most

solutions since most solid in liquid (water) solutions are endothermic (ΔH – heat of solution is positive)

- a. Heats of solutions (ΔH) – the energy change when a solute dissolves into a solvent. Negative sign means energy is given off and thus is exothermic. Positive sign means energy is taken in and thus is endothermic.
 4. Solids have a high entropy, when dissolved entropy increases thus its following a natural tendency
 5. When gases dissolve in water the entropy decreases therefore the process must be exothermic. As the temperature of water rises oxygen becomes less soluble and fish have a hard time breathing. The mass of a gas that will dissolve in a liquid at a given temperature varies directly with the partial pressure of that gas (Henry's law – $c = kP$ where c is the molar concentration (M) of the dissolved gas; P is the pressure (atm) of the gas over the solution and k is a constant that is temperature dependent with units of mole /L· atm.
 - a. Soda is a good example of this. The bottles are sealed in a chamber in which the partial pressure of CO_2 is much higher than that of the atmosphere (10atm). Some of the excess CO_2 dissolves in the soda. When you open the container the partial pressure of CO_2 above the solution drops, and the drink fizzes as the CO_2 bubbles out of solution. When a gas rapidly escapes from a liquid in which it is dissolved it is said to exhibit effervescence.
 6. Most solids having a positive ΔH are more soluble in hot water, why?
- E. Measuring concentrations
1. Molarity (M) is a concentration measurement equal to the number of moles of the solute per liter of solution. For a solution of known molarity, a measurement of volume is also a measurement of the number of particles of solute.
 - a. Standard solutions are those that have the concentration of the solute in a solution with a high degree of certainty. These are used by environmental chemists as a reference for comparison with the conc. Of dissolved oxygen in lake river and ocean waters.
 2. Molality (m) is a concentration measurement equal to the number of moles of the solute per kilogram of solvent. This is useful in studying colligative properties (those that depend on the number of particle present).
 3. The mole fraction is a comparison of moles of one component to the total number of moles of solution.
 4. Mass percent is the grams of solute per 100 grams of solution

5. Normality is the number of chemical equivalents per liter of solution. An equivalent is the quantity, in grams, that supplies or acquires 1 mole of electrons in a chemical reaction.

F. There are nine possible solution combinations

SOLVENT	SOLUTE	COMMON EXAMPLES
GAS	GAS	He-O ₂ (deep sea diver's gas)
GAS	LIQUID	air- water (humidity)
GAS	SOLID	air-naphthalene (mothballs)
LIQUID	GAS	water-CO ₂ (carbonated bev)
LIQUID*	LIQUID*	water-acetic acid (vinegar)
LIQUID	SOLID	water-salt (seawater)
SOLID	GAS	Pd-H ₂ (gas stove lighter)
SOLID	LIQUID	Ag - Hg (dental amalgam)
SOLID	SOLID	gold - silver (ring) alloys

*Two liquids that are mutually soluble in all proportions are miscible.

II. Colligative and colloidal properties

- A. Colligative properties are those properties that depend on the number of particles in solution not the type.

1. Vapor pressure
2. Freezing point depression
3. Boiling point elevation
4. Osmotic Pressure

- B. Some solute particles take up space on the liquid surface normally occupied by the solvent. These particles decrease the opportunity for the solvent particles to escape (evaporate) from the surface of the liquid, thus lowering the vapor pressure. Thus if the solute is nonvolatile, the vapor pressure of the solution is lower than the vapor pressure of the pure solvent. The lowering of the vapor pressure of the solvent varies directly with the number of solute particles present.

1. A French chemist, Francis Raoult, first stated this principle that the vapor pressure of a solution varies directly as the mole fraction of the solvent.

$$\text{Mathematically } P_{I \text{ solution}} = X_{I \text{ solvent}} \times P^{\circ}_{I \text{ solvent}}$$

Where $P_{I \text{ solution}}$ is the vapor pressure of the solution or the partial pressure of the solvent over a solution; $X_{I \text{ solvent}}$ is the mole fraction of the solvent in the solution; and $P^{\circ}_{I \text{ solvent}}$ is the vapor pressure of the pure solvent.

- a. Raoult's law describes an ideal solution in which all intermolecular attraction are the same.
- b. The ratio of molecules (solute : solvent) in a liquid solution will not always be the same ratio for the vapor.
- c. We can use Raoult's law to determine the decrease in vapor pressure, ΔP , where $\Delta P = X_2 P^{\circ}_1$; where X_2 is the mole fraction of the solute.

- C. Using colligative properties
1. Since the presence of a nonvolatile solute lowers the vapor pressure of a solution it in turn raises the boiling point of the solution since it will take more energy to have more solvent particles reach the vapor phase to equal the atmospheric pressure. Entropy has increased therefore there are more ways for the energy to be dispersed. Uses?
 2. The same idea can be used for the freezing point of a solution. Since the freezing point is the temperature at which the vapor pressure of the solid and liquid are equal, if the solute now lowers the vapor pressure of the liquid the freezing point of the solution is lowered. The solute particles are decreasing the concentration of solvent molecules. The solute particles are getting in the way of crystal formation Uses?
 3. These changes depend only on the concentration of the solute particles and not the chemical nature of the solute. How would the number of particles differ in an ionic solution and a molecular solution? The concentration of particles in the ionic solution depends on the number of ions in the compound. The molality of the solution is the key to determine the freezing point depression and the boiling point elevation.
 - a. $\Delta T_f = mK_f$ where ΔT is the change in freezing point(C^0) and m is the molality of the solution and K_f is the freezing point depression constant for the solvent ($K_{f\text{ water}} = 1.86 C^0 / \text{molal}$)
 - b. $\Delta T_b = mK_b$ where ΔT is the change in boiling point(C^0) and m is the molality of the solution and K_b is the boiling point elevation constant for the solvent ($K_{b\text{ water}} = 0.51 C^0 / \text{molal}$)
 - c. To account for ionic solutes multiply mK by the number of ions in formula (van't Hoff Factor).
 4. Molar mass can be determined using the boiling point elevation and freezing point depression. Just remember the units and poof its magic!
 5. Use of differences in vapor pressure.
 - a. Distillation is a physical process of separating substances that have different boiling points. The boiling point of each mixture is the temperature at which the sum of the two vapor pressures equals 1 atm, 760mm Hg, or 101.3 kPa. At each of these points, however, the vapor phase would be richer in the more volatile component. Refer to the liquid-vapor phase diagram in your text.
- D. Osmotic pressure
1. The pressure needed to prevent the net flow of solvent from pure solvent into a solution of the solvent.

