Chapter.1

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Solutions

Solution is a homogeneous mixture of two or more chemically non-reacting substances whose composition can be varied with certain limits.
A solution containing only one solute dissolved in a solvent is called binary solution.

A Solvent is the component of the solution which is present in larger amount by mass than the other component, termed as solute.

⇝ Solvent determines the physical state in which solution exist.

Types of solution :
Depending upon the physical state of solvent various types of solution are :-

1). Solid Solution is a solution in which the solvent is solid and solid, liquid or gas can be solute.

eg. Solid in solid → Alloys
Liquid in Solid → Amalgam of Hg with Na.
Gas in solid → H_2 in Pd , Cu in Au.

2). Liquid solution is a solution in which the solvent is liquid and solid, liquid or gas component can be solute.

eg. Solid in Liquid → Glucose dissolved in H_2O
Liquid in Liquid → Ethanol dissolved in H_2O
Gas in Liquid → Oxygen dissolved in H_2O

3. <u>Gaseous Solutions</u> is solution in which the solvent is gas and solid, liquid or gas can be solute.

eg. Solid in gas → Camphor in N_2
liquid in gas → $CHCl_3$ in N_2
gas in gas → Mixture of O_2 and N_2.

Concentration Terms :-

Volume related
(temperature dependent)

- % by volume
- wt by Volume
- Molarity
- Normality

Mass related
(T independent)

- wt/wt %
- Mole fraction
- Molality
- PPM or PPB

① wt by wt %

$$\boxed{wt/wt\ \% = \frac{\text{mass of solute (g)}}{\text{mass of solution g}} \times 100}$$

▷ A solution of NaCl in water 5% (wt/wt).
→ 5g of NaCl present in 100g solution.

② Volume by volume %

$$\boxed{V/V\ \% = \frac{\text{volume of solute (mL)}}{\text{volume of solution (ml)}} \times 100}$$

▷ A HCL solution is 7 %. (V/V%)
→ 7 mL of HCL is present in 100 ml of solution.

③. wt by volume %

$$\boxed{wt/V\ \% = \frac{\text{mass of solute (g)}}{\text{volume of solution (mL)}} \times 100}$$

▷ A sugar solution is 3% (wt/V)
→ 3g of sugar dissolved in 100ml water.

④. Mole fraction :-
(X)
Moles of a particular component divided by total moles of all component.

$$\boxed{X_A = \frac{n_A}{n_A + n_B}}$$

A+B → solution.

Note:- $X_A + X_B = 1$

5. Parts per Million (PPM)

$$\boxed{\text{No. of PPM} = \frac{\text{mass of solute(g)}}{\text{mass of solution(g)}} \times 10^6}$$

▷ Sugar 2 PPM in a solution.
2 g sugar in 10^6 g of solution.

6. Parts per Billion (PPB)

$$\boxed{\text{No. of PPB} = \frac{\text{mass of solute(g)}}{\text{mass of solution(g)}} \times 10^9}$$

7. Molarity (M) : Number of moles of solute present in 1 L solution.

$$\boxed{\text{Molarity} = \frac{\text{no. of moles of solute}}{\text{Volume of solution (L)}}}$$

On dilution ;

[n = MV] $\boxed{M_1V_1 = M_2V_2}$

Molarity of Mixture ;

$$\boxed{M = \frac{M_1V_1 + M_2V_2}{V_1 + V_2}}$$

8. Molality (m) : Number of moles of solute present in 1 kg solvent.

$$\boxed{m = \frac{\text{no. of moles of solute}}{\text{mass of solvent in kg}}}$$

9. Equivalent Mass :

$$\boxed{\text{Equivalent mass} = \frac{\text{Molecular mass}}{\text{valency factor } X}}$$

valency factor for
Acid → basicity
Base → acidity
Salt → total +ve charge on cation.

Note:
$$\boxed{\text{Number of gram equivalent} = \frac{\text{mass}}{\text{Equivalent mass}}}$$

also,
$$\boxed{\text{Number of gram equivalent} = \text{no. of moles} \times X}$$

10. (N)
Normality : Number of gram equivalent of solute which are present in 1 L solution.

$$\boxed{N = \frac{\text{no. of gram equivalent of solute}}{\text{volume of solution}}}$$

also, $N_1V_1 = N_2V_2$

11. Mass Fraction : Mass of given component per unit mass of solution.

$$\boxed{X_A = \frac{m_A}{m_A + m_B}}$$

Solubility :-

The maximum amount of solute that can be dissolve in a specified amount of solvent at a particular temperature.

