Colligative Properties

DEPRESSION OF FREEZING POINT OF SOLUTIONS

The freezing point of a liquid is the temperature at which the solid phase begins to separate out from the liquid. At this temperature solid and liquid phases are in equilibrium and have equal vapour pressures.

A solution freezes at a temperature lower than that of the pure solvent. This is due to the lowering of the vapour pressure of a solution as a result of addition of a small amount of nonvolatile solute.

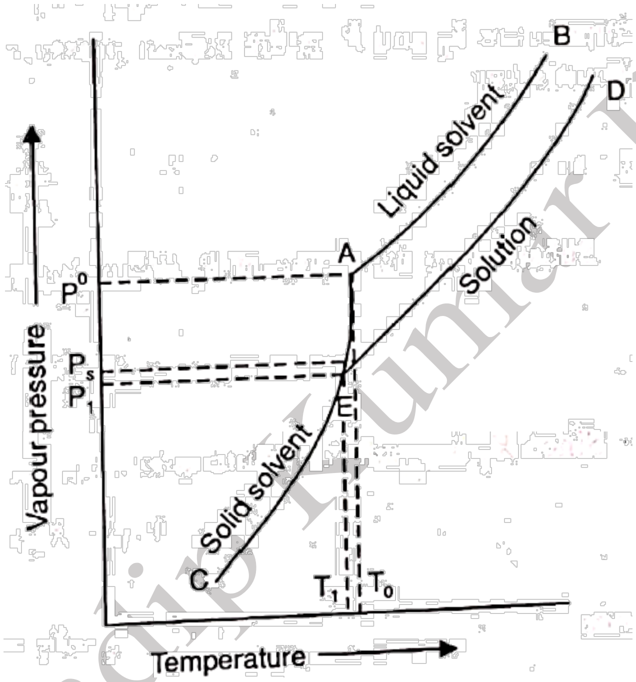

Fig. 3: Depression of freezing point of a solvent

Figure 3 shows the vapour pressure as a function of temperature for the solution and the pure solvent. CA is the sublimation curve of the solid solvent and AB represents the vapour pressure curve of the pure liquid solvent. These two curves intersect at point A, where the vapour pressures of the solid solvent and liquid solvent are equal. The temperature T_0 corresponding to this vapour pressure P^0 is the freezing point of the pure solvent.

The vapour pressure curve of the solution of a nonvolatile solute will be lower than that of the pure solvent and is represented by DE. This curve intersects the sublimation curve at point E, where the solution will have the same vapour pressure as the pure solid solvent. Hence T_1 is the freezing point of the solution and is lower than T_0.

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The depression of freezing point of the solution is given by $\Delta T_f = T_0 - T_1$. The magnitude of ΔT_f depends on the solvent and the of the solute. Let P^0 be the vapour pressure of the solid and pure solvent at temperature T_0 and P_1 the vapour pres-sure of the solution at temperature T_1. Since points A and E lie on the same vapour pressure curve, they must both be related by Clausius-Clapeyron equation.

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

$$= \frac{\Delta H_{sub,\,m}}{R}\left[\frac{T_0 - T_1}{T_0 T_1}\right]$$

$$\ln\frac{P_0}{P_1} = \frac{\Delta H_{sub,\,m}}{R}\left[\frac{T_0 - T_1}{T_0 T_1}\right] \qquad \text{..............................(25)}$$

Again for solution, P_s is the vapour pressure at temperature T_0 and P_1 is the vapour pressure at temperature T_1, therefore,

$$\ln\frac{P_s}{P_1} = -\frac{\Delta H_{vap,\,m}}{R}\left[\frac{T_1 - T_0}{T_0 T_1}\right] = \frac{\Delta H_{vap,\,m}}{R}\left[\frac{T_0 - T_1}{T_0 T_1}\right] \qquad \text{..............................(26)}$$

On subtracting (26) from (25), we get

$$\ln P^0 - \ln P_s = \frac{(\Delta H_{sub,\,m} - \Delta H_{vap,\,m})(T_0 - T_1)}{R T_0 T_1} \qquad \text{..............................(26)}$$

But $\Delta H_{sub,\,m} - \Delta H_{vap,m} = \Delta H_{fus,m}$ the molar enthalpy of fusion of solvent.

