Solutions Part - I

## Vapour Pressure and Colligative Properties

1.4: Vapour Pressure

i.   The transformation of liquid to vapour form is vapourisation. Evaporation of a liquid is **endothermic process.** It is explained on the basis of Kinetic molecular theory. The vapour molecules have a higher potential energy than the liquid molecules at the same temperature.

ii. The number of molecules escaping from the liquid surface in one second is called Rate of evaporation. It depends on
    i)   Nature of liquid
    ii)   Surface area of liquid
    iii) Temperature
    iv)   Flow of air current over the surface

iii. Rapid evaporation results in decrease in temperature leading to intense cooling. This technique is used in the liquification of air and real gases.

iv . When a liquid and its vapour are in equilibrium with each other, the pressure exerted by the vapour over the liquid surface is known as the vapour pressure of the liquid.

v.   Vapour pressure of a liquid will be more, if the intermolecular forces of the liquid are less. Such liquids are called volatile liquids.

    Eg: - Ether, Methyl alcohol, acetone, benzene, Carbon tetrachloride, Carbon disulphide

vi. Vapour pressure of a liquid will be less, if the intermolecular forces are strong. Such liquids are called non-volatile liquids.

Eg. Aniline, Nitrobenzene, water, mercury etc

vii. The vapour pressure of a liquid depends upon the nature of the liquid and temperature. With an increase in temperature the vapour pressure of a liquid increases exponentially.
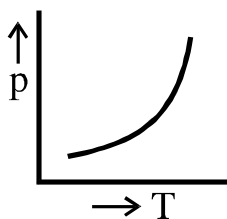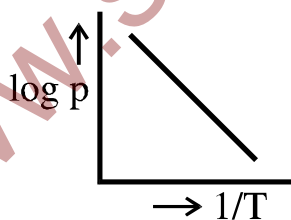

The relationship between the vapour pressure and the temperature of the liquid is given by **Clausius** and **Clapeyron as**

$$\log \frac{P_2}{P_1} = \frac{\Delta H_v}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

ΔH_v = Enthalpy of vapourisation of liquid; R= gas constant;

P_2 = vapour pressure at T_2 and P_1= vapour pressure at T_1

A graph is plotted between log p vs 1/T gives straight line with negative slope.

viii. The temperature at which vapour pressure of a liquid becomes equal to the atmospheric pressure is called Normal boiling point of that liquid. When the external pressure is decreased the boiling point of a liquid also decreases.

ix   The vapour pressure of a solution of a nonvolatile solute is less than the vapour pressure of the pure solvent at the same temperature. This phenomenon is known as lowering of vapour pressure.

x.   If P_0 is the vapour pressure of the pure solvent and P_S is the vapour pressure of the solution at the same temperature then, $P_0 - P_S$ = lowering in vapour pressure

Relative lowering of vapour pressure = $(P_0 - P_S)/P_0 = n/N+n$

xi.   "The vapour pressure of a solution of a non-volatile solute is directly proportional to the mole fraction of the solvent in the solution". $P_S = P_0 X_{solvent}$

xii.   Lowering of vapour pressure is directly proportional to mole fraction of solute

xiii.   Lowering of vapour pressure increases with increase in temperature

1.5; Raoult's Law

i.   Raoult Law states that "the relative lowering of vapour pressure of a solution is equal to the mole fraction of the solute in the solution".

. $(P_0 - P_S)/P_0 = n/N+n$

Where n is the number of moles of the solute. And N is the number of moles of the solvent. In a dilute solution n is very small compared to N.

Hence N+n can be taken as equal to N. Then

$$\frac{P_0 - P_S}{P_0} = \frac{n}{N} = \frac{w/m}{W/M} = \frac{w.M}{W.m}$$

w   = Weight of the solute

m   = molecular weight of the solute

W   = weight of the solvent

M   = molecular weight of the solvent

*As relative lowering of vapour pressure is equal to mole fraction of solute, it is independent of temperature

ii. Limitations of Raoults law: - Raoults law is applicable

    i) To dilute solutions only

    ii) T o non-volatile and non-electrolytic solutes only

    iii) To the solute which does not undergo either ionisation (or) association.

    iv) To ideal solution only (i.e., no chemical interactions between solute and the solvent.)

iii. Relative lowering of vapour pressure is determined by Ostwald and Walkers method. The vapour pressure of solution from Ostwald's method can be determined from the following equation.

