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STUDY COURSE MATERIAL
CHEMISTRY
SESSION-2020-21
CLASS-XII

DAY-1

❖ TEACING MATERIAL

Solutions vapour pressure, Raoult's Law, molecular weight determination from lowering of vapour pressure, elevation of boiling point and depression of freezing point, surface tension and viscosity. Surface chemistry: Elementary concepts in adsorption, colloids, emulsions, surfactants and miscelles (definition and examples only).

Introduction: -

A solution is a homogeneous mixture of the (or more) substances, the composition of which may vary between certain limits.

The component which is present in large quantity is called solvent and the component which's small in quantity is called solute.

A solution consist of two components is called binary solution.

Methods of expressing the strength of solution :-

Mass percentage : It may be defined as number of parts by mass of solute per hundred parts by mass of solution

Mass percentage $\dfrac{wt.to\ solute}{wt\ of\ solution}\times 100$

Volume percentage : It may be defined as number of parts by volume of solute per hundred parts by volume of solution.

Volume percentage $=\dfrac{Volume\ of\ solute}{Volume\ of\ Solution}\times 100$

Molality: Molality of a solution is defined as the number of moles of solute dissolved in 1kg of the solvent.

$$m=\dfrac{no.\ of\ moles\ of\ solute}{weight\ of\ solvent\ (in\ kg)}$$

Molarity: The molarity of a solution gives the number of gram molecules of the solute present in one litre of the solution. Thus, if one gram molecule of a solute is present in 1 litre of the solution, the concentration of the solution is said to be one molar.

$$M = \frac{no.\ of\ moles\ of\ solute}{volume\ of\ solution\ in\ lit}$$

Normality : The normality of a solution gives the number of gram equivalents of the solute present in one litre of the solution, thus, if the one gram equivalent of a solute is present in one litre of the solution, the concentration of the solution is said o be one normal.

$$N = \frac{no.\ of\ gm\ eqivalents\ of\ solute}{volume\ of\ solution\ (in\ lit)}$$

Mole fraction : The mole fraction of any component in a solution is the ratio of the number of moles of that component to the total number of moles of all components present in the solution

$$X_{solute} = \frac{n}{n+N}\ and\ X_{solvent} = \frac{N}{n+N}$$ n = moles of solute and N = moles of solvent.

Note: sum of the mole fractions of all the components in the solution is equal to unity.

Illustration 1: **A solution of ethanol in water is 10% by volume. If the solution and pure ethanol have densities of 0.9866 g/cc and 0.785 g/cc respectively, find the per cent by weight**

Solution:

Volume of ethanol = 1 ml; vol. of solution = 100 ml.

Weight of ethanol = Volume $\times$ Density

$= 10 \times 0.785 = 7.85\ g$

Weight of solution $= 100 \times 09866 = 98.66\ g$

$\therefore$ Weight per cent $= \dfrac{7.85}{98.66} \times 100$

$= \mathbf{7.95\%}$

Illustration 2: **5 g of NaCl is dissolved in 1000 g of water. If the density of the resulting solution is 0.997 g per cc, calculate molality, morality, normality and mole fraction of the solute.**

Solution:

Mole of NaCl $= \dfrac{5}{58.5} = 0.0854\ (Mol.\ wt.\ of\ NaCl = 58.5)$

Molality $= \dfrac{Moles}{Wt.of\ solvent\ in\ gram} \times 1000$

$= \dfrac{0.0854}{1000} \times 1000 = 0.0854\ m$

Volume of the solution $= \dfrac{Wt.in\ gram}{Density\ in\ gram/cc} = \dfrac{1005}{0.997}\ cc$

Again by definition

Molarity $= \dfrac{Moles}{Volume\ of\ solution\ in\ litre}$

$= \dfrac{0.0854}{1.008} = \mathbf{0.085M}$

$\therefore$ Normality $= 0.085\ N\ (for\ NaCl.\ eq.\ wt. = mol.\ wt.)$

Further, mole of $H_2O = \dfrac{1000}{18} = 55.55$

(1000 gram of water = 1000 ml of water, because density = 1 g/cc)

Total mole = Mole of NaCl + Mole of H_2O

$= 0854 + 55.55 = 55.6409$

$$\text{Mole fraction of NaCl} = \frac{Moles\ of\ NaCl}{Total\ moles} = \frac{0.0854}{55.6409} = \mathbf{1.53 \times 10^{-3}}$$

❖ CLASSROOM PRACTICE PAPER

1. Calculate mole fractions of urea and water if 2.0 g of urea is dissolved in 31.4 g of aqueous solution.

2. Calculate mole fraction of solute in an aqueous 4 *m* solution assuming the density of the solution as 1.0 g/ mL.

3. The molarity and molality of a solution are M and *m* respectively. If the molecular weight of the solute is M´, calculate the density of the solution in terms of M, *m* and M´.

4. When 400 g of a 20% solution was cooled, 50 g of the solute precipitated. What is the per cent concentration of the remaining solution?

5. 1 g of NaCl is dissolved in 10 g of a solution, the density of which is 1.07 g/cc. Find the molality and molarity of NaCl.

6. Calculate the molarity of water.

7. Calculate the molality and molarity of a solution of ethanol in water if the mole fraction of ethanol is 0.05 and the density of solution is 0.997 g/cc.

