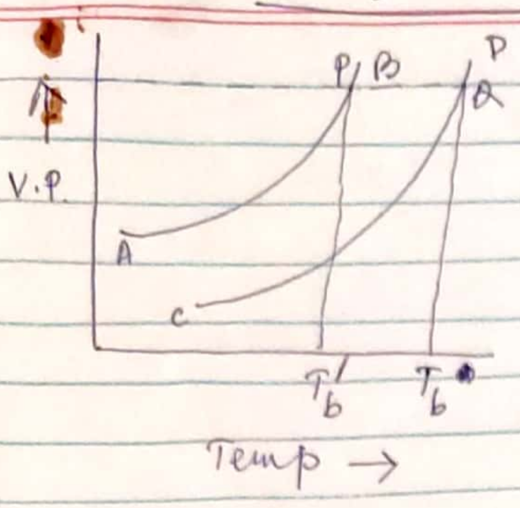
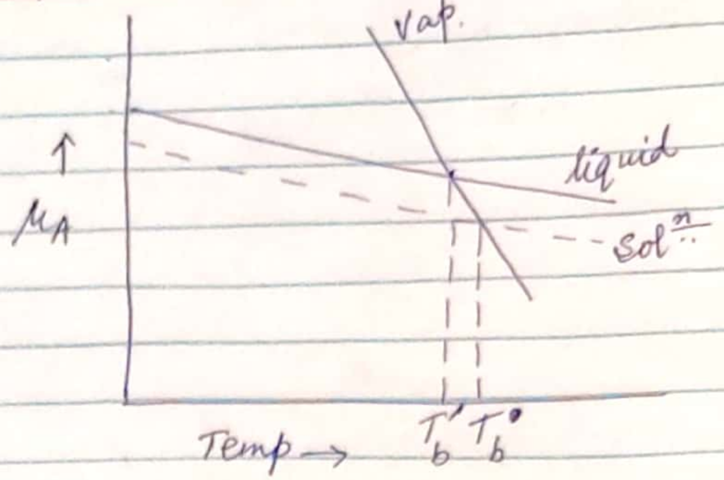
Elevation of boiling point :





Consider, a sol^n that is in eq^lm with the vapour phase of the pure solvent. The eq^lm condition is that,

$$\underset{\text{solvent in sol}^n}{\mu}(T_b, P, x) = \overset{\text{pure solvent}}{\mu^\circ_{vap}}(T_b, P) \quad \text{---- (i)}$$

T_b = b.pt. of sol^n

If the sol^n is ideal,

$$\overset{\text{solvent}}{\mu^\circ}(T_b, P) + RT_b \ln x = \mu_{vap}(T_b, P)$$

$$\text{or,} \quad \ln x = \frac{\mu_{vap}(T_b, P) - \mu^\circ(T_b, P)}{RT_b} \quad \text{---- (ii)}$$

The molar Gibbs free energy of vaporization is

$$\Delta G_{vap} = \mu_{vap}(T_b, P) - \mu^\circ(T_b, P) \qquad l \rightarrow V$$

$$\therefore \text{(ii)} \Rightarrow \quad \ln x = \frac{\Delta G_{vap}}{RT_b} \quad \text{---- (iii)}$$

Eqn (iii) has the same functional form as that of depression of freezing point except that the sign is changed on the R.H.S. This difference in sign indicates that the fz. pt. is depressed while the boiling pt. is elevated.

