

## Solutions

### Expressing Concentration of Solutions :

#### 1) Mass Percentage :

$$\text{Mass \% of component} = \frac{\text{Mass of component in solution}}{\text{Total mass of solution}} \times 100$$

Example :

$$10\% \text{ of w/w glucose solution means:} \\ 10 \text{ g of Glucose} + 90 \text{ g of water} = 100 \text{ g of solution} \\ (\text{or})$$

$$100 \text{ g of glucose} + 900 \text{ g of water} = 1000 \text{ g of solution.}$$

→ Commercial bleaching solution contains 3.62 mass percentage of sodium hypochlorite in water.

#### 2) Volume Percentage (v/v) :

$$\text{Volume \% of component} = \frac{\text{Volume of component}}{\text{Total volume of solution}} \times 100$$

→ For example, 10% of ethanol solution in water means:   
 10 ml of ethanol + 90 ml of water = 100 ml of solution.

→ A 35% (v/v) solution of ethylene glycol, an antifreeze, is used in cars for cooling the engine. [At this concentration, the antifreeze lowers the freezing point of water to 255.4 K (-17.6°C)]

### 3) Mass By Volume Percentage (w/v)

Mass by volume percentage =  $\frac{\text{mass of solute}}{\text{volume of solution}} \times 100$

For example, 10% w/v means

10g of solute + Vml of solvent = 100ml of solution.

\* Commonly used in medicine and pharmacy.

4) Parts per million (ppm:  $10^6$ )

Parts per million =  $\frac{\text{No. of parts of compound}}{\text{Total no. of parts of all compound in solution}} \times 100$

→ When a solute is present in trace quantities.

→ Can also be expressed as mass to mass, volume to volume and mass to volume

→ For example : A litre of sea water (which weighs 1030 g) contains about  $6 \times 10^{-3}$  g of dissolved Oxygen ( $O_2$ ).

or 5.8 g per  $10^6$  g (5.8 ppm)

## 5) Mole Fraction:

Mole fraction of a component = 
$$\frac{\text{No. of moles of component}}{\text{Total no. of moles of all components}}$$

For a binary mixture A + B :  $\frac{x_A}{x_B} = \frac{n_A}{n_B}$

For a mixture containing 'i' components:

$$\frac{x_0}{l} = \frac{n_0}{n_1 + n_2 + \dots + n_i} = \frac{n_i}{\sum n_j}$$

$$\chi_1 + \chi_2 + \chi_3 + \dots + \chi_p = 1$$

Molarity (M):

"Molarity (M) is defined as number of moles of solute dissolved in one litre (or one cubic decimetre) of solution".

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution in litre}}$$

Molality:

Molality (m) is defined as the number of moles of solute per kilogram (kg) of the solvent.

$$\text{Molality (m)} = \frac{\text{Moles of solute}}{\text{Mass of solvent in kg.}}$$

Numericals:

2.1) Calculate mole fraction of ethylene glycol  $C_2H_6O_2$  in solution containing 20% of  $C_2H_6O_2$  by mass.

$$20 \text{ g } C_2H_6O_2 + 80 \text{ g } H_2O.$$

$$\text{Molar mass of } C_2H_6O_2 = 12 + 12 + 6 + 16 + 16 \\ = 62 \text{ g mol}^{-1}$$

$$\eta = \frac{\text{given mass}}{\text{Molar mass}}$$

$$\text{Moles of } C_2H_6O_2 = \frac{20}{62} = 0.322 \text{ mol.}$$

$$\text{Moles of } H_2O = \frac{80}{18} = 4.444 \text{ mol.}$$

4761 201100

2856

3640

3239

3080

$$\chi_{\text{glycol}} = \frac{n_{\text{C}_2\text{H}_6\text{O}_2}}{n_{\text{C}_2\text{H}_6\text{O}_2} + n_{\text{H}_2\text{O}}}$$

$$= \frac{0.322}{0.322 + 1.444} = \frac{0.322}{4.766}$$

$$= 0.0675$$

$$\chi_{\text{water}} = 1 - \chi_{\text{glycol}} = 0.9325$$

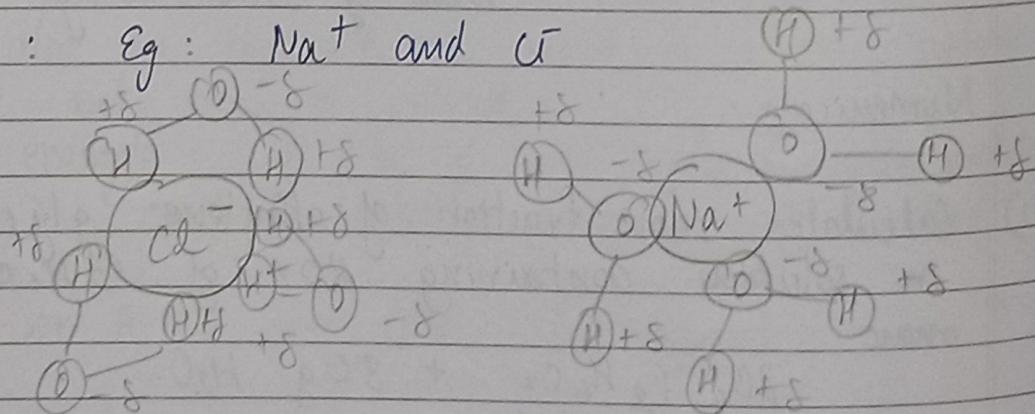
Solubility of solid in liquid:

"like dissolves in like")

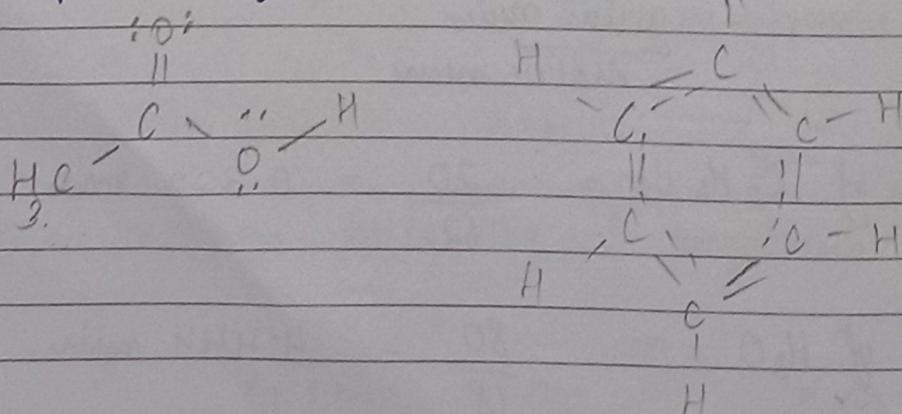
Polar solute  $\rightarrow$  Polar solvent

Non polar solute  $\rightarrow$  Non polar solvent.