❖ VIDEO-LINKS

https://youtu.be/Dza81cr_-Ko

❖ PPT LINKS

https://www.slideshare.net/mobile/HoneyJeanDuvidoo/chemistry-of-solutions-9267874

❖ TEACING MATERIAL

Vapour pressure of Solution

Consider a pure liquid in a breaker is covered with a jar. Some molecules of the liquid surface evaporate and fill the vacant space available to them. The molecules in the vapour phase move randomly in the vacant space, during this motion, they strike the surface of the liquid and condensed. This process of evaporation and condensation. The pressure exerted by vapour over the liquid surface at equilibrium is called vapour pressure of the liquid

If solute is non volatile solid or liquid the vapour pressure of solution is equal to partial vapour pressure of solvent in the solution and if the solute is volatile solid or liquid, then vapour pressure will be equal to the sum of partial vapour pressure of solute and that of solvent.

Raoult's Law

This law is applied for a solution of liquid in liquids and can be stated as follows.
"The partial vapour pressure of any component in the solution is directly proportional to its mole fraction".
$P_A \propto X_A$ Where, P_A = Partial vapour pressure of A

$P_A = KX_A$ $\qquad\qquad\qquad$ X_A = Mole fraction of A in solution

For pure liquids $X_A = 1$

Then $K = P_A^0$ where P_A^0 is the vapour pressure of component A in the pure state

Hence, $P_A = X_A P_A^0$

Similarly for component B, $P_B = X_B P_B^0$

Raoult's Law in combination with Dalton's Law of Partial Pressure

Assuming that vapours of a liquid is behaving like an ideal gas, then according to Dalton's law of partial pressure the total pressure P_T is given by

$P_T = P_A + P_B$

$or\ P_T = X_A P_A^\circ + X_B P_B^\circ = P_B^\circ + \left(P_A^\circ - P_B^\circ \right) X_A$

$[\because X_B = 1 - X_A]$

Illustration 3:   **The vapour pressure of ethanol and methanol are 44.5 mm and 88.7 mm Hg respectively An ideal solution is formed at the same temperature by mixing 60 g of ethanol with 40g of methanol. Calculate total vapour pressure of the solution.**

Solution.   Number of moles of ethanol $= \dfrac{60}{40} = 1.5$

                       Number of moles of methanol $= \dfrac{40}{32} = 1.25$

                       $X_A = \dfrac{1.25}{1.25 + 1.3} = 0.4545$,

$$X_B = 1 - 0.4545$$

$$= 0.545$$

$$Let\ A = CH_3OH$$

$$B = C_2H_5OH$$

Total pressure of the solution

$$P_T = X_A P_A^o + X_B P_B^o$$

$$P_T = X_A P_A^o + X_B P_B^o$$

$$= 0.4545 \times 88.7 + 0.545 \times 44.5$$

$$= 40.31 + 24.27$$

$$= \mathbf{64.58\,mm\ 49}$$

Composition of the Vapour

The composition of the liquid and vapour that are in mutual equilibrium are not necessarily the same, the common sense suggest that the vapour pressure should be richer in the more volatile component. This expectation can be confirmed as follows: Let the mole fractions of A and B in vapour phase is Y_A and Y_B then from Dalton's law,

$$Y_A = \frac{P_A}{P_T} \ldots\ldots\ldots\ldots\ldots\ldots \ (1)$$

and $Y_B = \dfrac{P_B}{P_T} \ldots\ldots\ldots\ldots\ldots . \ (2)$

Provided the mixture of vapours behaves as an ideal gas   Rewriting equation (1)

$$Y_A = \frac{X_A P_A^0}{P_B^0 + \left(P_A^0 - P_B^0\right) X_A} \quad \text{and,} \quad Y_B = 1 - Y_A$$

Illustration 4:   **What is the composition of the vapour which is in equilibrium at 30ºC with a benzene-toluene solution with fraction of benzene of 0.400?**

$$\left(P_b^o = 119\ torr\ and\ P_t^o = 37.0\,torr\right)$$

Solution: Total pressure of the solution is given by $P_T = X_b P_b^o + X_t^o P_t^o$

$$= 0.4 \times 119 + 0.6 \times 37 = 47.6 + 22.2$$

$$= 69.8\ torr$$

Applying Dalton's law for mole fraction is vapour phase

$$Y_b = \frac{P_b}{P_T} = \frac{47.6}{62.4} = 0.763 \qquad Y_t = 1 - 0.763 = 0.237$$

Composition of Vapours of Solution

When the vapours of solution (containing liquids A and B) is condensed, the compositions of liquids A and B in the condensate remains same. The vapours over condensate can again recondense and composition of A and B in condensate (2) remains same as it was in vapour phase over condensate (1).