Dissolution :-

when solute is added continuosly in in solvent (liquid) ; the concentration of solution keeps on increasing. This process is known as dissolution.

Crystallisation :- when solute particles starts colliding and get separated out of solution. This is known as crystallisation.

Saturated Solution :

When no more solute dissolves in solution at a given temperature because the rate of dissolution becomes equal to rate of crystallisatio and dynamic equilibrium is achieved is called Saturated Solution.

An Unsaturated solution is one in which more solute can be dissolved at same temperature.

Solubility of a solid in a liquid :-

The solubility of a solid in a liquid at any temperature is defined as the maximum amount of the solid (solute) in grams which can dissolve in 100g of liquid (solvent) to form saturated solution at a specific temperature.

Factors affecting solubility :

1). Nature of solute and solvent.
2). Temperature.

Note: Pressure has very little effect on solubility of solid in a liquid solid and liquids are highly incompressible.

1) Nature of solute and solvent :

'Like dissolves like' this implies that solid solute dissolves in solvent which is chemically similar. Polar (ionic) solute dissolve in polar solvent and Non-Polar solute · dissolve in non-polar solvent.

ii) Effect of temperature on solubility :

The substance in which the process of dissolution is exothermic, the solubility decreases with increase in temperature.

The substance in which process of dissolution is endothermic, the solubility increases with increase in temperature.

Solubility of Gas in a liquid :-

The solubitity of any gas in a particular liquid is the volume of gas that can be dissolved in unit volume of liquid to form saturated at particular temperature and pressure of 1 atm.

Factors affecting solubility :

1). Nature of gas and solvent
2). Effect of temperature
3). Effect of Pressure.

1) Nature of gas and solvent :

The greater solubility of gases in solvent is due to their chemical similarity with solvent.

Gases like N_2, H_2, O_2 etc. dissolve in water only to a small extent and CO_2, HCl, NH_3 are highly soluble.

II) Effect of temperature :
The solubility of gases decreases with increase in temperature. Temperature ↑ ; solubility ↓
Because on heating, kinetic energy cause more motion in gas molecules which break intermolecular bonds and escape from solution.

III) Effect of Pressure (Henry's Law) :-

The solubility of gases increases with increase in pressure.

Henry's Law :-
This law states that, at a constant temperature, solubility of a gas in a liquid is directly proportional to the partial pressure of the gas present above the surface of liquid or solution.

or

The partial pressure of a gas in vapour phase (p) is directly proportional to the mole fraction (χ) of the gas in solution.

$$\because \quad p \propto \chi$$

$$\boxed{p = K_H \chi}$$

K_H is Henry's constant.
Different gases have different values of K_H at same temperature and in same solvent.

- K_H is function of nature of gases.

- Greater value of K_H ; lower the solubility.

$$\frac{P}{\uparrow K_H} = \chi \downarrow \quad ; \quad \text{solubility} \downarrow ; \chi \downarrow$$

- Value of K_H increases with increase of temperature implying that the solubility decreases with increase in temperature.

K_H ↑ ; temperature ↑
χ ↓ ; solubility ↓
$\because$ temperature ↑ : solubility ↓

That's why aquatic life prefer cold water.

Applications of Henry's Law:

1). In production of carbonated beverages.
To increase the solubility of CO_2, the bottles are sealed under high pressure.
When sealed open CO_2 bubbles come out because partial pressure of CO_2 decreases.

2). Scuba divers depends on compressed air for their O_2 supply.
At depth, Pressure ↑, solubility ↑
As come upper side of sea, O_2 dissolved into blood will used up in metabolic process, but N_2 form bubbles as divers comes to atm pressure. This cause Bends or decompression sickness. To avoid this, cylinders are filled with air diluted with Helium.

iv) For Mountain Climbers :-

At high altitude, the partial pressure of O_2 is less than ground level. Thus, low O_2 concentration in blood and tissue, resulting anoxia, in which they feel weak and unable to think properly.

