

## UNIT-2

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### Solutions

**Solution**  $\Rightarrow$  A solution is a homogenous mixture of two or more substances whose composition can be varied within certain limits.

**Binary solution**  $\Rightarrow$  The solution having two components is known as binary solution.

**Solute**  $\Rightarrow$  The component which is present in a small quantity in solution is known as solute.

**Solvent**  $\Rightarrow$  The component which is present in a large quantity in solution is known as solvent.

**Types of solutions**  $\Rightarrow$

1) **Aqueous solution**  $\Rightarrow$  The solutions in which water is solvent are called aqueous solution.

2) **Non-aqueous solution**  $\Rightarrow$  The solutions in which water is not solvent are called non-aqueous solution.

**Concentration of a solution**  $\Rightarrow$  Concentration of a solution is defined as the amount of solute dissolved in a given quantity of solvent.

Methods to express the concentration of a



Solution  $\Rightarrow$

- 1) Strength of a solution  $\Rightarrow$  It is the amount of solute in grams dissolved per litre of the solution.

units  $\rightarrow \text{gml}^{-1}$

- 2) Mass percentage  $\Rightarrow$  The mass % of a component in a given solution is the mass of that component present in 100 gm of the solution.

Mathematically  $\rightarrow$

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

- 3) Volume percentage  $\Rightarrow$  The volume % of a component in a given solution is the volume of the component per 100 parts by volume of the solution.

- 4) ppm  $\rightarrow$  (Parts per million) It is the part of the component per million of part of the solution.

Mathematically  $\rightarrow$

$$\text{ppm of A} = \frac{\text{Mass of A}}{\text{Total mass of solution}} \times 10^6$$

This method is used to express the concentration of dilute solution.

- 5) Molarity  $\Rightarrow$  (M) It is the number of moles of solute dissolved per litre of the solution.

Mathematically  $\rightarrow$

$$\text{Number of moles} = \frac{\text{mass}}{\text{molecular mass}}$$

$$\text{Molarity (M)} = \frac{\text{No. of moles of solute}}{\text{vol. of solution in litre}}$$



$$M = \frac{\text{No. of moles of solute}}{\text{volume of solution in ml/cm}^3} \times 1000$$

Eg: → A solution of NaOH is prepared by dissolving 8g of NaOH in 500 ml of water. Calculate the molarity of the solution.

Sol: →

Amount of NaOH = 8g  
 Volume of solution = 500ml  
 Moles of NaOH =  $\frac{\text{Mass of NaOH}}{\text{Molar mass}}$   
 $= \frac{8}{40} = \frac{1}{5} \text{ mol}$

$$\begin{aligned} \text{Molarity} &= \frac{\text{moles of NaOH}}{\text{vol. of the solution in ml}} \times 1000 \\ &= \frac{1 \text{ mol}}{5 \times 500 \text{ ml}} \times 1000 \text{ ml l}^{-1} \\ &= \frac{1 \text{ mol}}{\frac{2500 \text{ ml}}{5}} \times 1000 \text{ ml l}^{-1} \\ &= \frac{2}{5} \text{ mol l}^{-1} \\ &= 0.4 \text{ M} \end{aligned}$$

units of molarity =  $\text{mol l}^{-1}$

6) Molality → (m) It is the number of moles of solute dissolved per kg of the solvent.  
 Mathematically →

$$\text{Molality (m)} = \frac{\text{No. of moles of solute}}{\text{Mass of solvent in kg}}$$



$$m = \frac{\text{No. of moles of solute}}{\text{mass of solvent in kg}} \times 1000$$

units of molality =  $\text{mol kg}^{-1}$

eg:  $\rightarrow$  2.5g of ethanoic acid ( $\text{CH}_3\text{COOH}$ ) (molar mass 60) in 75g of benzene. Calculate the molality of the solution.

$$\text{No. of moles} = \frac{\text{mass}}{\text{molar mass}}$$

$$= \frac{2.5}{60}$$

$$= \frac{25}{10 \times 60} = \frac{25}{600} = \frac{1}{24}$$

$$\text{Molality} = \frac{\text{No. of moles of solute} \times 1000}{\text{mass of solvent in g}}$$

$$= \frac{1}{24 \times 75} \times 1000$$

$$= \frac{1}{1800} \times 1000$$

$$= \frac{5}{9} = 0.56$$

1\* Molality is more effective method to express the concentration than molarity.

$\Rightarrow$  Molarity  $\rightarrow$  It is the no. of moles of solute dissolved per litre of the solution.

Mathematically  $\rightarrow$



$$\text{Molarity (M)} = \frac{\text{No. of moles of solute}}{\text{vol. of solution in litre}}$$

$$\text{or} = \frac{\text{No. of moles of solute}}{\text{vol. of solution in ml/cm}^3} \times 1000$$

of  
 Molality  $\rightarrow$  It is the no. of moles of solute dissolved per kg of the solvent.  
 Mathematically  $\rightarrow$

$$\text{Molality (m)} = \frac{\text{No. of moles of solute}}{\text{Mass of the solvent in kg}}$$

$$\text{or} = \frac{\text{No. of moles of solute}}{\text{mass of the solvent in g}} \times 1000$$

Molarity depends upon volume which changes with change in temperature but molality depends upon mass which do not changes with change in temperature. Thus molality is more effective method to express the concentration than molarity.

7) Normality  $\rightarrow$  (N) It is the number of gram equivalent of solute dissolved per litre of the solution.

Mathematically  $\rightarrow$

$$\text{Normality (N)} = \frac{\text{No. of gram equivalent of solute}}{\text{vol. of solution in litre}}$$

$$\text{or} = \frac{\text{No. of gram equivalent of solute}}{\text{vol. of solution in ml/cm}^3} \times 1000$$



$$\text{No. of gram equivalent mass} = \frac{\text{Mass}}{\text{Equivalent mass}}$$

$$\text{Equivalent mass for acid} = \frac{\text{Molar mass}}{\text{Basicity}} \\ (\text{no. of } H^+ \text{ ion given by acid})$$

$$\text{For base} = \frac{\text{Molar mass}}{\text{Acidity (OH}^- \text{ ion given by base)}}$$

$$\text{For salts} = \frac{\text{Molar mass}}{\text{valency of metal ion}}$$

eg:  $\rightarrow$  4g of NaOH is dissolved in 250 ml of solution. Calculate the normality of solution.