Vapour, Liquid, Solution, Condensate (1), Condensate (2)
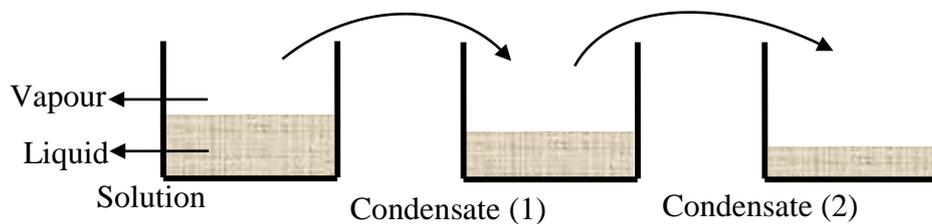
Illustration 5: **Liquids A and B form an ideal solution. The vapour pressure of A and B at 100°C are 300 and 100mm Hg respectively. Suppose that vapour above solution is composed of 1 mole of A and 1 mole of B is collected and condensed. This condensate is then heated at 100°C and vapours are again condensed to from a liquid L. What is the mole fraction of A in the vapour of L?**

Solution: Vapour pressure due to vapours above solution

$$P_T = X_A P_A^o + X_B P_B^o, P_T = 300 X_A + 100 X_B$$

It is given that in vapour phase each of A and B are one mole each hence each of ten have mole fraction 0.5 in vapour phase

$$0.5 = \frac{300 X_A}{P_T} \text{------------------ (1)}$$

$$0.5 = \frac{100 X_B}{P_T} \text{------------------ (2)}$$

and $X_A + X_B = 1$ --------------- (3)

Solving equation (1), (2) and (3), we get

$X_A = 0.25$ and $X_B = 0.75$

$$P_T = 300 \times 0.25 + 100 \times 0.75 = 75 + 75 = 150 mm$$

After condensation of vapours in condensate (1)

$X'_A = 0.5, \ X'_B = 0.5$

$$P'_T = 0.5 \times 300 + 0.5 \times 100$$

$$= 150 + 50 = 200 mm$$

Mole fraction of A & B in vapour phase of condensate

$$Y'_A = \frac{P_A}{P'_T} = \frac{150}{200} = 0.75$$

$$Y'_B = 1 - 0.75 = 0.25$$

When the vapours of the condensate (1) will again be vapourised in condensate (2) liquid L

$X_A'' = 0.75 \quad X_B'' = 0.25$, where X_A'' and X_B'' are mole fraction of A and B in liquid L

$$P_T'' = 300 \times 0.75 + 100 \times 0.25 = 225 + 25 = 250 mm$$

And mole fraction of A in vapour phase of the condensate (2) is given by

$$Y_A'' = \frac{225}{250} = \textbf{0.9}$$

1. The vapour pressure of benzene at 25°C is 639.7 mm of Hg and the vapour pressure of solution of a solute in benzene at the same temperature is 631.9 mm of mercury. Calculate the molality of the solution.

2. The vapour pressure of pure benzene at a certain temperature is 640 mmHg. A nonvolatile non-electrolyte solid weighing 2.175 g is added to 39 g of benzene. The vapour pressure of the solution is 600 mmHg. What is the molecular weight of the solid substance?

3. The vapour pressure of a dilute solution of glucose ($C_6H_{12}O_6$) is 750 mm of Hg at 373 K. Calculate (i) molality, and (ii) mole fraction of the solute.

4. The vapour pressure of pure benzene at 88°C is 957 mm and that of toluene at the same temperature is 379.5 mm. Calculate the composition of a benzene – toluene mixture boiling at 88°C.

5. Benzene and toluene form an ideal solution. The vapour pressure of benzene and toluene and respectively 75 mm and 22 mm at 20°C. If the mole fractions of benzene and toluene in vapour are 0.63 and 0.37 respectively, calculate the vapour pressure of the ideal mixture.

6. Benzene and toluene form nearly ideal solutions. If at 300 K, $p_{toluene}^0 = 32.06$ mm and $p_{benzene}^0 = 103.01$ mm.
   (a) Calculate the vapour pressure of a solution containing 0.6 molefraction of toluene.
   (b) Calculate the mole fraction of toluene in the vapour for this composition of liquid.

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❖ **PPT LINKS**

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DAY-3

❖ **TEACING MATERIAL**

Ideal and Non-Ideal Solution

The solutions which obey Raoult's law at all compositions of solute in solvent temperature are called **ideal solution.**

Ideal solutions can be obtained by mixing two components with identical molecular size, structure and should have almost same inter molecular attraction e.g., two liquids A and B form an ideal solution when A-A and B-B molecular attractions will be same and hence A-B molecular attraction will be almost same as A-A and B-B molecular attraction.

An ideal solution should have following characteristics

1.   It should obey Raoult's law i.e., $P_A = X_A P_A^o$ and $P_B = X_B P_B^o$

2. $\Delta H_{mixing} = 0$, i.e. no heat should be absorbed or evolved during mixing

3. $\Delta V_{mixing} = 0$, i.e. = no expansion or contraction on mixing

Examples of heat ideal solutions

(i)   Ethyl chloride and ethyl bromide

(ii)   n-hexane and n-heptane

(iii) CCl_4 and $SiCl_4$

The solutions which deviate from ideal behaviour are called **non ideal solution** or **real solution** and they do not obey Raoult's law over entire range of composition. It has been found that increasing dilution, a non ideal solution tend to be ideal.