Vapour Pressure :

Vapour Pressure of a liquid or solution is the pressure exerted by the vapours in equilibrium with liquid or solution at a particular temperature.

Factors affecting vapour Pressure :-

1). Nature of ~~of~~ liquid.
weaker the intermolecular forces, greater the amount of vapour pressure.

$$\boxed{\text{vapour pressure} = \frac{1}{\text{force of attraction between molecule}}}$$

2) Temperature
Higher the temperature, greater the vapour pressure.

Vapour Pressure of Liquid - Liquid solution :-

For a solution of liquid - liquid, as both the component of solution are volatile, each component form vapour pressure above the liquid.

This is governed by Raoult's law :-

In a solution of volatile liquids the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution.

According to Raoult's law,

$p_A \propto x_A$

$p_A = p^\circ_A x_A$, where p°_i is vapour pressure of pure component one, at same temperature.

Similarly, for other

$$p_B = p^\circ_B x_B$$

By Dalton's law of partial pressure,

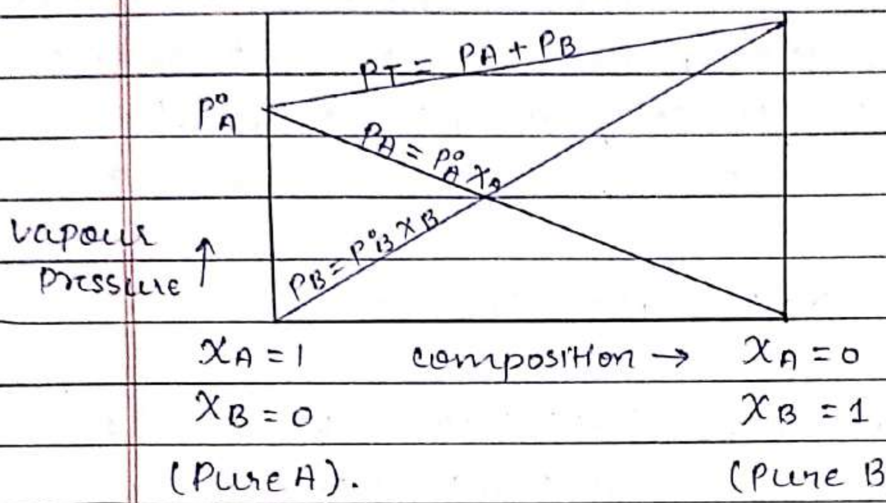
$$\begin{aligned} p_{Total} &= p_A + p_B \\ &= p^\circ_A x_A + p^\circ_B x_B \\ &= p^\circ_A (1 - x_B) + p^\circ_B x_B \\ &= p^\circ_A - p^\circ_A x_B + p^\circ_B x_B \\ &= p^\circ_A + x_B (p^\circ_A - p^\circ_B) \end{aligned}$$

$$\boxed{p_{Total} = p^\circ_A + x_B (p^\circ_A - p^\circ_B)}$$

If y_A and y_B represent the mole fraction of the component A and B respectively in vapour phase, then

$$\boxed{y_A = \frac{p_A}{p_{Total}}} \quad , \quad \boxed{y_B = \frac{p_B}{p_{Total}}}$$

Graph :



Raoult's Law as a special case of Henry Law:

According to Raoults law,

$$P_1 = P_1^o x_1$$

and, Henry's Law

$$P = K_H x$$

On comparing both equation we can say that Raoult's law becomes a special case of Henry's law in which K_H becomes equal to P_1^o. Only constant differs.

Vapour Pressure of Solution of Solid in Liquid :-

On adding non-volatile solute in a solution it is is observed that presence of non-volatile solute reduces the escaping tendency of solvent molecule into vapour phase and thus lower the vapour pressure of the solvent.

According to Raoult's law
Vapour pressure of solvent in solution (P_s)
= Mole fraction of solvent in solution (x_1) × Vapour pressure of pure solvent ($P°$)

Non volatile solute do not contribute in total vapour pressure of the solution.