sol. Equivalent mass of NaOH =  $\frac{\text{Molar mass}}{\text{acidity}}$

$$= \frac{40}{1} = 40$$

$$\text{No. of gram equivalent} = \frac{\text{mass}}{\text{molar mass}}$$

$$= \frac{4}{40} = \frac{1}{10}$$

$$\text{Normality} = \frac{\text{No. of gram equivalent}}{\text{vol. of sol. in ml}} \times 1000$$

$$= \frac{1}{10 \times \frac{250}{5}} \times 1000 = \frac{2}{5}$$

$$= 0.4$$



8) Mole fraction  $\rightarrow$  It is the ratio of no. of moles of a component to the total no. of moles of component present in the solution. It is denoted by  $x$ .  
Mathematically  $\rightarrow$  let us consider a solution having two component A & B

$$x_A = \frac{n_A}{n_A + n_B}$$

[Here  $n_A =$  no. of moles of A  
 $n_B =$  no. of moles of B]

$$x_B = \frac{x_B}{x}$$

$$x_B = \frac{n_B}{n_A + n_B}$$

The sum of mole fraction of all the component in a solution = 1 (unity)

eg:  $\rightarrow$  A solution contain 25% of water, 25% ethanol ( $C_2H_5OH$ ) and 50% of Acetic acid ( $CH_3COOH$ ). Calculate the mole fraction of each component.

Sol:  $\rightarrow$  Let the mass of solution = 100g  
 $\therefore$  mass of water = 25g  
mass of ethanol = 25g  
mass of acetic acid = 50g

$$\text{No. of moles of water} = \frac{25}{18} = 1.39$$

$$\text{No. of moles of ethanol} = \frac{25}{46} = 0.54$$

$$\text{No. of moles of acetic acid} = \frac{50}{60} = \frac{5}{6}$$

$$= 0.84$$



$$\text{Mole fraction of water} = \frac{1.39}{1.39 + 0.54 + 0.84}$$

$$= \frac{1.39}{2.77}$$

$$= 0.5$$

$$\text{Mole fraction of ethanol} = \frac{0.54}{2.77}$$

$$= 0.19$$

$$\text{Mole fraction of acetic acid} = \frac{0.84}{2.77}$$

$$= 0.3$$

$$\text{Sum of all mole fractions} = 0.5 + 0.19 + 0.3$$

$$= 0.99$$

eg:  $\rightarrow$  Calculate the molarity of pure water. (density = 1g per ml)

Sol.  $\text{density} = \frac{\text{mass}}{\text{volume}}$  [mass of 1000 ml of water =  $\frac{1 \times 1000}{1000}$ ]

$$\text{No. of moles} = \frac{\text{mass}}{\text{molar mass}}$$

$$= \frac{500}{18} = \frac{55.5}{9}$$

$$= 55.5 \text{ (molarity)}$$

eg:  $\rightarrow$  Calculate molarity of solution contains 0.5g of NaOH dissolved in 500 cm<sup>3</sup> of the solution.

Sol. Amount of NaOH = 0.5g  
Volume of the solution = 500 cm<sup>3</sup>



$$\text{Moles of NaOH} = \frac{\text{mass}}{\text{molar mass}}$$

$$= \frac{0.5}{40}$$

$$= \frac{5}{40 \times 10^2}$$

$$= \frac{1}{80} = 0.0125$$

$$\text{Molarity} = \frac{\text{Moles of NaOH}}{\text{Vol. of the solution in cm}^3} \times 1000$$

$$= \frac{0.0125}{800} \times 1000$$

$$= 0.0125 \times 2$$

$$= 0.025$$

eg: → A sugar syrup of weight 214.2g contains 34.2g of sugar ( $C_{12}H_{22}O_{11}$ ). Calculate

(i) molality (ii) mole fraction

Sol.

$$\text{weight of sugar syrup} = 214.2g$$

$$\text{weight of sugar in syrup} = 34.2g$$

$$\text{weight of water in syrup} = 214.2g - 34.2g = 180.0g$$

$$\text{moles of sugar} = \frac{34.2}{342} = \frac{342}{342 \times 10} = \frac{1}{10}$$

$$= 0.1$$

(ii)  $\text{Mass molality} = \frac{\text{No. of moles of solute}}{\text{mass of solvent in g}} \times 1000$

$$= \frac{0.1}{180} \times 1000$$



$$= \frac{1}{18 \times 10^3} \times 10^5$$

$$= \frac{10^5}{18 \times 10^3} = \frac{10^2}{18} = \frac{5}{9} = 0.56$$

(ii) Moles of sugar =  $\frac{34.2}{342} = 0.1$

Moles of water =  $\frac{180}{18} = 10$

mole fraction of sugar =  $\frac{0.1}{10 + 0.1}$

$$= \frac{0.1}{10.1}$$

$$= \frac{1 \times 10}{101 \times 10^2}$$

$$= \frac{1}{101} = 0.0099$$

\* Calculate the mole fraction of ethanol and water in a sample of rectified spirit which contains 92% ethanol by mass.

Sol  $\rightarrow$  let the weight of rectified spirit = 100g

$$\therefore \text{Mass of ethanol} = 92\text{g}$$

$$\text{Mass of water} = 100 - 92 = 8\text{g}$$

$$\text{No. of moles of ethanol} = \frac{92}{\frac{46}{23}} = 2$$

$$\text{No. of moles of } \overset{\text{water}}{\text{ethanol}} = \frac{8}{\frac{18}{9}} = \frac{4}{9} = 0.44$$



$$\begin{aligned}
 \text{Mole fraction of ethanol} &= \frac{2}{2+0.4} \\
 &= \frac{2}{2.4} \\
 &= \frac{2 \times 100}{24} \\
 &= \frac{40}{24} \\
 &= \frac{2 \times 10}{24} \\
 &= \frac{20}{24} = \frac{5}{6} \\
 &= 0.84
 \end{aligned}$$

it

$$\begin{aligned}
 \text{mole fraction of water} &= \frac{0.4}{2+0.4} \\
 &= \frac{0.4}{2.4} \\
 &= \frac{4 \times 10}{10 \times 24} \\
 &= \frac{4}{24} = \frac{1}{6} \\
 &= 0.17
 \end{aligned}$$

eg → 2.82 g of glucose is dissolved in 30g of water  
calculate the mole fraction of glucose and water.