For non ideal solutions,

(i) $P_A \neq X_A P_A^o$, $P_B \neq X_B P_B^o$ i.e, they do not obey Raoult's law

(ii) $\Delta H_{mixing} \neq 0$

(iii) $\Delta V_{mixing} \neq 0$

Here we may have two cases

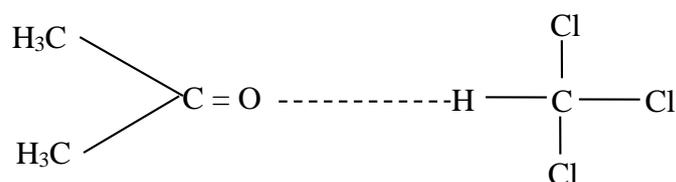**(A)**   When (i) $\begin{array}{c} P_A > X_A P_A^o \\ P_B > X_B P_B^o \end{array}$

(ii) $\Delta H_{mix} > 0$

(iii) $\Delta V_{mix} > 0$

Such a solution show positive deviation from Raoult's Law and the observed boiling point of such solutions is found to be less than the calculated value. e.g. cyclohexane and ethanol. In ethanol the molecules are held together due to hydrogen bonding, when cyclohexane is added to ethanol the molecules of cyclohexane tend to occupy the space between ethanol molecules due to which some hydrogen bonds break due to which molecular attraction between cyclohexane and ethanol is reduced and hence show higher vapour pressure.

$$H_5C_2\!-\!\overset{\displaystyle H}{\underset{}{O}}\cdots H\!-\!\underset{\displaystyle C_2H_5}{O}\cdots\cdots H\!-\!O\!-\!C_2H_5$$
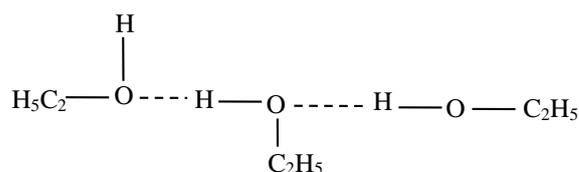
(B)   (i) $P_A < X_A P_A^o$, $P_B < X_B P_B^o$

(ii) $\Delta H_{mix} < 0$

(iii) $\Delta V_{mix} < 0$

Solution of above two show negative deviation from Raoult's law and their observed boiling point is found to be higher than the calculate value e.g. When acetone and chloroform are mixed together a hydrogen bond is formed between them which increases inter molecular attraction between them and hence decreases the vapour pressure.

$$H_3C \diagdown$$
$$\qquad C = O \text{-----------} H \text{---} \overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}} \text{---} Cl$$
$$H_3C \diagup$$

1. Which pair will show positive and negative deviation from Raoult's Law.

   (a) Methanal and Chloroform   (b) Methanol and Cyclopentane

2. Cyclohexane and ethanol at a particular at a particular temperature have vapour pressure of 280 nm and 168 nm respectively. If these two solutions having mole fraction value of cyclohexane equal to 0.32 are mixed and the mixture has a total vapour pressure of 376 nm, will the mixture be an ideal solution?

Colligative Properties:

The properties of dilute solutions which depend only on number particle of solute present in the solution and not on their identity are called **Colligative properties** (denoting depending upon collection).

We shell assume here that the solute is non volatile, so it does not contribute to the vapour. We shell also assume that the solute does not dissolve in solid solvent, that is the pure solid solvent separates when the solution is frozen, the latter assumption is quit drastic, although it is true of many mixture, it can be avoided.

Colligate properties are the properties are the properties of only dilute solution which are supposed behave as ideal solutions. The various Colligativ properties are:

1.   Lowering of vapour pressure
2.   Osmotic pressure
3.   Elevation of boiling point
4.   Depression of freezing point

Lowering of Vapour Pressure by a Non -Volatile Solute

It has been known for a long time that when non volatile solute is dissolved in a liquid, the vapour pressure of the solution become lower than the vapour pressure of the pure solvent. In 1886, the French chemist, Francois Raoult, after a series of experiments on a number of solvents including water, benzene and ether, succeeded in establishing a relationship between the lowering of vapour pressure of a solution and the mole fraction of the non-volatile solute.

Let us consider a solution obtained by dissolving n moles of a non volatile solute in N moles of a volatile solvent. Then mole fraction of the solvent $X_1 = N/(n+N)$ and mole fraction of the solute $X_2 = N/(n+N)$.

Since the solute is non-volatile, it would negligible vapour pressure. The vapour pressure of the solution is, therefore merely the vapour pressure of the solvent. According to Raoult's law, the vapour pressure of a solvent (p_1) in an ideal solution is given by the expression;

$$P_1 = X_1 P_1^0 \quad \ldots\ldots\ldots\ldots\ldots (1)$$

Where P_1^o is the vapour pressure of the pure solvent. Since $X_4 + X_2 = 1$, Eq. 1 may be written as

$$P_1 = (1 - X_2) P_1^o \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

or $P_1 / P_1^o = 1 - X_2$ $\qquad$ or $\dfrac{P_1^o - P_1}{P_1^o} = X_2 \quad \ldots\ldots\ldots\ldots\ldots (3)$

The expression on the left hand side of Equation (3) is usually called the relative of lowering vapour pressure. Equation (3) may thus be stated as: '**The relative lowering of vapour pressure of a solution containing a non-volatile solute is equal to the mole fraction of the solute present in the solution.**

This is one of the statements of the **Raoult's law'.**

Since mole fraction of the solute, x_2 is given by $n/(N+n)$, Equation (3) may be expressed as

$$\frac{P_1^o - P_1}{P_1^o} = \frac{n}{N+n} \quad \ldots\ldots\ldots\ldots.. (4)$$

It is evident Equation (4) that the lowering of vapour pressure of a solution depends upon the number of moles (and hence on the number of molecules) of the solute and not upon the nature of the solute dissolved in a given amount of the solvent. Hence, lowering of vapour pressure is a Colligative property.

