Class ⇒ B.Sc. (Part-I) subsidiary
Subject ⇒ Chemistry
Chapter ⇒ Colligative properties
Topic ⇒ Raoult's law of lowering of vapour pressure.

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Colligative properties

Lattin word,

Colligare = to bind together

The colligative properties are properties that depend only on the number of solute particles in a solution, but are independent of the nature of those particles.

Dilute solutions containing non-volatile solute exhibit the following properties.

(i) Lowering of vapour pressure
(ii) Elevation of the boiling point
(iii) Depression of the freezing point
(iv) osmotic pressure

Raoult's law of lowering of vapour pressure

The vapour pressure of a pure solvent is decreased when a non-volatile solute is dissolved in it.

If P is the vapour pressure of the solvent and Ps that of the solution.

The lowering of vapour pressure = $(P - P_s)$

The lowering of vapour pressure relative to the vapour pressure of the pure solvent is called relative lowering of vapour pressure. Thus,

Relative lowering of vapour pressure $= \frac{P - P_s}{P}$

According to the Raoult's law,

The relative lowering of the vapour pressure of a dilute solution is equal to the mole fraction of the solute present in dilute solution.

Raoult's law can be expressed mathematically in the form

$$\frac{P-P_s}{P} = \frac{n}{n+N}$$

Where n = no. of moles or molecules of solute.

N = no. of moles or molecules of solvent.

Derivation of Raoult's Law

The vapour pressure of the pure solvent is caused by the no. of molecules evaporating from its surface.

When a non-volatile solute is dissolved in soln, the presence of solute molecules in the surface blocks a fraction of the surface where no evaporation can take place. This causes the lowering of vapour pressure.

The vapour pressure of the soln is therefore, determined by the no. of molecules of the solvent present at any time in the surface which is proportional to the mole fraction.

i.e.

$$P_s \propto \frac{N}{n+N}$$

Where N = moles of solvent

n = moles of solute.

or $$P_s = K\frac{N}{n+N} \quad \text{——— (1)}$$

K is proportionality factor

In case of pure solvent $n=0$ and hence

Mole fraction of solvent $= \frac{N}{n+N} = \frac{N}{0+N} = 1$

from eqn ①, the vapour pressure $P = K$
Therefore, the eqn ① assumes the form

$$P_s = P \frac{N}{n+N}$$

or $$\frac{P_s}{P} = \frac{N}{n+N}$$

$$1 - \frac{P_s}{P} = 1 - \frac{N}{n+N}$$

$$\frac{P - P_s}{P} = \frac{n}{n+N}$$

This is Raoult's law.

Determination of Molecular Mass from vapour Pressure lowering

The molecular mass of a non-volatile solute can be determined by measuring the lowering of vapour pressure $(P - P_s)$ produced by dissolving a known weight of it in a known weight of the solvent.

If w gm of solute is dissolved in W gm of solvent, m and M are molecular masses of solute and solvent, then,

$$\text{No. of moles of solute}(n) = \frac{w}{m}$$

$$\text{No. of moles of solvent}(N) = \frac{W}{M}$$

Substituting these values in the Raoult's law equation,

$$\frac{P - P_s}{P} = \frac{n}{n+N}$$

$$\frac{P - P_s}{P} = \frac{w/m}{w/m + W/M} \quad \text{——— ①}$$

for very dilute solution, the no. of moles (molecules)

of solute (w/m) is very small, it can be neglected in the denominator. Then,

The eqn (1) can be written as

$$\frac{P-P_s}{P} = \frac{wM}{mW} \quad \text{———} \quad (2)$$

Knowing the experimental value of $\frac{P-P_s}{P}$ and the molecular mass of the solvent (M), the molecular weight of solute (m) can be calculated.