$$\begin{aligned}
 \text{Sol.} \rightarrow \text{Moles of glucose} &= \frac{2.82}{180} \\
 &= \frac{282}{180 \times 100} \\
 &= \frac{47}{180 \times 50} \\
 &= \frac{47}{60 \times 50} \\
 &= \frac{47}{3000} \\
 &= 0.0157
 \end{aligned}$$

$$\text{Moles of water} = \frac{5}{3} = 1.67$$

$$\begin{aligned}
 \text{Mole fraction of glucose} &= \frac{0.0157}{0.0157 + 1.67} \\
 &= \frac{0.0157}{1.6857} \\
 &= \frac{157}{16857} = 0.009
 \end{aligned}$$

$$\begin{aligned}
 \text{Mole fraction of water} &= \frac{1.67}{1.6857} \\
 &= \frac{167 \times 10000}{16857 \times 100} \\
 &= \frac{167 \times 100}{16857}
 \end{aligned}$$



$$= \frac{16700}{16857}$$

$$= 0.991$$

★ Henry's law  $\rightarrow$  Henry's law explain the effect of pressure on the solubility of gas in liquid. According to this law the solubility of a gas in a liquid at a particular temperature is directly proportional to the pressure of the gas in equilibrium with solution.

If the solubility express in terms of mass and 'm' be the mass of gas dissolve in liquid then mathematical according to Henry's law

$$m \propto P$$

$$m = KP \quad \left[ \begin{array}{l} \text{where } K \text{ is constant and } P \\ \text{is pressure} \end{array} \right]$$

If the solubility express in terms of mole fraction then according to Henry's law

$$x \propto P$$

$$x = K' P$$

$$P = \frac{1}{K'} x$$

$$P = K_H x$$

where  $K_H$  is  $K'$  as Henry's constant  
 $x$  is mole fraction and  
 $P$  is partial pressure

Applications of Henry's law  $\rightarrow$

1. In the production of carbonated beverages.
2. In deep sea diving



3. At high altitudes
4. In the function of lungs

\* vapour pressure of a liquid  $\Rightarrow$  The pressure exerted by the vapours on the liquid surface in equilibrium with the liquid at a given temperature is  $\kappa$  / as vapour pressure of a liquid.

Factors on which vapour pressure depends  $\Rightarrow$

- 1> Nature of liquid  $\rightarrow$  The liquid having greater intermolecular forces have less vapour pressure and the liquid having weak intermolecular force have more vapour pressure.
- 2> Temperature  $\Rightarrow$  The vapour pressure of the liquid increases with increase in temperature.

\* When a non-volatile solute is added to a liquid its vapour pressure decreases.

\* Raoult's law  $\Rightarrow$

- A) For volatile solute and volatile solvent  
According to this law for a solution containing volatile liquids the partial vapour pressure of each component in the solution is equal to the product of the vapour pressure of that component in pure state and its mole fraction.



Let us consider a solution containing volatile liquids A and B  
Acc. to Raoult's law

$$P_A = P_A^\circ \chi_A$$

where  $P_A$  = vapour pressure of A in solution  
 $P_A^\circ$  = vapour pressure of A in pure state  
 $\chi_A$  = mole fraction of A

$$P_B = P_B^\circ \chi_B$$

$P_B$  = vapour pressure of B in solution  
 $P_B^\circ$  = vapour pressure of B in pure state  
 $\chi_B$  = mole fraction of B

$$P = P_A + P_B$$

$$= P_A^\circ \chi_A + P_B^\circ \chi_B$$

$P$  = Total vapour pressure of the solution  
 $P_A$  = vapour pressure of A in solution  
 $P_B$  = vapour pressure of B in solution

(B)

For a solution containing non-volatile solute and volatile solvent  $\rightarrow$  For a solution containing non-volatile solute and volatile solvent A

The vapour pressure of a solution  
 $P = P_A + P_B$  [  $P_A$  = vapour pressure of solvent  
 $P_B$  = vapour pressure of solute ]

Since the solute is non-volatile  
 $\therefore$  its vapour pressure = 0  
 i.e.  $P_B = 0$   
 $\therefore P = P_A$  [  $P_A = P_A^\circ \chi_A$  ]

W.K.T  $P = P_A^\circ \chi_A$



Thus for a solution containing volatile solvent and non-volatile solute. The vapour pressure of a solution is equal to the product of vapour pressure of solvent in pure state and its mole fraction.

- \* Ideal and non-ideal solutions →  
 Ideal solution → The solutions which obeys the Raoult's law at all concentrations are called ideal solutions.

∴ For ideal solutions

$$P_A = P_A^\circ \times X_A$$

$$P_B = P_B^\circ \times X_B$$

$$P = P_A + P_B$$

$$P = P_A^\circ X_A + P_B^\circ X_B$$

$P_A$ = vapour pressure of solvent
$P_B$ = vapour pressure of solute
$P_A^\circ$ = vapour pressure of solvent in pure state
$P_B^\circ$ = VP of solute in pure state
$X_A$ = mole fraction of solvent
$X_B$ = mole fraction of solute

In ideal solution →

- 1) The intermolecular interactions b/w the component in ideal solution is of same magnitude as the intermolecular interaction in pure components.
- 2) For ideal solutions  $\Delta_{\text{mixing}} H = 0$   
 i.e. there is no heat change on mixing
- 3) For ideal solution  $\Delta_{\text{mixing}} V = 0$   
 i.e. there is no volume change on mixing

Non-ideal solutions → The solutions which do not obey Raoult's law at all concentrations are called non-ideal solutions.



For non-ideal solutions

$$P_A \neq P_A^0 X_A$$

$$P_B \neq P_B^0 X_B$$

$$P \neq P_A + P_B$$

$$P \neq P_A^0 X_A + P_B^0 X_B$$

- $P_A = VP$  of solvent
- $P_B = VP$  of solute
- $P_A^0 = VP$  of solvent in pure state
- $P_B^0 = VP$  of solute in pure state
- $X_A =$  mole fraction of solvent
- $X_B =$  mole fraction of solute

For non-ideal solution

- 1) The intermolecular interaction b/w the component in non-ideal solution is of different magnitude as the intermolecular interaction in pure components.
- 2) For non ideal solution  $\Delta_{mixing} H \neq 0$
- 3) For non ideal solution  $\Delta_{mixing} V \neq 0$ .

