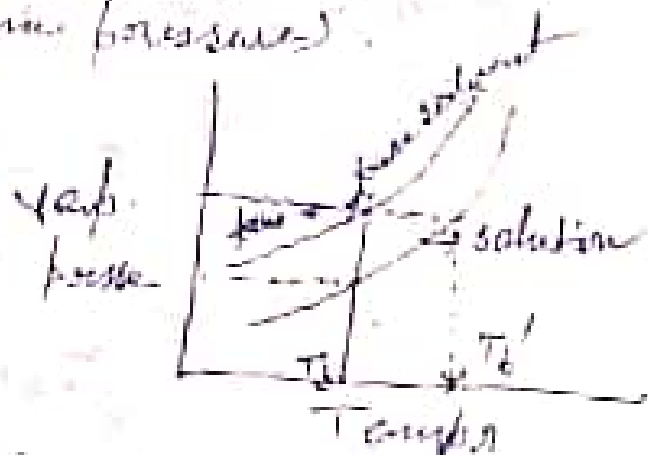


(HONS)
Elevation of boiling point.

Boiling temp^{re} is that temp^{re} at which the vapour pressure of liquid is equal to the external pressure (i.e. 1 atm pressure).

* (1)



The quantitative relation between the elevation of boiling point and the concentration of the solution can be derived thermodynamically.

Consider a solution which is in equilibrium with the vapour ~~phase~~ of the pure solvent.

We have the following equilibrium

at the boiling point of the solution
 solvent in solution \rightleftharpoons vapour of pure solvent

At eqm,

$$p_1(\text{soln}) (T_b, p) = p_1(\text{pure}) (T_b, p)$$

$T_b = \text{b.p. of the solution.}$

(1)

At constant pressure, boiling temp. is a function of x_1 i.e. fraction of the solvent in solution.

For an ideal solution we have

$$\mu = \mu^{\circ} + RT \ln X_{\text{solvent}}$$

$$\mu_{\text{pure}} = \mu^{\circ} + RT \ln x_1$$

$$\mu_{\text{pure}} = \mu_{\text{pure}} + RT \ln x_1 \quad \text{--- (2)}$$

$$\therefore \ln x_1 = \frac{\mu_{\text{pure}} - \mu_{\text{pure}}}{RT} \quad \text{--- (3)}$$

$$\ln x_1 = \frac{-\Delta \mu_{\text{vap}}}{RT} \quad \text{--- (4)}$$

$\Delta \mu_{\text{vap}} = \mu_{\text{pure}} - \mu_{\text{pure}}$, it is molar free energy of evaporation of the pure solvent at temp T_b and pressure P .

This relation is the relation between composition of the solution and the boiling point.

Differentiating equ (4) w.r.t. to x_1 at const. P we get

$$\frac{d}{dx_1} \ln x_1 = \frac{d}{dx_1} \left[\frac{-\Delta \mu_{\text{vap}}}{RT} \right]$$

$$0 = \frac{1}{x_1} = \frac{1}{R} \left\{ \frac{\partial \ln(a_1/T_b)}{\partial T_b} \right\}_P \left(\frac{\partial T_b}{\partial x_1} \right)_P$$

$$\therefore dG = v dp - e dt \quad (5)$$

$$dp = \bar{v} dp - \bar{s} dt$$

$$d\mu_p = - \bar{s} dt$$

$$d(\mu)_p = - \frac{\Delta H_m}{T} dt$$

$$d(\ln a_1)_p = - \frac{\Delta H_m}{T^2} dt$$

$$\left\{ \frac{\partial}{\partial T} (\ln a_1/T) \right\}_P = - \frac{\Delta H_m}{T^2} \quad (6)$$

\(\therefore\) Above eqn (6) becomes

$$\frac{1}{x_1} = - \frac{\Delta_{vap} H_{1,m}}{RT_b^2} \left(\frac{\partial T_b}{\partial x_1} \right)_P \quad (7)$$

$$\text{or, } \frac{dx_1}{x_1} = - \frac{\Delta_{vap} H_{1,m}}{RT_b^2} dT_b \text{ (constant)} \quad (8)$$

where $\Delta_{vap} H_{1,m}$ is the molar enthalpy of vapourisation of the pure solvent at temp. T_b .

