01. SOLUTIONS (Sem-01)

Homogenous mixture of two or more substances is called solution. The substance which is present in large proportion is termed the 'Solvent' while the other which is present in smaller proportion is called 'Solute'.

Types of solutions :- depending upon the physical state of the solute & the solvent, binary solutions are divided into 9 types.

Types of Solutions

solute	solvent	Example.
(i) Solid	liquid	Salt or sugar in water
(ii) Liquid	Liquid	Alchohol in water
(iii) Gas	Liquid	soda water (CO₂ in H₂0)
(iv) Solid	Solid	Alloys like brass, bronze etc .
(v) Liquid	Solid	Hydrates, jellies.
(vi) Gas	Solid	Dissolved gases in transition metals & minerals; (re, Hydrogen in palladium)
(vii) Solid	Gas	Smoke (carbon particles in air)
(viii) Liquid	Gas	Moisture in air
(ix) Gas	Gas	Water vapour in air (humidity), cooking gas, air.

Azeotropic mixture : "A mixture of 2 or more liquids which boils at a constant temperature and distills over completely at the same temperature without change in composition is known as "Azeotropic Mixture".

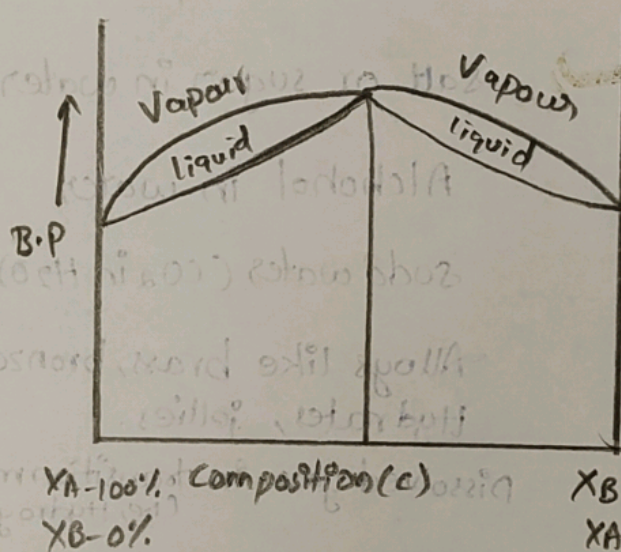Azeteoropic mixtures although boil at a constant temperature

Azeotropic mixtures are of two types :

1) maximum azeotropic mixtures
2) minimum azeotropic mixtures.

(1) Maximum Azeotropic mixtures : The Boiling point of Azeotropi
is more than that of its composition. These mixtures shows n
deviations from Raults law.

The mixture which evaporates at max. boiling point wi
changing their composition at constant temperature is kno
as " Maximum Azeotropic mixtures".

Ex : Max. Boiling point of $HCl + H_2O$ is 108.5C.

XA-100% Composition(c)   XB-100%.
XB-0%.   XA-0%.

(2) Minimum Azeotropic Mixtures : The Bioling point of the azeo
mixture is less than that of its compositions. These mixture
shows positive deviations from Rauolt's law.

The mixture which evaporates at minimum biolin
point without changing their composition at constant temper
is known as " minimum azeotropic mixtures".

Ex : The B.P of $C_2H_5OH + H_2O$ is 98.1C

$X_A = 100\%$ Composition (C) $X_B = 100\%$
$X_B = 0\%$ $X_A = 0\%$
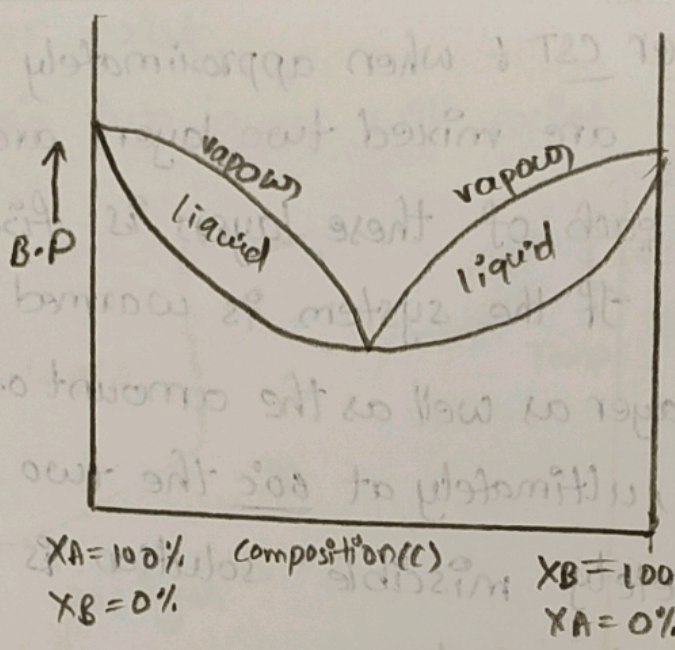
Partially Miscible Liquids : There are number of liquid pairs which are only partially miscible with one another. If a little amount of phenol (or) aniline (or) ether is added to water at ordinary temperature. It will dissolve completely but if the addition is continued a state is reached when no further dissolution occurs and the two liquid layers are formed.

"The solutions of different compositions co-existing with one another are termed "conjugate solutions".

Critical solution temperature (CST):- The temperature at which the two partially miscible liquids become completely miscible is called "Critical solution temperature (or) consolute temperature of the system.

partially miscible liquids may be classified into 3 types depending upon their CST.

(i) partially miscible liquids having upper CST.

(ii) partially miscible liquids having Lower CST.

(iii) partially miscible liquids having upper & lower CST.

i) **System with an upper CST :** when approximately equal am[ount]
of phenol in water are mixed two layers are produce[d]
The composition of each of these layers is fixed at a[n]
given temperature. If the system is warmed the amo[unt]
of phenol in water layer as well as the amount of water
phenol layer increase, ultimately at **66°c** the two layers be[come]
the same and completely miscible solution is formed.

Ex:- phenol – water system.
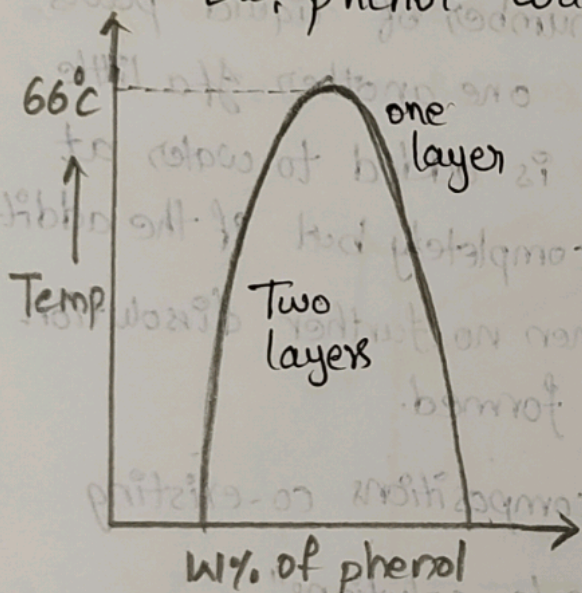
⇒ The plot leads to the follow[ing]

⇒ At and above 66°c phenol [&]
water are completely miscible.
whatever may be their compositi[on]

⇒ At any temperature below 66°c
the composition of the system lies
in the range of the curve

ii) **System with Lower CST :** When approximately equal a[m]
-ounts of Triethyl amine (TEA) and water are mixed, a part[ial]
miscible solution is formed. The mutual solubility of th[e]
liquids increases with decrease in temperature. Thus, coo[ling]
the system to 18.5°c causes the 2 components to become
completely miscible with each other, so this temperatu[re]
called lower consolute temperature;

Ex:- Tri ethyl amine & water.