So, vapour pressure of solution = vapour pressure of the solvent in solution.

$$\because \quad \frac{P_s}{P°} = x_1 \quad \text{eq} ① \quad \left(P_s \propto x_1 \right)$$

Mole fraction of solvent $= x_1 = \dfrac{n_1}{n_1 + n_2}$

Substituting value of x_1 in equation 1.

$$\frac{P_s}{P°} = \frac{n_1}{n_1 + n_2}$$

$$\boxed{\frac{P° - P_s}{P°} = \frac{n_2}{n_1 + n_2}}$$

$P° - P_s$ expresses lowering of vapour pressure.
and $\dfrac{P° - P_s}{P°}$ is called relative lowering of vapour pressure.

Hence, we can define that,
'The relative lowering of vapour pressure of a solution containing a non-volatile solute is equal to mole fraction of solute in the solution

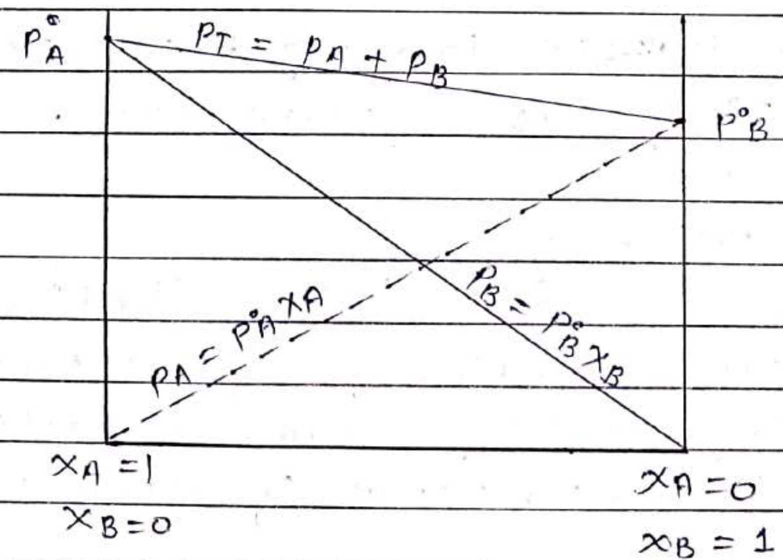
IDEAL AND NON - IDEAL SOLUTIONS :-

1. IDEAL Solution

- Obeys Raoult's law under all condition of temperature and concentration.
- no change in volume on mixing. $\Delta V_{mix} = 0$
- no change in ethalpy. $\Delta H_{mix} = 0$
  [no heat absorbed or evolved]
- Intermolecular interaction between the components are of same magnitude as the pure component.

Example :

(i). Benzene + Toluene
(ii). n - Hexane + n - Heptane
(iii). Ethyl bromide + Ethyl chloride
(iv). Chlorobenzene + Bromobenzene.