Polar: Eg:  $\text{Na}^+$  and  $\text{Cl}^-$



Non polar: Eg:  $\text{C}_2\text{H}_6$ , Ethanoic acid  $\text{CH}_3\text{COOH}$



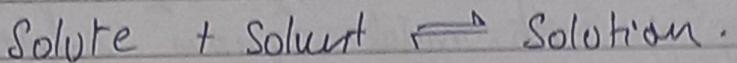
### Dissolution:

When a solid solute is added to the solvent, some solute dissolves and its concentration increases in solution. This process is known as dissolution.

### Crystallization:

Some solute particles in solution collide with the solid solute particles and get separated out of the solution. This process is known as crystallisation.

A stage is reached when the two processes occur at same rate,  $\rightarrow$  Equilibrium



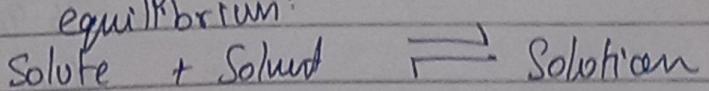
### Saturated Solution:

Solution in which no more solute can be dissolved at the same temperature and pressure is called a saturated solution.

Solubility: The solution which is in dynamic equilibrium with undissolved solute is the saturated solution and contains the maximum amount of solute dissolved in a given amount of solvent. Thus the concentration of solute in such a solution is its solubility (depends upon T & P)

### Factors affecting Solubility:

Consider the equilibrium:



Effect of temperature: Le Chateliers Principle.

→ It has significant effect on solubility.

→ If  $\Delta H_{sol} > 0 \rightarrow$  Forward direction

→ If  $\Delta H_{sol} < 0 \rightarrow$  backward direction

Effect of pressure:

→ It does not have any significant effect on solubility of solids in liquids ( $\because$  solids and liquids are highly incompressible).

Calculate

4) ~~Constituents~~ Mass of urea  $\text{NH}_2\text{CONH}_2$  required in making ~~2.5 kg~~ of  $0.25$  molal aqueous solution.

$$\text{Molar mass: } (2 \times 14) + (4 \times 1) + 12 + 16 \\ = 28 + 4 + 12 + 16 = 60 \text{ g/mol}$$

1000 g of water contains 0.25 moles of (urea)  $\text{NH}_2\text{CONH}_2$

$$\Rightarrow \text{Mass of urea} = 0.25 \times 60 = 15 \text{ g.}$$

$$15 \text{ g of urea} + 1000 \text{ g of water} = 1015 \text{ g of solution}$$

In 1015 g of solution, 15 g of urea is present

$$\text{In 2500 g of solution: } \frac{15}{1015} \times 2500 \\ = 36.94 \text{ g}$$

$\begin{array}{r} 25 \\ 15 \\ \hline 125 \\ 1015 \\ \hline 25 \\ 25 \\ \hline 0 \\ 3694 \end{array}$ 
  
 $\begin{array}{r} 1015 \\ 3045 \\ \hline 7050 \\ 6090 \\ \hline 9600 \\ 4135 \\ \hline 4650 \end{array}$

- 5) Calculate a) molality b) molarity c) mole fraction  
 d) KI if density of 20% (m/m) aqueous KI is 1.202 g ml<sup>-1</sup>.

$$\text{Molar mass} = 39 + 127 = 166 \text{ g mol}^{-1}$$

20% aqueous solution of KI means 20g of KI in 100g of solution

20g of KI is present in 80g of water.

a) Molality =  $\frac{\text{Moles of KI}}{\text{Mass of water (kg)}} = \frac{20/166}{80 \times 10^{-3}}$

$$\frac{1506}{664/1000} = \frac{20}{166 \times 80/4} \times 10^3 = \frac{1000}{664} = 1.506 \text{ m}$$

b) Density = 1.202 g ml<sup>-1</sup>

$$\text{Volume of 100g} = \frac{\text{Mass}}{\text{Density}}$$

$$V = \frac{100}{1.202} = 83.19 \text{ ml}$$

$$= 83.19 \times 10^{-3} \text{ L}$$

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

$$\frac{20000}{116 \times 83.19} = \frac{20 \times 10^3}{166 \times 83.19} - 1.44 \text{ M}$$

$$\frac{138}{138} \frac{12000}{1200} = \frac{138}{138} \frac{620}{620} \frac{552}{552} \frac{680}{680}$$

(c) Mole fraction:

$$\text{No. of moles of KI} = \frac{20}{166} = 0.1204 \text{ moles.}$$

$$0.1204 \text{ moles.}$$

$$\text{No. of moles of water} = \frac{18}{18} = 1.00 \text{ moles.}$$

$$\chi_{\text{KI}} = \frac{n_{\text{KI}}}{n_{\text{KI}} + n_{\text{H}_2\text{O}}} = \frac{0.1204}{1.00} = 0.1204$$

$$\chi_{\text{H}_2\text{O}} = 1 - 0.1204 = 0.8796$$

### Solubility of gases in liquids

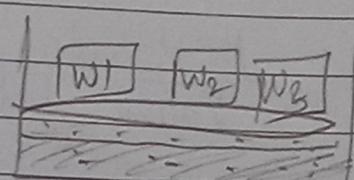
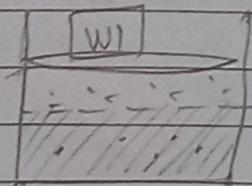
→ Solubility of Oxygen in water : very very less.