Air → [Solution] $\xrightarrow{P_S}$ [Solvent] $\xrightarrow{P°}$ [Anhydrous CaCl$_2$] → Air
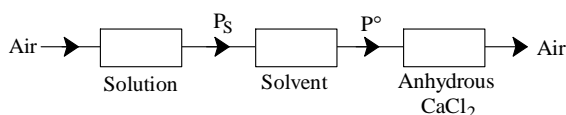
Loss in wt. of solution $\propto P_S$

Loss in wt. of solvent $\propto (P° - P_S)$

Gain in wt. of CaCl$_2$ $\propto p°$

$$\frac{P° - P}{P°} = \frac{\text{Loss in mass of solvent bulb}}{\text{Loss in mass of (solution bulb + solvent bulb)}}$$

1.6- **Ideal Solution:** It is the solution

(I) Which obey Raoult's law at all temperatures and concentrations

(II) In which no heat is evolved or absorbed when components are mixed to form the solution

i.e $\Delta H_{mix} = 0$

(III) In which there is no change in volume when components are mixed. i.e $\Delta V_{mix} = 0$

(iv) In ideal solution the X -Y intermolecular interactions are the same as X -X and Y -Y

inter molecular interactions

Examples to ideal solutions

(i) Benzene and toluene

(ii) Ethyl bromide and ethyl chloride

(iii n - Heptane and n- hexane

(iv) Chlorobenzene and Bromobezene

1.7-non-ideal solution

The Solution which does not obey Raoult's law or $\Delta V_{mix} \neq 0$ and $\Delta H_{mix} \neq 0$ is called a non-ideal solution. These are of two types

(I): **Showing Positive Deviations**: solutions in which X- Y inter - molecular interactions are weaker than X – X and Y -Y intermolecular interactions show positive deviation from Raoult's law. For these $\Delta V_{mix} > 0$ and $\Delta H_{mix} > 0$

Ex; **mixtures of**

Carbon tetrachloride +benzene, Ethyl alcohol + Water, Carbon tetrachloride + chloroform

Acetone +Ethyl alcohol, Acetone + Benzene etc

(II) **Showing Negative Deviations:** solutions in which X- Y inter - molecular interactions are stronger than X – X and Y -Y intermolecular interactions show negative deviation from Raoult's law. For these $\Delta V_{mix} < 0$ and $\Delta H_{mix} < 0$

Examples: mixture of

Chloroform + Acetone, Chloroform + Benzene, Chloroform + Diethyl ether, Acetone + Aniline, HCl + Water etc

1.8. A mixture of two or more components which boils at constant temperature without change in composition is called an azeotrope. Non ideal solutions form azeotropes.

I. **Azeotropic Mixture with Minimum Boiling Point**

These are formed by liquids showing positive deviation. An intermediate composition of liquids having highest vapour pressure, hence lowest boiling point gives this azeotrope. This azeotropic mixture has lower boiling point than either of the pure component

eg. Rectified spirit (ethanol 95.6% + 4.4%water) boils at 351.5 K.

II. **Azeotropic Mixture with Maximum Boiling Point**

These are formed by liquids showing negative deviation. An intermediate composition of liquids having minimum vapour pressure, hence highest boiling point gives this azeotrope. This azeotropic mixture has higher boiling point than either of the pure components.

E.g. Water & $HNO_3 \left(HNO_3 68\% + H_2O 32\% \right)$ boils at 393.5K

Colligative Properties

The properties of dilute solutions which depend on the number of particles (ions or molecules) of the solute dissolved in the solution but not on the nature of solute are called colligative properties.

They are

i) Relative lowering of vapour pressure (RLVP) of solution

ii) Elevation in the boiling point of the solution

iii) Depression in the freezing point of the solution

iv) Osmotic pressure of the solution

All the colligative properties can be used to determine the molecular weight of non-volatile solute. But the best method by using Osmotic pressure

1. Relative lowering of vapour pressure (RLVP) of solution

i. According to Raoult Law the relative lowering of vapour pressure of a solution is equal to the mole fraction of the solute in the solution.

    i.e . $(P_0-P_S)/P_0 = n/N+n$

    Where n is the number of moles of the solute. And N is the number of moles of the solvent. In a dilute solution n is very small compared to N.
    Hence N+n can be taken as equal to N. Then

ii.

$$\frac{P_0 - P_S}{P_0} = \frac{n}{N} = \frac{w/m}{W/M} = \frac{w.M}{W.m}$$

   w   = Weight of the solute

    m   = molecular weight of the solute

    W   = weight of the solvent

    M   = molecular weight of the solvent

    *As relative lowering of vapour pressure is equal to mole fraction of solute, it is independent of temperature

iii. Relative lowering of vapour pressure is determined by Ostwald and Walkers method. The vapour pressure of solution from Ostwald's method can be determined from the following equation.
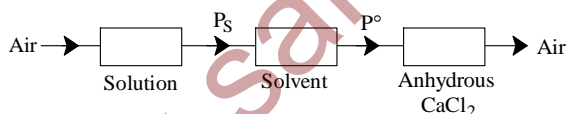
    Loss in wt. of solution $\propto P_S$

    Loss in wt. of solvent $\propto (P^\circ - P_S)$

    Gain in wt. of $CaCl_2$ $\propto p^\circ$

$$\frac{P^\circ - P}{P^\circ} = \frac{\text{Loss in mass of solvent bulb}}{\text{Loss in mass of (solution bulb + solvent bulb)}}$$

2. Elevation of boiling point

i) When a non-volatile solute is dissolved in the pure solvent its boiling point increases.

