

PHYSICAL CHEMISTRY



CLASS-XII
CHAPTER NAME: SOLUTIONS

LECT-01

Sub Concepts:
Introduction, types of Solution, Concentration of solutions.

CHANGING YOUR TOMORROW

Learning Outcome

- Students will be able to acknowledge the concept of solution.
- Students will be well-acquainted with types of solution based on physical state of matter.
- They will easily understand what is concentration of solution.
- This basic idea will create a grip among the students to browse, the different methods to express the concentration of solution.
- Students will able solve the problems based concentration.

CONTENTS:

1. INTRODUCTION

2. CLASSIFICATION OF SOLUTION

3. CONCENTRATION

INTRODUCTION :

- Solutions are homogeneous mixtures of two or more than two components.
- By homogenous mixture we mean that its composition and properties are uniform throughout the mixture.
- Generally, the component that is present in the largest quantity is known as solvent. Solvent determines the physical state in which solution exists.
- One or more components present in the solution other than solvent are called solutes.
- Solutions which contain only two components in it are called Binary Solutions.

Types of Solutions:

| Type of Solution | Solute | Solvent | Common Examples |
|--------------------------|------------------------|----------------------------|--|
| Gaseous Solutions | Gas Liquid Solid | Gas Gas Gas | Mixture of Oxygen and Nitrogen gases. Chloroform mixed with Nitrogen gas. Camphor in Nitrogen gas. |
| Liquid Solutions | Gas Liquid Solid | Liquid Liquid Liquid | Oxygen dissolved in water. Ethanol dissolved in water. Glucose dissolved in water. |
| Solid Solutions | Gas Liquid Solid | Solid Solid Solid | Solution of hydrogen in Palladium. Amalgam of mercury with sodium. Copper dissolved in gold. |

Methods of Expressing Concentration of a Solution:

- **Mass Percentage (%w/w):** “It represents mass of a component present in 100 g of solution.

$$\text{Mass percentage} = \frac{\text{Mass of the Solute}}{\text{Mass of Solution}} \times 100$$

- **Volume percentage (%v/v):** “It represents volume of a component in 100 mL of solution”

$$\text{Volume percentage of a component} = \frac{\text{Volume of the Solute}}{\text{Volume of Solution}} \times 100$$

- **Mass by volume percentage (%w/v):** “It represents mass of solute in grams present in 100 mL of solution”

$$\text{Mass by volume percentage of a component} = \frac{\text{Mass of the Solute}}{\text{Volume of Solution}} \times 100$$

Methods of Expressing Concentration of a Solution:

➤ **Parts per Million (ppm):**

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

➤ **Mole Fraction (x):** “It represents the moles of a solute present in one mole of solution

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

➤ If a binary solution contains two components A and B and if the no. of moles of A is n_a and no. of moles of B be n_b .

$$\text{Then mole fraction of A} = x_a = \frac{n_a}{n_a + n_b} \quad \text{Then mole fraction of B} = x_b = \frac{n_b}{n_a + n_b}$$

Methods of Expressing Concentration of a Solution:

- It is obvious that sum of mole fractions of all the components in a solution will be unity i.e

$$x_a + x_b = 1$$

- **Molarity(M):** It represents no. of moles of solute present in 1 L of solution.

$$\text{Molarity} = \frac{\text{No. of moles of Solute}}{\text{Volume of Solution in litres}}$$

Units of Molarity are mol/L also represented by 'M' or 'Molar'.

Methods of Expressing Concentration of a Solution:

- **Molality(m):** It represents no. of moles of solute present per kg of solvent”

$$\text{Molality} = \frac{\text{No. of moles of Solute}}{\text{Mass of Solvent in Kg}}$$

Units of molality are mol/kg which is also represented by ‘m’ or ‘molal’.

- . Dilution Law If a solution is diluted by adding solvent to it, then the amount of solute remains constant and we can write:

$$M_1 V_1 = M_2 V_2 ;$$

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PHYSICAL CHEMISTRY



CLASS-XII

CHAPTER NAME: SOLUTIONS

LECT-02

Sub Concepts:

Solubility, Solubility of solid in liquid, Solubility of gas in liquid.

CHANGING YOUR TOMORROW

Learning Outcome

- Students will be able to acknowledge the concept of Solubility.
- Students will be well-acquainted with the solubility of solid in liquid.
- They will easily understand the factors affecting solubility of solid in liquid.
- Students can able acknowledge about the solubility of gas liquid.
- They will easily understand the factors affecting solubility of gas in liquid.