Q. Difference b/w ideal and non-ideal sol.

Ideal solutions	Non ideal solutions
1) The solutions which obeys Raoult's law at all concentration	The solutions which do not obey Raoult's law at all concentrations.
2) The intermolecular interaction b/w the component is of same magnitude as the intermolecular interaction in pure components.	The intermolecular interaction b/w the component is of different magnitude as the intermolecular interaction in pure components.
3) $\Delta_{mixing} H = 0$	$\Delta_{mixing} H \neq 0$
4) $\Delta_{mixing} V = 0$	$\Delta_{mixing} V \neq 0$



\* Types of non-ideal solution  $\rightarrow$

There are two types of non-ideal solutions

- 1) Non-ideal solution with +ve deviation
- 2) Non-ideal solution with -ve deviation

Non-ideal solution with +ve deviation  
 when the intermolecular interaction in solutions are weak than the intermolecular interactions present in pure component.  
 Then the non-ideal solution is k/as non-ideal solution with +ve deviation.

$$\therefore P_A > P_A^0 X_A$$

$$P_B > P_B^0 X_B$$

$$P > P_A + P_B$$

For non-ideal solution with +ve deviation

$\Delta_{\text{mixing}} H$  and  $\Delta_{\text{mixing}} V$  are +ve

i.e.  $\Delta_{\text{mixing}} H > 0$

$$\Delta_{\text{mixing}} V > 0$$

Non-ideal solution with -ve deviation  
 when the intermolecular interaction in solutions are stronger than the intermolecular interaction present in pure component.  
 Then the non-ideal solution is k/as non-ideal solution with -ve deviation.

$$\therefore P_A < P_A^0 X_A$$

$$P_B < P_B^0 X_B$$

$$P < P_A + P_B$$

For nonideal solution with -ve deviation

$\Delta_{\text{mixing}} H$  and  $\Delta_{\text{mixing}} V$  is -ve

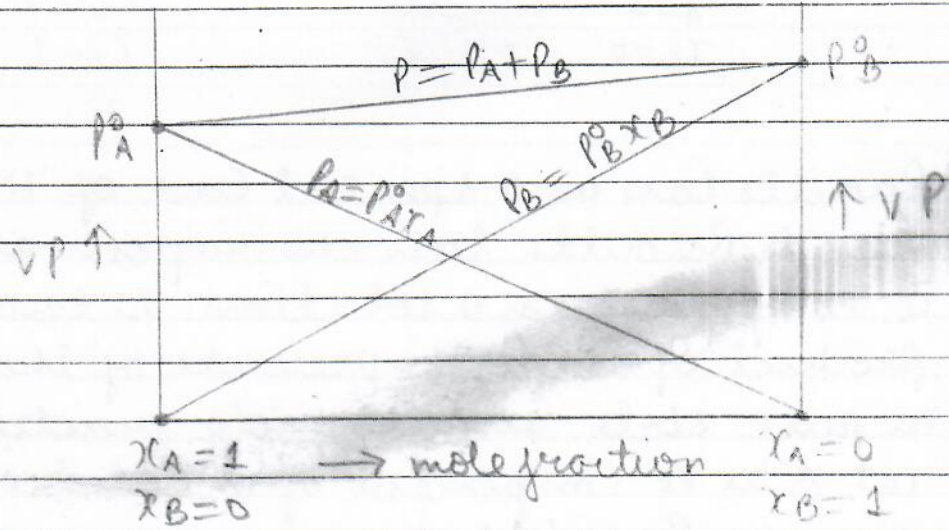
i.e.  $\Delta_{\text{mixing}} H < 0$

$$\Delta_{\text{mixing}} V < 0$$



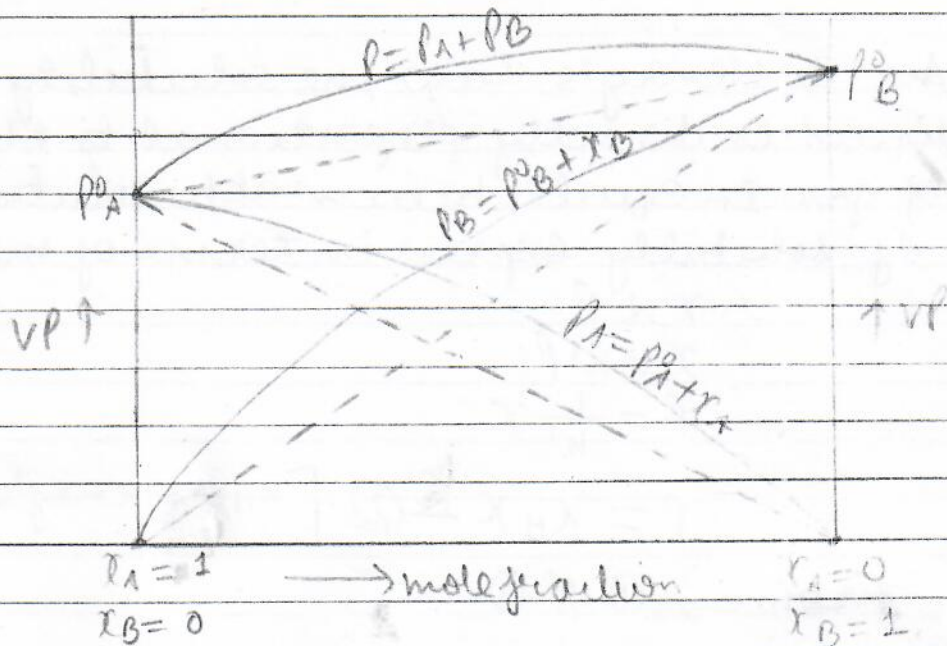
\* Graphical representation of ideal and non-ideal solutions →

Ideal solution → Graphical representation can be explain by plotting a graph b/w mole fraction and vapour pressure.



