

Deviation of Raoult's Law :-

The vapour pressure of a dilute solution is directly proportional to the mole fraction of the solvent.

Thus, $P \propto x_1$

$$\text{or, } P = K \cdot x_1 \\ = K \times \frac{n_1}{n_1 + n_2} \quad \text{--- (I)}$$

Where x_1 is the mole fraction of the solvent.

$n_1 =$ no. of moles of solvent.

$n_2 =$ " " " " Solute.

$K =$ Proportionality Constant.

In the case of pure solvent, if $n_2 = 0$

$$\text{So, } P^0 = K \times \frac{n_1}{n_1} \\ \text{because } n_2 = 0.$$

$$\text{So, } K = P^0 \quad \text{--- (II)}$$

Hence, from (I) and (II), we get

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

$$\text{or, } \frac{P}{P^0} = \frac{n_1}{n_1 + n_2} \quad \text{--- (III)}$$

$$\text{or, } 1 - \frac{P}{P^0} = 1 - \frac{n_1}{n_1 + n_2}$$

$$\text{or, } \frac{P^0 - P}{P^0} = \frac{n_1 + n_2 - n_1}{n_1 + n_2}$$

Therefore, $\frac{p_0 - p}{p_0} = \frac{n_2}{n_1}$

$$\text{or, } \frac{\Delta P}{p_0} = \frac{n_2}{n_1}$$

$$\text{or, } \Delta P = \frac{p_0 n_2}{n_1} \quad \text{--- (III)}$$

$$\text{Also here } n_1 = \frac{w_1 n_1}{M_1}, \quad n_2 = \frac{w_2}{M_2}$$

$$\text{So, we can write } \Delta P = p_0 \frac{w_2}{M_2} \times \frac{M_1}{w_1} \quad \text{--- (IV)}$$

For a Particular Solvent at a given temp.

We write, p_0 and M_1 is a constant quantities.

$$\text{Hence, } \Delta P \propto \frac{w_2}{M_2 \cdot w_1} \quad \text{--- (V)}$$

$$\text{or, Also from, } \Delta T_f \propto \frac{w_2}{M_2 \cdot w_1}$$

$$\text{or, } \Delta T_f = K \cdot \frac{w_2}{M_2 \cdot w_1} \quad \text{--- (VI)}$$

Where K is a Proportionality Constant Known as F.P. Constant.

$$\text{if } \frac{w_2}{M_2} = 1 \text{ mol, } w_1 = 1 \text{ g.}$$

$$\text{So, } \Delta T_f = K \quad \text{--- (VIIa)}$$

Thus, the F.P. Constant is

depression in F.P. observed by dissolving 1 mol of a solute in 1 g of a solvent.

Generally, the mass of solvent is taken as 1 g or 1 kg.

$$\text{Thus, when, } \frac{w_2}{M_2} = 1 \text{ mole, } w_1 = 1000.$$

$$\Delta T_f = K \cdot \frac{1}{1000} = K_f \quad \text{--- (VIIb)}$$

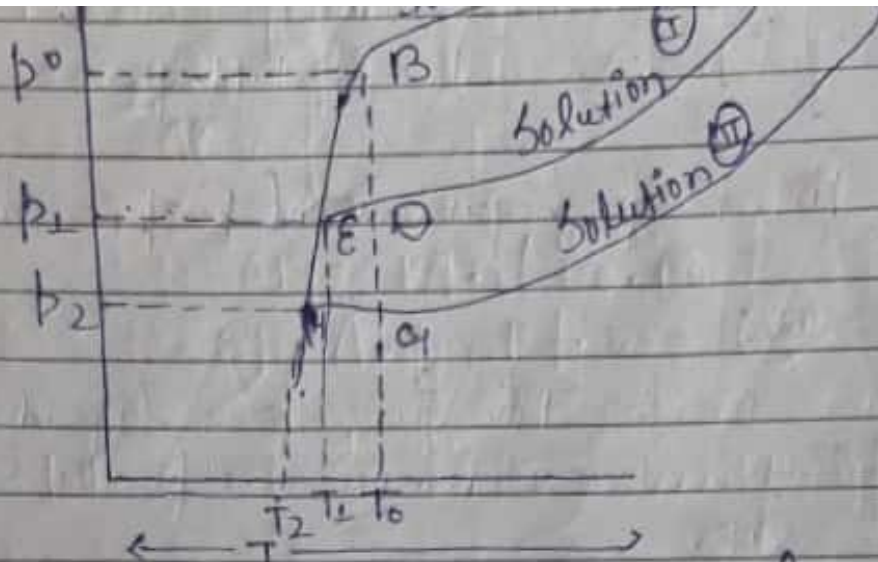
$$\text{So, that } K = 1000 K_f$$

$$\text{Hence, from the eq. } \Delta T_f = \frac{1000 K_f \times w_2}{M_2 \cdot w_1} \quad \text{--- (VIIc)}$$

Hence the constant K_f is called molar freezing point depression constant or cryoscopic constant.

$$\text{When } \frac{w_2}{M_2} = 1 \text{ mol and } w_1 = 1000 \text{ g}$$

from eq (VIIc),



p° and T_0 and v.P and F.P for solvent.

p_1 " T_1 " " " " " " Solution (I).

p_2 " T_2 " " " " " " " " (II).

Since the solutions are fairly dilute, the Curve ED and HG are considered as parallel straight lines.

Hence the triangles BHG and BEO are

similar.

$$\begin{aligned} \text{So, } \frac{BG}{BO} &= \frac{GH}{OE} \\ \frac{p - p_2}{p - p_1} &= \frac{T_0 - T_2}{T_0 - T_1} \\ \frac{\Delta P_2}{\Delta P_1} &= \frac{\Delta T_2}{\Delta T_1} \\ \Delta P &\propto \Delta T \quad \text{--- (I)} \end{aligned}$$