

SOLUTION

- Solutions are homogeneous mixtures of two or more than two components. The substances forming the solution are called components of the solution.
- The component present in smaller amount is called solute and the other present in large amount in which solute is dissolved is called solvent.

TYPES OF SOLUTION

- Depending upon the nature of solute and solvent solutions are classified as:

Gaseous solutions (in which gas act as solvent eg) mixture of O₂ and N₂).

Liquid solutions (in which liquid act as solvent eg) O₂ dissolved in Water)

Solid solutions (in which solid act as solvent or present in large amount eg) alloys.)

- Different methods to express the concentration of solution

→ Molarity [M]

It is defined as the number of moles of solute dissolved in one litre of the solution

$$\text{Molarity (M)} = \frac{\text{Number of moles of solute} \times 1000}{\text{Volume of solution (ml)}}$$

- Molarity is a function of Temperature and changes with change in temperature because Volume depends upon temperature.

→ Molality (m)

It is defined as the Number of moles of solution solute per kg of the solvent.

$$m = \frac{\text{NO. of moles of solute}}{\text{mass of solvent (g)}} \times 1000.$$

→ Normality (N)

$$N = \frac{\text{NO. of gram equivalents of solute}}{\text{Volume of solution (ml)}} \times 1000.$$

[Gram equivalents = $\frac{W_2}{\text{Eq. wt.}}$, where W_2 = mass of
of solute and Eq. weight = $\frac{\text{Molecular mass}}{\text{Valency}}$, where
solute]

MOLE FRACTION (x)

- It is the Number of moles of one component to the Number of moles of all components present in the solution
- For a binary solution having solvent 1 and solute 2.

$$\text{Mole fraction of solute}, \quad x_2 = \frac{n_2}{n_1 + n_2}$$

Similarly, mole fraction of solvent

$$x_1 = \frac{n_1}{n_1 + n_2}$$

$$x_1 + x_2 = 1$$

NOTE Mass %, ppm, molality and mole fraction do not change with change in temperature while molality decreases with rise in temperature.

→ Parts per million (ppm)

- when a solute is present in trace quantities, the conc.
is expressed in ppm.

$$\text{Parts per million} = \frac{\text{No. of parts of component} \times 10^6}{\text{Total No. of parts of all comp. of the soln.}}$$

→ Mass per cent (w/w)

$$\text{Mass per cent} = \frac{\text{Mass of component}}{\text{Total mass of solution}} \times 100$$

→ Volume per cent (v/v)

$$\text{Volume per cent} = \frac{\text{Vol. of the component}}{\text{Total volume of soln.}} \times 100$$

→ Mass by volume percentage (w/v)

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

→ Relation b/w Molarity and Molality

$$m = M \times 1000$$

$$(1000 \times d) - (M \times M_2)$$

where, m is the molality and M_2 is the molar mass of component 2 (generally solute), and d is the density of solution (in g cm^{-3})

(NOTE) $M_1 V_1 = M_2 V_2$ similarly, $N_1 V_1 = N_2 V_2$

SOLUBILITY

Solubility of a substance is its maximum amount of solute that can be dissolved in a specified amount of solvent.

- It depends on Nature of solute, solvent, temperature and pressure
- Depending on solubility, solution can be saturated or unsaturated.

→ Saturated Solution

Saturated solution is the solution in which no more solute can be dissolved at the same temperature and pressure.

→ UNSATURATED Solution

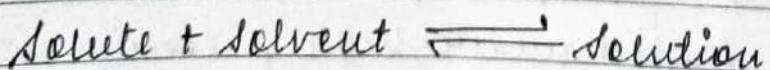
An unsaturated solution is the one in which more solute can be dissolved at the same temperature.

NOTE On dissolving the solid solute in a solvent, its concentration increases, this is dissolution.

While when some soluble particles in solution collide with the other solid solute particles and get separated out of the solution, this process is called crystallisation.

→ Dynamic Equilibrium

- Dynamic equilibrium is the condition when No. of solute particles going into the sol^l" is equal to the solute particles separating out i.e., dissolution and crystallisation occur at the same rate.



From Le Chatelier's principle, if in a nearly saturated solⁿ, the dissolution process is endothermic ($\Delta_{sol}H > 0$), the solubility should increase with rise in temp. and if it is exothermic ($\Delta_{sol}H < 0$), the solubility should decrease.

→ Henry's Law.