→ Solubility of  $\text{H}_2$  &  $\text{NH}_3$  gas in water

→ high

→ Solubility of Gas in liquid is greatly affected by Pressure and Temperature.

→ The solubility of gas increase with increase in pressure.



8  
Henry's law:

"The solubility of a gas in a liquid is directly proportional to the pressure of the gas". ( $s \propto p$ )

Dalton's Law: The solubility of a gas in a liquid solution is a function of partial pressure of the gas ( $s \propto p$ )

Other words: "The mole fraction of gas in the solution is proportional to the partial pressure of the gas over the solution" ( $x \propto p$ )

Most commonly used Henry's law:

"The partial pressure of the gas in vapour phase ( $p$ ) is proportional to the mole fraction of gas ( $x$ ) in the solution."

$$p = K_H x$$

$K_H$  depends on temperature, pressure, nature

Characteristics of  $K_H$ :

- $K_H$  depends on nature of gas, pressure and Temperature
- Different gases → different  $K_H$  values at same temperature.
- ↑ the  $K_H$  at given  $p$ , ↓ is the  $s$  ( $K_H \propto 1/s$ )
- ↑ the  $T$ , ↑ is  $K_H$ , and thus ↓ the  $s$

(Aquatic species are more soluble comfortable in cold water than hot water)

## Applications of Henry's Law:

- 1) Solubility of  $\text{CO}_2$  in soft drinks and soda water
  - 2) Scuba divers  $\rightarrow$  bends
  - 3) high altitude climbers  $\rightarrow$  anoxia
- Air bubble formed in circulatory system ( $\text{N}_2$ )  $\rightarrow$  bends.
  - hypoxia  $\rightarrow$  insufficient blood cloth of part of brain  $\rightarrow$  anoxia

## Limitations of Henry's Law:

Henry's law is applicable only when:

- a) The pressure of the gas is not too high and temperature is not too low.
- b) the gas should not undergo any chemical change.
- c) the gas should not undergo ionization or dissociation in the solution.

## Effect of Temperature on Solubility:

- $\rightarrow$  Solubility of  $G$  in  $L$  is similar to condensation, thus it is an endothermic process.
- $\rightarrow$  Thus  $S \propto T$  (Le Chatelier's Principle)

## Vapour Pressure of Liquid Solutions:

## i) Vapour pressure of liquid-liquid solutions:

Raoult's Law:

"For 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."

thus for component 1:  $p_1 \propto x_1$  and  $p_1 = p_1^0 x_1$

for component 2:  $p_2 \propto x_2$  and  $p_2 = p_2^0 x_2$ .

where  $p_1^0$  and  $p_2^0$  are the vapour pressure of pure components 1 and 2 respectively.

Vapour Pressure: The pressure of a gas at equilibrium with the liquid in a closed system is known as the vapour pressure  
 → characteristic physical property.

For a solution containing two liquids 1 and 2 ...

$$p_1 \propto x_1 \quad \therefore p_1 = p_1^0 x_1$$

$$\text{Similarly } p_2 \propto x_2 \quad \therefore p_2 = p_2^0 x_2$$

where  $p_1$  and  $p_2$  are partial pressures of comp. 1 and 2 in the solution.

$p_1^0$  and  $p_2^0$  are partial pressures of pure components 1 and 2.

$x_1$ ,  $x_2$  are mole fractions of 1 and 2 in the solution.

According to Dalton's law of partial pressures...

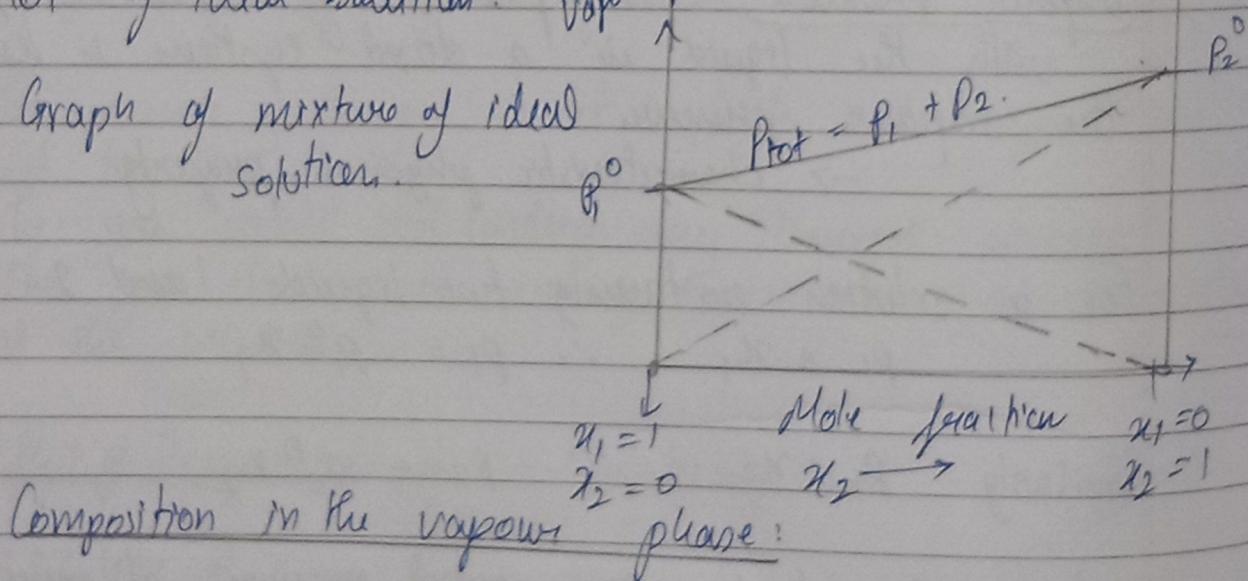
$$\begin{aligned}P_{\text{tot}} &= P_1 + P_2 \\&= P_1^\circ x_1 + P_2^\circ x_2 \\&= P_1^\circ (1 - x_2) + P_2^\circ x_2 \\&= P_1^\circ + (P_2^\circ - P_1^\circ) x_2.\end{aligned}$$

Conclusion :

- $P_{\text{tot}}$  can be related to the  $x$  or any one component.
- $P_{\text{tot}}$  over the solution  $\propto x_2$ .
- Dependence on  $P_1^\circ$  and  $P_2^\circ$ ,  $P_{\text{tot}}$  decreases or increases with increase of  $x_1$ .