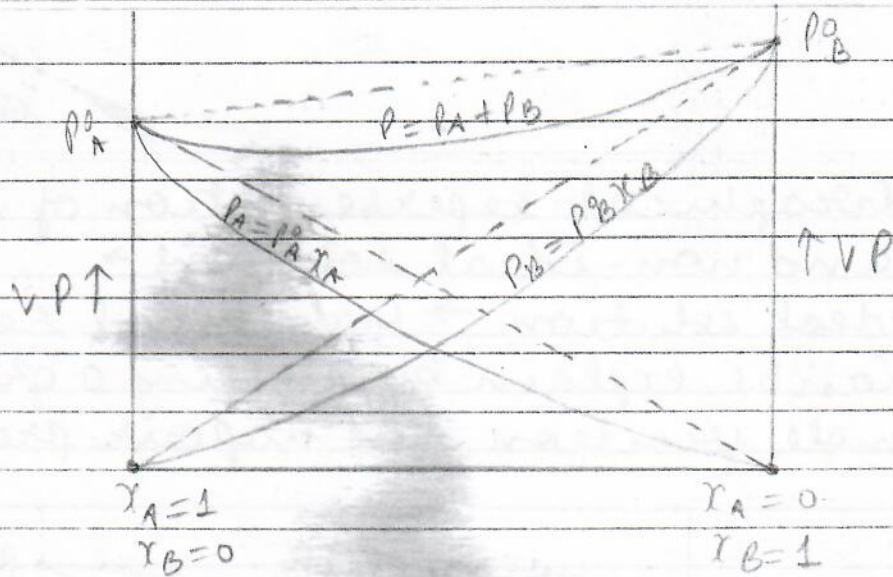
Non-ideal solution →

(A) Non ideal solution with +ve deviation



(B) Non-ideal solution with -ve deviation





\* Raoult's law as a special case of Henry's law →  
Acc. to Raoult's law the vapour pressure of a component in a solution is equal to the product of vapour pressure of that component in pure state and its mole fraction.  
Let A be a component of a solution then acc. to Raoult's law

$$P_A = P_A^0 \chi_A \quad \left[ \begin{array}{l} P_A = \text{VP of A component in sol.} \\ P_A^0 = \text{VP of A component in pure state} \\ \chi_A = \text{mole fraction of A} \end{array} \right]$$

— (1)

Acc. to Henry's law the solubility of gas in liquid is directly proportional to the pressure of gas in equilibrium with solution.

If solubility express in terms of mole fraction

$$\begin{aligned} \therefore x \propto P \\ x = k' P \\ P = \frac{1}{k'} x \end{aligned}$$

$$P = k_H x \quad \text{--- (2) } [k_H = \text{Henry's constant}]$$

From eq. (1) & (2)



We can say that Raoult's law is special case of Henry's law.

Azeotrope or Azeotropic mixture  $\rightarrow$  The liquid mixture or solution which boils at constant temperature and can be distilled unchanged in composition are called as Azeotrope or Azeotropic mixture.

\* Colligative properties  $\Rightarrow$  The properties of solution which depends only upon the number of solute particles and are independent to the nature of solute particles are called as Colligative properties.

Following are the colligative properties  $\Rightarrow$

- (1) Relative lowering of vapour pressure
- (2) Elevation in boiling point
- (3) Depression in freezing point
- (4) Osmotic pressure

Relative lowering of vapour pressure  $\rightarrow$  When a non-volatile solute is added to a volatile solvent its vapour pressure decreases. This is called as relative lowering of vapour pressure.

Let us consider a volatile solvent A and non-volatile solute B. Then acc. to Raoult's law the vapour pressure of A is equal to the vapour pressure of that component in pure state and its mole fraction



$$P_A = P_A^0 x_A \quad \left[ \begin{array}{l} P_A = \text{VP of solvent in solution} \\ P_A^0 = \text{VP of solvent in pure state} \\ x_A = \text{mole fraction of solvent} \end{array} \right]$$

$$\frac{P_A}{P_A^0} = x_A \quad \text{--- (1)}$$

Subtract on both side from 1

$$1 - \frac{P_A}{P_A^0} = 1 - x_A$$

$$\left( \frac{P_A^0 - P_A}{P_A^0} \right) = x_B$$

$$\left[ \begin{array}{l} \therefore \text{w.k.T } x_A + x_B = 1 \\ x_B = 1 - x_A \end{array} \right]$$

$\left( \frac{P_A^0 - P_A}{P_A^0} \right)$  represents relative lowering of vapour pressure.

Thus relative lowering of vapour pressure when a non-volatile solute is added to a volatile solvent is equal to the mole fraction of solute -

$\Rightarrow$  Show that relative lowering of vapour pressure is a colligative property.

Proof  $\rightarrow$  when a non volatile solute is added to a volatile solvent the relative lowering of vapour pressure is equal to the mole fraction of solute.

$$\left( \frac{P_A^0 - P_A}{P_A^0} \right) = x_B \quad \left[ \begin{array}{l} P_A = \text{VP of solvent in sol.} \\ P_A^0 = \text{VP of solvent in pure state} \\ x_A = \text{mole fraction of solvent} \end{array} \right]$$

$$\text{w.k.T } x_B = \frac{n_B}{n_A + n_B} \quad \left[ \begin{array}{l} n_A = \text{no. of moles of solvent} \\ n_B = \text{no. of moles of solute} \end{array} \right]$$

$$\therefore \frac{P_A^0 - P_A}{P_A^0} = \frac{n_B}{n_A + n_B}$$

It is clear from above equation that relative lowering of vapour pressure depends upon



number of moles of solute particles -  
∴ it is a colligative property.

⇒ Determination of molecular mass of solute using relative lowering of vapour pressure →

w.k.T relative lowering of vapour pressure is equal to the mole fraction of solute.

i.e.  $\left( \frac{P_A^0 - P_A}{P_A^0} \right) = X_B$  
 $P_A = \text{VP of solvent in sol.}$   
 $P_A^0 = \text{VP of solvent in pure state}$   
 $X_B = \text{mole fraction of solute}$

w.k.T  $X_B = \frac{n_B}{n_A + n_B}$  
 $n_A = \text{no. of moles of solvent}$   
 $n_B = \text{no. of moles of solute}$

$\frac{P_A^0 - P_A}{P_A^0} = \frac{n_B}{n_A + n_B}$  
 $\therefore \text{No. of moles} = \frac{\text{mass}}{\text{molecular mass}}$

Substituting the value of  $n_A$  and  $n_B$  in above equation =

$n_B = \frac{W_B}{M_B}$   
 $n_A = \frac{W_A}{M_A}$

$\frac{P_A^0 - P_A}{P_A^0} = \frac{\frac{W_B}{M_B}}{\frac{W_A}{M_A} + \frac{W_B}{M_B}}$

For dilute solution  
 $W_A \gg W_B$   
∴  $\frac{W_B}{M_B} \ll \frac{W_A}{M_A}$   
and can be neglected

$\frac{P_A^0 - P_A}{P_A^0} = \frac{W_B}{M_B} \times \frac{M_A}{W_A}$

$$M_B = \frac{W_B \times M_A}{\left( \frac{P_A^0 - P_A}{P_A^0} \right) W_A}$$

This equation represents the molecular mass of solute.