- It states that, at a constant temperature, the solubility of a gas in liquid is directly proportional to the partial pressure of the gas present above the surface of liquid or solution.

$$S \propto p \text{ or } p = k_H \cdot S.$$

Unit of solubility is same as concentration.

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

$$p \propto x \text{ or } p = k_H \cdot x$$

- If we draw a graph b/w partial pressure of the gas v/s mole fraction of the gas in solution, we get straight line whose slope is given by k_H .

- Higher the value of k_H at a given pressure, the lower is the solubility of the gas in the liquid.
Solubility of gases increases with ↑ of pressure.

→ Applications of Henry's law.

(i) To increase the solubility of CO_2 in soft drinks and soda water, the bottle is sealed under high pressure.

(P.P) To avoid bends and the toxic effect of high concentration of N_2 in the blood, the cylinders used by scuba divers are filled with air diluted with H_2 .

→ RAOULT'S LAW

This law states that for a solution of volatile liquids, the partial vapour pressure of each component in the solution is directly proportional to its mole fraction.

For component 1, $p_1 \propto x_1$ or $p_1 = p_1^{\circ} x_1$

component 2, $p_2 = p_2^{\circ} x_2$

$$p_{\text{total}} = p_1 + p_2 = p_1^{\circ} x_1 + p_2^{\circ} x_2 \quad (\text{as } x_1 + x_2 = 1)$$

$$p_{\text{total}} = (1 - x_2)p_1^{\circ} + x_2 p_2^{\circ}$$

$$p_{\text{total}} = p_1^{\circ} + (p_2^{\circ} - p_1^{\circ})x_2$$

where p_1° and p_2° are the vapour pressures of pure component 1 and 2 respectively.

If y_1 and y_2 are the mole fraction of the component 1 and 2 respectively in vapour phase, then

$$p_1 = y_1 \times p_{\text{total}}$$

$$p_2 = y_2 \times p_{\text{total}}$$

→ Ideal Solutions

- Ideal solutions obey Raoult's law over entire range of concentrations. For these solution $\Delta_{\text{mix}}H = 0$ and $\Delta_{\text{mix}}V = 0$

- In binary solution, if A-B interactions are nearly equal to A-A or B-B interaction then it is an ideal soln.

e.g) n-heptane & n-heptane, benzene and toluene

Non-Ideal Solutions

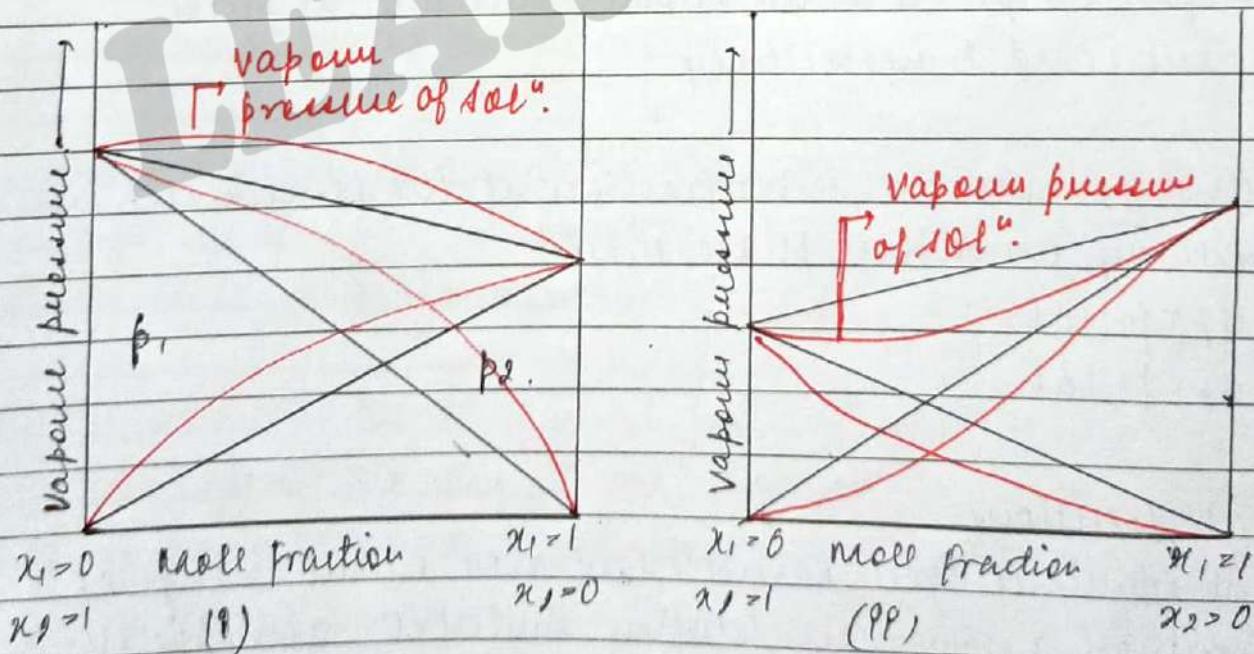
- Non-Ideal solutions do not obey Raoult's law over entire range of concentration. For such solutions,

