Colligative Properties

Dr. Sandip Kumar Rajak

ELEVATION OF BOILING POINT OF A SOLUTION

Boiling point of a solution is the temperature at which the vapour pressure of the liquid is equal to the external pressure, usually one atmospheric pressure. The addition of a nonvolatile solute to the solvent lowers its vapour pressure and thereby elevates the boiling point of the solution. The difference between the boiling point of the solution and the pure solvent is known as the elevation of boiling point of the solution. The elevation of boiling point of the solution depends on the nature of the solvent and the concentration of the solute. Boiling point elevation can be readily understood in terms of the lowering of vapour pressure. Figure 2 shows the variation of vapour pressure with temperature of pure solvent (curve AB) and solution (curve CD). Since the vapour pressure of the solution is lower than that of the pure solvent, the vapour pressure temperature curve for the solution thus lies below the curve for the pure solvent.

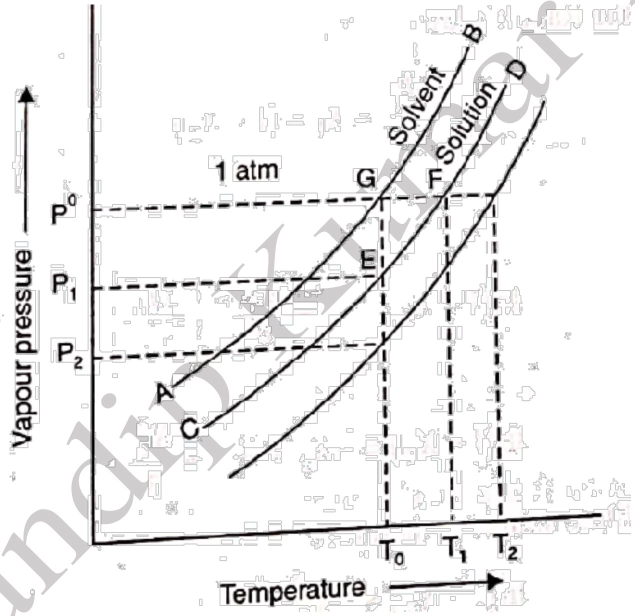

Fig. 2 : Elevation of boiling points

Let T_0 be the boiling point of the pure solvent at one atmospheric pressure. At this temperature, the solution lower vapour pressure than one atmosphere and hence it will not boil. With increase of temperature, say to T_1, the vapour pressure of the solution rises to one atmosphere and the solution boils. This means that the solution has a higher boiling point than that of the pure solvent. Thus $T_1 - T_0 = \Delta T_b$ represents the elevation in the boiling point of solution. Points G and E represent the vapour of pure solvent and solution respectively at the same temperature, T_0 . The lowering in vapour pressure is given by

$$P^0 - P^1 = \Delta P = GE$$

Since points E and F lie on the vapour pressure curve of the solution at temperature T_0 and T_1 then from Clausius Clapeyron equation we have

$$\ln \frac{P^0}{P_1} = \frac{\Delta H_{\text{vap},\,m}}{R}\left[\frac{1}{T_0} - \frac{1}{T_1}\right]$$

$$= \frac{\Delta H_{\text{vap},\,m}}{R}\left[\frac{T_1 - T_0}{T_1 T_0}\right] \qquad \text{.......................... .... (11)}$$

where P_1 is the vapour pressure of the solution at temperature T_0 while P^0 is the vapour pressure at T_1, $\Delta H_{\text{vap, m}}$ is the enthalpy of vapourization per mole of the solvent. For a dilute solution, T_0 and T_1 are not very different and therefore, $T_0T_1 \approx T_0^2$ and hence Eq. (11) reduces to

$$\ln \frac{P^0}{P_1} = \frac{\Delta H_{\text{vap},\,m}}{R}\left[\frac{\Delta T_b}{T_0^2}\right]$$

$$\ln \frac{P_1}{P^0} = -\frac{\Delta H_{\text{vap},\,m}}{R}\left[\frac{\Delta T_b}{T_0^2}\right] \qquad \text{............ .... (12)}$$