Eg: - sea water boils at greater than $100°C$.

ii) The difference between boiling points of solution containing a non- volatile solute (T_s) and the pure solvent T_o is called elevation of boiling point $\Delta T_b = T_s - T_o$.

iii) Liquids with high boiling point have low vapour pressures and are less volatile.

iv) Elevation of boiling point is directly proportional to molality of the solution. i.e.

$\Delta T_b \propto m$ $\Delta T_b = K_b.m = K_b \left[\dfrac{w}{M} \times \dfrac{1000}{W} \right]$

K_b = molal elevation constant of the solvent or ebullioscopic constant

m = molality w = wt.of solute

W = wt. of solvent   M = Mol.wt.of solute

v) Molal elevation constant is equal to the elevation in boiling point observed for 1 molal solution.

vi) K_b value changes from one solvent to another solvent and changes with temperature.

For water $K_b = 0.52$degree.Kg/mole,

For CCl_4 $K_b = 5$deg.kg/mole

Units of K_b: K .Kg mole^{-1}

$K_b = \dfrac{RT_b^2}{1000 \cdot L_v}$

Where K_b =   molal elevation constant.

R   =   Gas constant

L_v =   Latent heat of vapourisation /gm of the solvent

vii) Elevation in boiling point is determined by Landsberger's method and Cottrell's method.

In Cottrell's method, Beckmann's thermometer is used to measure the elevation of boiling point but not absolute boiling temperatures.

Beckmann thermometer contains a reservoir of mercury at one end and usual bulb at the other end. The two ends are internally connected through the capillary. Over a range of temperature, -6^oC to 300^oC, the elevation can be determined by adjusting the amount of mercury in the bulb.

3. Depression in the freezing point of the solution

i)   The temperature at which the pressure of a liquid is equal to that of the solid is called freezing point.

ii)   When a non - volatile solute is dissolved in a solvent, the freezing point of the solvent decreases.

Eg. Sea water freezes below $0°C$.

iii)   Water taken in automobile radiators is mixed with glycerol (or) glycol to decrease its Freezing point to prevent the formation of ice when surrounding temperature falls.

IV)   The depression in Freezing point is given by $\Delta T_f = T_o - T_s$, T_0= F.P. of pure solvent and T_s = F.P. of solution

v)   Depression in Freezing point is directly proportional to molality of the solution.

$\Delta T_f \propto m$

$$\Delta Tf = Kf \; X \; m = K_f \times \frac{w}{M} \times \frac{1000}{W}$$

w, W are weights of solute and solvent respectively

M = mol. wt. of solute and

K_f = molal depression constant of the solvent or cryoscopic constant

$$K_f = \frac{RT_f^2}{1000L_f}$$

R = Gas constant

T_f = Freezing point of the solvent in Kelvin

L_f = Latent heat of fusion.

vi) Depression in freezing point is determined by Beckmann's method and Rast's camphor method.

    i) In Rast's method pure camphor is used as solvent because of high cryoscopic constant value. It is applicable for solid in solid type of solution.

4. Osmotic pressure of the solution

i) The passage of solvent molecules from a solution of low concentration into a solution of higher concentration through a semi permeable membrane is known as osmosis.

ii) Semi permeable membrane is one which allows the solvent molecules to pass through but not solute particles.

    eg. Cellophane paper, cell walls, pig's gall bladder etc. Copper ferrocyanide i.e Cu_2 [Fe $(CN)_6$] also acts as a semi permeable membrane.

iii. Exosmosis is the outward flow of water from a cell into an aqueous solution through a semi permeable membrane.

    eg. Grape in NaCl solution

iv) Endosmosis is the inward flow of water in to cell from an aqueous solution through a semi permeable membrane.

    Eg: Grape in water

v) Egg free from outer shell placed in distilled water enlarges (haemolysis) and when placed in NaCl solution shrinks (plasmolysis) due to endomosis and exosmosis respectively.

vi. a) The excess pressure which must be applied to a solution to prevent the flow of the solvent into the solution through the semi permeable membrane is called osmotic pressure. (OR)

Pressure developed due to osmosis is called osmotic pressure.

b) Osmotic pressure is directly related to molar concentration and temperature.