Hence Eq. (26) becomes

$$\ln\frac{P^0}{P_s} = \frac{\Delta H_{fus,\,m}\Delta T_f}{RT_0T_1}$$

$$\ln\frac{P_s}{P^0} = -\frac{\Delta H_{fus,\,m}\Delta T_f}{RT_0T_1} \qquad \text{..............................(27)}$$

Since the solution is dilute, $T_0T_1 \approx T_0^2$. Again P^0 is the vapour pressure of the pure solvent at temperature T_0 and P_s is the vapour pressure of the solution at the same temperature. Therefore, from Raoult's law

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

Substituting this value of $P_s/ P_0)$ in Eq. (27), we get

$$(1-X_2) = -\frac{\Delta H_{fus,\,m} \Delta T_f}{RT_0^2}$$

Since X_2 is small for dilute solutions, therefore

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

Hence
$$-X_2 = -\frac{\Delta H_{fus,m}}{R} \frac{\Delta T_f}{T_0^2}$$

or
$$\Delta T_f = \frac{RT_0^2 X_2}{\Delta H_{fus,m}} \qquad \text{................................(28)}$$

THERMODYNAMIC DERIVATION OF DEPRESSION OF FREEZING POINT OF SOLUTIONS

When a solution freezes, pure solid solvent and the solution with solute present at a mole fraction are in equilibrium. The chemical potentials of the solvent must be the same in both phases, viz., solid and liquid phases

$$\mu^0(s) = \mu(l)$$

The chemical potential of the solvent in the solution is given by

$$\mu(l) = \mu^0(l) + RT \ln X_1$$

where X_1 is the mole fraction of the solvent in the solution.

On rearranging, we get

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$$\frac{\mu^0(l) - \mu^0(s)}{RT} = -\ln X_1$$

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

$$-\ln(1-X_2) = \frac{\Delta G_{fus,m}}{RT}$$

$$= \frac{\Delta H_{fus,m} - T\Delta S_{fus,m}}{RT}$$

$$= \frac{\Delta H_{fus,m}}{RT} - \frac{\Delta S_{fus,m}}{R} \qquad \text{.................................(29)}$$

when $X_2 = 0$ the freezing point is that of pure liquid, T_f

$$\ln(1) = \frac{\Delta H_{fus,m}}{RT_f} - \frac{\Delta S_{fus,m}}{R}$$

and

$$0 = \frac{\Delta H_{fus,m}}{RT_f} - \frac{\Delta S_{fus,m}}{R} \qquad \text{.................................(30)}$$

On subtracting Eq. (30) from Eq. (29), we get

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

Since X_2 is small ($X_2 << 1$) therefore In $(1 - X_2)$ can be written as $\ln(1 - X_2) \approx - X_2$, so

$$X_2 = \frac{\Delta H_{fus,m}}{R}\left[\frac{1}{T} - \frac{1}{T_f}\right]$$

$$= \frac{\Delta H_{fus,m}}{R}\left[\frac{T_f - T}{T_f\, T}\right]$$

$$= \frac{\Delta H_{fus,m}}{R T_f^2}\,\Delta T_f \qquad (\because T_f = T) \qquad \text{..................................(31)}$$

where ΔT_f the depression in the freezing point of the solvent.

$$X_2 \approx \frac{n_2}{n_1} = \frac{W_2 M_1}{M_2 W_1}$$

$$\text{m(molarity)} = \frac{1000 W_2}{M_2 W_1}$$

and hence Eq. (28) or Eq. (31) reduces to

$$\Delta T_f = \frac{R T_0^2 m M_1}{\Delta H_{fus,m}\, n_1}$$

$$= K_f\, m \qquad \text{................................(32)}$$

$$\therefore K_f = \frac{R T_0^2}{\Delta H_{fus,m}\, n_1} = \frac{R T_0^2}{\Delta H_{fus,m}}\,\frac{M_1}{1000} \qquad \text{................................(33)}$$

and is known as the molal freezing point constant or cryoscopic constant of a solvent.

