

Freezing Point Depression

(1)

The difference between the freezing point of the pure solvent and the solution containing the non-volatile solute is called depression of freezing pt.

If T_0 is the freezing point of pure solvent and T_f is freezing point depression.

Let us consider the freezing of pure liquid solvent (1). At its freezing point there is equilibrium between solid and liquid. When a non-volatile solute is added (2) to the liquid phase, the proportion of molecules bouncing against the solid phase decreases (i.e. the solvent molecules which are capable of being captured and added to the crystal lattice), the escaping tendency of solvent molecules from liquid to solid has diminished but the reverse process i.e. escaping tendency from solid to liquid is unaffected. The "crystals" of solvent begin to dissolve. ^{momentarily eqn} - To prevent this dissolution of solvent & to restore equilibrium, temperature is lowered. At some lower temperature, the two escaping tendency $S \rightleftharpoons L$ again match & equilibrium is attained.

The chemical potential of solid solvent (1) must be equal to its chemical potential in the liquid phase at new concentration.

$$\mu_1^s = \mu_1^l = \mu_1^{*l} + RT \ln x_1^l \quad \text{--- (1) (2)}$$

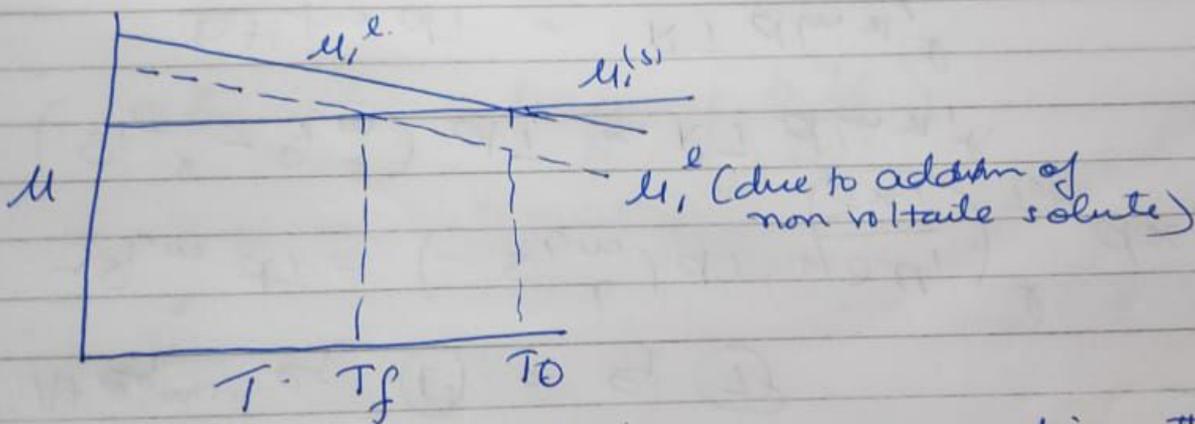
μ_1^{*l} → chemical potential of pure liquid 1

x_1^l = mole fraction of liquid (solvent) in solution

When a solute is added, $\ln x_1^l$ decreases,

∴ Temp is lowered in compensation so that μ_1^s & μ_1^{*l} both rises. But it is found that μ_1^{*l} rises faster than μ_1^s because the molar "entropy" of liquid is greater than that of solid & the ordering effect of temp. drop is more pronounced.

At lower temp, large rise in μ_1^{*l} & small drop in $\ln x_1^l$ (due to addition of solute) balance the small rise in μ_1^s & eq (1) is balanced



for a change (small) temp & composition, the equilibrium condition requires that

$$d\mu_1^s = d\mu_1^l$$

$$\mu_1^s = f(T, P) \quad \text{--- (2)}$$

$$\mu_1^l = f(T, P, x_1) \quad \text{--- (3)}$$

$$d\mu_1^s = \left(\frac{\partial \mu_1}{\partial T} \right)_P dT + \left(\frac{\partial \mu_1}{\partial P} \right)_T dP \quad \text{--- (4)}$$

$$d\mu_1^l = \left(\frac{\partial \mu_1}{\partial T} \right)_P^l dT + \left(\frac{\partial \mu_1}{\partial P} \right)_T^l dP + \left(\frac{\partial \mu_1}{\partial x_1} \right)^l dx_1$$