$\pi = CRT$ where π - Osmotic pressure, C is molarity,

T = absolute temperature

$$\pi = \frac{n}{V}RT \; ; \; \pi V = \frac{W}{M_{solute}}.RT \; ; \; \pi = hdg$$

vii)   Solutions having same osmotic pressure are known isotonic solutions. Isotonic solutions generally have the same molar concentrations

($C_1 = C_2$) at a given temperature.

Eg. Blood is isotonic with Normal saline (0.9% NaCl   i.e 0.16M NaCl solution).

viii)   The solution having lower osmotic pressure is known as hypotonic solution (<0.9% NaCl solution, cells-swell) and that having higher osmotic pressure is known as hypertonic solution (>0.9% NaCl solution, cells-shrinks)

ix)   Osmotic pressure method is widely used to determine molecular masses of proteins, polymers and other macro molecules.

x)   Osmotic pressure is determined by Morse and Frazer's method and Berkeley and Hartley's method.

II.   i) The colligative properties of solutions depend on the total number of solute particles present in solution. Since the electrolytes ionise to give more than one particle per formula unit in solution, the colligative effect of an electrolytic solution is greater than that of a non - electrolyte of the same molar concentration.

Eg. Osmotic pressure of 1M NaCl solution > 1M Urea solution

ii) For different solutes of same molar concentration, the colligative properties have the greater value for the solution which gives more number of particles on ionization.

Eg. Osmotic pressure of 1M AlCl$_3$ solution > 1M CaCl$_2$solution >1M NaCl solution

iii) For different molar concentrations of the same solute, the colligative property has greater value for the more concentrated solution.

Eg. Osmotic pressure of 3M AlCl $_3$ solution>2M AlCl $_3$ solution>1M AlCl $_3$ solution

iv) For solutions of different solutes having same percentage strength, the colligative property has greater value for the solute with least molecular weight.

III. Abnormal Molar masses

i) Certain solutes in solution are found to associate, leads to a decrease in the number of particles in the solutions. Thus, it results in a decrease in the values of colligative properties. The colligative properties are inversely related to the molecular mass.

For example, acetic acid dissolved in benzene shows a molecular mass of 120 (normal molecular mass is 60), because acetic acid form dimers in solution due to hydrogen bonding.
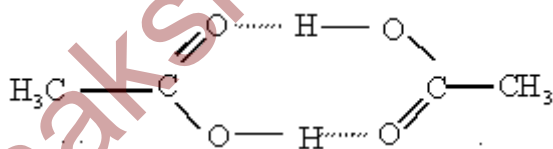
ii) Electrolytes dissociate in solution to give two or more particles (ions). Such solutions exhibit higher values of colligative properties. The molecular masses of such substances as calculated from colligative properties will be less than their normal values.

For example, KCl dissociates into K^+ and Cl^- ions when dissolved in water (On the basis of colligative properties) equal to half of its normal molecular mass, i.e., 74.5/2 or 37.25. However, the molecular mass of KCl is found to be 40.3 by

studies of depression in freezing point. The difference in the two values is due to the fact that there are strong attractive forces present between the oppositely charged ions of the strong electrolyte in solution. These electrical forces hold together a number of the ion pairs. Thus, such electrolytes are incompletely dissociated.

IV. Van't Hoff factor

Certain solutes that undergo dissociation (or) association in solution are found to show abnormal molecular mass. The extent of dissociation (or) association of solutes in solution is determined by Van't Hoff factor.

$$i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}} = \frac{\text{Observed colligative property}}{\text{Normal colligative property}}$$

i) For solutes showing dissociation,

   a) The Van't Hoff factor i >1.

   b) Colligative properties α No of particles after dissolution in solution

   c) Exp. (or) observed c.p > calculated (or) normal (or) theoretical C.P

   d) Exp. M.wt < Normal M.wt

ii) For solutes showing association the Van't Hoff factor i < 1

iii) For ideal solutions with no association or dissociation of solute the Van't Hoff factor i = 1

iv. If a molecule of solute on dissociation gives 'n' ions and is the degree of dissociation

Van't Hoff factor (i)

$$= \frac{\text{No.of moles of particles after dissociation}}{\text{Normal No.of moles of particles if there is no dissociation}} = 1 + \alpha (n - 1)$$

Degree of dissociation $(\alpha) = \frac{i - 1}{n - 1}$

v) If a solute A forms associated molecules $(A)_n$ and is the degree of association then,

Van't Hoff factor (i) = $1 - \alpha\left[1 - \dfrac{1}{n}\right]$

Degree of association $(\alpha) = \dfrac{(1-i)\,n}{n-1}$

vi.   a) Elevation of B.P. $T_b = iK_b m$

        b) Depression of F.P. $T_f = iK_f m$

        c) Osmotic pressure = $iMRT$