Furthermore, according to the Raoult's law

$$\frac{P_1}{P^0} = X_1 = (1 - X_2)$$

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hence Eq. (12) becomes

$$\ln(1-X_2) = -\frac{\Delta H_{\text{vap},m}}{R}\left[\frac{\Delta T_b}{T_0^2}\right]$$

$$\ln(1-X_2) = -X_2 + \frac{X_2^2}{2} - \frac{X_2^3}{3} + \ldots$$

.... (13)

and X_2 is small in case of a dilute solution, therefore

$\ln(1 - X_2) \approx - X_2$

hence Eq. (13) becomes

$$-X_2 = -\frac{\Delta H_{\text{vap},m}}{R}\left[\frac{\Delta T_b}{T_0^2}\right]$$

or

$$\Delta T_b = \frac{RT_0^2 X_2}{\Delta H_{\text{vap},m}}$$

.... (14)

THERMODYNAMIC DERIVATION OF BOILING POINT ELEVATION OF SOLUTIONS

The Chemical potential μ_l of the solvent in a dilute solution of a non-volatile solute (behaving as an ideal solution) is given by

$$\mu_l = \mu_l^0 + RT \ln X_1$$

where the subscript 'l' refers to the liquid phase and X_1 is the mole fraction of the solvent and μ_l^0 is the chemical potential of pure solvent. At the boiling point of the solution where the equilibrium exists with vapour at a pressure of 1 atm

$$\mu_l = \mu_v^0$$

where μ_l^0 is the chemical potential of pure vapour. Thus, at the boiling point of the solution one can write

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$$\mu_v^0 = \mu_l = \mu_l^0 + RT \ln X_1$$

On rearranging, we get,

$$RT \ln X_1 = \mu_v^0 - \mu_l^0$$

$$\ln X_1 = \ln(1 - X_2) = \mu_v^0 - \mu_l^0 = \frac{\Delta G_{vap,\, m}}{RT} \qquad \text{.......... ....} \quad (15)$$

Here $\Delta G^0_{vap,\, m}$ is the molar Gibbs free energy of vapourization of pure solvent and X_2 is the mole fraction of the solute in the solution.

Since

$$\Delta G_{vap,\, m} = \Delta H_{vap,m} - T\Delta S_{vap,m}$$

Therefore, Eq. (15) becomes

$$\ln(1 - X_2) = \frac{\Delta H_{vap,\, m}}{RT} - \frac{\Delta S_{vap,\, m}}{R} \qquad \text{.......... ....} \quad (16)$$

When $X_2 = 0$, $T = T_b$ = boiling point of the pure solvent and from Eq. (16), we have

$$\frac{\Delta H_{vap,\, m}}{RT_b} = \frac{\Delta S_{vap,\, m}}{R} \qquad \text{.......... ....} \quad (17)$$

Comparison of equation 16 and 17 yields

$$\ln(1-X_2) = \frac{\Delta H_{vap,\, m}}{R}\left[\frac{1}{T} - \frac{1}{T_b}\right]$$

Since the solution is very dilute $X_2 << 1$, therefore, ln $(1-X_2)$ can be written as

$$\ln(1-X_2) \approx -X_2$$

and hence we obtained

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$$-X_2 = \frac{\Delta H_{vap,\,m}}{RT_b}\left[\frac{1}{T}-\frac{1}{T_b}\right] = -\frac{\Delta H_{vap,\,m}}{RT_b}\left[\frac{1}{T_b}-\frac{1}{T}\right]$$

$$X_2 = \frac{\Delta H_{vap,\,m}}{RTT_b}(T-T_b)$$

$$= \frac{\Delta H_{vap,\,m}}{RT_b^2}\Delta T_b$$

(as $T \approx T_b$)

Where ΔT_b is the elevation of boiling point of the solution.

or

$$\Delta T_b = \frac{RT_b^2 X_2}{\Delta H_{vap,\,m}} \qquad \text{........ ....} \quad (18)$$

Equations (14) or (18) give the elevation of boiling point of a solution in terms of the molar enthalpy of vapourization of the solvent, the boiling point of the solvent, and mole fraction of the solute in solution. Since T_0 and ΔH_{vap} are constant for a given solvent, therefore the elevation of boiling point of the solution is directly proportional to the mole fraction of the solute and is independent of the nature of the solute.