⇒ At and below 18.5°c the two liquids are completely
miscible in all proportion. i-e, the system is homogene[ous]

ly one layer exist.

→ Above 18.5°C two layers will exist.

Two layers

Temp ↑

18.5°C   one layer

% Triethylamine

(or)

Temp ↑

Two layers

one layer

W% of TEA
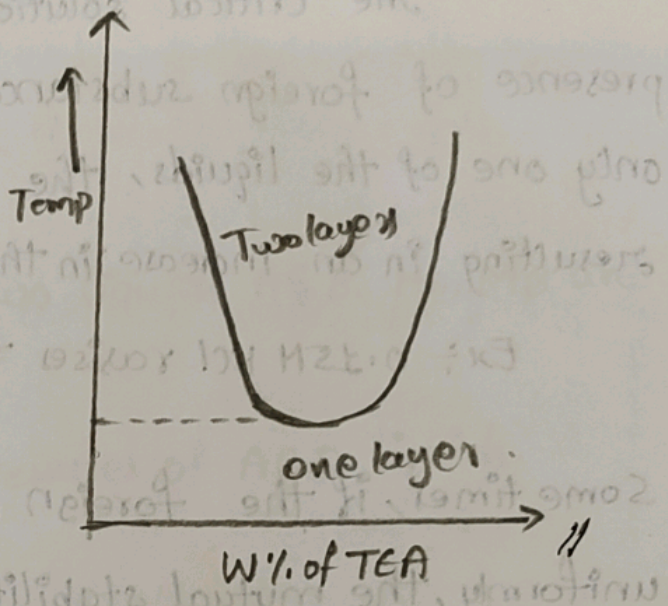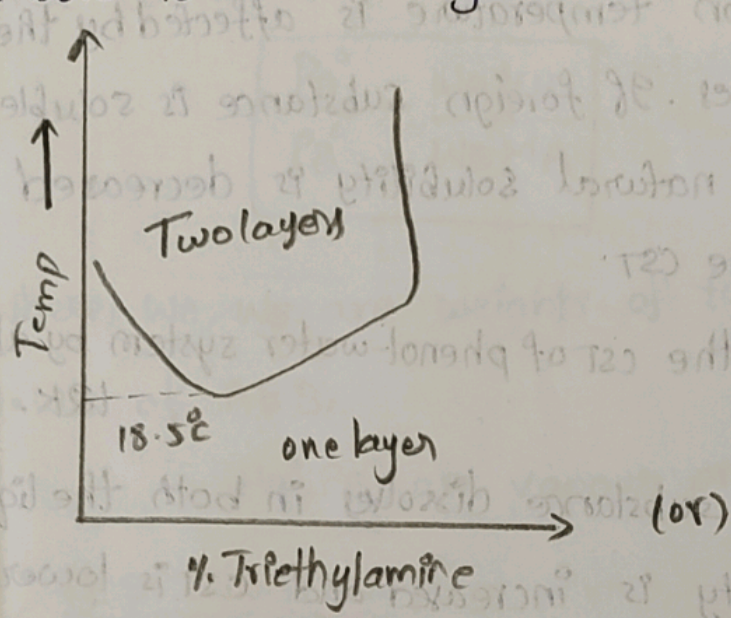
i) **System with an upper and lower CST:-** In this type of system the natural solubility of the two liquids increases with increase of temperature as well as decrease of temperature.

At normal temperature, when an approximately equal amount of Nicotin in water are mixed, a partially miscible liquid is formed. when temperature raises to 208°c (or) decreases to 60.8°c causes the completely miscible solutions. Hence, these two temperatures are maximum CST and minimum CST respectievely.

Ex:- Nicotine - water system.

→ These liquids are miscible at a certain higher temp (upper CST) as well as at a certain lower temp (Lower CST). B/w these two limiting temperatures, They are partially miscible.

208°c   one layer

Temp

Two

layer

60.8°c

one layer

W% of Nicotine
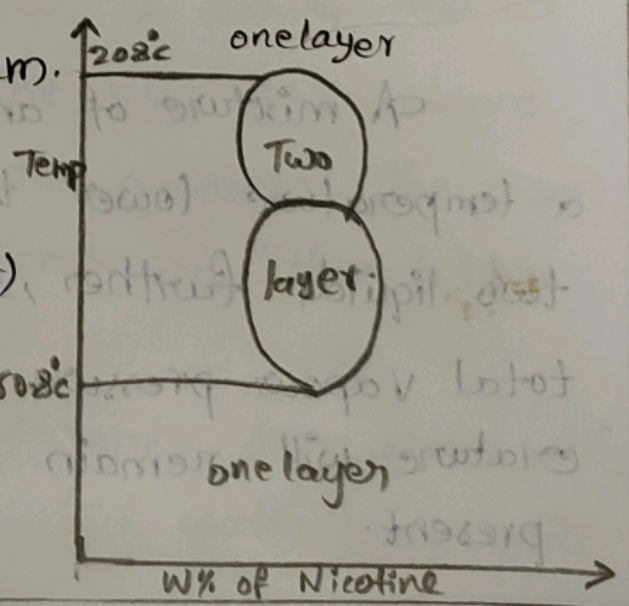
Effect of impurity on consulate temperature:

The critical solution temperature is affected by th presence of foreign substances. If foreign substance is solubl only one of the liquids, the natural solubility is decreased resulting in an increase in the CST.

Ex: 0.15M KCl raises the CST of phenol-water system by 12K.

Some times, if the foreign substance dissolves in both the li uniformly, the mutual stability is increased and CST is lowe

Ex: 0.083N sodium oleate decreases the CST of phenol- water system to 329.7K.

Completely immiscible Liquids:

Immiscible liquids are th which do not mix with each other at all. In these liquids, component liquid exerts its own vapour pressure indeper of the presence of the other. Hence total vapour pressure the two pure constituents.

$$P = P_A + P_B$$

P_A & P_B are the vapour pressures of pure liquids A & B respectievely the same temperature.

A mixture of any two immiscible liquids will bo a temperature lower than the boiling point either of th two liquids further, since, when the mixture is boilin total vapour pressure remains the same, the boiling te orature will remain constant so long both liquids ar present.