Plot of ideal solution: Vapour pressure

Graph of mixture of ideal solution.



Composition in the vapour phase:

- The composition of vapour phase in equilibrium with the solution is determined by the partial pressure of the components.
- If  $y_1$  and  $y_2$  are the mole fractions of the components 1 and 2 respectively in the vapour phase, using Dalton's law of partial pressures.

$$P_1 = Y_1 P_{\text{total}}$$

$$P_2 = Y_2 P_{\text{total}}$$

In general  $P_i = Y_i P_{\text{tot}}$

Raoult's Law as a Special Case of Henry's Law:

Raoult's Law:  $P_i = P_i^0 X_i$

Henry's Law:  $P_i^0 = K_H X_i^0$

→ In the solution of a gas in a liquid, when one of the components is so volatile that it exists as a gas, then Raoult's law becomes a special case of Henry's Law.

→ Comparing the two equations:  $P_i^0$  is similar to  $K_H$ .

Vapour Pressure of solid in liquid solutions:

- 1) When only solvent is present, pressure exerted by solvent vapour molecules is  $P^0$ .
- 2) When non-volatile solute is added, solute molecules share the surface and affect the evaporation and hence the vapour pressure decreases to  $P$ .
- 3) If more solute is added, the vapour pressure decreases even more.

Liquid - Liquid solution on the basis of Raoult's law can be classified into.

1) Ideal Solution:

The solution which obey Raoult's law over the entire range of concentration, temperature and pressure are known as ideal solutions.

Elaboration:  $A, B \rightarrow 2$  liquids.

Dipole Interactions:  $A - A$

$B - B$

$A - B$ .

Properties:

1) Enthalpy of mixing,  $\Delta H_{\text{mix}} = 0$  (i.e., no heat change occurs on mixing)

2) Volume of mixing  $\Delta V_{\text{mix}} = 0$  (i.e., volume of solution is equal to sum of volumes of two liquids exactly)

$\rightarrow$  If  $A - A$  and  $B - B$  are nearly equal to  $A - B$ , ideal solution is formed.

$\rightarrow$  Perfectly ideal solution - rare.

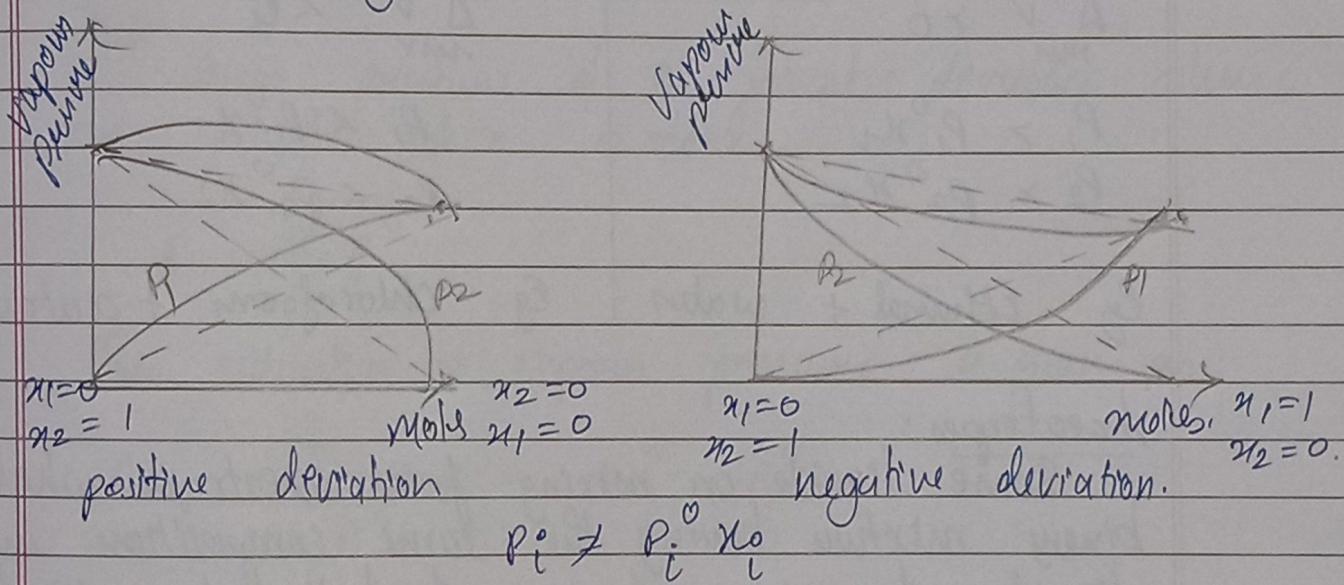
Eg: n-hexane - n-heptane  
benzene - toluene }  $\rightarrow$  nearly ideal  
bromoethane - chloroethane }

Non Ideal Solution:

"When a solution does not obey Raoult's law over the entire range of concentration, then it is called non-ideal solution."

Thus the vapour pressure is either higher (+ve deviation) or lower (-ve deviation) contrary to as expected Raoult's law!

### Positive and Negative Deviation:



### Positive deviation:

Eg: Ethanol, Acetone  
 $A - B$ .

- $A - B$  is weak as compared to  $A - A$  and  $B - B$ . (+ve deviation)
- molecules move out of solution into vapour phase.

### Negative deviation:

Eg: Chloroform - Acetone  
 $A - B$

- $A - B$  is strong, individual molecules cannot go into vapour phase.

Positive deviation

 $A-A$  and  $B-B > A-B$ 

$$\frac{\Delta H}{\text{mix}} > 0$$

$$\frac{\Delta V}{\text{mix}} > 0$$

$$P_1 > P_1^0 \chi_1$$

$$P_2 > P_2^0 \chi_2$$

Negative Deviation

 $A-A$  and  $B-B < A-B$ 

$$\frac{\Delta H}{\text{mix}} < 0$$

$$\frac{\Delta V}{\text{mix}} < 0$$

$$P_1 < P_1^0 \chi_1$$

$$P_2 < P_2^0 \chi_2$$

Eg: Ethanol + water

Eg: chloroform + acetone.