At const P , $dP = 0$ eq (4) & (5) becomes (3)

$$d\mu_1^{(s)} = \left(\frac{\partial \mu_1}{\partial T} \right)_P^s dT = -S_{1,m}^s dT \quad \text{--- (6)}$$

$$d\mu_1^{(l)} = \left(\frac{\partial \mu_1}{\partial T} \right)_P^l dT + \left(\frac{\partial \mu_1}{\partial x_1} \right)_{T,P}^l dx_1 = (-S_{1,m}^l) dT + \left(\frac{\partial \mu_1}{\partial x_1} \right)_{T,P}^l dx_1$$

At eqⁿ eq (6) = eq (7) --- (7)

$$-S_{1,m}^s dT = (-S_{1,m}^l) dT + \left(\frac{\partial \mu_1}{\partial x_1} \right)_{T,P}^l dx_1$$

$$(S_{1,m}^l - S_{1,m}^s) dT = RT d \ln x_1^l$$

$$\frac{\Delta H_{fus}}{T} dT = RT d \ln x_1^l$$

$$\int_1^n \left\{ d \ln x_1^l \right\} = \int_{T_0}^{T_f} \frac{\Delta H_{fus}}{RT^2} dT$$

$$\ln x_1 = - \frac{\Delta H_{fus}}{R} \left[\frac{1}{T_f} - \frac{1}{T_0} \right]$$

$$\ln x_1 = - \frac{\Delta H_{fus}}{R} \left[\frac{T_0 - T_f}{T_f T_0} \right] \quad \text{--- (7a)}$$

$$\ln x_1 = - \frac{\Delta H_{fus}}{R} \frac{\Delta T}{T_f T_0} \quad \text{--- (8)}$$

$$\Delta T_f = \frac{\ln x_1 T_f T_0}{- \frac{\Delta H_{fus}}{R}}$$

eq (7) can also written in a form

$$\ln x_1 = - \frac{\Delta H_{\text{fusion}}}{R} \left(\frac{1}{T_f} - \frac{1}{T_0} \right)$$

$$- \frac{R}{\Delta H_f} \ln x_1 = \left(\frac{1}{T_f} - \frac{1}{T_0} \right)$$

$$- \frac{R}{\Delta H_f} \ln x_1 = \frac{T_0 - T_f}{T_f T_0}$$

$$T_f T_0 \left(- \frac{R}{\Delta H_{\text{fusion}}} \ln x_1 \right) = T_0 - T_f$$

$$T_f T_0 \left(- \frac{R}{\Delta H_{\text{fm}}} \ln x_1 \right) + T_f = T_0$$

$$T_f \left(1 - \frac{R T_0}{\Delta H_{\text{fm}}} \ln x_1 \right) = T_0$$

$$T_f = \frac{T_0}{\left(1 - \frac{R T_0}{\Delta H_f} \ln x_1 \right)}$$

$$\therefore x_1 + x_2 = 1 \quad \Rightarrow \quad x_1 = 1 - x_2$$

$$T_f = \frac{T_0}{\left[1 - \frac{R T_0}{\Delta H_f} \ln(1 - x_2) \right]}$$

$$= \frac{T_0}{\left(1 + \frac{R T_0 x_2}{\Delta H_f} \right)}$$

This gives the variation of freezing pt of solution with concⁿ. As proportion of solution ↑, T_f ↓ decreases.

For very dilution solution i.e. amt of solute is very less

$$\ln x_1 = \ln(1 - x_2) = -x_2 - \frac{1}{2}x_2^2 - \frac{1}{3}x_2^3$$

For very dilute solution, 2nd, 3rd power goes off

$$\ln x_1 = -x_2$$

For this type of solution T₀ ≈ T_f = T₀²

Eq (8) can be written

$$-x_2 = -\frac{\Delta H_{fus}}{R} \left[\frac{\Delta T_f}{T_0^2} \right]$$

$$x_2 = \frac{\Delta H_{fus}}{R} \frac{\Delta T_f}{T_0^2}$$

$$\frac{x_2}{n_1 + n_2} = \dots \quad \text{--- (9)}$$

ΔT_f in eq (9) depends on the amt of solute (n₂) is added to given solvent n₁.
 ∴ ΔT_f is a colligative prop. & it doesn't contain any other characteristic of solute but its mole fraction or n₂

(6)

For dilute solution $x_2 = \frac{m M_1}{1000}$, M_1 , Molecular wt of solvent, m = molality of the solution

$$\Delta T_f = \frac{R T_0^2 M_1 m}{1000 \Delta H_{fus}} = K_f m \quad \text{--- (10)}$$