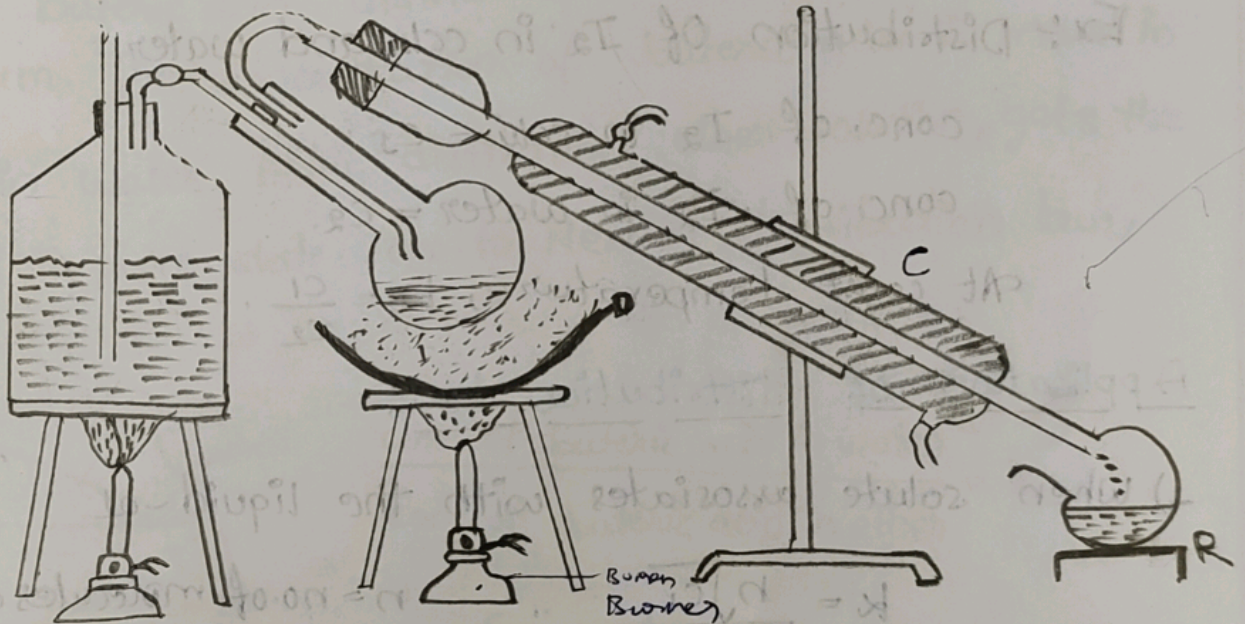The relative proportions of the two liquids in the distillate can be calculated as partition of efficient:

$$\boxed{\dfrac{P_A^\circ}{P_B^\circ} = \dfrac{W_A M_B}{W_B M_A}}$$

Where, W_A, W_B are weights of two liquids A & B. M_A, M_B are M.wts of A & B,

P_A°, P_B° are vapour pressures of A & B liquids.

DISTILLATION:-

As in the above distillation diagram the flask containing inpure liquid to be purified is slowly heated and a current of steam picksup the volatile substance from the liquid and passes it in to the condensor. The steam liquid vapours condense in the condensor and thus trickle down in the reciever.

The pure liquid is then seperated from water with the help of a seperating funnell in which water and liquid

(pure) form two seperate layers and hence collected seper

The relative amounts of the organic substance water in the distillate depend on their molecular weig and water vapour pressures at the boiling point.

$$\frac{\text{weight of distilled water}}{\text{weight of substance distilled}} = \frac{M.w \text{ of } H_2O \times \text{part. press of wate}}{M.w \text{ of substance} \times \text{parthial press of subs}}$$

Nernst Distribution law:

" At constant temperature, a solute distributes it between two miscible solvents only in a particular ratio."

Ex: Distribution of I_2 in ccl_4 and water.

conc. of I_2 in ccl_4 = c_1

conc. of I_2 in water = c_2.

At const temperature, $K_D = \dfrac{c_1}{c_2}$.

Application of distribution law:-

1) When solute assosiates with the liquid-01

$$K = \frac{n\sqrt{c_1}}{c_2}$$

n = no.of molecules associated

c_1 = con. of solute in liq-1

c_2 = con. of solute in liq-

k = dissosiation constar

2) When solute assosiates with liquid-02.

$$K = \frac{c_1}{n\sqrt{2}}$$

3) When solute dissosicates in liquid-01

$$k = \frac{c_1(1-\alpha)}{c_2}$$

α = extent of dissosiation

4) When solute dissosciate in both the solvents,

$$k = \frac{C_1(1-\alpha_1)}{C_2(1-\alpha_2)}$$

Application of Nernst distribution law in solvent extraction:-

If an organic compound is distributed in an organic solvent and water, that substance is more soluble in organic solvent while less in water.

Ex: Buteric acid is distributed in water and Ether. Take the above mixture in a seperating funnel and shake it. After some time buteric acid distributes in both the solutions, and equilibirium. The concentration of buteric acid is more in ther than in water. After distillation ether solution, gets the buteric acid in pure state. acc. to Nernst distribution law,
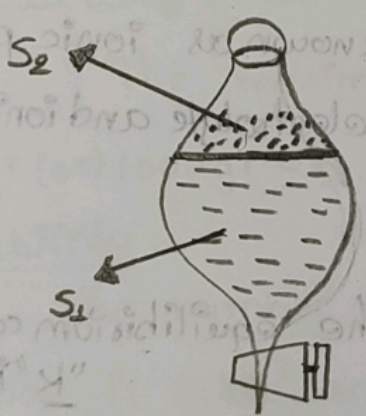
$$\frac{conc.\ of\ buteric\ acid\ in\ water}{conc.\ of\ buteric\ acid\ in\ ether} = K_D.$$

$$H_2O + H^+ \longrightarrow OH$$

S_1 = water phase

S_2 = organic phase

Limitations of distribution law :-

1) This law applicable at const temperature only.

2) Solute must distributes in two solutions equally.

3) Solute neither associates nor dissosiates with either of solvents.

4) Two solvents must be immiscible.

01) what are azeotropes? and explain HCl-H₂O₂ and ethanol

system?

02) write the effect of impurity on consulate temperatu

LONG QUESTIONS

(4)

01) write about steam distillation.

02) write the defination and types of azeotropic mixtures.

03) what is Nernst distribution law and it applications.

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2. IONIC EQUILIBRIUM

Ionic product :- The product of concentrations of cation

anion at a particular temperature is called ionic prod

Ionic product of Water :-

The product of concentrations of H^+ and OH^- ions i

water at a particular temperature is known as ionic pro

of water. pure water is a very weak electrolyte and ionise
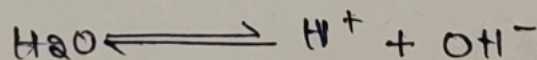
$$H_2O \rightleftharpoons H^+ + OH^-$$

According to law of mass action. The equilibrium cons

"K" is

$$k = \frac{[H^+][OH^-]}{[H_2O]}$$

$$\Rightarrow k[H_2O] = [H^+][OH^-]$$

But, $k[H_2O] = k_w$ then

$$\boxed{k_w = [H^+][OH^-]}$$

where, k_w = Ionic product of water.

