1. A sol^{n} containing 0.5126 gm of naphthalene (molar mass 128.2 gm/mol) in 50 gm CCl_4, yields a bl. pt. elevation of 0.~~0~~402 K, while a sol^{n} of 0.6216 gm of an unknown solute in the same mass of the solvent gives a ~~b.pt~~ elevation of 0.647K. Find the molar mass of the unknown solute.

Ans: Mass of dissolved naph. = 0.5126 gm

Mass of solvent = 50 gm

Molality of the sol^{n} $= m = \frac{n_2}{m_1} = \frac{m_2/M_2}{m_1}$

$$= \frac{0.5126 \cancel{g}/128.2 \text{ gm/mol}}{0.050 \text{ kg}}$$

$= 0.07997$ mol/kg.

Again $\Delta T_b = K_b m$

$$K_b = \frac{\Delta T_b}{m} = \frac{0.402}{0.07997} = 5.027 \text{ K kg/mol.}$$

Let, M_2 = molar mass of unknown substance.

Now Molality, $m = \frac{m_2/M_2}{m_1} = \frac{0.6216/M_2}{.050}$

$$= \frac{12.432}{M_2} \text{ gm/kg.}$$

Again, $\Delta T_b = 0.647$ K.

$$\therefore 0.647 = K_b \times m$$

$$= 5.027 \times \frac{12.432}{M_2}$$

$\therefore M_2 = 96.59$ gm/mol.

Relation of relative lowering of vapour pressure with other colligative properties:-

$$\boxed{\frac{p^\circ - p}{p^\circ} = x_2} \quad \text{---------- ①}$$

$$\ln x_1 = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_b^*} - \frac{1}{T_b}\right) \quad \text{--- ②}$$

$$\ln x_1 = \frac{\Delta H_{fus}}{R}\left(\frac{1}{T_f^*} - \frac{1}{T_f}\right) \quad \text{--- ③}$$

$$V\pi = -RT\ln x_1 \quad \text{--- ④}$$

$$\ln(1 - x_2) = -\frac{\Delta H_{vap}}{R}\left(\frac{T_b - T_b^*}{T_b T_b^*}\right)$$

$$\therefore\ -x_2 = -\frac{\Delta H_{vap}}{R}\,\frac{\Delta T_b}{T_b T_b^*}$$

$$\boxed{x_2 = \frac{\Delta H_{vap}}{R}\,\frac{\Delta T_b}{T_b^{*2}}}$$

Similarly, $\boxed{x_2 = \frac{\Delta H_{fus}}{R}\left(-\frac{\Delta T_f}{T_f^{*2}}\right)}$ (where $-\Delta T_f = T_f - T_f^*$)

And, $V\pi = -RT\ln(1 - x_2)$.

$$V\pi \approx RTx_2$$

$$\boxed{x_2 = \frac{V\pi}{RT}}$$

$$\therefore\ x_2 = \frac{p^* - p}{p^*} = \frac{\Delta H_{vap}}{R}\,\frac{\Delta T_b}{T_b^{*2}}$$

$$= \frac{\Delta H_{fus}}{R}\,\frac{(-\Delta T_f)}{T_f^{*2}}$$

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

Ques: The addition of 3 gm of a substance to 100 gm of CCl_4 raises the boiling pt of CCl_4 by 0.60 K, $K_b = 5.03$ K mol^{-1} kg. Calculate the fr. pt. depression ($K_f = 31.8$ K kg mol^{-1}), the relative v.p. lowering the o.p. of the sol^{n} at 298K, & the molar mass of the substance. The density of CCl_4 is 1.59 gm/cm^3.

Ans: The given data are —

$m_1 = 100$ gm, $m_2 = 3$ gm, $\Delta T_b = 0.60$ K,

$K_b = 5.03$ K kg mol^{-1}, $K_f = 31.8$ K kg mol^{-1},

M_1 (CCl_4) = 154 gm/mol.