Azeotropes:

Some liquids on mixing form azeotropes which are binary mixtures having the same composition in liquid and vapour phase and boil at a constant temperature.

→ The components cannot be separated by fractional distillation.

\* Minimum boiling azeotrope: +ve deviation  
(ethanol + water: approximately 95% by volume of ethanol)

\* Maximum boiling azeotrope: -ve deviation.  
(nitric acid + water: 68% Nitric acid and 32% water by mass) with boiling point 393.5 K.

## Colligative Properties:

Properties which depend on the number of solute particles irrespective of their nature are called colligative properties.

## Relative Lowering of Vapour Pressure:

Vapour pressure of a solvent decreases when a non volatile solute is added.

$$P_i = x_i P_i^0$$

The reduction of vapour pressure is given as:

$$\Delta P_i = P_i^0 - P_i = P_i^0 - P_i^0 x_i \\ = P_i^0 (1 - x_i)$$

Knowing that  $x_2 = 1 - x_1$ ,

$$\Delta P_i = P_i^0 x_2.$$

In a solution containing several non-volatile solutes, the lowering of vapour pressure depends on the sum of mole fractions of different solutes.

$$\frac{\Delta P_i}{P_i^0} = \frac{P_i^0 - P_i}{P_i^0} = x_2.$$

→ The relative lowering of vapour pressure is equal to the mole fraction of the solute.

$$\frac{P_1^0 - P_1}{P_1^0} = \frac{n_2}{n_1 + n_2} \quad \left[ \text{Since } \frac{n_2}{n_1 + n_2} = \frac{n_2}{n_1 + n_2} \right]$$

for dilute solutions,  $n_2 \ll n_1$ , neglecting  $n_2$  in denominator.

$$\frac{P_1^0 - P_1}{P_1^0} = \frac{n_2}{n_1} = \frac{w_2 \times M_1}{M_2 \times w_1}$$

$w_1$ ,  $w_2$  are mass,  $M_1$ ,  $M_2$  are molar mass of solvent and solute respectively.

(2.6) The vapour pressure of pure benzene at a certain temperature is 0.850 bar. A non volatile, non electrolyte solid weighing 0.5 g when added to 39.0 g of benzene (molar mass 78 g mol<sup>-1</sup>), vapour pressure of the solution being 0.845 bar. What is the molar mass of solid substance.

Given:

$$P_1^0 = 0.850 \text{ bar}$$

$$P = 0.845 \text{ bar}$$

$$M_1 = 78 \text{ g mol}^{-1}$$

$$w_2 = 0.5 \text{ g}$$

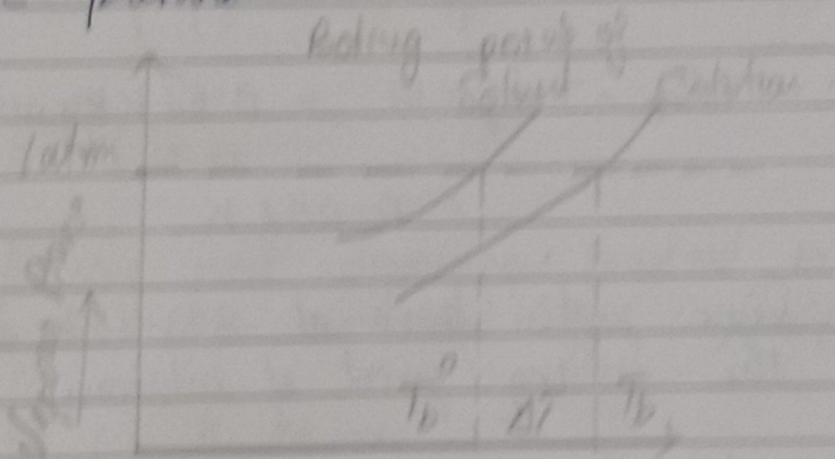
$$w_1 = 39 \text{ g}$$

$$\frac{0.850 - 0.845}{0.850} = \frac{0.5 \times 78}{M_2 \times 39}$$

$$M_2 = \frac{1000 \times 0.5 \times 18 \times 0.85}{10 \times 0.005} \\ = 170 \text{ g mol}^{-1}$$

## 2] Elevation of Boiling Point

Boiling point : It is the temperature at which vapour pressure of the liquid is equal to the atmospheric pressure.



Let  $T_b^0$  be boiling point of pure solvent and  $T_b$  be the boiling point of solution. The increase in boiling point  $\Delta T_b = T_b - T_b^0$  is known as elevation of boiling point.

$$(a) \Delta T_b \propto m$$

$$\Delta T_b = k_b \cdot m$$

$k_b$  is called boiling point elevation constant or molal elevation constant or ebullioscopic constant

Q) 18g of glucose,  $C_6H_{12}O_6$  is dissolved in 1 kg of water in a sauspan. At what temperature will water boil at 1.013 bar?  $k_b$  for water is 0.52  $K \text{ kg mol}^{-1}$

$$\text{Moles of glucose} = \frac{18g}{180 \text{ g mol}^{-1}} = 0.1 \text{ mol}$$

$$\text{No. of kilograms of solvent} = 1 \text{ kg.}$$

$$\text{Thus molality of glucose solution} = 0.1 \text{ mol kg}^{-1}$$

For water, change in boiling point

$$\Delta T_b = k_b \times m = 0.52 \text{ K kg mol}^{-1} \times 0.1 \text{ mol kg}^{-1}$$

$$= 0.052 \text{ K}$$

Since water boils at 373.15 K at 1.013 bar,  
the boiling point of solution will be

$$373.15 + 0.052 = 373.202 \text{ K.}$$

Depression of Freezing Point:

The freezing point of a substance is defined as the temperature at which the vapour pressure of the substance in its liquid phase is equal to its vapour pressure in solid phase.

A solution will freeze when its vapour pressure equals the vapour pressure of pure solid solute.