CONTENTS:

1. SOLUBILITY

2. SOLUBILITY OF SOLID IN LIQUID

3. SOLUBILITY OF GAS IN LIQUID

SOLUBILITY:



- Solubility of a substance is its maximum amount that can be dissolved in a specified amount of solvent at a specified temperature.
- It depends upon the nature of solute and solvent as well as temperature and pressure

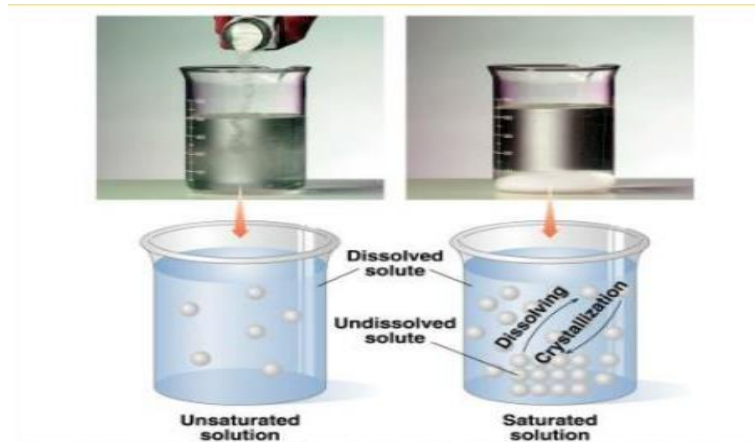
SOLUBILITY:

- It is observed that polar solutes dissolve in polar solvents and non polar solutes in nonpolar solvents.
- In general, a solute dissolves in a solvent if the intermolecular interactions are similar in the two or we may say like dissolves like.
- When a solid solute is added to the solvent, some solute dissolves and its concentration increases in solution. This process is known as dissolution.

- Some solute particles in solution collide with the solid solute particles and get separated out of solution. This process is known as crystallisation.
- A stage is reached when the two processes occur at the same rate. Under such conditions, number of solute particles going into solution will be equal to the solute particles separating out and a state of dynamic equilibrium is reached.



- At this stage the concentration of solute in solution will remain constant under the given conditions, i.e., temperature and pressure.
- Similar process is followed when gases are dissolved in liquid solvents. Such a solution in which no more solute can be dissolved at the same temperature and pressure is called a saturated solution.
- An unsaturated solution is one in which more solute can be dissolved at the same temperature. 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.



Factors affecting the solubility of a solid in liquid :

- 1. Nature of solute and solvent** : Like dissolves like. For example, While sodium chloride and sugar dissolve readily in water, naphthalene and anthracene do not. On the other hand, naphthalene and anthracene dissolve readily in benzene but sodium chloride and sugar do not.
- 2. Temperature** : In a nearly saturated solution, If ($\Delta_{sol}H > 0$), the solubility increases with rise in temperature and If ($\Delta_{sol}H < 0$) the solubility decreases with rise in temperature.
- 3. Effect of pressure** : Does not have any significant effect as solids and liquids are highly incompressible.

Solubility of a Gas in a Liquid:

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

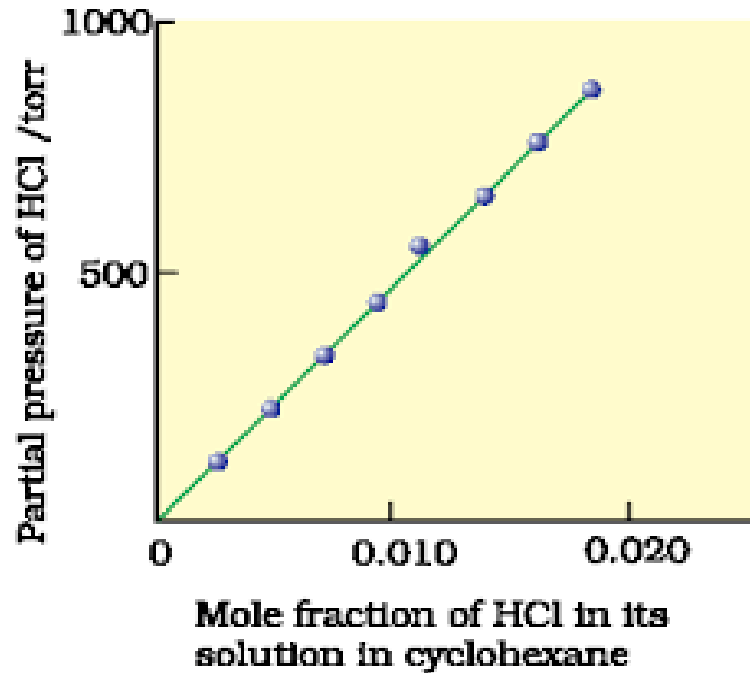
Vapour pressure \propto escaping tendency

- On increasing the temperature of the liquid the escaping tendency of the molecules increases and the vapour pressure increases.
- Henry's law. The law states that at a constant temperature, the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas present above the surface of liquid or solution.
- The mole fraction of gas in the solution is proportional to the partial pressure of the gas over the solution.
- "The partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution

$$p = K_H x$$

Here K_H is the Henry's law constant.