ρ_1 (CCl_4) = 1.59 gm/cc.

Since, $\Delta T_b = K_b m$

$$\therefore m = \frac{\Delta T_b}{K_b} = \frac{0.60 K}{5.03 \text{ K kg mol}^{-1}}$$

$$= 0.12 \text{ mol/kg}.$$

Since $m = \frac{n_2}{m_1} = \frac{m_2}{M_2 m_1}$ $\underline{m = w}$

$$\therefore M_2 = \frac{m_2}{m\, m_1} = \frac{3 \text{ gm}}{0.12 \text{ mol/kg} \times (100 \text{ gm})}$$

$$= 0.25 \text{ kg/mol}.$$

Now, $-\Delta T_f = K_f m = (31.8 \text{ K kg/mol}) \times .12 \text{ mol/kg}$

$$= 3.82 \text{ K}$$

$$\frac{\Delta P}{\Delta P^*} = x_2 = \frac{n_2}{n_1 + n_2} = \frac{m_2/M_2}{(m_1/M_1) + (m_2/M_2)}$$

$$= \frac{0.003 \text{ kg} / 0.25 \text{ kg/mol}}{(0.1 \text{ kg} / 0.154 \text{ kg mol}^{-1}) + (0.003 \text{ kg} / 0.25 \text{ kg/mo}}$$

Application of van't Hoff Factor :

(i) Degree of association : is defined as the fraction of the total number of molecules which combine to form bigger molecules.

Consider, 1 mole of solute A dissolved in a definite volume of the solvent. Suppose, 'n' molecules of solute A combine to form the associated molecules, $(A)_n$ according to the eq.

$$nA \rightleftharpoons A_n$$

Let, 'α' is the degree of association. Then,

the number of associated moles $= \frac{\alpha}{n}$

The number of unassociated moles $= 1-\alpha$

Total number of moles in solⁿ. $= 1-\alpha+\frac{\alpha}{n}$

For normal behaviour, i.e., if there is no association, the no. of moles would have been one.

Since, the colligative effect is proportional to the number of particles are proportional to the number of moles, the van't Hoff factor, 'i' is given by,

$$i = \frac{\text{observed colligative effect}}{\text{Normal colligative effect}}$$

$$i = \frac{1-\alpha+\frac{\alpha}{n}}{1} = \frac{1-\alpha\left(1-\frac{1}{n}\right)}{1}$$

$$\boxed{\alpha = \frac{1-i}{1-1/n}}$$

The value of 'i' can be calculated from the eq^{n},

$$i = \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}}$$

when association is complete, i.e., $\alpha = 1$, $i = \frac{1}{n}$,
" no " , $\alpha = 0$, then $i = 1$.

(ii) <u>degree of dissociation</u> : is defined as the fraction of the total number of molecules which dissociate, i.e., break into simpler molecules / ions.

Consider, 1 mole of electrolyte A_xB_y which partly dissociates in sol^{n} yielding 'x' ions of A^{y+} and 'y' ions of B^{x-}. Let, 'α' be the degree of dissociation. Then the disso^{n} eqlm in sol^{n} is represented as:

$$\begin{array}{ccccc} A_xB_y & \rightleftharpoons & xA^{y+} & + & yB^{x-} \\ 1-\alpha & & x\alpha & & y\alpha \end{array}$$

The total no. of moles at eqlm $= x\alpha + y\alpha + 1 - \alpha$
$= 1 + \alpha(x + y - 1)$

for, Normal behaviour, no. of moles = 1.

$$\therefore \; i = \frac{1 + \alpha(x+y-1)}{1}, \quad \alpha = \frac{i-1}{x+y-1}$$

The Van't Hoff Equation :

The eqm condition is that the chemical potential of water must have the same value on each side of the membrane at every depth in the beaker. This quality of chem. pot. is achieved by a pressure difference on the 2 sides of the membrane.