According to Raoult's Law, when a non volatile solid is added to the solvent, its vapour pressure

decreases and now it would become equal to that of solid solvent at low temperature. Thus the freezing point of solvent decreases.

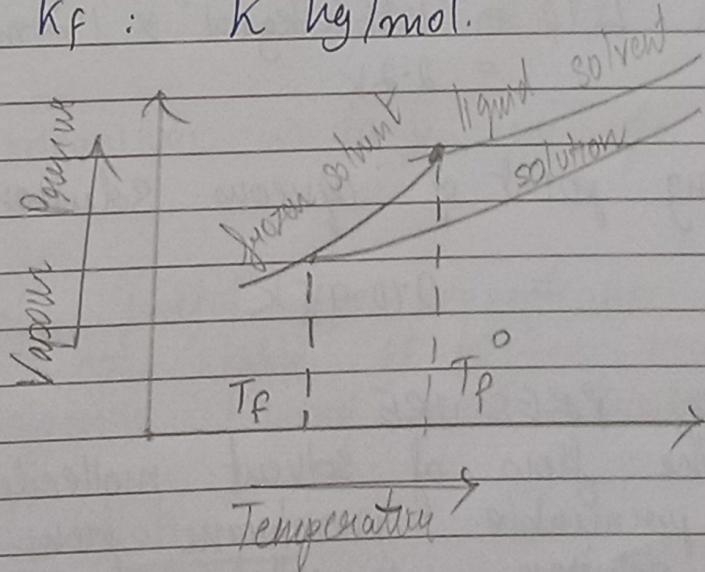
Let  $T_f^0$  be freezing point of pure solvent and  $T_f$  be its freezing point when non volatile solute is dissolved in it. The decrease in freezing point  $\Delta T_f = T_f^0 - T_f$  is known as depression in freezing point.

$$\Delta T_f \propto m$$

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

$K_f \rightarrow$  freezing point depression constant (or) molal depression constant (or) cryoscopic constant.

Unit of  $K_f$  :  $K \text{ kg/mol}$ .



- Q] 45g of ethylene glycol ( $(\text{CH}_2\text{O})_2$ ) is mixed with 60g of water. Calculate (a) freezing point depression (b) freezing point of the solution.

Depression in freezing point is related to the molality, therefore the molality of the solution with respect to ethylene glycol

$$\text{Molality} = \frac{\text{No. of moles of ethylene glycol}}{\text{Mass of water in (kg)}}$$

$$\text{Moles of ethylene glycol} = \frac{45}{62 \text{ g mol}^{-1}} = 0.73 \text{ mol}$$

$$\text{Mass of water in kg} = \frac{600}{1000 \text{ g kg}^{-1}} = 0.6 \text{ kg.}$$

$$\text{Hence molality of ethylene glycol} = \frac{0.73}{0.6} = 1.2 \text{ mol kg}^{-1}$$

Freezing point depression:

$$\Delta T_f = 1.86 \text{ K kg mol}^{-1} \times 1.2 \text{ mol kg}^{-1} \\ = 2.2 \text{ K}$$

$$\text{Freezing point of aqueous solution} = 273.15 - 2.2 \\ = 270.95 \text{ K}$$

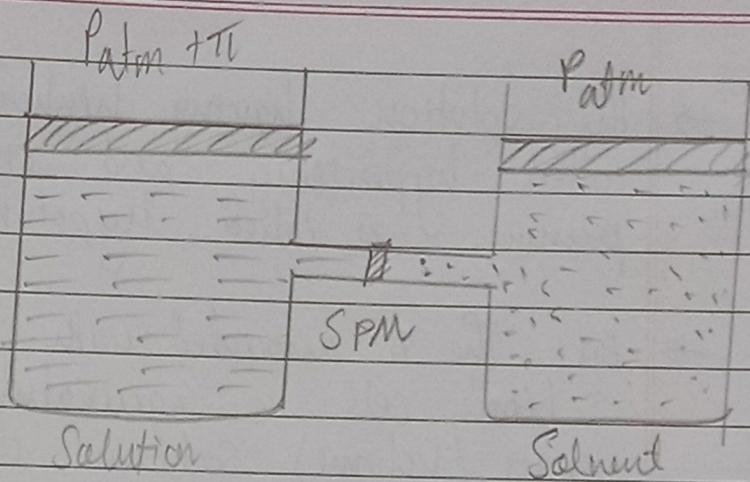
4]

OSMOTIC PRESSURE:

The flow of solvent molecules through a semi-permeable membrane from pure solvent to the solution is called osmosis.

The osmotic pressure of a solution is the excess pressure that must be applied to a solution to prevent osmosis.

$$\begin{aligned} \Pi &= CRT \\ &= \left(\frac{n_2}{V}\right) RT \end{aligned}$$



Uses:

→ Widely used to determine molar masses of proteins, polymers and other macro molecules.

Advantages over other methods:

→ The pressure measurement is around the room temperature and the molarity of the solution is used instead of molality.

→ Its magnitude is large even for very dilute solutions.

Particularly useful for biomolecules as they are generally not stable at higher temperatures and polymers having poor solubility.

Different Solutions:

Two solutions having same osmotic pressure at a given temperature are called isotonic solutions.

→ The solution having higher osmotic pressure is called hypertonic and one with lower osmotic pressure is called hypotonic.

→ Eg: The  $\pi$  associated with the fluid inside the blood cell is equivalent to that of 0.9% (mass / volume) sodium chloride solution, called normal saline solution and it is safe to inject intravenously. less or more will be hypo or hypertonic solutions.

Examples:

→ A raw mango placed in concentrated salt solution loses water via osmosis and shrivels into a pickle.

→ Wilting flowers revive when placed in fresh water. A carrot that has become limp because of water loss into the atmosphere can be placed into the water making it firm once again. Water will move into them through osmosis.

→ When placed in water containing less than 0.9% (mass / volume) salt, blood cells collapse due to loss of water by osmosis.

