

Generic Elective-3

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Section A - Physical Chemistry

Important questions

Long Questions & Short questions.

1. Define vapour pressure? State and explain Raoult's law for volatile solutes & non-volatile solutes.

Ans:- Vapour pressure of a liquid/solution is the pressure exerted by the vapours in equilibrium (when rate of evaporation is equal to rate of condensation) with the liquid/solution at a particular temperature.

For a solution of liquid-liquid, as both the components of the solution are volatile, each component will form vapour above the solution. When equilibrium is reached each component will exert a vapour pressure called partial pressure whose value depends upon the mole fraction of the component in solution and vapour pressure of that component in pure state.

Raoult's law states that in a solution, the vapour pressure of a component at a given temperature is equal to the mole fraction of that component in the solution multiplied by the vapour pressure of that component in the pure state.

$$P_A = x_A P_A^0 \quad \text{and} \quad P_B = x_B P_B^0$$

P_A → v.p of A component in solution

$x_A \rightarrow$ mole fraction of A component in solution.

$P_A^0 \rightarrow$ v.p of A component in its pure state.

$P_B^0 \rightarrow$ v.p of B component in pure state

$P_B \rightarrow$ v.p of B component in solution

$x_B \rightarrow$ mole fraction of B component

If P is the total pressure of the system at same temp.

$$\text{Then, } P = P_A + P_B = x_A P_A^0 + x_B P_B^0$$

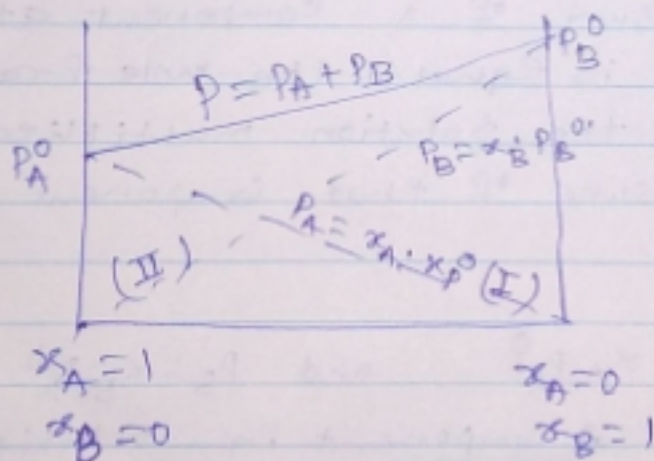
$$\begin{aligned} P &= (1 - x_B) P_A^0 + x_B P_B^0 \\ &= (P_B^0 - P_A^0) x_B + P_A^0 \end{aligned}$$

When $x_A = 1$ i.e. the liquid is pure A

$$P_A = P_A^0$$

When $x_B = 1$ i.e. the liquid is pure B

$$P = P_B^0$$



$$P = (P_B^0 - P_A^0) x_B + P_A^0$$

Since P_A^0 and P_B^0 are constant at a particular temperature. So that total vapour pressure is a linear function of the mole fraction x_B . Thus a st. line should be obtained when P is plotted against x_A or x_B .

Raoult's law as explained above is applicable only if two components (volatile liquids) form a solution. This law is not applicable if the two liquids are not completely miscible.

Raoult's law for Non volatile solute

For non-volatile solutes quantitatively the effect of adding a solid (non-volatile) on the lowering of vapour pressure can be derived

$$P_s = x_1 \cdot P_A^0$$

x_1 → mole fraction of solvent

Mole fraction of solute is not dependent, because it is non-volatile solute

P_s → vapour pressure of solvent in the solution

$$\frac{P_s}{P_A^0} = x_1$$

$$\text{or } P_s \propto x_1 \quad \text{or } x_1 = \frac{n_1}{n_1 + n_2}$$

$$\frac{P_s}{P^0} = x_1 = \frac{n_1}{n_1+n_2}$$

$$1 - \frac{P_s}{P^0} = 1 - \frac{n_1}{n_1+n_2}$$

$$\Delta P = \frac{P^0 - P_s}{P^0} = \frac{n_2}{n_1+n_2}$$

$P^0 - P_s \rightarrow$ lowering of v.p

$\frac{P^0 - P_s}{P^0} \rightarrow$ Relative lowering of vapour pressure.

$$\frac{n_2}{n_1+n_2} = x_B = \text{Mole Fraction of solute}$$

The relative lowering of vapour pressure of a solution containing a non-volatile solute is equal to the mole fraction of the solute in the solution.