Graph of Henry's Law:



Characteristics of K_H :

- K_H is a function of the nature of the gas.
- Higher the value of K_H at a given pressure, the lower is the solubility of the gas in the liquid.
- K_H values increase with increase of temperature indicating that the solubility of gases increases with decrease of temperature.

Application of Henry's Law:

- To increase the solubility of CO_2 in soft drinks and soda water, the bottle is sealed under high pressure.
- Scuba divers must cope with high concentrations of dissolved gases while breathing air at high pressure underwater. Increased pressure increases the solubility of atmospheric gases in blood.
- When the divers come towards surface, the pressure gradually decreases. This releases the dissolved gases and leads to the formation of bubbles of nitrogen in the blood. This blocks capillaries and creates a medical condition known as bends, which are painful and dangerous to life.
- To avoid bends, as well as, the toxic effects of high concentrations of nitrogen in the blood, the tanks used by scuba divers are filled with air diluted with helium (11.7% helium, 56.2% nitrogen and 32.1% oxygen).
- At high altitudes the partial pressure of oxygen is less than that at the ground level. This leads to low concentrations of oxygen in the blood and tissues of people living at high altitudes or climbers. Low blood oxygen causes climbers to become weak and unable to think clearly, symptoms of a condition known as anoxia.

LECTURE-04:

Raoult's Law:

Vapour Pressure of Liquid-Liquid Solutions

- **Raoult's Law:** According to this law, the partial pressure of any volatile constituent of a solution at a constant temperature is equal to the vapour pressure of pure constituent multiplied by the mole fraction of that constituent in the solution.
- Let a solution containing two volatile components 1 and 2 with mole fractions x_1 and x_2 respectively. Suppose at a particular temperature, their partial vapour pressures are p_1 and p_2 and the vapour pressure in pure state are p_1^0 and p_2^0 . Thus, according to Raoult's Law, for component 1.

$$p_1 \propto x_1$$

So, $p_1 = p_1^0 x_1$, Similarly for component 2, $p_2 = p_2^0 x_2$

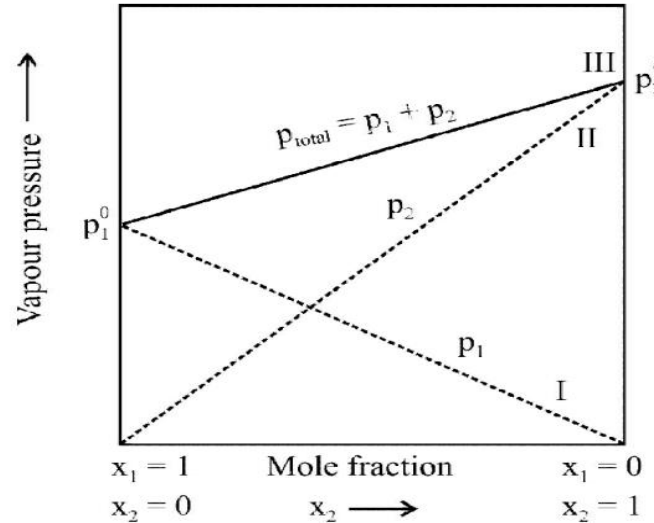
$$P_{total} = P_1 + P_2$$

$$P_{total} = p_1^0 x_1 + p_2^0 x_2$$

$$= p_1^0 (1 - x_2) + p_2^0 x_2$$

$$= p_1^0 + (p_2^0 - p_1^0) x_2$$

Plot of Vapour pressure and mole fraction for an Ideal Solution



The plot of vapour pressure and mole fraction of an ideal solution at constant temperature. The dashed line I and II represent the partial pressure of the components. It can be seen from the plot that p_1 and p_2 are directly proportional to x_1 and x_2 , respectively. The total vapour pressure is given by line marked III in the figure.