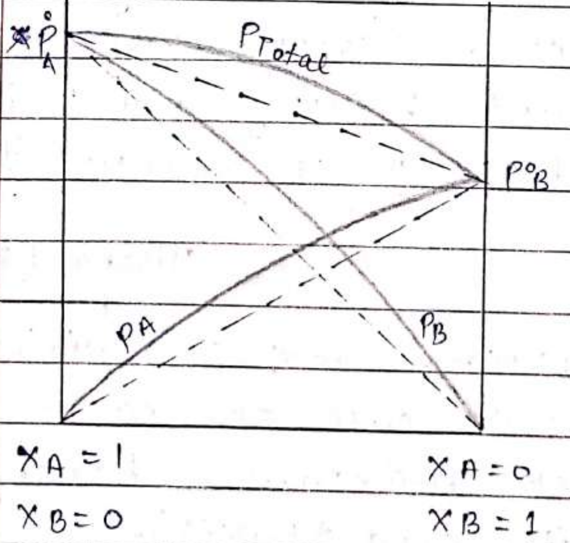


2. NON-IDEAL Solution (do not obeys Raoult's law).

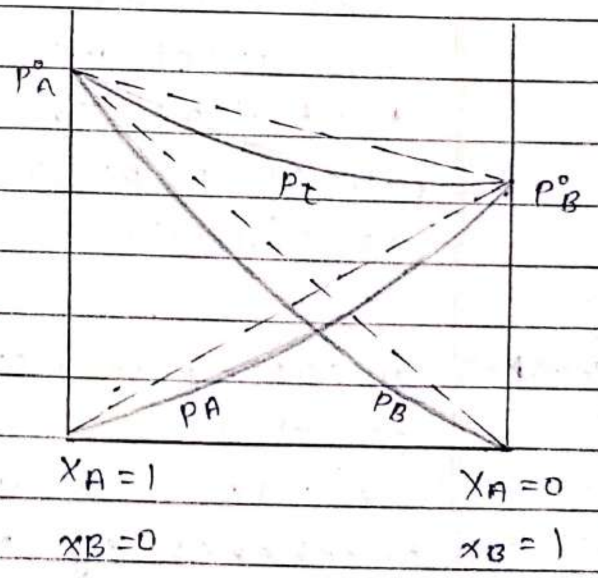
Showing positive Deviation	Showing negative Deviation
• The interaction between the components are less than in the pure component.	• The interaction between the components are greater than the pure pure component.
• ΔV_{mix} = +ve	• ΔV_{mix} = −ve
• ΔH_{mix} = +ve	• ΔH_{mix} = −ve
• $P_A > x_A P^\circ_A$, $P_B > x_B P^\circ_B$	• $P_A < x_A P^\circ_A$, $P_B < x_B P^\circ_B$
• Form minimum boiling azeotropes.	• Form maximum boiling azeotropes.

Graphs :

→ +ve deviation



→ negative deviation



Non Ideal Solution examples -

① Positive Deviation.
- → Acetone + Carbon disulphide
- → Methyl alcohol + H_2O
- → Acetone + Ethyl alcohol.
- → Acetone + Benzene.
- → Ethyl alcohol + H_2O
- → ~~$CHCl_3$~~ Carbon tetra chloride + Chloroform
- → CCl_4 + Benzene
- → CCl_4 + Toulene.

② Negative Deviation -
- → $CHCl_3$ + Benzene
- → $CHCl_3$ + Diethyl ether
- → Acetone + Aniline
- → $HCl + H_2O$
- → $HNO_3 + H_2O$
- → Acetic acid + Pyridine
- → $HI + H_2O$

Azeotropic or Constant Boiling Mixture -
An azeotropic is a liquid mixture that has constant boiling point and whose vapour has same composition as liquid.

(ethanol + water)
↑
imp In case of +ve deviation, we get minimum azeotropes and in case of negative deviation we get maximum boiling azeotropes (eg. Nitric acid + water).

Colligative Properties :

The properties which depend on the number of solute particles relative to total number of particles present in solution irrespective of their nature. Such properties are called colligative properties.

These are -

1. Relative lowering of vapour pressure
2. Elevation in boiling point
3. Depression in freezing point
4. Osmotic pressure of solution

1. Relative lowering of vapour pressure :

When a non-volatile solute is dissolved in a solvent, the vapour pressure of the solution is lower than that of pure solvent.

It was derived earlier ;

$$\boxed{\frac{p^{\circ} - p_s}{p^{\circ}} = \frac{n_2}{n_1 + n_2}} \quad \text{or} \quad \boxed{\frac{P_1^{\circ} - P_1}{P_1^{\circ}} = x_2}$$

or

$$\boxed{\frac{p^{\circ} - p_s}{p_s} = \frac{n_2}{n_1}}$$

↳ this formula can be used for dilute as well as concentrated solutions.

2. Elevation in Boiling point :

When a non.volatile solute is added to a solvent the resulting solution has a higher boiling point than that of pure solvent.

→ Boiling point is the temperature at which the vapour pressure of solution become equal to atmospheric pressure.