eg:  $\rightarrow$  The vapour pressure of pure benzene at certain temperature is 0.850 bar. A non volatile solid of weight 0.50 g is added to 39.0 g of benzene (molecular mass = 78). Then the vapour pressure of solution becomes 0.845 bar. What is the molecular mass of solid.

sol:  $\rightarrow$  Acc. to Raoult's law

$$\frac{P^{\circ}_A - P_A}{P^{\circ}_A} = X_B = \frac{W_B \times M_A}{M_B \times W_A} \quad (\text{for dilute sol.})$$

$$W_B = \frac{M_B \times (P^{\circ}_A - P_A) \times W_A}{P^{\circ}_A \times M_A}$$

$$W_B = 0.50 \text{ g}, W_A = 39.0 \text{ g}, P_A = 0.845 \text{ bar}, P^{\circ}_A = 0.850 \text{ bar}$$

$$M_A = 78$$

$$M_B = \frac{0.50 \times 78}{\left(\frac{0.850 - 0.845}{0.850}\right) \times 39.0}$$

$$= \frac{0.50 \times 78 \times 0.850}{(0.850 - 0.845) \times 39.0}$$

$$= \frac{0.50 \times 78 \times 850}{0.005 \times 39.0}$$

$$= \frac{50 \times 78 \times 850}{100 \times 5 \times 39}$$

$$= \frac{8 \times 78 \times 85}{8 \times 39}$$

$$= \frac{2170}{39}$$

$$= 170 \text{ g mol}^{-1}$$



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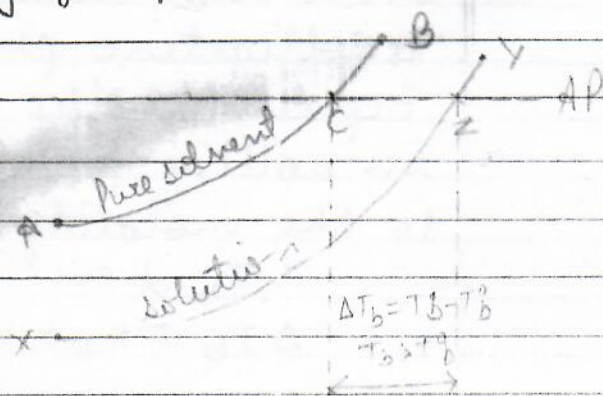
Elevation in boiling point  $\Rightarrow$

When a non-volatile solute is added to a volatile solvent its boiling point increases. This is called elevation in boiling point.

BP  $\rightarrow$  of a liquid is a temperature at which its vap becomes = the atmospheric pressure.

l.) The elevation in boiling point can be explained by plotting graph b/w VP and temperature.

In graph, AB represents vapour pressure of pure solvent. At point C the vapour pressure<sup>VP</sup> of pure solvent becomes = atmospheric pressure. Therefore, temperature correspond to C is  $T_b^0$



$T_b^0$  which is boiling point of pure solvent.

Curve XY represents vapour pressure of a solution at point Z the vapour pressure of solution becomes = atmospheric pressure.

$\therefore$  Temperature correspond to Z is  $T_b$  which is called boiling point of solution.

$$\text{As } T_b > T_b^0$$

$\therefore$  elevation in boiling point =  $\Delta T_b = T_b - T_b^0$

Experimentally it is found that elevation in boiling point is directly proportional to the molality of the solution.



Mathematically

$$\Delta T_b \propto m$$

where  $m$  is molality of solution

$$\Delta T_b = K_b m \quad \left[ \begin{array}{l} \text{where } K_b \text{ is constant and } K_b \text{ as} \\ \text{molal elevation constant or} \\ \text{ebullioscopic constant} \end{array} \right]$$

If  $m = 1$  then  $\Delta T_b = K_b$

Thus, molal elevation in boiling constant is equal to the elevation in boiling point when the molality of a solution is unity.

⇒ Show that elevation in boiling point is a colligative property -

Experimentally it is found that elevation in boiling point is directly proportional to the molality of the solution -

$$\therefore T_b \propto m$$

$$\Delta T_b = K_b m$$

where  $\Delta T_b =$  elevation in BP  
 $K_b =$  molal elevation constant  
 $m =$  molality of the solution

$$\text{W.K.T } m = \frac{\text{No. of moles of solute}}{\text{mass of solvent in gm}} \times 1000$$

$$= \frac{w_B}{w_A} \times 1000$$

On putting value of  $m$  in above equation

$$\Delta T_b = \frac{K_b \times w_B \times 1000}{w_A}$$

It is clear from above equation that elevation in boiling point depends upon number of moles of solute or number of solute particles.

∴ Elevation in boiling point is a colligative property -



⇒ Determination of ~~sol~~ molecular mass of solute from elevation in boilingpoint → Experimentally it is found that elevation in boiling point is directly proportional to the molality of solution.

$$\therefore \Delta T_b \propto m$$

$$\Delta T_b = K_b m$$

$$w \cdot K \cdot T \quad m = \frac{w_B}{w_A} \times 1000$$

On putting value of m in above equation

$$\Delta T_b = \frac{K_b \times w_B}{w_A} \times 1000$$

$$w \cdot K \cdot T \quad w_B = \frac{w_B}{M_B}$$

$$\Delta T_b = \frac{K_b \times \frac{w_B}{M_B} \times 1000}{w_A}$$

$$w_A = \frac{K_b \times \frac{w_B}{M_B} \times 1000}{\Delta T_b \times w_A}$$

eg: → 18g of glucose (molecular mass = 180) is dissolved in 1 kg of water. At what temperature will the solution boil ( $K_b$  for water = 0.52 K kg mol<sup>-1</sup>)

$$sol. \Rightarrow \Delta T_b = \frac{K_b \times w_B}{w_A \times M_B} \times 1000$$

$$w_B = 18g, w_A = 1000g, M_B = 180, K_b = 0.52$$

$$\Delta T_b = \frac{0.52 \times 18}{1000 \times 180} \times 1000$$

$$= \frac{0.52 \times 18}{100 \times 180} = \frac{13}{250} = \frac{13}{250} = 0.052 K$$

$$\Delta T_b = T_b - T_b^0$$

$$T_b = \Delta T_b + T_b^0$$



$$T_b = 0.052 + 373.15$$

$$= 373.202$$

∴ Boiling point of solution = 373.202 K

eg. → The boiling point of benzene is 353.23 K when 1.80 g of a non-volatile solute was dissolved in 90 g of benzene. The boiling point raise to 354.11 K. Calculate the molecular mass of non volatile solute. ( $K_b$  for benzene = 2.53 K kg mol<sup>-1</sup>)