Relation between Dalton's Law and Raoult's Law

Mole fraction in vapour phase If y_1 and y_2 are the mole fractions of the components 1 and 2 respectively in the vapour phase then, using Dalton's law of partial pressures:

$$P_1 = y_1 P_{total}$$

$$P_2 = y_2 P_{total}$$

In general

$$P_i = y_i P_{total}$$

Similarity between Raoult's Law and Henry's Law

- According to Raoult's Law

$$p_i = x_i p_i^o$$

- In solution of gas in liquid, one of the component is so volatile that it exists as a gas. Its solubility according to Henry's law is

$$p = K_H x$$

- Thus Raoult's law becomes a special case of Henry's law in which K_H becomes equal to p_i^o

LECTURE-05: Ideal and Non-Ideal Solutions

Ideal solutions : An ideal solution is the solution in which each component obeys Raoult's law under all conditions of temperatures and concentrations.

Properties of Ideal solutions :

- $\Delta H_{\text{MIXING}} = 0$
- $\Delta V_{\text{MIXING}} = 0$
- Intermolecular attractive forces between the A-A and B-B are nearly equal to those between A-B.

Eg. solution of benzene and toluene,
solution of n-hexane and n-heptane

Non-Ideal Solutions: Deviation from Ideal Behaviour

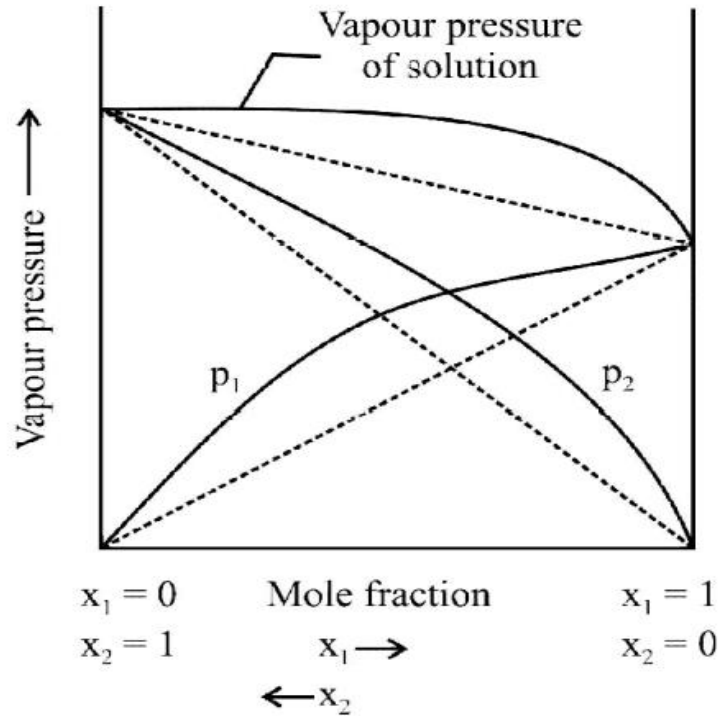
Non – ideal solutions : When a solution does not obey Raoult’s law over the entire range of concentration, then it is called non-ideal solution.

Solutions showing positive deviation from Raoult’s Law :

- Solvent-Solute(A-B) type of force is weaker than Solute-Solute(B-B) & Solvent-Solvent(A-A) forces.
- The vapour pressure is higher than predicted by the law.
- $\Delta H_{\text{MIXING}} > 0$
- $\Delta V_{\text{MIXING}} > 0$

Eg. ethanol and acetone, carbon disulphide and acetone

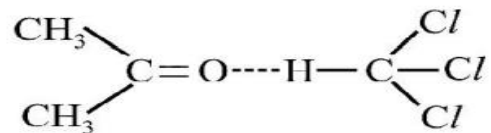
Graph showing positive Deviation from Ideal Behaviour



Solutions showing negative deviations from Raoult's law :

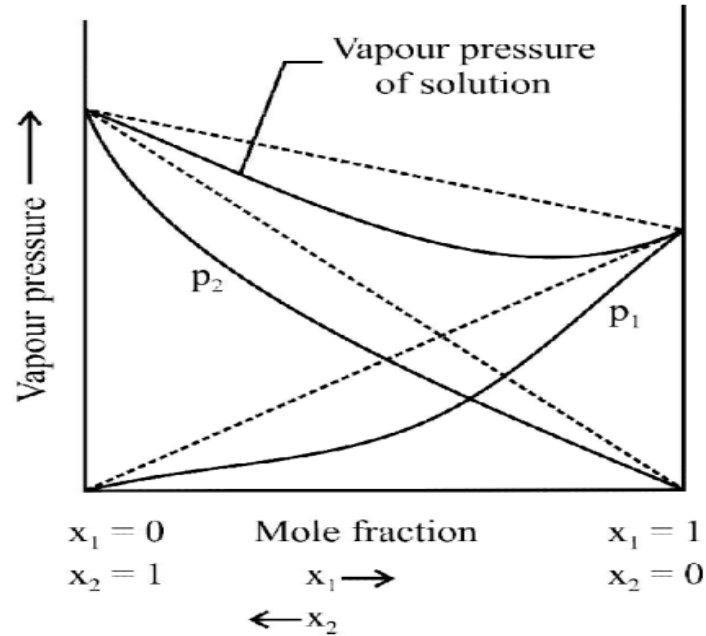
- Solvent-Solute(A-B) type of force is stronger than the other two.
- The vapour pressure is lower than predicted by the law
- $\Delta H_{\text{MIXING}} < 0$
- $\Delta V_{\text{MIXING}} < 0$