2. The flow is a result of an unequal passing of particles between a semipermeable membrane. This is the type of membrane that will allow small particles to pass through, but will stop large molecules
3. A cell is an aqueous solution enclosed in a semipermeable membrane. The fluid that surrounds the cell must have the same osmotic pressure as the fluid within the cell. If the cell has a lower solvent concentration than the surroundings, then the fluid will flow into the cell and burst, hemolysis. If the cell has a higher solvent concentration than the surrounding fluid, the fluid will flow from the cell and shrivel up, crenation. Another example is a pickle - cucumber placed in brine, lost water by osmosis, and shriveled. Limp veggies placed in water to become firm.
4. Osmotic pressure can be expressed in an equation since it is a colligative property.
 - a. $\Pi = MRT$ where Π is the osmotic pressure M = molarity, R is the ideal gas constant ($0.0821 \text{ Latm/moleK}$ or 8.31 LkPa/moleK), and T is the Kelvin temperature.

E. Debye-Hückel Theory

1. This deals with the fact that solutions are not ideal solutions and thus they will deviate from theoretical boiling point elevation and freezing point depression predictions.
2. As a solution becomes more concentrated in the solute, the number of ionic particles increases. Due to the increase in the number of particles in solution and solvation, clustering of solvent particles around solute particles, the ionic activity decreases. The depressions and elevations are not as great as predicted. Also, the ions are now interacting with each other more often and are not actually 100% dissociated thus not interfering with the solvent as much.

F. Colloids

1. Means glue-like; mixtures composed of two phases of matter, the dispersed phase and the continuous phase. They are in between suspensions and solutions,
2. Colloid particles are larger than the single atoms, ions, or molecules of solutions, smaller than suspension particles (which can be seen under a microscope and settle out on standing).
3. Any substance can be used to produce a colloid. They will not pass through a membrane.
4. Classification
 - a. Aerosols - liquids and solids dispersed in gases ex. Fog and smoke
 - b. Foams - gases dispersed in liquids ex. Whipped cream and marshmallows.
 - c. Emulsions - liquids dispersed in liquids or solids ex. Mayonnaise, and cheese.

- d. Sols - solids dispersed in liquids or other solids ex. Jellies, paints, pearls, opals
- e. Gels - are sols that have set.

5. Size

TYPE	PARTICLE SIZE	PERMANENCE
SOLUTION	< 1 nm	permanent
COLLOID	> 1 nm but < 100nm	permanent
SUSPENSION	> 100nm	settle out

6. Properties

- a. Tyndall effect - the scattering of light by colloidal particles
- b. Brownian motion - continuous random motion, due to constant collisions with the smaller molecules of the medium.
- c. Adsorption - solid and liquid surfaces tend to attract and hold substances with which they come in contact. Because of colloids small size, they have an extremely large surface to mass ratio which makes them excellent adsorption materials (adsorbents).
- d. Electrophoresis - electrical field applied to colloid, positive particles are attracted to cathode, negative particles to the anode. This is called electrophoresis. Can be used to separate amino acids and peptides.
- e. Hydrophilic and Hydrophobic Colloids
Colloids can be hydrophilic (water loving) or hydrophobic (water fearing). Hydrophilic will dissolve in water while hydrophobic will clump in water. Colloids can be composed of both on opposite ends. Soap molecules have both ends, one, hydrophobic, is attracted to the dirt, surrounds it with hydrophilic end pointing out so it can dissolve in water thus “washing” the dirt away.

7. Uses (misc.)

- a. Semipermeable membranes used to separate ions and colloids used in kidney dialysis.
- b. Reverse osmotic pressure so solvent flows from solution to solvent - used to purify water.

G. Solution equilibrium

- 1. The point at which the number of particles leaving the crystal surface equals the number returning to the surface is called solution equilibrium. When the rate of dissolving equals the rate of crystallization.
- 2. A solution that contains the maximum amount of dissolved solute at a given temperature is called a saturated solution.

3. A solution that contains more solute than a saturated solution can normally hold at a given temperature is called a supersaturated solution. This occurs when there is no special surface for the solid to begin crystallizing
4. The amount of solute that can dissolve in a given amount of solvent at a given temperature at saturation is called solubility.
5. Solubility can be changed by altering the temperature.
6. Differing solubilities can be used to separate different substances in the same solution. We use precipitation as an analytical tool by carefully choosing the reagent to precipitate only one of the substances present at one time. For example Group I ion precipitation HCl is used to Ppt the three ions in this group, Ag^+ , Pb^{++} , and Hg^{++} . Lead is separated by adding hot water which dissolves the lead chloride, then other reagents are used to separate silver and mercury.