The value of kc increases with temperature

units of k_w = mole^2 lit^{-2}

since, pure water is neutral $[H^+] = [OH^-]$

k_w at $25°C = 1.0 \times 10^{-14}$ (mole/lit)^2

① k_w at $10°C = <1.0 \times 10^{-14}$ (mole/lit)^2

k_w at $50°C = >1.0 \times 10^{-14}$ (mole/lit)^2

The solution will be acidic in nature, when $[H^+] > [OH^-]$ then,

$[H^+] > 1.0 \times 10^{-7} M$ (M = molar)

$[OH^-] < 1.0 \times 10^{-7} M$.

The solution will be basic in nature, when $[OH^-] > [H^+]$ then,

$[OH^-] > 1.0 \times 10^{-7} M$

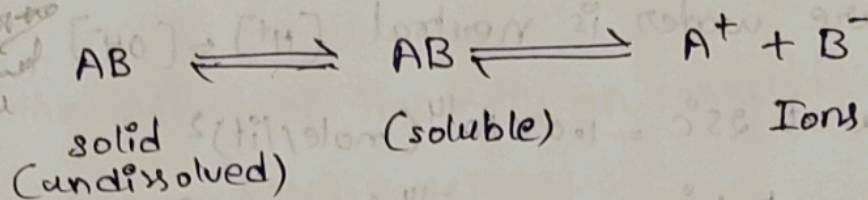$[H^+] < 1.0 \times 10^{-7} M$.

Solubility : ①

The maximum amount of salt that can dissolve in 100gr (or) 1000gr of solvent at room temperature is called its solubility.

The number of moles of solute dissolved in one litre of solution is called molar solubility. The sparingly soluble salts are almost insoluble.

The solution containing the salt dissolved state in an amount which is greater than the solubility amount of the salt at room temperature is called saturated solution. A saturated solutions contains salt in the solid form and in dissolvedform. Hence, these exist two dynamic equilibirra in the solution.

Dissolved salt $\rightleftharpoons$ ion of the salt

undissolved salt $\rightleftharpoons$ dissolved salt

$$AB \rightleftharpoons AB \rightleftharpoons A^+ + B^-$$

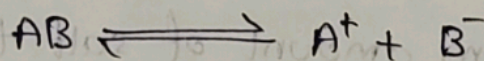| solid | (soluble) | Ions |
| (undissolved) | | |

② The categories of salts based on their solubility in

if solubility > 0.1M $\longrightarrow$ salt is highly soluble

solubility < 0.1M $\longrightarrow$ sparingly soluble.

0.01 < solubility < 0.1M $\longrightarrow$ slightly soluble.

Solubility product (Ksp):-

" The product of the ionic concentration in a saturated
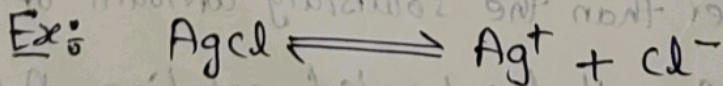-on of a soluble electrolyte at constant temperature is call
solubility product!"

$$AB \rightleftharpoons A^+ + B^-$$

$$K = \frac{[A^+][B^-]}{[AB]}$$

$$k[AB] = [A^+][B^-]$$
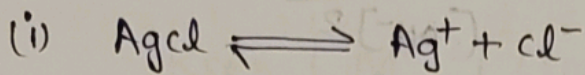
But k (AB) = Ksp.

Then Ksp = $[A^+][B^-]$

Ex: $AgCl \rightleftharpoons Ag^+ + Cl^-$

$$Ksp = [Ag^+][Cl^-]$$

Solubility of Agcl is low in concentrated solution.

RELATION BETWEEN SOLUBILITY (S) AND SOLUBILITY PRODUCT (ksp):-

(i) $AgCl \rightleftharpoons Ag^+ + Cl^-$

$$k = \frac{[Ag^+][Cl^-]}{[AgCl]}$$

Relation
$Ksp = x^x . y^y . s^{x+y}$

$$Ksp = [Ag^+][Cl^-] \quad ③$$

if the solubility of $[Ag^+] = S$

and if the solubility of $[Cl^-] = S$

then, $Ksp = [Ag^+][Cl^-]$
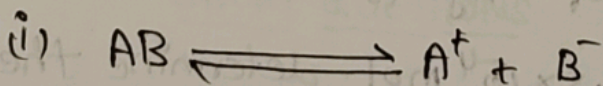
$$Ksp = S.S$$

$$\therefore \boxed{Ksp = S^2}$$

(ii) $Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$
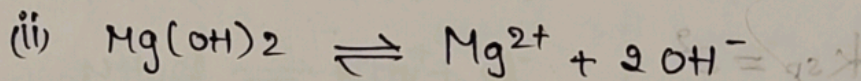
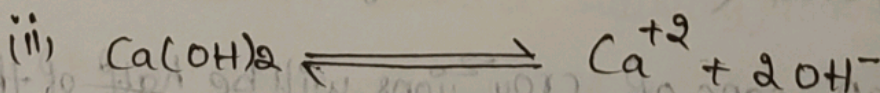$$Ksp = [Mg^{2+}][OH^-]^2$$

$$= S.(2S)^2 \Rightarrow S.4S^2$$

$$\boxed{Ksp = 4S^3}$$

Calculations based on solubility product:-

Some times an ion remains, after precipitation if it is in excess. Remaining concentration can be determined as.

(i) $AB \rightleftharpoons A^+ + B^-$

$$[A^+]_{left} = \frac{Ksp(AB)}{[B^-]}$$

(ii) $Ca(OH)_2 \rightleftharpoons Ca^{+2} + 2OH^-$

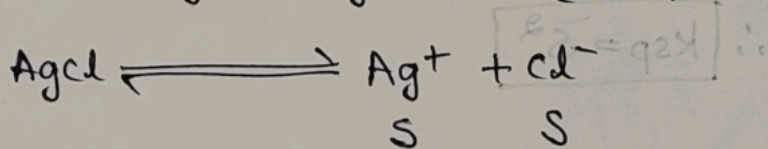$$\left[Ca^{+2}\right]\text{left} = \frac{Ksp\ \left[Ca(OH)_2\right]}{\left[OH^-\right]^2}$$

(iii) percentage precipitation of anion.

$$= \left[\frac{\text{Initial concentration} - \text{left concentration}}{\text{Initial concentration}}\right] \times 100$$

PROBLEMS

(1) The solubility product of silver chloride is 1.5625×10^{-10} at $25°C$. it solubility.

