Colligative properties :- The colligative effect of an electrolyte solution is always greater than that of a non-electrolyte of the same molal concentration

To represent, Van't Hoff suggested the use of a factor i.

The ratio of the colligative effect produced by an electrolyte solution to the corresponding effect for the same concentration of a non-electrolyte solution.

$$i = \frac{\Delta T_f}{(\Delta T_f)_0 \text{ (nonelectrolyte)}} \quad - ①$$

$$\Delta T_f = i (\Delta T_f)_0$$

$(\Delta T_f)_0$ = value of depression of freezing point of the electrolyte solution assuming no ionization.

$$(\Delta T_f)_0 = \frac{1000 \times K_f \times w}{mW} \qquad \therefore \Delta T_f = i \times \frac{1000 K_f w}{Wm}.$$

a similar relation: $(\Delta T_b)_0 = \frac{1000 \times K_b \times w}{mW}$ $\therefore \Delta T_b = i \times \frac{1000 K_b w}{mW}$

$$\therefore i = \frac{\Delta T_f}{(\Delta T_f)_0} = \frac{\Delta T_b}{(\Delta T_b)_0} = \frac{\Delta p}{\Delta p_0} = \pi/\pi_0.$$

$$i = \frac{\text{Actual number of particles}}{\text{Number of particles for no ionization.}}$$

The degree of dissociation is the fraction of an electrolyte which is dissociated into ions in aqueous solution. If an electrolyte is 50% dissociated, its degree of dissociation is 0.5. The degree of dissociation is usually represented by α.

Suppose 1 mole of an electrolyte is capable of forming ν (nu) ions on complete dissociation. If the degree of dissociation be α, the total number of particles in solution are:

No. of undissociated molecules $= 1 - \alpha$

No. of ions produced $= \alpha\nu$

$\therefore$ Total number of particles $= 1 - \alpha + \alpha\nu$

Hence $\quad i = \dfrac{1 - \alpha + \alpha\nu}{1}$

or $\quad i - 1 = \alpha(\nu - 1)$

$$\boxed{\alpha = \frac{i - 1}{\nu - 1}}$$

Relation between van't Hoff factor and degree of dissociation.

Example : Solution of 1.5g Barium nitrate in 0.1kg of water freezes at 272.720 K. Calculate the apparent degree of dissociation of the salt. Given $K_b = 1.86$; MW of $Ba(NO_3)_2 = 261$.

Calculation: $[\Delta T_f]_0 = \frac{1000 K_f w}{mW} = \frac{1000 \times 1.5 \times 1.86}{261 \times 0.1 \times 1000}$

$= 0.1068\,°C.$

$$\begin{array}{r} 273.000\,K \\ 272.720\,K \\ \hline 0.280\,K \end{array}$$

Calculation of i ; $i = \frac{\Delta T}{(\Delta T)_0} = \frac{1 - 0.720}{0.1068} = \frac{0.280}{0.1068}$

Calculation of α ; $\alpha = \frac{i - 1}{\nu - 1}$.

$Ba(NO_3)_2 \longrightarrow Ba^{2+} + 2NO_3^-$

1 formula units yields 3 ions on dissociation (ie $\nu = 3$)

$$\alpha = \frac{\frac{0.280}{0.1068} - 1}{3 - 1} = 0.81 = 81\%.$$

Osmosis :- Flow of solvent from dilute solution to concentrated solution, (with SPM).

Theories of semi permeability :-

(a) Molecular sieve theory : SPM consists of lots of fine pores - acts as molecular sieves.

animal membrane - chemical interaction.

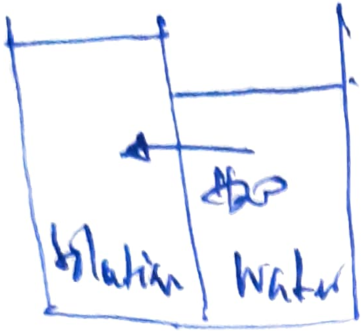
(b) Membrane Solution theory : few groups such as $-COOH$; $-OH$, $-NH_2$ dissolve water molecules thru hydrogen bonding. dissolved water passes into the solution to equalize concentration.

(c) Vapor pressure theory :- SPM - many fine holes or capillaries. the walls are not wetted by water or solution. Solution in one end and water at the other, separated by a small gap.