When m = 1, $K_f = \Delta T_f$. The molal depression constant can thus be defined as the depression in the freezing point of of unit *molality*. Since K_f is constant for a given solvent, therefore the depression in freezing point of a solution is dependent on the concentration of the solute and not on the nature of the solute. It is for this reason the depression of freezing point is a colligative property.

For water $T_0 = 273.16K$, $M_1 = 1.8 \times 10^{-2}\ kgmol^{-1}$, $\Delta H_{fus,\ m} = 6031\ J\ mol^{-1}$, K_f can be calculated from Eq. (33) as

$$K_f = \frac{(8.3124 JK^{-1}mol^{-1})(273.16K)^2(18 g\ mol^{-1})}{1000\ g\ Kg^{-1})(6031\ Jmol^{-1})}$$

$$= 1.857\ K\ Kg\ mol^{-1}$$

Determination of Molar mass from Freezing Point Depression

From Eq. (32), it is possible to calculate the molar mass of the solute as

$$\Delta T_f = K_f m$$
$$= K_f \left(\frac{1000 W_2}{M_2 W_1}\right)$$

or

$$M_2 = \frac{1000 W_2 K_f}{W_1 \Delta T_f} \qquad \text{.................................(34)}$$

Hence, to calculate the molar mass of the solute, K_f for the solvent be known. The value of K_f is obtained either from the equation (32) using a dilute solution or computed from equation (33). Different solvent have their specific molal freezing point constant.

Problem 1: The lowering of freezing point of benzene was 2.33 K when 4.12×10^{-4} kg of a solute of unknown molar mass was dissolved in 9.31×10^{-3} kg of benzene. Calculate the molar mass of the solute. Molal depression constant for benzene is 5.1 K kg mol^{-1}.

Solution: Here,

$\Delta T_f = 2.33$ K $\qquad K_f = 5.1$ K kg mol^{-1}

$M_2 = ?$ $\qquad W_1 = 9.31 \times 10^{-3}$kg

$W_2 = 4.12 \times 10^{-4}$ kg

We know,

$$\Delta T_f = K_f \frac{W_2 \times 1000}{M_2 \times W_1}$$

or

$$M_2 = \frac{K_f W_2 1000}{W_1 \Delta T_2}$$

$$= \frac{\left(5.1 \text{ K kg mol}^{-1}\right)\left(4.12 \times 10^{-4} \text{ kg}\right)\left(1000 \text{ g kg}^{-1}\right)}{\left(9.31 \times 10^{-3} \text{kg}\right)\left(2.33 \text{ K}\right)}$$

$$= 96.87 \text{ g mol}^{-1}$$

$$M_2 = 9.687 \times 10^{-2} \text{kg mol}^{-1}$$

Problem 2 : There are two solutions of a certain non-volatile solute X in a solvent Y. The molalities of these solutions are m_1 and m_2. If K_f and K_b for the solvent are 1.8 and 0.9 (K kg mol^{-1}), then for equal values ΔT_f for m_1 and ΔT_b for m_2, calculate the ratio of m_1 and m_2.

Solution:

$$\Delta T_f = 1.8\ m_1$$

and $\qquad \Delta T_b = 0.9\ m_2$

But $\qquad \Delta T_f = \Delta T_b$, hence

$$1.8\ m_1 = 0.9\ m_2$$

or

$$\frac{m_1}{m_2} = \frac{1}{2}$$