(A) Let, the solubility of AgCl be S (mole/lit)

$$AgCl \rightleftharpoons Ag^+ + Cl^-$$
$$\qquad\qquad S \qquad S$$

$$Ksp = S^2$$

$$1.5625 \times 10^{-10} = S^2$$
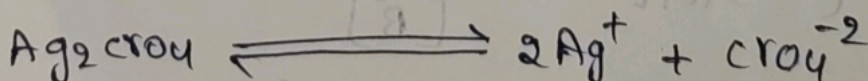
$$S = 1.25 \times 10^{-5}\ mol/lit.$$

M.wt of AgCl = 143.5

$$\text{Solubility} = M.wt \times S$$

$$= 143.5 \times 1.25 \times 10^{-5}$$

$$= 1.079 \times 10^{-3}\ g/lit.$$

(2) The concentrations of Ag^+ ion in a saturated soluti of Ag_2CrO_4 at $20°C$ 1.5×10^{-4} mol. determine the ksp of Ag_2CrO_4 at $20°C$.

sol.

$$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{-2}$$

acc. to eqn conc of CrO_4^{-2} ions will be half of the conc. Ag

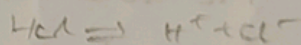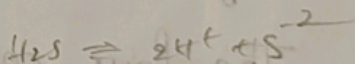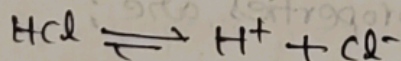$$[Ag^+] = 1.5 \times 10^{-4} m \qquad [Cro_4^{2-}] = 0.75 \times 10^{-4} m$$

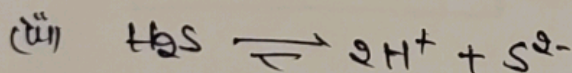$$Ksp = [Ag^+]^2 [Cro_4^{-2}]$$

⑤
$$= (1.5 \times 10^{-4})^2 (0.75 \times 10^{-4})$$

$$Ksp = 1.6875 \times 10^{-12}.$$

Common ion effect:- "a decrease in ionisation of weak electrolyte caused by the addition of a strong electrolyte having an ion common with weak electrolyte"

Ex: decrease of ionisation of NH_4OH (or) $(NH_4)_2CO_3$ in presence of NH_4Cl, CH_3COOH in presence of CH_3COONa and H_2S in presence of HCl.

(i) $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$

(ii) $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$

(iii) $H_2S \rightleftharpoons 2H^+ + S^{2-}$

$HCl \rightleftharpoons H^+ + Cl^-$
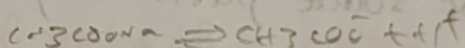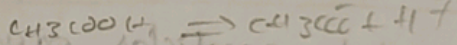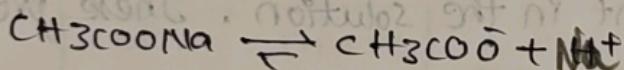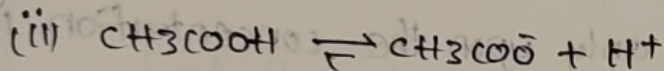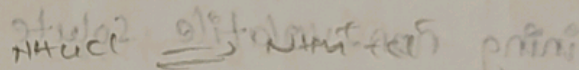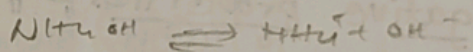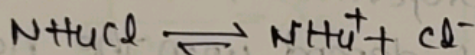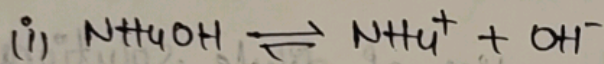
common ion effect is of great importance in analytical chemistry, specially in qualitative and quantitative analysis.

SHORT QUESTIONS

1. Explain about ionic product of water.
2. write a short notes on solubility.
3. write the calculations based on solubility product
4. Explain about common ion effect.

o1. what is solubility product and explain the relation b
solubility (s) and solubility product (ksp).

03. DILUTE SOLUTIONS

A solution may be defined as a homogenous mixt
two or more substances. The substance which is to be dis
is called a solute, while the medium in which the solute
persed to get a homogenous solution is called the solvent
-ution in which a small amount of solute is present is calle
dilute solution (while) which large amount of the solute is preser
called as a concentrated solution.

★ Colligative properties :- " The properties of dilute solutions
ining non-volatile solute do not depend upon the nature of
solute dissolved but depend only upon the concentration i-e
no-of solute particles present in the solution. These propertie
called colligative properties.

The four colligative properties are :
1) Lowering of vapour pressure
2) Elevation in bioling point
3) Depression in freezing point
4) Osmatic pressure.

(1) Lowering of vapour pressure :- when a non-volatile so
is dissolved in the pure solvent (liquid), the vapour pre
of the liquid is lowered. The vapour pressure of the soluti
will be less than that of the pure solvent.

If p^0 is the vapour pressure of the solvent and p is the vapour pressure of the solution.

lowering of vapour pressure $= p^0 - P.$

lative lowering of Vapour pressure and Raoult's Law :-

The ratio of lowering of vapour pressure to the vapour pressure of pure solvent is called the relative lowering of v.p.

$$\text{Relative lowering of vapour pressure} = \frac{p^0 - P}{p^0}$$

Raoult's Law :- "The relative lowering of vapour pressure of a dilute solution x containing non volatile solute is equal to the mole fraction of the solute present in the solution.

$$\frac{p^0 - P}{p^0} = X_2$$

$$\boxed{X_2 = \text{mole fraction of} \\ \text{Solute } X_2 = \frac{n_2}{n_1 + n_2}}$$

$$\boxed{\frac{p^0 - P}{p^0} = \frac{n_2}{n_1 + n_2}}$$

$\Rightarrow n_2 = $ no. of moles of a solute.

where,

$P_0 = $ Vapour pressure of pure solvent.

$P = $ Vapour pressure of solution.

$n_1 = $ no. of moles of solvent

$n_2 = $ no. of moles of solute.

In dilute solution quantity of solute is less. Hence, neglec ts value from the denominator.

$$\therefore \quad \boxed{\frac{P_0 - P}{P} = \frac{n_2}{n_1}}$$

this is known as "Condensed Raoult's Law"

Derivation of Raoult's law :-

According to Raoult's law, "The vapour pressure of a solvent ideal solution is equal to its mole fraction (x_1) multiplied vapour pressure of the solvent (P^0)".

$$P = x_1 P^0 \underline{\hspace{2cm}} (1)$$

$$x_1 + x_2 = 1$$

$$x_1 = 1 - x_2 \underline{\hspace{2cm}} (2)$$

Substitute (2) in (1),

$$P = (1-x_2) P^0$$

$$\frac{P}{P^0} = (1-x_2)$$

$$x_2 = 1 - \frac{P}{P^0}$$

$$\frac{P^0 - P}{P^0} = x_2$$

but

$$\boxed{x_2 = \frac{n_2}{n_1 + n_2}}$$

$$\frac{P^0 - P}{P^0} = \frac{n_2}{n_1 + n_2}$$

when compared to n_2, n_1 is greater,

$n_2 <<< n_1$, then we neglected n_2 from the denon

$$\frac{P^0 - P}{P^0} = \frac{n_2}{n_1}$$

$$\frac{P^0 - P}{P^0} = \frac{\dfrac{w}{mw}}{\dfrac{W}{Mw}}$$

$$\boxed{\frac{P^0 - P}{P^0} = \frac{w}{mw} \times \frac{Mw}{W}}$$

Deviations of Raoult's law:

1) Raoults law is applicable only to very dilute solutions. which approximate to the ideal behaviour.