Sol. →

$$T_b^0 = 353.23$$

$$w_B = 1.80$$

$$w_A = 90$$

$$T_b = 354.11$$

$$K_b = 2.53$$

$$\Delta T_b = T_b - T_b^0$$

$$= 354.11 - 353.23$$

$$= 0.88$$

$$M_B = \frac{K_b \times w_B}{\Delta T_b \times w_A \times M_B} \times 1000$$

$$= \frac{2.53 \times 1.80}{0.88 \times 90} \times 1000$$

$$= \frac{2.53 \times 1.80}{0.88 \times 90} \times 1000$$

$$= \frac{2.53 \times 1.80}{0.88 \times 90} \times 1000$$

$$= \frac{2.53}{0.44}$$

$$= 57.5 \text{ g mol}^{-1}$$



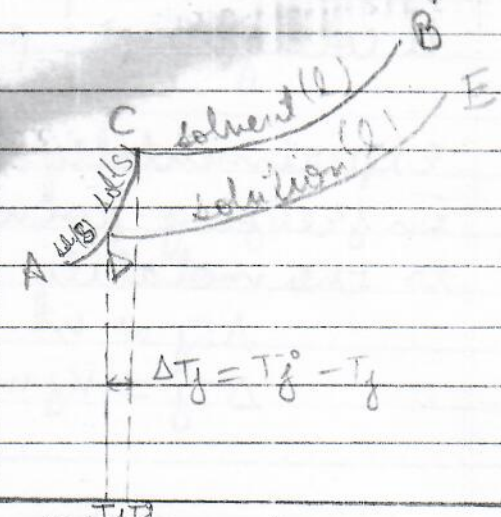
Depression in freezing point  $\Rightarrow$  when a non-volatile solute

is added to a volatile solvent its freezing point decreases. This is called depression in freezing point.

Freezing point  $\rightarrow$  The temperature at which solid and liquid state of a substance have same VP is called as freezing point.

The depression in freezing point can be explained by plotting graph between VP and temperature.

Curve AC represents the vapour pressure of pure solvent in solid state and CB represents the VP of pure solvent in liquid state. At point C the VP of solid state



and liquid state of pure solvent becomes equal. Therefore temperature corresponds to C i.e.  $T_f^0$  is called as freezing point of pure solvent.

Curve AD represents the VP of sol. in solid state and DE represents the VP of solution in liquid state. At point D the VP of solid and liquid state becomes equal.

Therefore temperature corresponds to D i.e.  $T_f$  is called as freezing point of solution.

$\therefore$  The depression in freezing point

$$\Delta T_f = T_f^0 - T_f$$



Experimentally it is found that depression in freezing point is directly proportional to the molality of solution.

$$\therefore \Delta T_f \propto m$$

$$\Delta T_f = K_f m \quad \left[ \begin{array}{l} \text{where } K_f \text{ is } K_{\text{molal depression}} \\ \text{Constant or Cryoscopic} \\ \text{Constant} \end{array} \right]$$

$$\text{If } m = 1$$

$$\Delta T_f = K_f$$

Then the molal depression constant is equal to the depression in freezing point when the molality of the solution is unity.

⇒ Show that depression in freezing point is a colligative property.

Experimentally it is found that depression in freezing point is directly proportional to the molality of solution.

$$\Delta T_f \propto m$$

$$\Delta T_f = K_f m \quad \left[ \begin{array}{l} \text{where } \Delta T_f = \text{depression in freezing point} \\ K_f = \text{Cryoscopic constant} \\ m = \text{molality of sol} \end{array} \right]$$

$$\text{W-K-T } m = \frac{\text{No. of moles of solute}}{\text{mass of solvent in g}} \times 1000$$

$$= \frac{n_B}{w_A} \times 1000 \quad \left[ \begin{array}{l} n_B = \text{no. of moles of solute} \\ w_A = \text{mass of solvent} \end{array} \right]$$

Putting the value of  $m$  in above equation

$$\Delta T_f = \frac{K_f \times n_B}{w_A} \times 1000$$

It is clear from the above equation that depression in freezing point depends upon no. of solute particles or no. of moles of solute.



∴ Depression in freezing point is a colligative property.

⇒ Determination of molecular mass of solute from depression in freezing point.  
Experimentally it is found that depression in freezing point is  $\propto$  the molality of sol.

$$\Delta T_f \propto m$$

$$\Delta T_f = K_f m$$

where  $K_f$  = Cryoscopic constant  
 $\Delta T_f$  = depression in freezing point  
 $m$  = molality of sol

$$w \cdot K \cdot T \cdot m = \frac{w_B}{w_A} \times 1000$$

$w_B$  = no. of moles of solute  
 $w_A$  = mass of solvent

Putting the value of  $m$  in above equation

$$\Delta T_f = \frac{K_f \times w_B}{w_A} \times 1000$$

$$w \cdot K \cdot T \cdot w_B = \frac{w_B}{M_B} \times w_A$$

$M_B$  = molar mass of solute  
 $w_B$  = mass of solute

$$\Delta T_f = \frac{K_f \times w_B}{w_A \times M_B} \times 1000$$

$$M_B = \frac{K_f \times w_B}{\Delta T_f \times w_A} \times 1000$$

eg: →  $100 \times \frac{w_B}{w_A}$  40.643g of a compound is added to 50ml of benzene (density =  $0.879 \text{ g ml}^{-1}$ ) lowers its freezing point from  $5.51^\circ\text{C}$  to  $5.03^\circ\text{C}$  if  $K_f$  for benzene is  $5.12 \text{ K kg mol}^{-1}$ . Calculate the molar mass of the compound.