$K_f = \frac{R T_0^2 M_1}{1000 \Delta H_{fus}}$ is called molal freezing

pt. depression constt

$$m = \frac{w_2}{M_2} \times \frac{1000}{w_1} \quad \text{--- (11)}$$

$$\Delta T_f = \frac{1000 K_f w_2}{M_2 w_1}$$

$$M_2 = \frac{1000 K_f w_2}{w_1 \Delta T_f}$$

$$M_2 = \frac{R T_0^2 M_1 w_2}{\Delta T_f \Delta H_{fus} w_1} \quad \text{--- (12)}$$

eq (12) helps in calculating the molar mass of solute -

Q1 Calculate the molal freezing pt depression constt for C_6H_6 if ΔH_f at 5°C is 9.83 kJ/mole

$$T_2 = 5 + 273 = 278 \text{ K}, \quad \Delta H_f = 9.830 \text{ J/mole}, \quad R = 8.3145 \text{ J/K/mole}$$

$$K_f = \frac{RT_2^2 M_1}{1000 \Delta H_f}$$

$$= \frac{8.3145 \text{ J/K/mole} \times (278 \text{ K})^2 \times (78 \text{ g/mole})}{1000 \text{ g kg}^{-1} \times 9830 \text{ J/mole}}$$

$$= 5.1 \text{ K mole}^{-1} \text{ kg}$$

Q2 Cal. the man of $\text{C}_2\text{H}_5\text{OH}$ which when dissolved in 100 g of H_2O , would just prevent the formation of ice at -10°C , $K_{f\text{H}_2\text{O}} = 1.86 \text{ K molal}^{-1}$

$$W_1 = 100 \text{ g}, \quad \Delta T_f = 10 \text{ K}, \quad K_f = 1.86 \text{ K kg mole}^{-1}$$

$$M_2 = 32 \text{ g/mole}$$

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

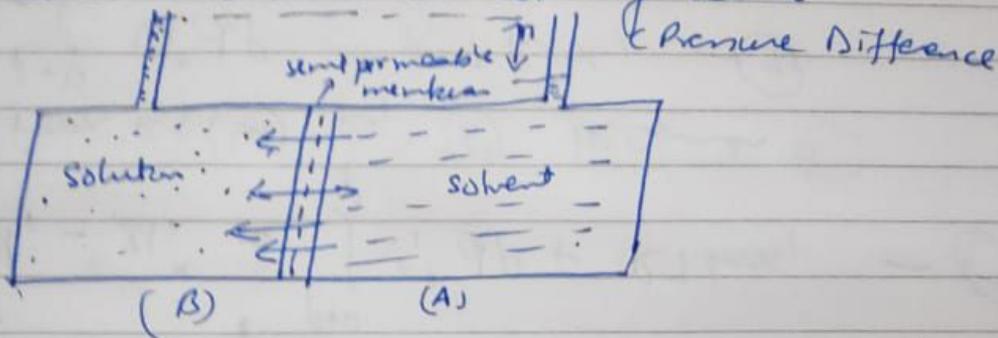
$$W_2 = \frac{\Delta T_f \times M_2 \times W_1}{K_f \times 1000}$$

$$= \frac{10 \text{ K} \times 32 \text{ g/mole} \times 100 \text{ g}}{1.86 \text{ K mole}^{-1} \text{ kg} \times 1000 \text{ g kg}^{-1}} = 17.20 \text{ g}$$

Man of $\text{C}_2\text{H}_5\text{OH}$ would prevent the formation of ice at -10°C

Osmosis & Osmotic Pressure

Let us consider a solution separated from the solvent by a semipermeable membrane which is permeable by solvent molecules but not by solute



Since the v. P. and chemical potential of pure solvent is higher than the ~~solvent~~ ^{solvent} molecules, therefore the solvent molecules ^{move} from chamber A to chamber B so that chemical potential become equal on both the chambers. This is known as osmosis and extra pressure which is developed on the solution side due to flow of pure solvent is called osmotic pressure. It is denoted by π . The flow of solvent molecules can be prevented by applying a high P on solution side. This pressure stop the osmosis & is known as osmotic pressure.

The chemical potential of solvent (1) in chamber A is greater than its μ of solution in chamber B

$$\mu_1^A > \mu_1(B) \quad \text{Before osmosis}$$

As osmosis takes place the P on solution side increases. At equilibrium the μ of solvent in two chambers becomes equal.