The increase in B.P. $\Delta T_b = T_b - T^\circ_b$ is known as elevation in boiling point.

$$\boxed{\Delta T_b = T_b - T^\circ_b}$$

From experiments,

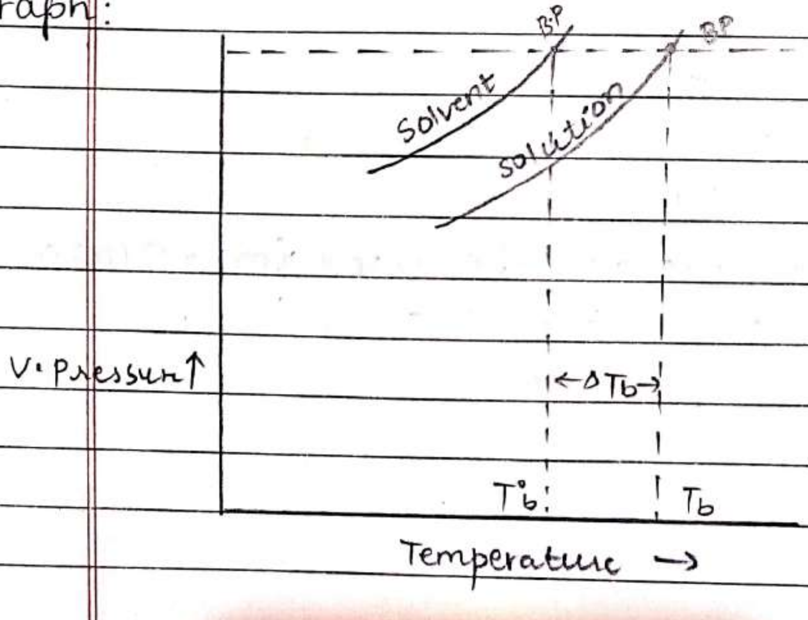
$\Delta T_b \propto m$ (molal conc. of solⁿ).

$$\boxed{\Delta T_b = K_b m}$$

where K_b is molal elevation constant and depends upon nature of solvent.

$$\boxed{\Delta T_b = \frac{K_b \times w_2 \times 1000}{M_2 \times w_1}}$$

Graph:



3. Depression in freezing Point :

when a non-volatile solid is added to the solvent its vapour pressure decreases and become equal to that of solid solvent at lower temperature. Thus, freezing point of solvent decreases.

Freezing point is the temperature at which vapour pressure of liquid state becomes equal to vapour pressure of solid state.

$$\boxed{\Delta T_f = T_f^\circ - T_f}$$

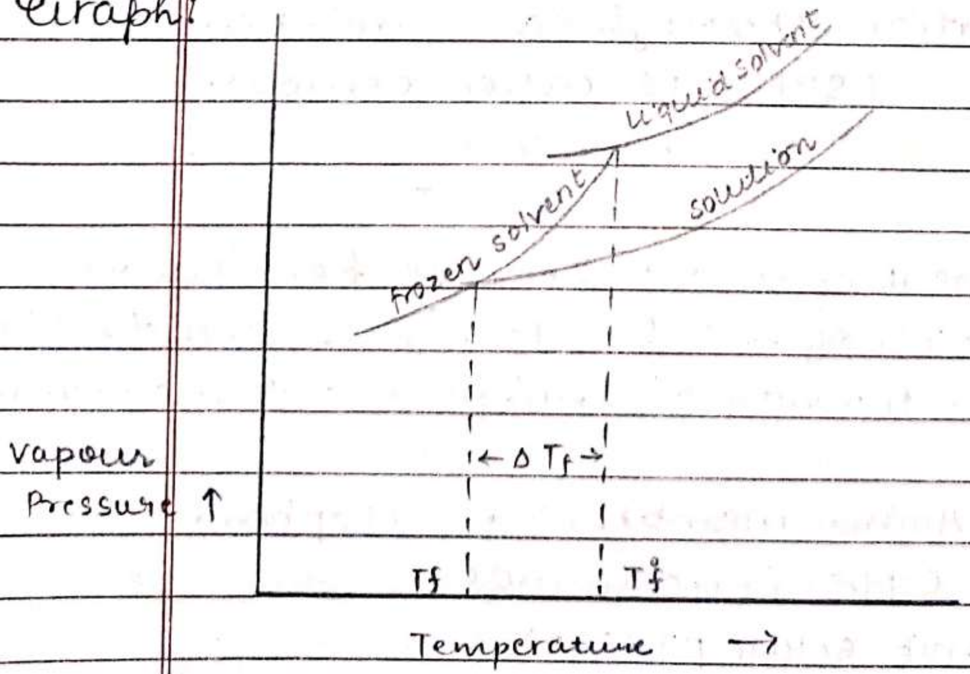
$$\Delta T_f \propto m$$

$$\boxed{\Delta T_f = K_f m}$$

where Kf is molal depression constant and depends on solvent.

