SOLUTIONS AND THEIR COLLIGATIVE PROPERTIES

1. Definitions:

   (a) Solvent and solute
   (b) Solubility and miscibility
   (c) Dilute and concentrated solutions
   (d) Unsaturated, saturated and supersaturated solutions

2. Concentration units of solutions:

   (a) mass percent - % by mass of A = (mass A/Total mass) x 100
   (b) Molarity - *M* = moles solute/Liter of solution
   (c) Molality - *m* = moles solute/1000 g of solvent
   (d) Mole fraction - X_A = moles of A/Total number of moles

3. Heats of solution (endothermic or exothermic)

   (a) Lattice energy ($\Delta H_{\text{lattice energy}}$) and heat of hydration ($\Delta H_{hydration}$)
   (b) Ionic compounds
   (c) Non-Ionic compounds
   (d) Gases

4. Effect of temperature on solubility

5. **Henry's Law** - the moderate solubility of gases in a liquid

$$P_{gas} = kX_{gas}$$

   where *k* is Henry's Law constant for a particular gas and is dependent on temperature and pressure.

6. **Raoult's Law** - the vapor pressure of a liquid in a solution is directly proportional to the mole fraction of that liquid in the solution. Raoult's law is obeyed by an *ideal solution*. An ideal solution is a solution of A and B in which the intermolelcular forces between A and A molecules, B and B molecules, and A and B molecules are all the same.

$$P_{total} = p_A + p_B = P°_A X_A^{liq} + P°_B X_B^{liq}$$

7. Properties of real solutions (i.e. solutions not obeying Raoult's Law

   (a) **Positive deviation from Raoult's Law**
      (i) P_{total} is greater than for an ideal solution
      (ii) Heat is absorbed when A and B are mixed (i.e. $\Delta H_{mixing} > 0$)
      (iii) $\Delta V_{mixing} > 0$
      (iv) A...B intermolecular forces are weaker than A...A and B...B
   (b) **Negative deviation from Raoult's law**
      (i) P_{total} is smaller than for an ideal solution
      (ii) Heat is evolved when A and B are mixed (i.e. $\Delta H_{mixing} < 0$)
      (iii) $\Delta V_{mixing} < 0$
      (iv) A...B intermolecular forces are stronger than A...A and B...B

8. Vapor pressure lowering by non-volatile molecular solutes

Because a molecular non-volatile solute has essentially zero vapor pressure, from Raoult's law the total vapor pressure of the solution is,

$$P_{total} = P°_{solvent}X_{solvent} = (1 - X_{solute})P°_{solvent}$$

since $X_{solvent} + X_{solute} = 1$

$$\Delta P = P°_{solvent} - P_{total} = X_{solute}P°_{solvent}$$
$$= (n_{solute}/(n_{solvent} + n_{solute}))P°_{solvent}$$

If we consider dilute solutions then $\Delta P \cong (n_{solute}/n_{solvent})P°_{solvent}$

Therefore, the lowering of the vapor pressure in a dilute solution of a non-volatile solute is directly proportional to the amount of the solute dissolved in a definite amount of solvent.

9. **Distillation**

(a) *simple distillation* - separation of a nonvolatile solute from a volatile solvent.

(b) *fractional distillation* - two volatile components that follow Raoult's law can be separated into its pure components by this method.

$$P_{total} = p_A + p_B = P°_A X_A^{liq} + P°_B X_B^{liq}$$

The composition of the vapor in equilibrium with the solution can be calculated as follows:

$$X_A^{vapor} = p_A/P_{total} \quad \text{and} \quad X_B^{vapor} = p_B/P_{total}$$

FOR IDEAL SOLUTIONS THE VAPOR IS ALWAYS RICHER THAN THE LIQUID IN THE MORE VOLATILE COMPONENT.

(c) *Systems that deviate from Raoult's law*

(1) positive deviation - such a system forms a **minimum boiling point azeotrope.** i.e. the azeotropic mixture has a boiling point lower than either of the two pure components.

(2) negative deviation - such a system forms a **maximum boiling point azeotrope.** i.e. the azeotropic mixture has a boiling point higher than either of the two pure components.

10. **Boiling point elevation and freezing point depression**

For ideal dilute solutions involving molecular solutes the boiling point elevation and freezing point depression can be approximated by using the following equations:

(b.p. elevation) $\Delta T_{bp} = K_b m$

(f.p. depression) $\Delta T_{fp} = K_f m$

where K_b is the molal boiling point elevation constant of the solvent, K_f is the molal freezing point depression constant for the solvent, and m is the concentration of the solute expressed as molality (moles of solute/kg of solvent). The numerical values of K_b and K_f for the solvent depend on the following properties of the solvent: molar mass, normal b.p. or freezing point, and heat of vaporization or heat of fusion. The above equations thus show that the f.p. depression and b.p. elevation depend on both the solvent and the solute in the solution.

11. **Osmotic pressure**

The osmotic pressure for an ideal dilute solution is approximated by the equation:

$$\pi = MRT$$

where π is the osmotic pressure (in atm), M is the molarity of the solute, R is the gas constant (0.0821 L-atm/mol-K) and T is the absolute temperature.

12. **Molar Mass determination**

Any of the colligative properties (vapor pressure, freezing point, boiling point or osmotic pressure) can be used to determine the molar mass of nonvolatile molecular substances. Each method has its limitations. Experimentally the f.p. or b.p. changes are easier to measure than pressure changes. Experimentally f.p. depression results are more reliable due to a variety of reasons which we will discuss in class.

13. **Colligative properties of electrolyte solutions**

$\Delta T_{bp} = iK_b m$ and $\Delta T_{fp} = iK_f m$ where "i" is called the van't Hoff factor.

$i = 1$ for non-electrolytes
$n > i > 1$ for weak electrolytes
$i = n$ for strong electrolytes

As a solution is made more dilute, the value of "i" for strong electrolytes approaches "n" (the whole number expected on the basis of complete dissociation).

Weak electrolytes do not dissociate completely and therefore their degree of dissociation can be expressed according to the following equation:

$$\% \text{ dissociation} = \left(\frac{i - 1}{n - 1}\right) \times 100$$

where "i" is the van't Hoff factor and "n" is the number of ions per formula unit of the electrolyte.

14. **Debye-Huckel Theory**

Interionic attraction make a solution behave as though the ion concentrations were less than they actually are,

$$a = \gamma c$$

where "a" is the activity of the ion. We can think of the activity as the *effective concentration* of the ion. γ is called the activity coefficient.

As the concentration ,c, becomes more dilute $\gamma \rightarrow 1$.