2) Raoult's law is applicable to solutions containing non-volatile solute only.

3) Raoult's law is not applicable to solutes which dissosiate or assosiate in the particular solution.

PROBLEMS

x·1) When a solution of sugar is prepared in water at 20°c, the vapour pressure of water (17.51mm). Increased by 0.0614mm. calculate (i) RLVP (ii) vapour pressure of the solution (iii) Mole fraction of water and sugar solution?

Sol:

$$P^0 = 17.55mm$$

Lowering of vapour pressure $P^0 - P = 0.0614mm$.

(i) Relative lowering of vapour pressure $= \dfrac{P^0 - P}{P^0}$

$$= \dfrac{0.0614}{17.51}$$

$$= 0.00351.$$

(ii) vapour pressure of the solution $P = P^0 - (P^0 - P)$

$$= 17.51 - 0.0614$$

$$= 17.4486 mm.$$

(iii) Calculation of mole fraction of the solute,

$$\dfrac{P^0 - P}{P^0} = X_2$$

$$0.00351 = X_2 \text{ (sugar)}$$

Hence, mole fraction of the solvent (water) = 1 - 0.00351

$$= 0.99649.$$

(Q2) The relative lowering of vapour pressure produced by di$\text{x}$ 72 grams of substance of 1kg of water is 0.009. What is molecular mass of the substance?

Sol:

RLVP = 0.009.

w = 72gr   W = 1kg = 1000gr

mw = ?   Mw = 18

$$\frac{p^0 - p}{p^0} = \frac{w}{mw} \times \frac{Mw}{W}$$

$$0.009 = \frac{72 \times 18}{mw \times 1000}$$

$$mw = \frac{72 \times 18}{0.009 \times 1000}$$

$$mw = 144.$$

✓ **Osmatic pressure :-**

Osmasis :- "The phenomenon in which pure solvent molecules pa through a semi permeable membrane from a solution of l concentration to a solution of higher concentration".

Osmatic pressure :- "The excess pressure which must be ap$\text{p}$ on a solution in order to prevent flow of solvent into th solution through the semi permeable membrane".

Isotonic solutions :- A pair of solutions having the same osmatic pressure are known as isotonic solutions. These sol$\text{l}$ ave the same molar concentration.

Measurement of osmatic pressure by Berkeley-Hartley's method:-

ghis method involves the determination of the excess pressure that is applied upon the solvent to prevent the entry of the solvent into the solution.
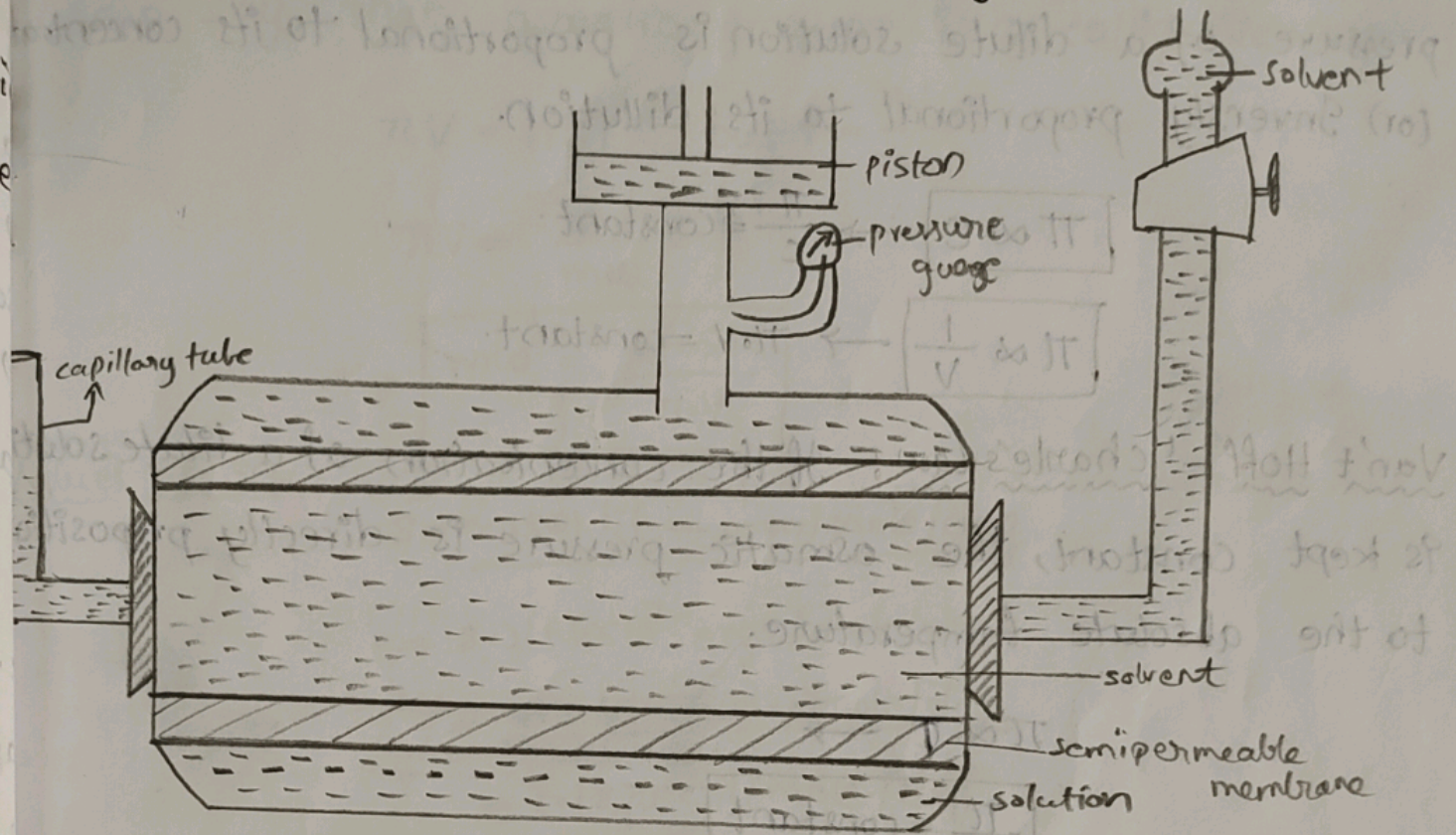
The apparatus consists of a porous pot having electrolytically deposited copper ferro cyanide semi permeable membrane in its walls. On one side it is connected to capillary tube and to a dropping funnel on the other side. The porous pot is fitted into a gun metal jacket provided with an air-tight piston. This piston is attached to the pressure guage. The porous pot is filled with the jacket is filled with solution whose osmatic pressure is to be determined. Internal pressure is applied to the solution through the piston to prevent the entry of the solution. That pressure is known as osmatic pressure.