For example, phenol and aniline, chloroform and acetone etc



Pressure composition curves for solution showing negative deviation

Pressure composition curves for solution showing negative deviation



Azeotropes and its Types

- Azeotropes are binary mixtures having the same composition in liquid and vapour phase and boil at a constant temperature.
- Minimum boiling azeotrope The solutions which show a large positive deviation from Raoult's law form minimum boiling azeotrope at a specific composition.
- For example, ethanol-water mixture containing approximately 95% of ethanol forms an azeotrope with boiling point 351.15 K.
- Maximum boiling azeotrope : The solutions that show large negative deviation from Raoult's law form maximum boiling azeotrope at a specific composition.
- Nitric acid and water mixture containing 68% nitric acid forms an azeotrope with a boiling point of 393.5K

LECTURE-06: Colligative Properties:

COLLIGATIVE PROPERTIES

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

There are four colligative properties:

1. Relative Lowering of vapour Pressure
2. Elevation in Boiling Point
3. Depression in freezing point
4. Osmotic pressure

Relative Lowering of vapour Pressure

- When a non-volatile solute is added to a solvent, the vapour pressure decreases.
- Nonvolatile means that the solute itself has little tendency to evaporate.
- Because some of the surface is now occupied by solute particles, there is less room for solvent molecules.
- This results in less solvent being able to evaporate
- The lowering of vapour pressure w.r.t. the vapour pressure of the pure solvent is called “Relative lowering in vapour pressure”
- The lowering of the vapor pressure depends on the number of solute particles that have been dissolved

According to Raoult's Law

$$p_1 = x_1 p_1^o$$

(1 represents Solvent and 2 represents Solute)

The lowering in vapour pressure (Δp_1) of solvent can be written as

$$\Delta p_1 = p_1^o - p_1 = p_1^o - p_1^o x_1 = p_1^o (1 - x_1)$$

Knowing that $x_2 = 1 - x_1$

$$\Delta p_1 = p_1^o x_2$$

(x_1 and x_2 are the mole fractions of solvent and solute respectively)

The above equation can be written as $\frac{\Delta p_1}{p_1^o} = x_2$

The above expression can be further expressed as

$$\frac{\Delta p_1}{p_1^o} = \frac{p_1^o - p_1}{p_1^o} = x_2$$

$$\Rightarrow \frac{p_1^o - p_1}{p_1^o} = \frac{n_2}{n_2 + n_1}$$

The expression in the left hand side of the above expression is called the relative lowering of vapour pressure and it is equal to mole fraction of solute.

Here n_2 and n_1 are the number of moles of solute and solvent respectively in a solution. For very dilute solutions $n_2 \ll n_1$. Neglecting n_2 in the denominator we get:

$$\frac{p_1^o - p_1}{p_1^o} = \frac{n_2}{n_1}$$
$$\Rightarrow \frac{p_1^o - p_1}{p_1^o} = \frac{w_2 \times M_1}{M_2 \times w_1}$$

Where w_2 and M_2 are mass and Molar mass of Solute and w_1 and M_1 are mass and Molar mass of Solvent respectively.

Lecture-07: Vapour pressure of solution of solids in liquids:

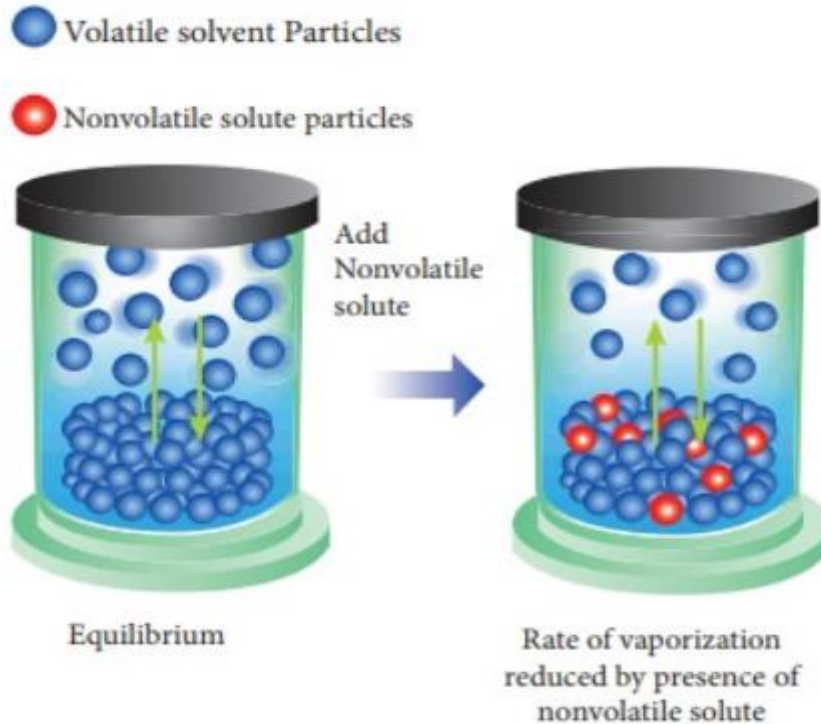
Vapour pressure of solution of solids in liquids

- Addition of a non-volatile solute to a solvent to give a solution results in the exertion of the vapour pressure of the solution uniquely from the solvent.
- This vapour pressure is lower than the vapour pressure of the pure solvent at a given temperature.
- The surface of the solution is occupied by both solute and solvent molecules which results in the reduction of the surface for the solvent molecules. As a result the apparent number of solvent molecules escaping from the surface is reduced. This in turn reduces the vapour pressure.
- The reduction of vapour pressure of solvent depends on the quantity of non-volatile solute present in the solution not on its nature.
- Raoult's law is applicable here also only for the volatile component.

$$P_{\text{solution}} = P^{\circ}_{\text{solvent}} x_A$$

Where x_A is the mole fraction of the solvent

Addition of Non-Volatile Solute Reduces the Rate of Vapourisation



LECTURE-08: Elevation in Boiling point:

- Boiling point of a liquid is the temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure.
- On addition of non-volatile solute the vapour pressure of the solvent decreases and therefore, to boil the solution the required temperature will be higher.
- So, there will be a rise in the boiling point of the solution.
- The increase in boiling point $\Delta T_b = T_b - T_b^o$ where T_b^o is the boiling point of pure solvent and T_b is the boiling point of solution is known as elevation of boiling point
- Expression for elevation in boiling point:

$$\Delta T_b = K_b m$$

- Where K_b is called the molal elevation constant or boiling point elevation constant or Ebullioscopic constant and m is the molality.

Determination of molar mass of solute from the expression of elevation in boiling point.

- Considering w_2 and M_2 are mass and Molar mass of Solute and w_1 and M_1 are mass and Molar mass of Solvent respectively, then molality can be expressed as:

$$m = \frac{w_2 / M_2}{w_1 / 1000} = \frac{1000 \times w_2}{M_2 \times w_1}$$

Substituting the above expression of Molality in the expression for Elevation in Boiling point:

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

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

Molal Elevation Constant:its Definition and expression

K_b is defined as elevation in boiling point produced when molality of solution is unity.It's unit is $K\ kg\ mol^{-1}$.

Determination of K_b :

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

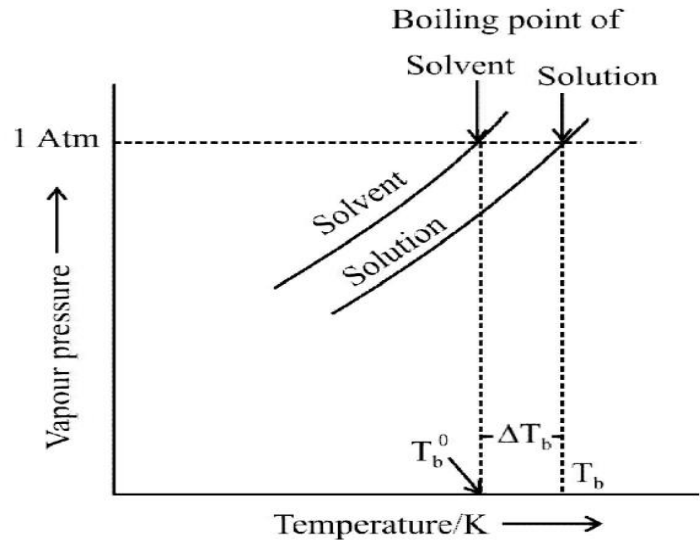
where: R = gas constant (8.314 JK/mol),

T_r = freezing temperature in K,

M_1 = Molar mass of solvent in Kg/mol,

$\Delta_{\text{vap}} H$ = enthalpy of vapourisation of solvent in J/mol.