At equilibrium, the Pressure on the solvent is P (9)
 while on solution side it is $(P + \pi)$

$$\mu_1^A(T, P) = \mu_1^A(T, P, x_1) \quad \text{--- (1)}$$

$$d\mu_1^B = \left(\frac{\partial \mu_1}{\partial T}\right)_{P, x_2} dT + \left(\frac{\partial \mu_1}{\partial P}\right)_{T, x_2} dP + \left(\frac{\partial \mu_1}{\partial x_1}\right)_{T, P} dx_1 \quad \text{--- (2)}$$

$$d\mu_1^A(T, P) = d\mu_1^\circ \quad \text{--- (3)} \Rightarrow \mu_1 = \mu_1^\circ \quad \text{--- (3a)}$$

At const T , $dT = 0$ for ideal solution
 $\mu_1 = \mu_1^\circ + RT \ln x_1$

$$\left(\frac{\partial \mu_1}{\partial x_1}\right)_{T, P} = \frac{RT}{x_1} \quad \text{--- (3)}$$

$$\left(\frac{\partial \mu_1}{\partial P}\right)_{T, x_2} = V_1^\circ \quad \text{(Molar volume of the solvent)} \quad \text{--- (4)}$$

sub. (3) & (4) in (2)

$$\int_{\mu_1^\circ}^{\mu_1} d\mu_1^B = \int_P^{P+\pi} V_1^\circ dP + \int_1^{x_1} RT d \ln x_1 \quad \text{--- (5)}$$

$$\mu_1 - \mu_1^\circ = \int_P^{P+\pi} V_1^\circ dP + RT \ln x_1 \quad \text{--- (6)}$$

from eq (3a) eq. (6) becomes

$$\int_P^{P+\pi} V_1^\circ dP = RT \ln x_1 \quad \text{--- (7)}$$

Since Molar volume of solvent is independent of pressure then V_1° is taken out from integral

$$-V_1^*(P+\pi - P) = RT \ln x_1 \quad (10)$$

$$-V_1^* \pi = RT \ln x_1 \quad (8)$$

For very dilute solutions $x_2 < 1$.

$$\ln x_1 = \ln(1-x_2) = -x_2$$

eq. (8) becomes

$$-V_1^* \pi = -RT x_2$$

$$\pi = \frac{RT x_2}{V_1^*} \quad (9)$$

$$\therefore x_2 = \frac{n_2}{n_1}$$

$$\pi V_1^* = RT \frac{n_2}{n_1}$$

$$\pi n_1 V_1^* = n_2 RT$$

Total volume of solution $V = n_1 V_1^* + n_2 V_2^*$

$$\therefore n_2 \ll n_1 \quad V \approx n_1 V_1^* \quad (10)$$

$$\pi V = RT n_2 \quad (11)$$

$$\pi = \frac{n_2}{V} RT = C_2 RT \quad \text{where } C_2 \text{ is } (12)$$

molar concⁿ of solute in the solution

$$\pi V = \frac{W_2}{M_2} RT$$

$$M_2 = \frac{W_2}{V} \frac{RT}{\pi} = C_2' \frac{RT}{\pi} \quad \text{where } C_2' \text{ is}$$

Concⁿ of solute in gms per unit volume of solution,
 M_2 is molar mass.

$$\pi V_1^* = \frac{RT}{1000} M_1 m_2 \quad \text{where } m_2 \text{ is molarity in eq (9)}$$

POCO

SHOT ON POCO F1

Application of osmotic Pressure

(11)

1. osmotic Pressure is imp. in biological and chemical systems.

(a) If 2 solutions are of equal concentration, they have same O.P. they are called isotonic.

(b) If 2 solutions have different concentrations, the more concentrated solution is said to be hypertonic and less concⁿ is called hypotonic.

When RBC are placed in hypotonic sol, water moves into the RBC. they swell & burst releasing hemoglobin and other protein molecules.

If RBC are placed in hypertonic solution, the intercellular water tends to move outside the cell to the more concⁿ solution known as crenation. RBC shrink and stop functioning.

That is why when intravenous injection is given to a patient, great care is taken to ensure that the concⁿ of solution to be must be equal to that of blood plasma.

(2) O.P. increases with amt of solute. The body fluid contains Na^+ & Cl^- ions. If more salt is taken, these ions will \uparrow which cause \uparrow of O.P. That is why patients of high B.P are advised to take less salt.

3) During throat trouble gargle with hypertonic saline H_2O gives relief - the extra H_2O accumulates and comes out into the saline H_2O by osmosis.

POCO

SHOT ON POCO F1

... in kidney the

saline H_2O gives relief - the extra H_2O accumulated comes out into the saline H_2O by osmosis

(4) The functioning of mammalian kidney, the intake of H_2O by fresh water fish through their gill membrane, the rising of H_2O in plants is governed by osmosis

(5) It is also useful in the determination of molar masses of macromolecules