Again,

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$$X_2 = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1} \quad \text{(For a Dilute solution)}$$

$$= \frac{W_2/M_2}{W_1/M_1}$$

$$= \frac{W_2 M_1}{W_1 M_2}$$

Substituting this value of X_2 in Eq. (18), we get

$$\Delta T_b = \left(\frac{RT_0^2}{\Delta H_{vap,m}}\right)\left(\frac{W_2 M_1}{W_1 M_2}\right)$$

.... (19)

Since the molality m of the solution is given as

$$m = \frac{1000 W_2}{W_1 M_2}$$

.... (20)

Therefore equation 19 becomes

$$\Delta T_b = \frac{RT_0^2 \, m M_1}{\Delta H_{vap,m} \, 1000}$$

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$$= \frac{RT_0^2 m}{\Delta H_{vap.m}\, n_1} \qquad \text{........ ....} \quad (21)$$

where $n_1 (= 1000/M_1)$ is the number of moles of 1000 g of solvent. For any solvent, the quantity $\frac{RT_0^2 M_1}{\Delta H_{vap.m}\, 1000}$ is constant and is equal to K_b known as the molal boiling point elevation or molal ebullioscopic constant .

$$K_b = \frac{RT_0^2}{\Delta H_{vap.m}\, n_1} = \frac{RT_0^2 M_1}{\Delta H_{vap.m}\, 1000} \qquad \text{........ ....} \quad (22)$$

Hence Eq. (20) becomes,

$$\Delta T_b = K_b m \qquad \text{........ ....} \quad (23)$$

It is clear from this equation that the elevation in boiling point of a solution is directly proportional to the molality of the solution.

For a solution, where m = 1, $\Delta T_b = K_b$ i.e., the molal elevation constant is therefore defined as the elevation in boiling point of a solution *unit molality*.

Equation (23) can be verified in three ways (i) the elevation of boiling point should be proportional to the molality of the solution, (ii) the proportionality constant K_b should be independent of the nature of the solute, and (iii) the value of K_b obtained from experiments and the one predicted by Eq. (22) should be in agreement.

For water, $\Delta H_{vap,\,m} = 40670 \text{J mol}^{-1}$, $T_0 = 373.16\text{K}$, $M_1 = 18\text{g mol}^{-1}$ and hence the value of K_b from Eq. (22)

$$K_b = \frac{RT_0^2 M_1}{\Delta H_{vap.m}\, 1000}$$

$$= \frac{(8.314 \text{ JK}^{-1}\text{mol}^{-1})(373.16 \text{ K})^2 (18 \text{ g mol}^{-1})}{(1000 \text{ g kg}^{-1})(40670 \text{ J mol}^{-1})}$$

$$= 0.513 \text{ kg mol}^{-1} \text{ K or } 0.513 \text{ K}/(\text{mol kg}^{-1})$$

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Molar Mass Determination from Boiling Point Elevation

From Eq. (23), it is possible to calculate the molar mass of the solute

$$\Delta T_b = K_b m$$

$$= K_b \frac{1000 W_2}{W_1 M_2}$$

$$M_2 = \frac{1000 W_2 K_b}{W_1 \, \Delta T_b} \quad \text{.................................(24)}$$

This equation permits us to calculate the molar mass of the solute since W_1, the mass of the solvent, W_2 the mass of the solute, ΔT_b the elevation of boiling point and K_b the ebullioscopic constant are known.

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