Vont Haff – Boyle's Law : "At constant temperature the osm
pressure of a dilute solution is proportional to its concer
(or) Inversly proportional to its dillution.

$$\boxed{\pi \propto C} \rightarrow \frac{\pi}{C} = constant$$

$$\boxed{\pi \propto \frac{1}{V}} \rightarrow \pi \cdot V = constant.$$

Van't Hoff – ' charle's law : If the concentration of a dilute s
is kept constant, the osmatic pressure is directly propo:
to the absolute temperature.

$$\pi \propto T \rightarrow$$

$$\boxed{\frac{\pi}{T} = constant}$$

General osmatic pressure for dilute solutions :-

acc. to van't Hoff - boyle's law, $\pi \propto \frac{1}{V}$

acc. to von't Hoff – charle's law, $\pi \propto T$

combining both the laws, $\pi \propto \frac{1}{V} \propto T$

$$\pi \propto \frac{T}{V}$$

$$\pi V = ST \qquad S = solution$$
$$Temperc$$

for 'n' moles, $\boxed{\pi V = n S T}$ Van't Hoff Equation

$$\pi = \frac{n}{V} \cdot ST$$

$$\pi = CST$$

since, the osmatic pressure of a solution at any
given temperature T, depends upon the no. of moles per ur

and independent of the the nature of the solvent. Hence, we can say that osmatic pressure is a colligative property.

$$\pi V = nST \quad \text{but } n = \frac{W}{mw}$$

$$\pi V = \frac{W}{mw} \cdot S \cdot T$$

$$\boxed{mw = \frac{W \cdot ST}{\pi \cdot V}}$$

Values of S:

$$S = 0.0821 \text{ lit} - atm/mole/deg.$$

$$= 8.3160 \times 10^7 \text{ ergs/mole/deg}$$

$$= 8.3160 \text{ Joules/mole/deg}$$

$$= 1.1870 \text{ cal/mole/deg}.$$

PROBLEMS

Ex: 1) Calculate the osmatic pressure of 0.01M solution of urea at 300K. (S = 0.0821 lit - atm/deg/mole)

ol:
$$C = 0.01M = 0.01 \text{ moles lit}^{-1}$$
$$S = 0.821 \text{ lit} - atm \text{ deg}^{-1} \text{mole}^{-1}$$
$$T = 300K.$$

$$\pi = CST$$
$$\pi = 0.01 \times 0.0821 \times 300$$
$$= 0.2463 \text{ atm}!$$

Ex: 2) Calculate the osmatic pressure of a 10% solution of cane sugar at 25°C. (R = 8.31 J K^{-1}mole^{-1})

sol: 10% solution of cane sugar means that it contains 10 gr of cane sugar per 100 cc of the solution.

$$\omega = 10 \text{gr}$$
$$V = 100 \, c \cdot c = \frac{1}{10} \text{lit}$$

$$mw = 342$$
$$S = 8.31 \, J. \deg^{-1} mole^{-1}$$

$$T = 25 + 273 = 298 K \cdot \pi = ?$$

acc. to von't Hoff. Equation,

$$\pi V = n S T$$

$$\pi V = \frac{\omega}{mw} \cdot S \cdot T$$

$$\pi = \frac{\omega}{mw} \times \frac{ST}{V}$$

substituting the values in the equation.

$$\pi = \frac{10}{342} \times \frac{8.31 \times 298 \times 10}{1}$$

$$= 724.09 \, J.$$

(3) **Elevation in Boiling point :—** Boiling point of a liquid ma
defined as the temperature at which its vapour pressure
equal to atmospheric pressure. Elevation in the boiling point
the solvent is due to the addition of a non-volatile solute
be readilly understood from the vapour pressure curves
pure solvent.

The boiling point of a pure solvent is given if
this solvent a small amount of non-volatile solute is
then the B.p of solution will be greater than the pure so

Let us consider the B.p of solution is T, the elevatio
Boiling point is $\boxed{\Delta T_b = T - T_0.}$

We should know that as the vapour pressure of any solution decreases its boiling point increases. when solute is added to the solvent it ↓ses the vapour pressure. Hence boiling point ↑ses. The increase in B·p by addition of non – volatile solute to a solvent is known as elevation of boiling point.

consider a pure solvent, solution-I and solution-II in which the conc. of solution II is greater than solution-I. If a graph is drawn between the vapour pressure and boiling points of these systems the curves formed are as shown in fig.

Let us consider T₀, T₁, T₂ are the boiling points of solvent, solution-I. solution-II. the corresponding vapour pressures are P₀, P₁. P₂ respectively.
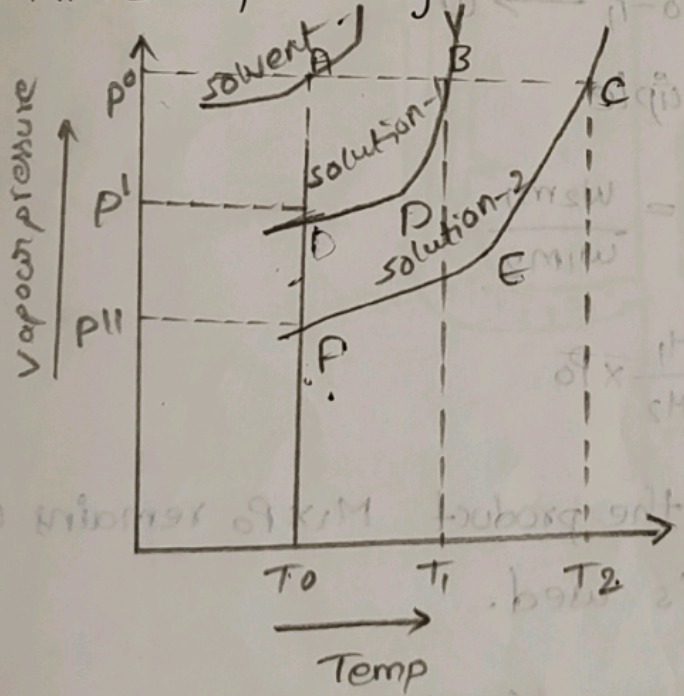
→ In the diagram, the curves BD and EF are parallel lines for the given systems. Hence the triangles ACF & ADB are equal triangles then,

$$\frac{AC}{AB} = \frac{AF}{AD}$$

from the diagram

$$AC = T_2 - T_0$$
$$AB = T_1 - T_0$$
$$AF = P_0 - P_2$$
$$AD = P_0 - P_1$$

→ Boiling point of pure solvent = T₀
→ Boiling point of solution – I = T₁
→ Boiling point of solution – II = T₂