Vapour pressure-Temperature curve showing Elevation in Boiling point



The vapour pressure curve for solution lies below the curve for pure water. The diagram shows that ΔT_b denotes the elevation of boiling point of a solvent in solution.

Depression In Freezing point

- The freezing point of a substance may be defined as the temperature at which the vapour pressure of the substance in its liquid phase is equal to its vapour pressure in the solid phase.
- 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 lower temperature. Thus, the freezing point of the solvent decreases.
- The decrease in freezing point $\Delta T_f = T_f^0 - T_f$ where T_f^0 is the freezing point of pure solvent and T_f is the freezing point of solution is known as elevation of boiling point.
- Expression for depression in freezing point:

$$\Delta T_f = K_f m$$

- Where K_f is called the molal depression constant or freezing point depression constant or Cryoscopic constant and m is the molality.

Calculation of molar mass of solute from the expression of depression in freezing point:

Considering w_2 and M_2 are mass and Molar mass of Solute and w_1 and M_1 are mass and Molar mass of Solvent respectively, then molality can be expressed as:

$$m = \frac{w_2 / M_2}{w_1 / 1000}$$

Substituting the above expression of molality in the expression of depression in freezing point.

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

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

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

Molal Depression Constant:its Definition and expression

K_f is defined as depression in freezing point produced when molality of solution is unity.The unit of K_f is $K \text{ kg mol}^{-1}$.

Determination of K_f :

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

where : R = gas constant (8.314 JK/mol),

T_f = freezing temperature in K,

M_1 = Molar mass of solvent in Kg/mol,

$\Delta_{\text{fus}} H$ = enthalpy of fusion of solvent in J/kg

Vapour pressure-Temperature curve showing Elevation in Boiling point

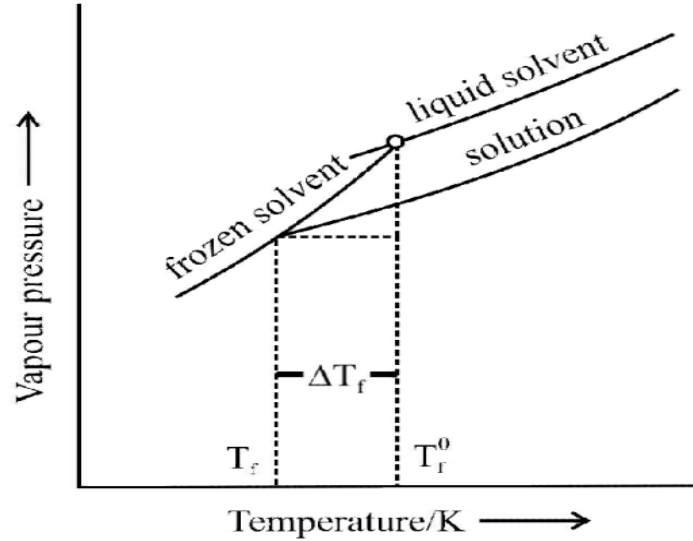


Diagram showing ΔT_f depression of the freezing point of a solvent in a solution.

LECTURE-09: Osmosis and Osmotic Pressure:

- When a pure solvent and solution are kept with a semipermeable membrane between them then the solvent particles pass through the membrane from the solvent side to the solution side. This phenomenon is called “Osmosis”.
- The semi-permeable membrane is a membrane that allows only small molecules to pass through and blocks the larger solute molecules.
- The osmotic pressure of a solution is the excess pressure that must be applied to a solution to prevent osmosis,