Consider the situation at the depth 'h' in figure. At this depth, the solvent is under a pressure p while the soln is under pressure $p+\pi$. If $\mu(T, p+\pi, x)$ is the chemical potential of the solvent in the soln under the pressure $p+\pi$ and $\mu^\circ(T,P)$ that of the pure solvent under the pressure p, then the eqm condition is

$$\mu(T, p+\pi, x_1) = \mu^\circ(T,P) \quad \ldots \text{(i)}$$

and

$$\mu^\circ(T, p+\pi) + RT\ln x_1 = \mu^\circ(T,P) \quad \ldots \text{(ii)}$$

The problem is to express the μ of the solvent under a pressure $p+\pi$ in terms of the μ solvent under a pressure p. From the fundamental eqn at constant T we have,

$dG = vdp \; \boxed{-sdT}$

for partial molar quantities, $dG = \bar{v}\,dp$ equal to μ,

$$d\mu^\circ = \bar{V}_1^\circ\,dp$$

vol. of pure solvent

Integrating, we have, $\mu^\circ(T, P+\pi) - \mu^\circ(T,P) = \int_{p}^{p+\pi} \bar{V}_1^\circ\,dp$ . . . (iii)

Then, eqn (ii) becomes,

$$\int_{P}^{P+\pi} \overline{V}_1^{\circ}\, dp + RT \ln x_1 = 0 \quad \cdots\cdots (iv)$$

In eqn (iv), $\overline{V}_1^{\circ}$ is the molar volume of pure solvent. If the solvent is incompressible, then $\overline{V}^{\circ}$ is independent of pressure and can be removed from the integral.

Then, $\boxed{\overline{V}_1^{\circ}\pi + RT \ln x_1 = 0}$ ------ ..(v)

This is the relation betn O.P. (π) and mole fraction of solvent (x) in the soln. Two assumptions are involved — ✓ i) soln is ideal

✓ ii) solvent is incompressible.

In terms of the solute concn,

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

If soln is dilute, then $x_2 \ll 1$, so logarithm may be expanded in series. Keeping only the 1st term,

$$\ln(1 - x_2) = -x_2 = -\frac{n_2}{\underset{\text{solvent}\to}{n_1} + n_2} \approx -\frac{n_2}{n_1}$$

Since $n_2 \ll n_1$ in dil. soln. Then eqn (v) becomes

$$RT\left(\cancel{-}\frac{n_2}{n_1}\right) = \cancel{-}\overline{V}_1^{\circ}\pi \qquad \pi = \frac{n_2 RT}{n_1 \overline{V}_1^{\circ}} \quad \cdots\cdots (vi)$$

By the addition rule, the volume of the ideal soln is

$$V_S = n_1\overline{V}_1^{\circ} + \cancel{n_2\overline{V}_2^{\circ}}.$$

If the soln is dilute, n_2 is very small, ∴ $\boxed{V_S \approx n_1\overline{V}_1^{\circ}}$

∴ Eqn (vi) is $\pi = \frac{n_2 RT}{V_S}$, or, $\boxed{\pi = cRT}$ --(vii)

$C = \frac{n_2}{V}$, the conc$^{\underset{..}{n}}$ of solute (mol/m³) in the sol$^{\underset{..}{n}}$.

Eq$^{\underset{..}{n}}$ (vii) is the V. H. eq$^{\underset{..}{n}}$ ~~of~~ for O. P.

In the V. H. eq$^{\underset{..}{n}}$, n_2 is the number of moles of solute. The solute molecules dispersed in the solvent are analogous to the gas molecules dispersed in empty space. The solvent is analogous to the empty space bet$^{\underset{..}{n}}$ the gas molecules.

Laws of O. P.