Integrating eqn (8), we get

$$\int_1^{x_1} \frac{dx_1}{x_1} = - \int_{T_b^0}^{T_b} \frac{\Delta_{vap} H_{1,m}}{R} \frac{dT_b}{T_b^2} \quad (9)$$

T_b^0 b.p. of pure solvent

Let $\Delta_{vap} H_{1,m}$

where T_1 and T_2 are the b.p. of solution and pure solvent respectively

As $\Delta_{\text{vap}} H_{\text{m}}$ is assumed to be independent of over the temperature range T_1 and T_2 , on integrating

the eqn (9) becomes

$$\ln x_1 = - \frac{\Delta_{\text{vap}} H_{\text{m}}}{R} \left(-\frac{1}{T_1} + \frac{1}{T_2} \right) \quad \dots (10)$$

$$\ln x_1 = + \frac{\Delta_{\text{vap}} H_{\text{m}}}{R} \frac{1}{T_1} - \frac{\Delta_{\text{vap}} H_{\text{m}}}{R T_2}$$

$$\frac{\Delta_{\text{vap}} H_{\text{m}}}{R} \frac{1}{T_1} = \ln x_1 + \frac{\Delta_{\text{vap}} H_{\text{m}}}{R T_2}$$

$$\therefore \frac{1}{T_1} = \frac{R \ln x_1}{\Delta_{\text{vap}} H_{\text{m}}} + \frac{1}{T_2} \quad (11)$$

$$\begin{aligned} \frac{R \ln x_1}{\Delta_{\text{vap}} H_{\text{m}}} &= \frac{1}{T_1} - \frac{1}{T_2} = \frac{T_2 - T_1}{T_1 T_2} \\ &= - \frac{\Delta T_1}{T_1^2} \quad [T_1 \approx T_2] \end{aligned}$$

$$\ln x_1 = - \frac{\Delta H_{\text{m}}}{R} \frac{\Delta T_1}{T_1^2} = - \frac{L V \cdot \Delta T_1}{R T_1^2}$$

Equation (1) can be used to compute the b.p. of a solution in which the amount fraction of solvent is x_1 .

$$T_1^0 = \text{b.p. of pure solvent}$$

ΔH_{vap} = molar enthalpy of vaporization of pure solvent, respectively.

$$\ln \frac{p}{p^0} = -\frac{L_v}{R} \frac{\Delta T_1}{T_1^2} \quad \left[\because p = p^0 \cdot x_1 \right]$$

$$\therefore x_1 = \frac{p}{p^0}$$

$$\therefore \ln \left(1 - \frac{p^0 - p}{p^0} \right) = -\frac{L_v}{R} \frac{\Delta T_1}{T_1^2} \quad \left[\because \frac{p^0 - p}{p^0} = x_2 \right]$$

as $\frac{p^0 - p}{p^0}$ is quite small, expanding and neglecting higher terms

$$\left[\ln(1-x) = -x + \dots \right]$$

$$\therefore -\frac{p^0 - p}{p^0} = -\frac{L_v \Delta T}{RT_1^2}$$

$$x_2 = \frac{L_v \Delta T}{RT_1^2}$$

$$\therefore \Delta T_1 = \frac{RT_1^2}{L_v} x_2$$

This is the relation between elevation of b.p. and concentration of the solute in soln.

$$X_2 = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1} \quad (\because n_1 \gg n_2)$$

$$= \frac{g/m}{W/H}$$

$$\Delta T_b = \frac{RT_b^2}{L_v} X_2 = \frac{RT_b^2}{L_v} \frac{g/m}{W/H}$$

$$= \frac{RT_b^2}{\frac{L_v}{H}} \frac{g}{m} \cdot \frac{1}{W}$$

$$= \left\{ \frac{RT_b^2}{1000 \times L_v} \right\} \left\{ \frac{g \times 1000}{mH} \right\} \quad \text{--- (1)}$$

L_v = latent heat of vap. per gm.

g = wt of solute

m = Mol wt of "

W = wt. of solvent

H = Mol wt. of "

$$\therefore \Delta T_b = K_b C_m \quad \text{--- (2)}$$

where $K_b = \frac{RT_b^2}{1000 L_v} \quad \text{--- (3)}$

$$C_m = \frac{g \times 1000}{m \times H} = \text{molality of the soln.} \quad \text{--- (4)}$$

According to the relation (2), Elevation of bp is proportional to the molality of the solution i.e. proportional to the no. of molecules of any solute per 1000 gm of solvent. It is thus a colligative.

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$$\ln \frac{p}{p^0} = - \frac{L_v}{R} \left[\frac{1}{T_b} - \frac{1}{T_b'} \right] = - \frac{L_v}{R} \frac{T_b' - T_b}{T_b \cdot T_b'}$$

L_v = latent heat of vaporization/mole

$$p = p^0 \cdot X_1$$

$$\begin{aligned} \therefore \ln X_1 &= - \frac{L_v}{R} \frac{T_b' - T_b}{T_b \cdot T_b'} \\ &= - \frac{L_v}{R} \frac{\Delta T_b}{T_b^2} \end{aligned}$$

property.

It is evident that equal molecular amounts of different solute substances dissolved in the same amount of a given solvent increases the b.p. to the same extent.

For a solution, where $\rho_{\text{sol}} = 1$

$\Delta T_b = K_b$ i.e. K_b is the elevation of b.

point for a solution of unit

molarity. Hence K_b is called

molar elevation constant or

ebullioscopic constant.

So the ρ K_b is the increase of b.pt.

of a solvent, when one mole of

the solute is dissolved per 1000

gm of the solvent.