Determination of Molar Masses from Lowering of vapour Pressure

It is possible to calculate molar masses of non-volatile non-electrolytic solutes by measuring vapour pressure of their dilute solutions.

Suppose a given mass, w gram, of a solute of molar mass m, dissolved in W gram solvent of mass M, lowers the vapour pressure from P_1^o to P_1. Then, by Equation (4)

$$\frac{P_1^o - P_1}{P_1^o} = \frac{n}{N+n} = \frac{w/m}{W/M + w/m} \quad \ldots\ldots\ldots\ldots\ldots.. (5)$$

Since in dilute solutions, n is very small as compound to N, Equation (5) may be put in the approximate form as

$$\frac{P_1^o - P_1}{P_1^o} = \frac{n}{N} = \frac{w/m}{W/M} = \frac{wM}{Wm} \quad \ldots\ldots\ldots\ldots.. (6)$$

or $m = \dfrac{wM}{W(P_1^o - P_1)/P_1^o}$

- **Limitations of Raoult's Law**

(i)   Raoult's law is applicable only to very dilute solutions.

(ii)   It is applicable to solutions containing nonvolatile solute only.

(iii)   it is not applicable to solutes which dissociate or associate in a particular solution.

Illustration 6: $\qquad$ **The density of 0.438 M solution of potassium chromate at 298 K is 1.063g cm^{-3}. Calculate the vapour pressure of water above this solution. Given : $P°(water) = 23.78\,mm$ Hg.**

Solution: A solution of 0.438 M means 0.438 mol of K_2CrO_4 is present in 1 L of the solution. Now,

Mass of K_2CrO_4 dissolved per litre of the solution $= 0.438 \times 194 = 84.972 g$

(Mass of 1L of solution $= 1000 \times 1.063 = 1063 g$)

Amount of water in 1L of solution $= \dfrac{978.028}{18} = 54.355 mol$

Assuming K_2CrO_4 to be completely dissociated in the solution, we will have;

Amount of total solute species in the solution $= 3 \times 0.438 = 1.314 mol$.

Mole fraction of water solution

$= \dfrac{54.355}{54.355 + 1.314} = 0.976$

Finally, Vapour pressure of water above solution

$= 0.976 \times 23.79 = \textbf{23.22mm Hg}$

❖ CLASSROOM PRACTICE PAPER

3. The vapour pressure of dilute solution of glucose $\left(C_6H_{12}O_6\right)$ is 750 nm Hg at 373 K. Calculate (i) molality and (ii) mole fraction of the solute.

4. Two liquids A and B form an ideal solution. At 300 K, the vapour pressure of a solution containing 1 mole of A and 3 moles of B is 550 mm of Hg. At the same temperature, if one mole of B is added to this solution, the vapour pressure of the solution increases by 10 mm of Hg. Determine the vapour pressure of A and B in their pure states.

5. What is the vapour pressure at 100°C of a solution containing 15.6 g of water and 1.68 g of sucrose $(C_{12}H_{22}O_{11})$?

❖ VIDEO-LINKS

https://youtu.be/eW7oHXd_ig8

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DAY-4

❖ TEACING MATERIAL

Boiling Point Elevation by a Non-Volatile Solute

The boiling point of a liquid is the temperature at which its vapour pressure becomes equal to 760mm (i.e. 1 atmospheric pressure). Since the addition of a non-volatile solute lowers the vapour pressure of the solvent, the vapour pressure of a solution is always lower than that of the pure solvent, and hence it must be heated to a higher temperature to make its vapour than the pure solvent. If T_b^o is the boiling point of the solvent and T_b is the boiling point of the solution, the difference in boiling points $\left(\Delta T_b\right)$ is called the **elevation of boiling point.**

Thus, $T_b - T_b^{\circ} = \Delta T_b$.

$\Delta T_b \; \alpha$ molality where ΔT_b = elevation of boiling point

n = no. of moles of non-volatile solute

N = Total no. of moles in the solution

This implies that the boiling point elevation in a dilute solution is directly proportional to the number of moles of the solute dissolved in a given amount of the solvent and is quit independent of the nature of the solute. Hence boiling point elevation is a Colligative property.
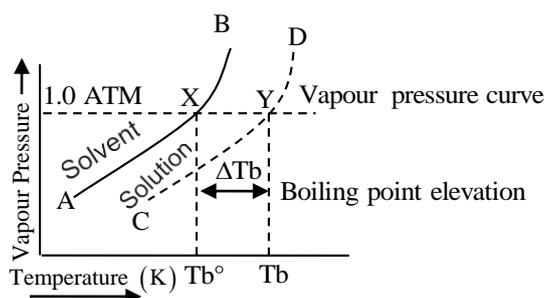
$\Delta T_b = K_b \times m$ k_b : molal elevation constant or Ebullioscopic constant

m: molality of the solution

<mark>Molal boiling point elevation constant or ebullioscopic constant</mark> of the solvent is defined as the elevation in boiling which may theoretically be produced by dissolving one mole of any solute in 1000g of the solvent.