$$\Delta H_{mix} \neq 0 \text{ and } \Delta V_{mix} \neq 0.$$

The vapour pressure is either higher (+ deviation) or lower (- deviation) than predicted by Raoult's law.

→ Positive and Negative Deviation

- In case of positive deviation from Raoult's law (e.g., mixture of ethanol and acetone, carbon disulphide and acetone), A-B (polar, solute-solvent) interactions are weaker than those of A-A or B-B interactions.
- While, negative deviation from Raoult's law (e.g., mixture of phenol and aniline, chloroform and acetone), A-B interactions are stronger than those of A-A or B-B.



(a) For positive Deviation, $\Delta H_{mix} = +ve$ and $\Delta V_{mix} = +ve$

(b) For Negative Deviation, $\Delta H_{mix} = -ve$ and $\Delta V_{mix} = -ve$

AZEOTROPS

Mixtures that have the same composition in liquid and vapour phase and boil at constant temperature like pure liquid are azeotropic mixtures.

- The solutions which show large negative deviation from Raoult's law, form maximum boiling azeotropes.

e.g) Nitric acid-Water.

- The solutions show large positive deviation from Raoult's law form minimum boiling azeotropes.

e.g) ethanol-Water mixture.

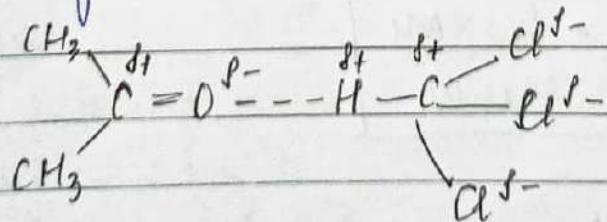
2011 Explain why a solution of chloroform and acetone shows Negative Deviation from Raoult's law?

Ans A mixture of chloroform and acetone forms a solution which shows Negative deviation from Raoult's law because chloroform molecule forms H-bonding with acetone molecule.

- Here solute is chloroform and solvent is acetone.

As a result A-B interaction becomes stronger than A-A and B-B interaction.

- This \downarrow the escaping tendency of molecules for each component which leads to the decrease in vapour pressure and resulting in Negative deviation from Raoult's law.



COLLIGATIVE PROPERTY

- The properties of solutions which depends only on the Number of solute particles, irrespective of their Nature relative to the total Number of particles present in solution are known as colligative properties.

$$\text{Colligative property} \propto \text{NO. of particles} \propto \frac{1}{\text{molar mass of solute}}$$

⇒ Relative lowering of vapour pressure (RLVP)

- When a non-volatile solute is dissolved in a solvent, vapour pressure of the solution becomes lower than that of the pure solvent which is known as relative lowering.
- The RLVP of a solution containing the non-volatile solutes is equal to the mole fraction of the solute at a given temperature.

- The expression for RLVP,

$$\frac{\Delta p_i}{p_i^0} = \frac{p_i^0 - p_i}{p_i^0} = x_2 \Rightarrow \frac{p_i^0 - p_i}{p_i^0} = \frac{u_2}{u_1 + u_2}$$

(since $x_2 = \frac{u_2}{u_1 + u_2}$)

$$\frac{p_i^0 - p_i}{p_i^0} = \frac{u_2}{u_1} \quad (\text{for dilute soln: } u_2 \ll u_1)$$

$$\left[\frac{p_i^0 - p_i}{p_i^0} = \frac{w_2 \times M_1}{M_2 \times w_1} \right]$$

⇒ Elevation in Boiling point

- The boiling point of a liquid is that temperature at which its vapour pressure becomes equal to the atm. pressure.
- The boiling point of a solution is always higher than the boiling point of the pure solvent in which the solution is prepared.