Sol: →  
 $w_B = 40.643 \text{ g}$   
 $T_f^\circ = 5.51^\circ\text{C}$   
 $T_f = 5.03^\circ\text{C}$   
 $K_f = 5.12$



$$\text{Density} = 0.87 \text{ g/ml}$$

$$\text{volume} = 50 \text{ ml}$$

$$\text{Density} = \frac{\text{mass}}{\text{vol.}}$$

$$\text{mass} = \text{density} \times \text{vol.}$$

$$W_A = 0.879 \times 50$$

$$= 43.95 \text{ g}$$

$$\Delta T_f = T_f^\circ - T_f$$

$$= 5.51 - 5.03$$

$$= 0.48^\circ$$

$$\therefore M_B = \frac{k_f \times W_B}{\Delta T_f \times W_A} \times 1000$$

$$= \frac{512 \times 0.643 \times 1000}{43.95 \times 0.48}$$

$$= \frac{512 \times 643 \times 1000 \times 100}{4395 \times 1000 \times 48}$$

$$= 156.06$$

Q.  $\rightarrow$  45g of ethylene glycol ( $C_2H_6O_2$ ) is mixed with 600g of water. Calculate

- (i) Freezing point depression
- (ii) The freezing point of solution.  
( $k_f$  for water =  $1.86 \text{ K kg mol}^{-1}$ )

$$\begin{aligned} C_2H_6O_2 &= 12 \times 2 + 1 \times 6 + 16 \times 2 \\ &= 24 + 6 + 32 \\ &= 62 \end{aligned}$$

$$W_B = \frac{\text{mass}}{\text{molar mass}} = \frac{45}{62}$$



$$\Delta T_f = \frac{k_f \times m_B}{W_A \times M_B} \times 1000$$

$$\Delta T_f = \frac{M_B \times k_f \times m}{W_A \times M_B}$$

$$= \frac{M_B \times k_f \times m}{W_A} \times 1000$$

$$= \frac{31 \times 9}{186} \times 45 \times 1000$$

$$= \frac{100 \times 600 \times 62}{2}$$

$$= \frac{31 \times 9}{2 \times 62}$$

$$= \frac{279}{124}$$

$$= 2.25 \text{ K An.}$$

$$\Delta T_f = T_f^\circ - T_f$$

$$T_f = T_f^\circ - \Delta T_f$$

$$= 273.15 - 2.25$$

$$= 270.90 \text{ K An.}$$

- (1) Application of depression in freezing point → Anti freezing substances are used in automobiles in the countries having very cold climate. These anti freezing substances decrease the freezing point of the fuel of automobiles. Generally ethylene glycol is used as anti freezing substance.
- (2) NaCl is added on snow to clear it because NaCl lowers the freezing point of water.



Osmotic pressure  $\rightarrow$

Osmosis  $\rightarrow$  The phenomenon of flow of solvent through a semi permeable membrane from pure solvent to solution is called osmosis.

Osmotic pressure  $\rightarrow$  The excess of pressure which must be applied to the solution to prevent the passage of solvent molecules into it through a semi-permeable membrane is called osmotic pressure. It is denoted by  $\pi$

Experimentally it is found that osmotic pressure is directly proportional to  
i) molar concentration ii) Temperature

$$\pi \propto CT$$

$$\pi = RCT \left[ \begin{array}{l} \text{where } R \text{ is } \text{U} \text{ gas constant} \\ \pi = \text{osmotic pressure} \\ T = \text{temperature} \\ C = \text{molar conc.} \end{array} \right]$$

$\Rightarrow$  show that osmotic pressure is a colligative property.

Experimentally it is found that osmotic pressure is  $\propto$  the (i) molar conc. and (ii) temperature.

$$\pi \propto CT$$

$$\pi = RCT \left[ \begin{array}{l} \text{where } \pi = \text{osmotic pressure} \\ R = \text{gas constant} \\ C = \text{molar conc.} \\ T = \text{temperature} \end{array} \right]$$

w.k - T molar concentration (C)

$$= \frac{\text{no. of moles of solute}}{\text{vol. of sol.}} = \frac{nB}{V}$$



on putting value of  $C$  in above equation

$$\pi = R \frac{n_B}{V} T$$

It is clear from above equation that osmotic pressure depends upon the no. of moles of solute or no. of solute particles  
 $\therefore$  Osmotic pressure is a colligative property

$\Rightarrow$  Determination of molecular mass of solute from osmotic pressure  $\rightarrow$

$$w \cdot k \cdot T \quad \pi \quad \& \quad C \quad T$$

$$\pi = RCT$$

where  $R$  = gas constant  
 $C$  = molar conc.  
 $T$  = temperature  
 $\pi$  = osmotic pressure

$$C = \frac{n_B}{V} \left[ \begin{array}{l} n_B = \text{no. of moles of solute} \\ V = \text{vol. of sol.} \end{array} \right]$$

$$\pi = R \frac{n_B}{V} T$$

$$w \cdot k \cdot T \quad n_B = \frac{w_B}{M_B} \left[ \begin{array}{l} w_B = \text{mass of solute} \\ M_B = \text{molar mass of solute} \end{array} \right]$$

$$\pi = R \frac{w_B}{M_B V} T$$

$$M_B = R \frac{w_B}{\pi V} T$$

\* Isotonic solutions  $\rightarrow$  The solutions having same conc. osmotic pressure are called isotonic solutions.

OR

Solutions having same molar concentration and temperature are called isotonic solutions.



Experimental determination of osmotic pressure  $\rightarrow$  Osmotic pressure can experimentally determined by Berkeley's Hartley method.

This method is based on the principle of that external pressure is applied on the solution to prevent the flow of solvent towards solution i.e. osmosis.

The apparatus consists of a porous pot which act as a semi permeable membrane. This porous pot is fitted with capillary tube at one end and water reservoir at other end. This porous pot contains water.

This porous pot is fitted in a bronze cylinder fitted with piston and pressure gauge containing solution.

This water from porous pot moves to the bronze cylinder and the level of water in capillary tube decreases. In order to maintain the level of water in capillary tube, pressure has to be applied on the piston. The pressure applied on the piston can be determine by pressure gauge. This pressure is the osmotic pressure of the solution.

\* vant Hoff's factor  $\rightarrow$  when a solute is dissolve in a solvent the extent of association and dissonation of solute in solution can be determine by a term  $i$  as vant Hoff's factor.



van't Hoff factor is the ratio of observed value of colligative property and to the normal value of colligative property. It is denoted by  $i$ .

$$i = \frac{\text{observed value of colligative property}}{\text{Normal value of colligative property}}$$

I case

If neither ~~is~~ association nor dissociation occurs then  $i = 1$

II case

For association,  $i < 1$

III case

For dissociation,  $i > 1$

In terms of molar mass

$$i = \frac{\text{Normal value of molar mass}}{\text{observed value of molar mass}}$$