Or $\Delta T_b = \dfrac{1000 \times K_b \times w}{m_1 \times W}$, where m_1 = molecular weight of solute and w and W are weights of solute and solvent.

Illustration 8: **A certain non-volatile non-electrolyte contains 40.0% carbon, 6.71% hydrogen and 53.3% oxygen. An aqueous solution containing 5% by mass of the solute boils at 100.15°C. $K_b\left(water\right) = 0.512K \; kg \; mol^{-1}$.**

Solution: First of all, we compute the empirical formula of the compound as shown in the following:

Element	%	Mass taken	No. of moles of element	Simple ratio
C	40	40g	$\dfrac{40}{12} = 3.33$	$\dfrac{3.33}{3.33} = 1$
H	6.7	6.7g	$\dfrac{6.7}{1} = 6.7$	$\dfrac{6.7}{3.33} = 2$
O	53.3	53.3g	$\dfrac{53.3}{16} = 3.33$	$\dfrac{3.33}{3.33} = 1$

Hence the empirical formula is CH_2O. Empirical formula mass $= 30g \ mol^{-1}$. Mass of solute = 5 g, mass of solvent $= 100 - 5 = 95g$

$$M = \frac{K_b}{\Delta T_b} \times \frac{m_2}{m_1} = \left[\frac{0.512 kgmol^{-1}}{0.15K}\right]\left[\frac{5g}{95g}\right] = 0.180 kgmol^{-1} = 180 \ g \ mol^{-1}$$

Let the molecular formula is $(CH_2O)_x$ $\qquad x = \dfrac{Molar \ mass}{Empirical \ mass} = \dfrac{180}{30} = 6$

Hence molecular formula $= \mathbf{C_6H_{12}O_6}$.

Depression of Freezing point by a Non-Volatile Solute

Freezing point is the temperature at which solid states of substance have the same vapour pressure. It is observed that the freezing point of the solution (T) containing non volatile solute is always less than the freezing point of the pure solvent (T_f^o). Thus

$$T_f^o - T_f = \Delta T_f$$

It can be seen that

$\Delta T_f \propto$ molality

That is freezing point depression of a dilute solution is directly proportional to the number of moles of the solute dissolved in a given amount of the solvent and is independent of the nature of solute or $\Delta T_f = K_f m$

k_f : molal freezing point depression constant of the solvent or cryoscopic constant m: molality of the solution

Molal freezing point depression constant of the solvent or cryoscopic constant, is defined as the depression in freezing point which may theoretically be produced by dissolving 1 mole of any solute in 1000g of the solvent

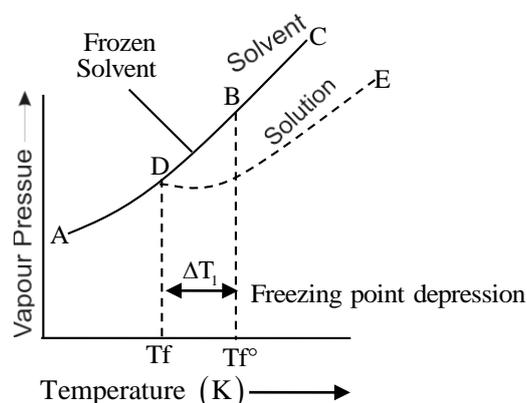or $\Delta T_f = \dfrac{1000 \times K_f \times w}{m_1 \times W}$

Where $m_1 = $ molecular weight of solute and w and W are weights of solute and solvent.

Illustration 9: **An aqueous solution containing 0.25 g of a solute dissolved in 20g of water freezing at –0.4ºC. Calculate the molar mass of the solute.** $K_f = 1.86 \ K \ kg \ mol^{-1}$.

Sol. $\Delta T_f = K_f \times m$

$$M = \frac{K_f \times w \times 1000}{wW \times \Delta T} = \frac{1.86 \times 0.25 \times 1000}{20 \times 0.42} = \mathbf{55.35 g/mol}$$

❖ CLASSROOM PRACTICE PAPER

1. If for a particular solution, $\Delta T_f = 0.73^o, K_f = 5.028 K.molality^{-1}$, what is the molality of the solution.

2. 2 g of benzoic acid, dissolved in 25 g of benzene, produces a freezing – point depression of 1.62°. Calculate the molecular weight. Compare this with the molecular weight obtained from the formula for benzoic acid, C_6H_5COOH. ($K_f = 4.90$)

3. What is the weight of 1 mole of a solute, 0.132 g of which in 29.7 g of benzene, gave a freezing – point depression of 0.108°C? (K_f for benzene = 5.12)

4. K_f for water is 1.86°C. m^{-1}. What is the molality of a solution which freezes at –0.192°C? Assuming no change in the solute by raising the temperature, at what temperature will the solution boil?