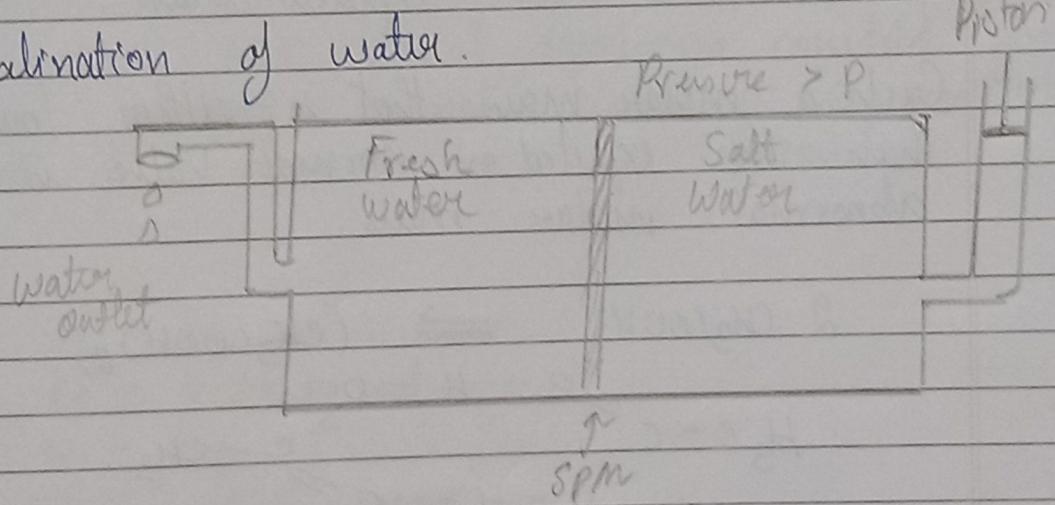
→ People taking a lot of salt or salty food experience water retention in tissue cells and intercellular spaces because of osmosis. Edema.

→ Preservation of meat by salting and of fruits by adding sugar protects against bacterial action.

### Reverse Osmosis and Water Purification:

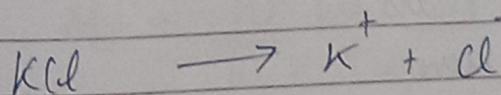
Application of pressure higher than osmotic pressure results into flow of solvent molecules from solution to pure solvent. This phenomenon is called reverse osmosis.

→ Desalination of water.



### ABNORMAL MOLAR MASS:

Tonic compounds when dissolved in water dissociate into cations and anions.



If 1 mol of KCl is dissolved, there would be two moles of particles in solution.

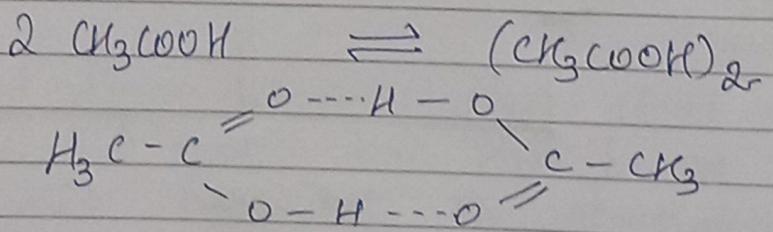
When there is dissociation, the experimentally determined molar mass is always lower than true value.

Molecules of ethanoic acid dimerize in benzene due to hydrogen bonding. In this case, the number of particles is reduced due to dimerization.

If all molecules of ethanoic acid associate in benzene,  $\Delta T_b$  or  $\Delta T_f$  for ethanoic acid will be half of normal value.

The molar mass calculated on basis of  $\Delta T_b/\Delta T_f$  will be twice than expected value.

Such a molar mass that is either lower or higher than the expected or normal value is called abnormal molar mass.



Van't Hoff factor ( $\gamma$ )

$$\gamma = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$$

$$= \frac{\text{Observed colligative property}}{\text{Calculated colligative property}}$$

$$\gamma = \frac{\text{Total no of moles of particles after dissociation}}{\text{No. of moles of particles before dissociation}}$$

$$\frac{P_2^o - P_1}{P_1^o} = i \cdot \frac{n_2}{n_1}$$

Elevation of Boiling point,  $\Delta T_b = i k_b m$

Depression of freezing point,  $\Delta T_f = i k_f m$

Osmotic pressure of solution  $\rightarrow \pi = i \frac{n_2 RT}{V}$

Q] 2g of benzoic acid ( $C_6H_5COOH$ ) dissolved in 25g of benzene shows a depression in freezing point equal to 1.62K. Molal depression constant for benzene is  $4.9 \text{ K kg mol}^{-1}$ . What is % dissociation of acid if it forms dimer in solution?

Given :

$$w_2 = 2 \text{ g}$$

$$k_f = 4.9 \text{ K kg mol}^{-1}$$

$$w_1 = 25 \text{ g}$$

$$\Delta T_f = 1.62 \text{ K}$$

$$\Delta T_f = k_f m = \frac{k_f \cdot n_2}{w_1} = \frac{k_f w_2}{M_2 w_1}$$

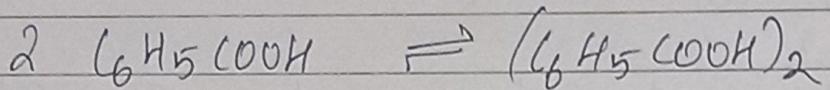
$$M_2 = \frac{k_f w_2}{w_1 \times \Delta T_f}$$

$$= \frac{4.9 \text{ K kg mol}^{-1} \times 2 \text{ g} \times 1000 \text{ g kg}^{-1}}{25 \text{ g} \times 1.62 \text{ K}}$$

$$= 241.98 \text{ g mol}^{-1}$$

Experimental molar mass of  $\gamma = 241.98 \text{ g mol}^{-1}$   
benzoic acid in benzene

Consider the equilibrium.



if  $\alpha$  represents degree of ionization of solute, then we would have  $(1-\alpha)$  mol of benzoic acid left in unsaturated form and correspondingly  $\frac{\alpha}{2}$  as ionized moles of

benzoic acid at equilibrium. The total no. of moles of particles in equilibrium.

$$= (1-\alpha) + \frac{\alpha}{2} = 1 - \frac{\alpha}{2}.$$

Total no. of moles of particles at equilibrium equals van't Hoff factor  $i$ ,

$$i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}} = \frac{122 \text{ g/mol}}{241.98 \text{ g/mol}}$$

$$1 - \frac{\alpha}{2} = \frac{122}{241.98}$$

$$\frac{\alpha}{2} = 1 - \frac{122}{241.98} = 1 - 0.504 = 0.496$$

$$\alpha = 2 \times 0.496 = 0.992.$$

The degree of ionization of benzoic acid = 99.2%.