- If T_b^o is the boiling point of pure solvent and T_b is the boiling point of solution, then the elevation in B.P. is

$$\Delta T_b = T_b - T_b^o$$

Elevation in boiling point.

$$\Delta T_b \propto m \quad (m = \text{molality})$$

$$\Delta T_b = k_b m.$$

$$\Rightarrow \boxed{\Delta T_b = \frac{k_b \times w_2 \times 1000}{M_2 \times w_1 (\text{gm})}}$$

$$k_b = R \times M_1 \times (T_b^o)^2$$

$$1000 \times \Delta \text{vap. H.}$$

where k_b = boiling point elevation const or molal elevation const or ebullioscopic const having unit kg/mol^2 .

⇒ Depression in Freezing point.

- The freezing point of a substance is that temp. at which the vapour pressure of the substance in its liquid phase is equal to its vapour pressure in solid phase.
- When a non volatile solute is added to a solvent, the freezing point of the soln. is always lower than that of pure solvent.
- The difference in freezing point is known as depression of Freezing point ΔT_f , $\Delta T_f = T_f^o - T_f$.

where T_f^o is the freezing point of pure solvent and T_f is the freezing point of solution.

Depression of freezing point.

$$\Delta T_f \propto m \quad \text{or} \quad \Delta T_f = k_f m$$

$$\boxed{\Delta T_f = \frac{k_f \times w_2 \times 1000}{M_2 \times w_1 (\text{gm})}}$$

where k_f is freezing point depression or molal depression or cryoscopic const having unit kg/mol^2 .

$$k_f = \frac{R \times M \times (T_f^0)^2}{1000 \times \Delta_{\text{fus}} H}$$

where R and M, are gas constant and molar mass of the solvent respectively.

- $\Delta_{\text{fus}} H$ and $\Delta_{\text{vap}} H$ are enthalpies of fusion and vapourisation of the solvent respectively.

OSMOSIS and OSMOTIC PRESSURE

- The process of flow of solvent molecules from solution of lower concentration to solution of higher conc. through semipermeable membrane is known as osmosis.
- The hydrostatic pressure which develops on account of osmosis is called Osmotic pressure or the excess pressure that must be applied on the solution to prevent osmosis is called Osmotic pressure.
- Osmotic pressure (π) is directly proportional to molality (c) of the solution at given temperature T.

$$\pi \propto c$$

$$\pi = CRT \quad \text{or} \quad \pi = \frac{n g RT}{V}$$

$$\Rightarrow \pi V = WRT \quad \text{or} \quad M_g = \frac{WRT}{V}$$

→ Osmotic pressure is used to determine molar masses of proteins, polymers and other macromolecules.

(I) Two solutions having same Osmotic pressure at a given Temperature are called Isotonic solutions.

(II), a solution having lower Osmotic pressure than the other solution is called Hypotonic while, the one with higher Osmotic pressure is called hypertonic.

(iii) people taking salty food, experience water retention in tissue cells and extracellular spaces due to osmosis. The resulting is called edema.

iv) **Reverse Osmosis** If a pressure larger than the osmotic pressure is applied to the solution side, then the pure solvent flows out of the soln. through the semipermeable membrane.

- It is used for the desalination of sea water.

→ **ABNORMAL Molar Mass.**

- For the substances undergoing association or dissociation, in the solution, molecular mass determined from colligative properties is different from expected value.
- This is known as abnormal molar mass. This change can be known by using Van't Hoff factor

→ **VAN'T HOFF FACTOR**

- It is the ratio of the experimental value of colligative property to the calculated value of colligative property.
- It is used to find out the extent of dissociation or association.

Van't Hoff factor,

$$\text{V.H.F.} = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$$

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

- If $i > 1$, solute undergoes dissociation, and if $i < 1$ solute undergoes association

→ For association, when molecules of solute form dimer, $n=2$
 Degree of association, $\alpha = \frac{i-1}{(i-1) + \frac{1}{n}}$ (where, $n = \text{No. of particles ass.)}$)

→ For dissociation of the solute AB, $n=2$
 Degree of dissociation, $\alpha = \frac{i-1}{i-1 + \frac{1}{n}}$

→ Inclusion of Van't Hoff factor modifies the equation for colligative property :

(i) Relative lowering of vapour pressure

$$\frac{p_i^0 - p_i}{p_i} = i \frac{\Delta \pi}{\Delta \pi_0}$$

(ii) Elevation of Boiling point

$$\Delta T_b = i k_b m$$

(iii) Depression in Freezing point

$$\Delta T_f = i k_f m$$

(iv) Osmotic pressure of solution

$$\pi = \frac{P_{ext} RT}{V}$$