① Temperature remaining constant, the O. P. (π) of a sol$^{\underset{..}{n}}$ is directly proportional to its conc$^{\underset{..}{n}}$ (C).

$$\pi = K_1 C \quad (K_1 \text{ is const})$$

Since, $C = \frac{1}{V}$, where V lit contain 1 gm-mole of solute, $\therefore \ \pi = \frac{K_1}{V}$ or, $\pi V = K_1$

② Conc$^{\underset{..}{n}}$ remaining const, the O. P. (π) of a sol$^{\underset{..}{n}}$ is directly proportional to absolute temperature (T).

$$\pi = K_2 T \quad (\text{where } K_2 = \text{Const.})$$

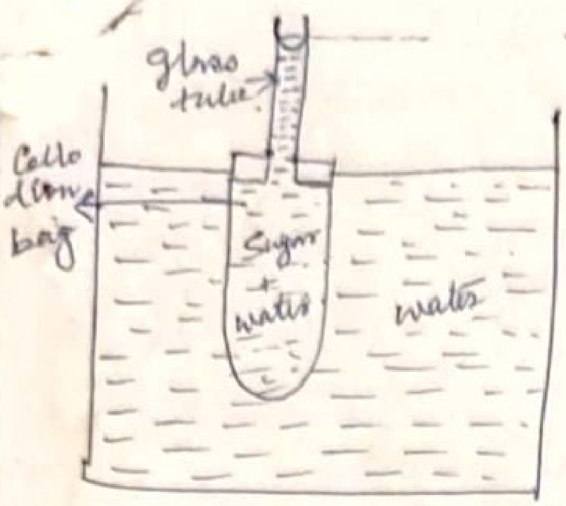
When both temp & conc$^{\underset{..}{n}}$ would vary,

$$\pi = CKT \quad (K = \text{Const.})$$

If the sol$^{\underset{..}{n}}$ contains n gm-moles of solute in V lit. of sol$^{\underset{..}{n}}$, we have,

$$\pi = \frac{n}{V} KT, \text{ or, } \boxed{\pi V = nKT}$$

Osmotic Pressure



The phenomenon of O.P. is shown by the figure. *

A collodion bag, ~~is~~ tied to a glass capillary tubing, is inserted. The bag is filled with a dil. sol. of sugar in water and immersed in a beaker of pure water. The level of sugar sol. rises untill it reaches a definite height, which depends on the conc^{n} of the sol^{n}. The hydrostatic pressure arises due to difference in levels of the sugar sol^{n} and pure water is the osmotic pressure of the sol^{n}. No sugar has escaped through the membrane into the pure water. The increase in vol. of the sol^{n} is due to the passage of H_2O through membrane. The collodion functions as a semipermeable membrane (which allows H_2O but does not allow sugar to pass).

We have to derive the relation between the pressure difference and the conc^{n} of the solution.

* The O.P. of a sol^{n} is the pressure reqd. to prevent osmosis when the sol^{n} is seperated from pure solvent by a semipermeable membrane.

* Osmosis is defined as the spontaneous flow of the solvent molecules through a semipermeable membrane into a sol^{n} or from a dil sol to concentrated one.

Solvent in solution ⇌ Solid solvent

Abnormal behaviour of solutions :

The experimental results for the colligative properties of sol^{n} are often differed from the theoretical values. This is due to 2 reasons :

(i) The sol^{n} are often not ideal, especially at higher conc^{n}.

(ii) The association or dissociation of solute molecules in sol^{n} also lead to departure from theo. value.

Non-ideality in sol^{n} :

The laws for dilute sol^{n} are derived from the Raoults' law, $p_i = x_i p_i^{\circ}$. It is valid for dil. sol^{n} only. But real sol^{n} obey Raoults' law only at high diln. At higher conc^{n}, sol^{n} exhibit considerable departure.

Association in sol^{n} :

Some solutes when dissolved in non-hydroxylic solvents like benzene, cyclohexane, CCl_4, nitrobenzene etc. remain associated. Thus, acetic ā, benzoic ā etc remain mostly as dimers in benzene sol^{n} (which is also known from the partition co-eff. experiments). This association ~~causes~~ decreases the number of solute particles less than if the solutes are present as single molecules.