Q) Calculate the mole fraction of benzene in solution containing 30% by mass in carbon tetrachloride.

Let the total mass of solution be 100g,  
mass of benzene is 30g.

Mass of carbon tetrachloride = 70g.

$$\text{Molar mass of benzene} = \frac{12(6) + 6}{78 \text{ g mol}^{-1}} = \frac{72}{78} = \frac{2}{3} = 0.6667$$

$$\text{No. of moles of C}_6\text{H}_6 = \frac{30}{78} = \frac{0.3846}{1} = 0.3846 \text{ mol.}$$

$$\text{No. of moles of CCl}_4 = \frac{70}{142} = \frac{0.4929}{1} = 0.4929 \text{ mol.}$$

$$\text{Mole fraction of C}_6\text{H}_6 \quad X_1 = \frac{n_1}{n_1 + n_2} = \frac{0.3846}{0.3846 + 0.4929} = \frac{0.3846}{0.8775} = 0.4371$$

$$= \frac{0.3846}{0.3846 + 0.4929} = \frac{0.3846}{0.8775} = 0.4371$$

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Q) Boiling point of water at 750mm Hg is 35100  
99.63°C. How much sucrose to be added.  
to 500g of water such that it  
boils at 100°C. Molal elevation  
constant for water is 0.52 K kg mol<sup>-1</sup>

$$= \frac{0.3846}{0.8775} = 0.4371$$

Ans: Here elevation of boiling point

$$\begin{aligned}\Delta T_b &= (100 + 273) - (99.63 + 273) \\ &= \cancel{0.37} \\ &= 0.37 \text{ K}\end{aligned}$$

Molar mass of sucrose ( $C_{12}H_{22}O_{11}$ )

$$M_2 = 342 \text{ g/mol}$$

Molar elevation constant  $k_b = 0.52 \text{ K kg/mol}$

We know that

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

$$\begin{aligned}w_2 &= \frac{\Delta T_b \times M_2 \times w_1}{k_b \times 1000} = \frac{0.37 \times 342 \times 500}{0.52 \times 1000} \\ &= 121.67 \text{ g (approx.)}\end{aligned}$$

∴ 121.67 g of sucrose is to be added.

Q] 19.5 g of  $CH_3COOH$  (Fluoro acetic acid) is dissolved in 500 g of  $H_2O$ ,  $\Delta T_f = 1^\circ\text{C}$ , calculate Vant Hoff factor and dissociation constant of fluoroacetic acid ( $K_f = 1.86$ )

$$\begin{aligned}\Delta T_f &= k_f \cdot m \\ &= \frac{k_f \times w_2 \times 1000}{w_1 \times M_2}\end{aligned}$$

Molar mass of

$$\text{CH}_2\text{FCOOH} = 78 \text{ g mol}^{-1} = M_2$$

32.

27

49

78

49

29

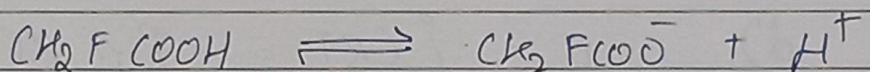
52

$$\Delta T_F = \frac{1.86 \times 1.95 \times 1000}{78 \times 500} = 0.93 \text{ K}$$

$$\frac{93}{93} \text{ K}$$

$$\bar{P} = \frac{\text{Observed } \Delta T_F}{\text{Calculated } \Delta T_F} = \frac{1}{0.93} = 1.0753$$

$$\begin{array}{r} 700 \\ 651 \\ 465 \\ 250 \\ 186 \end{array}$$



$$n = 2$$

$$\alpha = \frac{i-1}{n-1} = \frac{1.0753-1}{2-1} = 0.0753$$

$$\begin{aligned} K_a &= \frac{C\alpha^2}{1-\alpha} \\ &= \frac{0.5 \times (0.0753)^2}{0.9247} \end{aligned}$$

$$\begin{aligned} \text{Molality} &= \frac{\text{No. of moles solute}}{\text{Mass of solvent (kg)}} \\ &= \frac{19.5 \times 1000}{78 \times 500} \text{ m} \\ &= 0.5 \text{ m} \end{aligned}$$

$$K_a = 3.04 \times 10^{-3}$$

Semi Permeable Membrane

- Cellular autotote
- Pig's bladder
- Parchment
- Cellophane.

## Important Formula: Association / Dissociation

$$a) \frac{P_A^0 - P_A}{P_A^0} = i X_B$$

$$b) \Delta T_b = i k_b m$$

$$c) \Delta T_f = i k_f m$$

$$d) \Pi = i \frac{n}{V} RT$$

$$e) \alpha = \frac{i-1}{n-1} \quad (\text{dissociation of electrolyte})$$

degree of dissociation

$n \rightarrow$  no. of ions produced / formula compound.

$$K_a = \frac{c \alpha^2}{1-\alpha}$$

$\alpha \rightarrow$  degree of dissociation.

Q) Determine the amount of  $\text{CaCl}_2$  ( $i^0 = 2.417$ ) dissolved in 2.5 L of water such that its osmotic pressure is 0.75 atm, at  $27^\circ\text{C}$ .

$$\Pi = i \frac{n}{V} RT$$

$$\frac{120}{1280}$$

$$\frac{\Pi}{i} = \frac{W}{MV} = \frac{0.75 \times 121 \times 2.5}{2.417 \times 8.314 \times 300}$$

$$W = \frac{\Pi MV}{i RT} = \frac{8.075 \times 121 \times 2.5}{4 \times 4 \times 2.417 \times 8.314 \times 100} = 36 \text{ g.}$$

$$= 36.826 \text{ g}$$