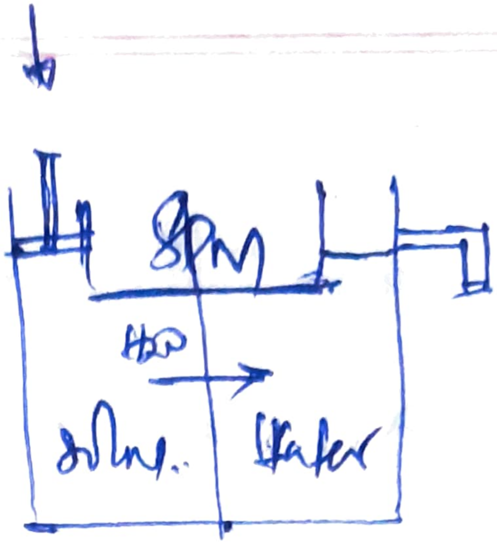
V.P of solution is lower than that of pure solvent, diffussion of vapor occurs from water to solution.

(d) Membrane bombardment theory :- Unequal bombardment pressure caused by solvent molecules. Fewer bombardment per unit area of surface on the solution side.

Reverse Osmosis :-

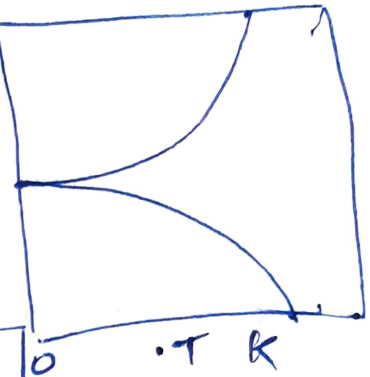


SPM
Normal



R.O.

Nernst heat theorem :-



- From Gibbs-Helmholtz eqn :-

$$\Delta G - \Delta H = T\left(\partial(\Delta G)/\partial T\right)_P \quad — ①$$

At absolute zero i.e, $T = 0$; $\boxed{\Delta G = \Delta H}$.

Richards by measuring EMF of cells at different temperatures found that $\partial\Delta G/\partial T$ decreases with decrease in temperature.

— Nernst heat theorem.

- Mathematically the theorem ;

$$\underset{T\to 0}{LT}\left[\partial\Delta G/\partial T\right]_P = \underset{T\to 0}{LT}\left[\partial\Delta H/\partial T\right]_P = 0 \quad — ②$$

From IInd law of TD ;

$$\left[\partial\Delta G/\partial T\right]_P = -\Delta S \rightarrow \text{entropy change} \quad - ③$$

$$\left[\partial\Delta H/\partial T\right]_P = \Delta C_p \text{ (Kirchoff eqn)} \; ④ \rightarrow$$ difference in heat capacitie of rxt r pdt.

from ②, ③, ④

$$\underset{T\to 0}{LT}\; \Delta S = 0 \text{ and } \underset{T\to 0}{LT}\; \Delta C_p = 0.$$

As temp is lowered to absolute zero ; ΔS and ΔCp tends to zero.

∴ 3rd law : $\underset{T\to 0}{LT}\; C_p = 0$; and $\underset{T\to 0}{LT}\; S = 0$.

for xline substances.

Determination of Absolute Entropies of solids, liquids and Gases.

- For a small change of a substance: the entropy change is $ds = dq/T$ - 1

At const P; then $(\partial S)_P = (\partial q)_P / T$ - 2

$$(\partial S/\partial T)_P = (\partial q/\partial T)_P \times 1/T \quad - 3$$

By definition: $(\partial q/\partial T)_P = C_P$ - 4

$$\therefore (\partial S/\partial T)_P = C_P \times 1/T \quad - 5$$

or at const pressure; $\boxed{dS = C_P/T \, dT}$. - 6.

For a perfectly crystalline substance, the absolute entropy $S=0$ at $T=0$; therefore

$$\int_{S=0}^{S=S} dS = \int_{T=0}^{T=T} (C_P/T)\, dT \quad - 7$$

or

Absolute entropy → $S_T = \int_0^T \frac{C_P dT}{T} = \int_0^T C_P \, d(\ln T)$.

Distribution Law:

Two immiscible solvents A and B for separate layers when in contact. When a solute X which is soluble in both solvents is added it gets distributed or partitioned between them. Molecules of X pass from solvent A to B and from solvent B to A. Finally a dynamic equilibrium is set up.

At equilibrium, the rate at which molecules of X pass from one solvent to the other is balanced. Experimentally it is found

$$\frac{\text{Concentration of X in A}}{\text{Concentration of X in B}} = \text{A constant.}$$

For example:- succinic acid in Ether and water.

C_1 (Ether)	C_2 (water)	C_1/C_2
0.0046	0.024	0.191
0.013	0.069	0.188

If a solute x distributes itself between two non-miscible solvents A and B at constant temperature and X is in the same molecular condition in both solvents.

$$\frac{\text{Conc. of } X \text{ in } A}{\text{Conc. of } X \text{ in } B} = K_D .$$