Osmosis

- Water
- Sugar

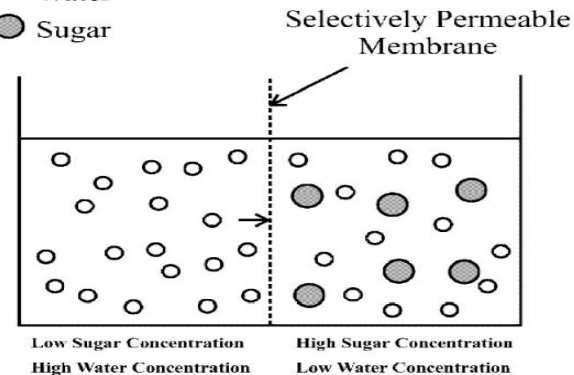
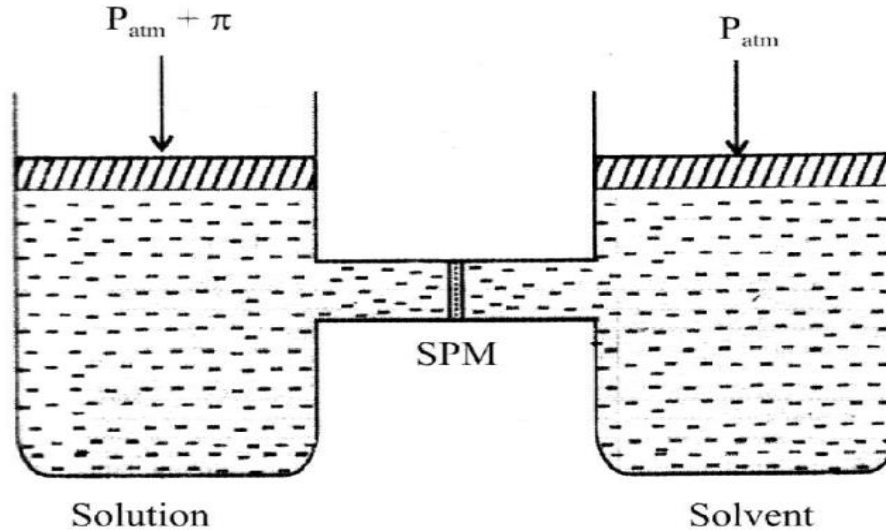


Diagram emphasizing on the concept of Osmotic Pressure



The excess pressure equal to osmotic pressure must be applied on the solution to prevent osmosis.

Expression for Osmotic Pressure

Expression : For dilute solutions, osmotic pressure is proportional to the molarity, C of the solution at a given temperature T. Thus:

$$\pi = C R T$$

Here π is the osmotic pressure and R is the gas constant.

Calculation of molar mass :

$$\pi = (n_2 / V) RT$$

Here V is volume of a solution in litres containing n_2 moles of solute. If w_2 grams of solute, of molar mass, M_2 is present in the solution, then $n_2 = w_2 / M_2$ and we can write,

$$\pi V = \frac{w_2 RT}{M_2}$$

or
$$M_2 = \frac{w_2 RT}{\pi V}$$

Types of Solutions with Osmotic Pressure

- Two solutions having same osmotic pressure at a given temperature are called **isotonic** solutions.
- The solution with lower concentration or lower osmotic pressure is known as “**Hypotonic**” with respect to more concentrated solution.
- The solution with higher concentration or higher osmotic pressure is known as “**Hypertonic**” with respect to dilute solution.
- **Reverse osmosis** : If a pressure larger than the osmotic pressure is applied to the solution side, the solvent will flow from the solution into the pure solvent through the semi permeable membrane. This phenomenon is called reverse osmosis.
- **Application** : Desalination of sea water : When pressure more than osmotic pressure is applied, pure water is squeezed out of the sea water through the membrane.

LECTURE-10: Abnormal Molar Mass and Van't Hoff's factor(i)

- When the molecular mass of a substance determined by studying any of the colligative properties comes out to be different than the theoretically expected value, the substance is said to show abnormal molar mass.

Abnormal Molar Masses are observed:

1. When the solute undergoes association or dissociation in the solution.
- **Van't Hoff's Factor(i)** : To calculate extent of association or dissociation, van't Hoff introduced a factor i , known as the van't Hoff Factor

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

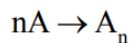
$$i = \frac{\text{Observed colligative property}}{\text{Calculated colligative property}}$$

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

Association and Dissociation of Particles in a Solution

Association :

Number of particles will always decrease due to association therefore $i < 1$.



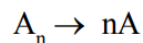
Let initial particles (n_i) = 1

Final number (n_f) = $1 - \alpha + \alpha/n$

van't Hoff factor, $i = n_f/n_i = 1 - \alpha + \alpha/n$

Dissociation :

The number of particles will always increase due to dissociation and hence $i > 1$.



Initial particle = 1

Final particles = $1 - \alpha + n\alpha$

$i = 1 - \alpha + n\alpha$

Modified Expressions of Colligative Properties in terms of Van't Hoff's Factor

Modified Expressions :

Relative lowering of vapour pressure of solvent,

$$\frac{p_1^0 - p_1}{p_1^0} = i \cdot \frac{n_2}{n_1}$$

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, $\pi = i n_2 RT/V$

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