2. What are ideal & non-ideal solution discuss with examples. Why it shows positive and negative deviation?

Ans: An ideal solution is that solution in which each component obeys under all conditions of temperature and concentration

An ideal solution will satisfy the following conditions:

(i) $\Delta V_{\text{mixing}} = 0$, There will be no change in volume on mixing the two components.

(ii) There will be no change in enthalpy
 $\Delta H_{\text{mixing}} = 0$

(iii) $P_A = x_A P_A^0$ and $P_B = x_B P_B^0$

(iv) $f_{A-B} = f_{A-A} = f_{B-B}$
 Intermolecular interaction between A-B components are same magnitude as the intermolecular interaction found in the pure A-A and B-B attractions.

Examples (i) Benzene + Toluene

(ii) n-Hexane + n-Heptane

(iii) Ethyl bromide + Ethyl chloride

(iv) Chloro benzene + Bromobenzene

Non-ideal solution - A solution which does not obey Raoult's law is called non-ideal solution.

For such solution

$$\Delta V_{\text{mixing}} \neq 0$$

$$\Delta H_{\text{mixing}} \neq 0$$

$$P_A \neq x_A \cdot P_A^0 \quad \text{or} \quad P_B \neq x_B \cdot P_B^0$$

$$f_{A-B} \neq f_{A-A} = f_{B-B}$$

A non-ideal solution is that solution in which solute and solvent molecules interact with one another with a different force than the forces of interaction between the molecules of the pure components.

Types of Non-ideal solution - There are two types

(i) Positive deviation $\Delta V_{mix} > 0$

$$\Delta H_{mix} > 0$$

$$P_A > x_A \cdot P_A^0 \quad \text{and} \quad P_B > x_B \cdot P_B^0$$

$$F_{A-B} < F_{A-A} \text{ or } F_{B-B}$$

Example (i) Acetone + Carbon disulphide

(ii) Acetone + Ethyl alcohol

(iii) Carbon tetrachloride + Benzene

(iv) Carbon tetrachloride + Toluene.

Non-ideal solutions showing negative deviation.

$$(i) \quad P_A < x_A P_A^0, \quad P_B < x_B P_B^0$$

$$P_{Total} < x_A P_A^0 + x_B P_B^0$$

$$(ii) \quad \Delta H_{mixing} = -ve$$

$$(iii) \quad \Delta V_{mixing} = -ve.$$

Example (a) Chloroform + Benzene

(b) Acetone + aniline.

(c) HCl + water.

Q (3) What are Colligative Properties?
Discuss different types Colligative Properties.

Ans:- Those Properties of ideal solutions which depend only on the number of particles of the solute dissolved in a definite amount of the solvent and do not depend on the nature of solute are called colligative Properties.

The important Colligative Properties are:

- (i) Relative lowering of vapour pressure.
- (ii) Osmotic pressure
- (iii) Elevation in boiling point
- (iv) Depression in Freezing point

Relative lowering of vapour pressure

When a non-volatile solute is dissolved in a solvent, the vapour pressure

of the solution is lower than that of the pure solvent. It was derived that the relative lowering of vapour pressure given by this equation.

$$\frac{p^0 - p_s}{p_A^0} = \frac{n_2}{n_1 + n_2}$$

Osmotic Pressure - The minimum hydrostatic pressure that has to be applied on the solution to prevent the entry of the solvent into the solution through the semi-perm membrane is called osmotic pressure.

$$\pi \propto c$$

$$\pi \propto T$$

$$\pi \propto c \times T$$

$$\text{or } \pi = R c T$$

R - Solution Constant

π - Osmotic Pressure.

c - Molar Concentration of solution.

T - Temperature.

$$\pi = c R T = \frac{n}{V} R T$$

$$\pi V = n R T$$

$$\text{or } \pi V = \frac{W}{M} R T \quad \text{or } M = \frac{W R T}{\pi V}$$

(9)

Elevation in Boiling Point - It is found that the boiling point of the solution is always higher than that of pure solvent. The increase is called the elevation in boiling point.

$$\Delta T_b = K_b \cdot m$$

K_b → molar elevation constant

ΔT_b → Increase in boiling point

m → molality of solution.

$$M_2 = \frac{1000 \times K_b \times W_2}{\Delta T_b \times W_1}$$

Depression in Freezing Point - Freezing point of a substance is the temperature at which the solid and the liquid forms of substance have the same vapour pressure.

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

$$M = \frac{1000 \times K_f \times W_2}{\Delta T_f \times W_1}$$

K_f → molar depression constant

m → molality of solution

ΔT_f → Depression in Freezing point.