   (K_b for H_2O = 0.515°C. m^{-1})

❖ VIDEO-LINKS

https://youtu.be/Dza81cr_-Ko

❖ PPT LINKS

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DAY-5

❖ TEACING MATERIAL

Osmosis and Osmotic Pressure

The phenomenon of the passage of pure solvent from a region of lower concentration (of the solution) to a region of its higher concentration through a semi-permeable membrane is called **osmosis.**

The driving force of osmosis is what is known as osmotic pressure. It is the difference the pressure between the solution and the solvent system or it is excess pressure which must be applied to a solution in order to prevent flow of solvent into the solution through the semi-permeable membrane. Once osmosis is complete the pressure exerted by the solution and the solvent on the semi-permeable membrane is same.
Van't Hoff equation for dilute solutions is (parallel to ideal gas equation)
$\pi V = nRT$
Where π = Osmotic pressure
V = volume of solution
n = no. of moles of solute that is dissolved
R = Gas constant
T = Absolute temperature

Isotonic Solutions

A pair of solutions having same osomotic pressures a called lsotonic solutions.
For isotonic solution, $\pi_1 = \pi_2$ (Primary condition)
Also,

$$\left.\begin{array}{l} C_1 = C_2 \\[2mm] \text{or } \dfrac{n_1}{v_1} = \dfrac{n_2}{v_2} \\[3mm] \text{or } \dfrac{w_1}{m_1 v_1} = \dfrac{w_2}{m_2 v_2} \end{array}\right\} \text{Secondary condition}$$

Illustration10: **Calculate the osmotic pressure of sucrose solution containing 1.75 gms in 150 ml of solution at 17°C.**

Solution: We know that

$$\pi V = nRT = \frac{W_B}{m_B} RT$$

$$\frac{W_B}{m_B} RT$$

$$\pi \times 0.15 = \frac{1.75}{342} \times 0.0821 \times 290$$

$$\pi = 0.812 \, \text{atm}$$

❖ CLASSROOM PRACTICE PAPER

1. A 5% solution (wt. /mol) of cane sugar is isotonic with 0.877% (wt/vol) of urea solution. Find m wt. of urea if the m.wt of sugar is 342.

2. Calculate the osmotic pressure of a decinormal solution of cane sugar at 0°C.

3. An aqueous solution contains 10 g of glucose (mol. wt. = 180) per 0.5 L. Assuming the solution to be ideal, calculate osmotic pressure at 25°C.

4. At 25°C a solution containing 0.2 g of polyisobutylene in 100 cc of benzene, developed a rise of 2.4 mm at osmotic equilibrium. Calculate the molecular weight of polyisobutylene if the density of the solutions is 0.88 g/cc.

5. The average osmotic pressure of human blood is 7.7 atm at 40°C.

   (a) What should be the total concentration of various solutes in the blood?

   (b) Assuming this concentration to be essentially the same as the molality, find the freezing point of blood. [K_f (H_2O) = 1.86]

Abnormal Molecular Weight and Van't Hoff Factor

Since Colligative properties depend upon the number of particles of the solute, in some cases where the solute associates or dissociates in solution, abnormal results molecular masses are obtained.

▪ **Van't Hoff factor**

Van't Hoff in order to account for all abnormal cases introduced a factor known as the Van't Hoff factor, such that

$$i = \frac{\text{Observed colligative property (actual)}}{\text{Theoretical colligative property (expected)}} = \frac{\text{No. of molecules actually present}}{\text{No. of molecules expected to be present}}$$

- **Association**

    There are many organic solutes, which in non-aqueous solution undergo association, that is, two or more molecules of the solute associate to from a bigger molecule. Thus the number of
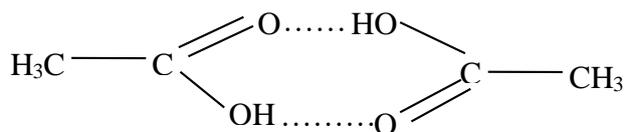
    effective molecules decreases and, consequently the osmotic pressure, the elevation of boiling point or depression of freezing point, is less than that calculated on the basic of a single molecule. Two examples are: acetic in benzene and chloracetic acid in naphthalene Aociation of acidic in benzene through hydrogen bonding

- **Degree of Association**

    The fraction of the total number of molecules which combine to from bigger molecule. Consider one mole of solute dissolved in a given volume of solvent. Suppose n simple molecule.

    i.e. $nA \rightleftharpoons (A)_n$

    Let α be the degree of association, then,

    The number of unassociated moles $= 1 - \alpha$

    The number of associated moles $= \alpha / n$

    Total number of effective moles $= 1 - \alpha + \alpha / n$

    $$i = \frac{1 - \alpha + \alpha / n}{1}$$

    $$\mathbf{i = 1 - \alpha(1 - 1/n)} \qquad \text{Obviously, i < 1}$$

Illustration 11: **Acetic acid (CH_3COOH) associates in benzene to form double molecules. 1.65 g of acetic acid when dissolved in 100g of benzene raised the boiling point by 0.36°C. Calculate the Van't Hoff Factor and the degree of association of acetic acid in benzene (Molal elevation constant of benzene is 2.57).**

Solution. Normal molar mass of acetic acid = 60

Observed molar mass of acetic acid.

$$M = K_b \frac{W_{solute}}{W_{solvent} \, (\text{in gms}) \Delta T} \times 1000$$

$$\frac{2.57 \times 1.65 \times 1000}{100 \times 0.36} = 118$$

$$\text{Van't Hoff Factor} = \frac{\text{Normal molar mass}}{\text{Observed molar mass}} = \frac{60 \text{ g mol}^{-1}}{118 \text{ gmol}^{-1}}$$

$$= 0.508$$

$$= 0.508 = 1 - \alpha(1 - 1/n) = 1 - \alpha\left(1 - \frac{1}{2}\right) = 1 - \alpha/2$$

$$\alpha/2 = 1 - 0.508 = 0.492 \therefore \alpha = 2 \times 0.492 = \mathbf{0.984}$$

Thus acetic acid is 98.3% associated in benzene.