$$\boxed{\Delta T_f = \frac{K_f \times w_2 \times 1000}{w_1 \times M_2}}$$

Graph:



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Constant K_f and K_b

The values of K_f and K_b can be asgertained from the following relations ,

$$K_f = \frac{R \times M_1 \times T_f^2}{1000 \times \Delta_{fus.}H}$$

$$K_b = \frac{R \times M_1 \times T_b^2}{1000 \times \Delta_{vap}H}$$

R is gas constant.

M_1 is Molar mass of solvent.

T_f is freezing point of pure solvent in K

T_b " boiling " " " " " ".

$\Delta_{fus}H$ represent enthalpy for fusion of solvent.

$\Delta_{vap}H$ " " vapourisation " ".

4. Osmotic Pressure ;

Osmosis : The movement of solvent molecule from their higher concentration to their lower concentration through a semi-permeable membrane (SPM) is called osmosis.

or

The movement of solvent molecules from lower concentration of solution to higher concentration of solution through a semi-permeable membrane

SPM → Animal membrane , cellophane , copper ferrocyanide.

↓

(do not permit solute particle)

Osmatic Pressure : (π)

The net movement of solvent molecule from solvent to solution can be stopped by applying some extra pressure over solution and that extra pressure over solution side which stops osmosis is called osmotic pressure.

$\pi \propto C/M$ (molarity of solution)

$\pi \propto T$ (Temperature in K).

$\pi = MRT$ or CRT

$\boxed{\pi = CRT}$ where, R is solution constant.

$R = 0.082$ atm L $mol^{-1} K^{-1}$

Diffusion : Resultant movement of any substance from region of higher concentration to lower concentration.

- Isotonic : Solution with equal osmotic pressures are called isotonic.
- Hypotonic : Solution have lower osmotic pressure than normal solution.
- Hypertonic : Solution have higher osmotic pressure than normal solution.

Reverse Osmosis : Reverse osmosis is a special type of filteration that uses a semi-permeable membrane that allows only pure water to pass through it, filtering the larger molecules or impurities.

→ applied pressure should be more than osmotic pressure (π).

Abnormal Malar Mass -

A malar mass that is either lower or higher than the expected or normal value is called as abnormal malar mass.

Weak electrolyte dissociate in water to form ions.

Van't Hoff Factor : (i)

It can be defined as -
ratio of concentration of particles formed when a substance is dissolved to a concentration of substance by mass.

- The extent to which a substance associates or dissociate in a solution is described by Van't Hoff factor.

$$i = \frac{\text{total number of moles of solute after dissocia}}{\text{total number of moles of solute before dissociat or Associat}}$$

$$i = \frac{\text{observed (actual) colligative Property}}{\text{calculated colligative property.}}$$

$$i = \frac{\text{normal molar mass}}{\text{observed molar mass}}$$

for example :

→ $K_4[Fe(CN)_6] \longrightarrow 4K^+ + [Fe(CN)_6]^{4-}$

initial	1	0	0
equilibrium	$1-\alpha$	4α	α

$$i = \frac{1-\alpha+4\alpha+\alpha}{1}$$

$$i = \frac{1+4\alpha}{1}$$

in case of dissociation i is greater than 1.

if dissociation 100%

$$i = \frac{1+4\times 1}{1} = 5 \qquad \boxed{i=5}$$

→ $2CH_3COOH \rightleftharpoons (CH_3COOH)_2$

initial	1	0
equilibrium	$1-\alpha$	$\alpha/2$

$$i = \frac{1-\alpha+\alpha}{1\times 2}$$

$$i = \frac{1}{2} \qquad \boxed{i=\frac{1}{2}}$$

in case of association value of i is less than unity.

1. $\frac{P_1^\circ - P_1}{P_1^\circ} = i \times \frac{n_2}{n_1}$
2. $\Delta T_b = i\, k_b\, m$
3. $\Delta T_f = i\, k_f\, m$
4. $\pi = i\, CRT$