The properties of dilute sol^{n} being colligative in nature, depend on the no. of solute particles and not

Depression of freezing pt.

At the freezing point of the sol^n, the eql^m is

Solvent in sol^n ⇌ Solid solvent.

The eql^m condition is

$$\mu_{1\,sol^n}(T_f, P) = \mu_1^*(s)\,(T_f, P).$$

T_f = freezing pt. of the sol^n

At a const. 'P', the temp. is a function of x_1, the mole fraction of the solvent. If the sol^n is ideal,

$$\mu_1(sol^n) = \mu_1^0 + RT_f \ln x_1$$

$$\therefore \mu_1^0 + RT_f \ln x_1 = \mu_1^*(s)$$

$$\ln x_1 = -\frac{\mu_1^0 - \mu_1^*(s)}{RT_f} = -\frac{\Delta G}{RT_f}$$

ΔG = molar free energy of fusion

Differentiating w.r. to x_1 at const. P,

$$\frac{\partial}{\partial x_1}\left[(\ln x_1)\right]_P = -\frac{1}{R}\left[\frac{\partial}{\partial T_f}\left(\frac{\Delta G}{T_f}\right)\right]_P \left(\frac{\partial T_f}{\partial x_1}\right)_P.$$

$$\therefore \frac{1}{x_1} = -\frac{1}{R}\left\{\frac{\partial}{\partial T_f}\left(\frac{\Delta G}{T_f}\right)\right\}\left(\frac{\partial T_f}{\partial x_1}\right)_P.$$

From Gibbs-Helmholtz eq^n,

$$\frac{1}{x_1} = +\frac{\Delta H_{fus}}{RT_f^2}\left(\frac{\partial T_f}{\partial x_1}\right)_P$$

[ΔH_{fus} = molar enthalpy of fusion for pure solvent]

Integrating,

$$\int_1^{x_1} \frac{dx_1}{x_1} = \frac{\Delta H_{fus}}{R\cancel{T_f}} \int_{T_f^*\,(\text{pure solvent})}^{T_f\,(sol^n)} \frac{dT_f}{T_f^2}$$

$$\therefore \ln x_1 = \frac{\Delta H_{fus}}{R}\left[-\left(\frac{1}{T_f} - \frac{1}{T_f^*}\right)\right] = \frac{\Delta H_{fus}}{R}\left[\frac{1}{T_f^*} - \frac{1}{T_f}\right]$$

$$\therefore \frac{1}{T_f} \,/\, \frac{1}{T_f^*} \,/$$

$$\therefore \ln(1-x_2) = -x_2 = \frac{\Delta H_{fus}}{R}\left(\frac{T_f - T_f^*}{T_f^* T_f}\right) \text{---(i)}$$

$(T_f - T_f^*)$ is the frz. pt. depression, $\Delta T_f = T_f - T_f^*$

T_f is close to T_f^*, $\therefore$ $T_f^* \cdot T_f = (T_f^*)^2$ for very dilute solⁿ (negligible error)

$$\text{(i)} \rightarrow \Delta T_f = -\frac{x_2 R (T_f^*)^2}{\Delta H_{fus}} \text{.....(ii)}$$

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

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

M_1 = solvent molar mass. (? kg/mol)

For very dilute solⁿ, $x_2 = M_1 \cdot m_2$ ↓ molality

$$\text{(ii)} \rightarrow \Delta T_f = -\frac{M_1 R (T_f^*)^2}{\Delta H_{fus}} \cdot m_2$$

$$\Delta T_f = -\boxed{K_f}\, m_2.$$

↓ solvent's molal-freezing point-depression constant.

where $K_f = \frac{M_1 R (T_f^*)^2}{\Delta H_{fus}}$