Now, differentiating both side w.r.to T_b at const P,

$$\frac{\partial}{\partial T_b}\left[(\ln x)\right]_P = \frac{\partial}{\partial T_b}\left(\frac{\Delta G_{vap}}{RT_b}\right)$$

$\Delta G = \Delta H - T\Delta S$

(from Gibb's Helmholtz eqn.)

$$= -\frac{\Delta H_{vap}}{RT^2}$$

$$\text{or, } \int_{\text{state 1 (Pure solvent)}}^{\text{state 2 (sol}^n)} d\ln x = -\frac{\Delta H_{vap}}{R}\int_{s-1}^{s-2}\frac{dT}{T^2}$$

(ΔH_{vap} is independent of temp.)

$$\ln\frac{x,2}{x,1} = \frac{\Delta H_{vap}}{R}\left[-\frac{1}{T}\right]_{T_b'}^{T_b^{*}}$$

$$\text{or, } \ln x = +\frac{\Delta H_{vap}}{R}\left[\frac{1}{T_b^{*}} - \frac{1}{T_b'}\right] = \frac{\Delta H_{vap}}{R}\left[\frac{T_b' - T_b}{T_b T_b'}\right]$$

$$\text{or, } \ln x = \frac{\Delta H_{vap}}{R}\times\frac{\Delta T_b}{T_b'^2}$$

Now, $\ln x_1 = \ln(1-x_2)$ [x_2 = mol. fraction of solute.]

Since sol^n is dilute, so x_2 is small.

Expanding and neglecting higher powers of x_2,

$$\ln(1-x_2) = -x_2$$

$$\therefore \cancel{-}x_2 = \cancel{+}\frac{\Delta H_{vap}}{R}\frac{\Delta T_b}{T_b'^2}$$

$$\frac{n_2}{n_1+n_2} \approx \frac{n_2}{n_1} = \frac{\left(\frac{n_2}{m_1}\right)}{M_1} = m \rightarrow \text{molality}$$

$\frac{\left(\frac{\text{mole}}{\text{wt}}\right)M_1}{M_1}$ x_B

$$\left[\; m_B = \frac{n_B}{n_A M_A} \quad (M_A = \text{Mol. wt of Solvent}) \;\right]$$

$$\therefore x_B = M_A m_B$$

$$\frac{M_1 m}{\cancel{M_1}} = \frac{\Delta H_{vap}}{R}\frac{\Delta T_b}{T_b^{*2}}$$

$$\Delta T_b = K_b m_B$$

$$\text{where } K_b = \frac{M_A R (T_b^{*})^2}{\Delta H_{vap}}$$

(where K_b = molal bl. pt. elevation const.)

$$\Delta T_b = m\left(\frac{T_b^{*2} R\, M_1}{\Delta H_{vap}}\right)$$

Integrating, $\int_{1}^{x_1} \frac{dx_1}{x_1} = -\frac{\Delta H_{vap}}{R} \int_{T_b^*}^{T_b} \frac{dT_b}{T_b^2}$

$\therefore \ln x_1 = -\frac{\Delta H_{vap}}{R} - \left(\frac{1}{T_b} - \frac{1}{T_b^*}\right)$

$= +\frac{\Delta H_{vap}}{R} \frac{(T_b^* - T_b)}{T_b T_b^*}$

$= -\frac{\Delta H_{vap}}{R} \frac{\Delta T_b}{T_b^{*2}}$ $\quad (\Delta T_b = T_b - T_b^*)$

$\ln x_1 \approx \ln(1-x_2) \approx -x_2 = \frac{\Delta H_{vap}}{R} \times \frac{\Delta T_b}{T_b^{*2}}$

$+x_2 = +\frac{\Delta H_{vap} \cdot \Delta T_b}{R T_b^{*2}}$

$x_2 = \frac{n_2}{n_1+n_2} \approx \frac{n_2}{n_1}$

Solute molality is $m_2 = \frac{n_2}{n_1 M_1}$

M_1 = Solvent molar mass (? Kg/mol)

for very dilute solⁿ,

$x_2 = M_1 \cdot m_2$.

$\therefore M_1 \cdot m_2 = \frac{\Delta H_{vap} \cdot \Delta T_b}{R T_b^{*2}}$

$\therefore \Delta T_b = \left(\frac{R T_b^{*2} M_1}{\Delta H_{vap}}\right) m_2$

$= K_b \cdot m_2$

↓

Solvent's molal boiling pt.-elevation const.

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