- **Dissociation**

    Organic acids, bases and salts in aqueous solutions undergo dissociation, that is, the molecules break down into positively and negatively charged ions. In such cases, the number of effective particles increases and, therefore, osmotic pressure, elevation of boiling point and depression of freezing point are much higher than those calculated on the basis of an undissociated single molecule.

- **Degree of Dissociation**

   Degree of dissociation means the fraction of the total number of molecules which dissociates, in the solution that is breaks into simple molecules or ions. Consider one mole of an univalent electrolyte like potassium chloride dissolved in a given volume of water. Let α be its degree of dissociation.

   Then the number of moles of KCl left undissociated will be $1-\alpha$. At the same time, α moles of K^+ ions and α moles of Cl^- ions will be produced, as shown below.

   $KCl \quad K^+ + Cl^-$

   $1-\alpha \qquad \alpha \qquad \alpha$
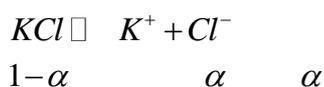
   Thus, the total number of moles after dissociation $= 1-\alpha+\alpha+\alpha = 1+\alpha$

   Hence $i = \dfrac{1+\alpha}{1}$

   Since, as already, mentioned, osmotic pressure, vapour pressure lowering, boiling point elevation or freezing point depressions vary inversely as the molecular weight of the solute of follows that

   $i = \dfrac{\text{Normal molar mass}}{\text{Observed molar mass}} = \dfrac{1+\alpha}{1}$

   $i = 1+\alpha = 1+(2-1)\alpha$

   In general, $\mathbf{i = 1+(n-1)\alpha,}$ Where, $n =$ number of particle (ions) formed after dissociation from the above formula, it is clear that $i > 1$

   Knowing, the observed molar mass and the Van't Hoff factor, i, the degree of dissociation, α can be easily calculated.

   Now, if we include Van't Hoff factor in the formula for colligative properties we obtain the normal results.

   1. Relative lowering of vapour pressure, $\dfrac{P_1^o - P_1}{P_1^o} = iX_2 = i\dfrac{n}{n+N}$

   2. Osmotic pressure, $\pi = iCRT$

   3. Elevation in boiling point, $\Delta T_b = i, \ 1000 \times K_b \times molality$

   4. Depression in freezing point, $\Delta T_f = i \ 1000 \times K_f \times molality$

Note: The value of i is taken as one when solute is non electrolyte

Illustration 12: **A 0.5 percent aqueous solution of potassium Chloride was found to freeze at 0.24ºC. Calculate the Van't Hoff factor and degree of dissociation of the solute at this concentration (K_f for water is 1.86).**

Solution:

$\Delta T_f \dfrac{i \times 1000 K_f w}{W.M}$ $\qquad\qquad\qquad 0.24 = \dfrac{i \times 1000 \times 0.5 \times 1.86}{100 \times 74.5}$

$i = \dfrac{0.24 \times 100 \times 74.5}{1000 \times 0.5 \times 1.86} = 1.923; \quad i = 1+(n-1)\alpha$

$1.923 = 1+(2-1)\alpha \quad 1.923 = 1+\alpha \quad \alpha = 1.923 - 1 = 0.923$

or $\alpha = 0.923 \ or \ 92.3\%$

1. A 0.01 *m* aqueous solution of $K_3[Fe(CN)_6]$ freezes at –0.062°C. What is the apparent percentage of dissociation ? (K_f for water = 1.86)

2. A 0.2 *m* aqueous solution of KCl freezes at –0.68°C, Calculate '*i*' and the osmotic pressure at 0°C. Assume the volume of solution to be that of pure H_2O and for H_2O is 1.86.

3. 1.1 g of $CoCl_3$. $6MH_3$ (mol. wt. = 267) was dissolved in 100 g of H_2O. The freezing point of the solution was –0.29°C. How many moles of solute particles exist in solution for each of solute introduced? K_f for $H_2O = 1.86°C. m^{-1}$.

4. 1.22 g of benzoic acid is dissolved in 100 g of acetone and 100 g of benzene separately. Boiling point of the solution in acetone increases by 0.17°C, while that in the benzene increases by 0.13°C; K_b for acetone and benzene is 1.7 K kg mol^{-1} and 2.6 K kg mol^{-1} respectively. Find molecular weight of benzoic acid in two cases and justify your answer.

5. 75.2 g of C_6H_5OH (phenol) is dissolved in a solvent of K_f = 14. If the depression in freezing point is 7 K then find the % of phenol that dimerises.

❖ **VIDEO-LINKS**

https://youtu.be/EEnbajugGfg

❖ **PPT LINKS**

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