then,
$$\frac{T_2 - T_0}{T_1 - T_0} = \frac{P_0 - P_2}{P_0 - P_1}$$

$$\frac{\Delta T_2}{\Delta T_1} = \frac{\Delta P_2}{\Delta P_1}$$

$$\frac{\Delta T_2}{\Delta P_2} = \frac{\Delta T_1}{\Delta P_1}$$

$$\frac{\Delta T}{\Delta P} = K \text{ (constant)}$$

From this the boiling points of different systems a directly proportional to the lowering of vapour pressure

$$\Delta T_b \propto P_0 - P.$$

Determination of Molecular weight of solute by elevation boiling point :-

We know that $\Delta T_b \propto P_0 - P_1 \longrightarrow$ ①

from Raoult's principle

$$\frac{P_0 - P}{P_0} = \frac{n_2}{n_1 + n_2} = \frac{W_2 m_1}{W_1 m_2}$$

then $P_0 - P = \dfrac{W_2 M_1}{W_1 M_2} \times P_0$

In the above equation, the product $M \times P_0$ remain -ant when the same solvent is used.

$$P_0 - P = \frac{W_2}{W_1 \times M_2} \times \text{constant}.$$

$$\therefore P_0 - P \propto \frac{W_2}{W_1 \times W_2} \longrightarrow ②$$

from eq ① & ② $\quad \Delta T_b \propto \dfrac{W_2}{W_1 \times M_2} \quad$ Then $\Delta T_b = K_b \times$

where k_b = molar elevation constant:

To define k_b consider $\dfrac{W_2}{M_2} = 1$ mole & $W_1 = 1$ kg then
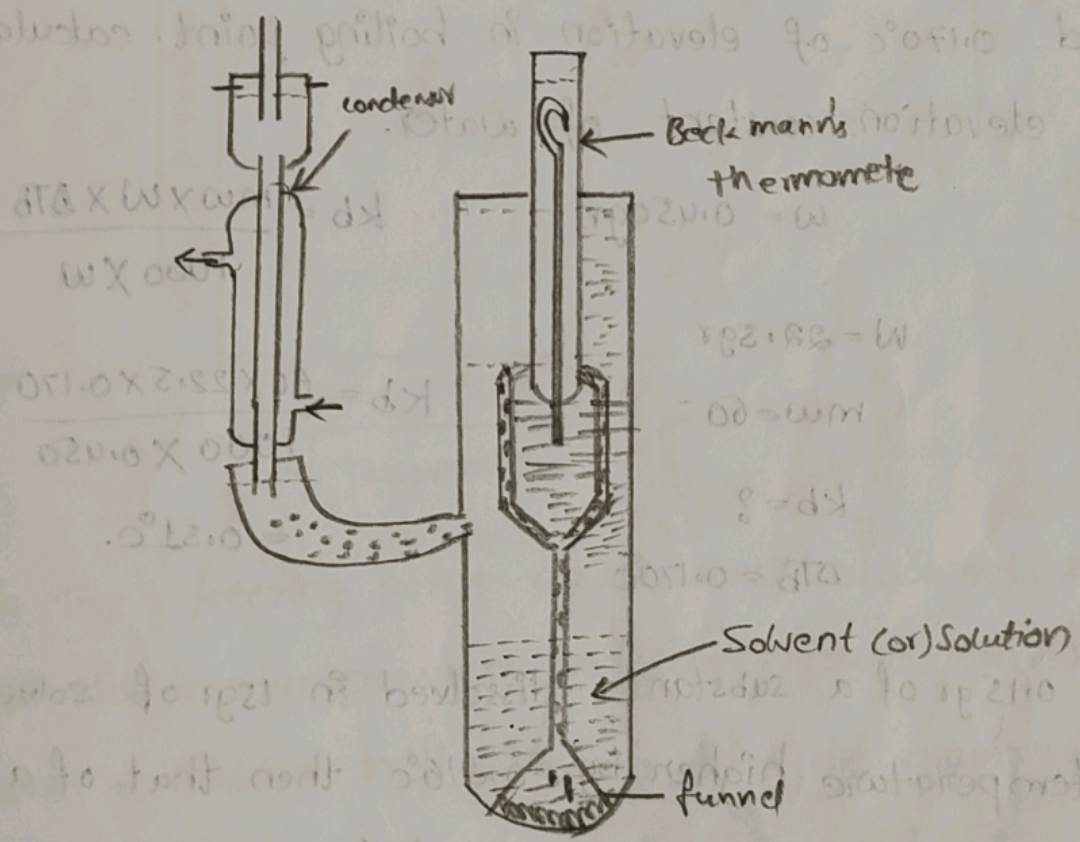
$$\boxed{\Delta T_b = k_b}$$ k_b = Molar elevation constant.

If the weight of the solvent is given in gms.

then $\Delta T_b = \dfrac{k_b \times W_2 \times 1000}{W_1 M_2}$

$\therefore$ $\boxed{M_2 = \dfrac{k_b \times W_2 \times 1000}{W_1 \times \Delta T_b}}$

Determination of elevation of boiling point by cottrell's method:-

Cotrells apparatus consists of graduated boiling tube containing solvent or solution, a condensor fitted. In the slide tube of the main graduated tube, the condensor returns the vapourised solvent to the boiling tube.

solvents is placed in the boiling tube having a few fra ments of a porous pot below the mouth of the funnel. The tube is heated on a small flame. Now, the temperature read is exactly that of the boiling liquid and the super heating is minimum. This is the B.P of the pure solvent.

Now, weighed amount of the solute is added to the solvent and boiling point of the solution is determine as that of the solvent.

PROBLEMS

Ex: 1) A solution of 0.450 gr. of urea (m.wt =60) in 22.5 of water showed 0.170°C of elevation in boiling point. calculate the molal elevation constant of water.

sol:

$w = 0.450 gr$

$W = 22.5 gr$

$mw = 60$

$kb = ?$

$\Delta T_b = 0.170°C$

$kb = \dfrac{mw \times W \times \Delta T_b}{1000 \times w}$

$kb = \dfrac{60 \times 22.5 \times 0.170}{1000 \times 0.450}$

$= 0.51°C$

Ex: 2) 0.15 gr of a substance dissolved in 15 gr of solvent boile at a temperature higher by 0.216°C then that of a pure solu calculate the molecular weight of the substance (kb= 2.16°c)

sol: Depression in freezing point :-

Freezing point is the temperature at which th liquid and the solid states of a substance are in equilibriu with each other

...the vapour pressure of a liquid is lowered by the addition of a non-volatile solute. In other words freezing point of a solution will be lower than the freezing point of the pure solvent.

* If T_0 is the freezing point of pure solvent and T is the freezing point of the solution. The difference in the two freezing points are called the depression in freezing point which is denoted by ΔT_f.

Depression in freezing point $\Delta T_f = T_0 - T$

ABE, ACF

$$\frac{AE}{EF} = \frac{BC}{CF}$$
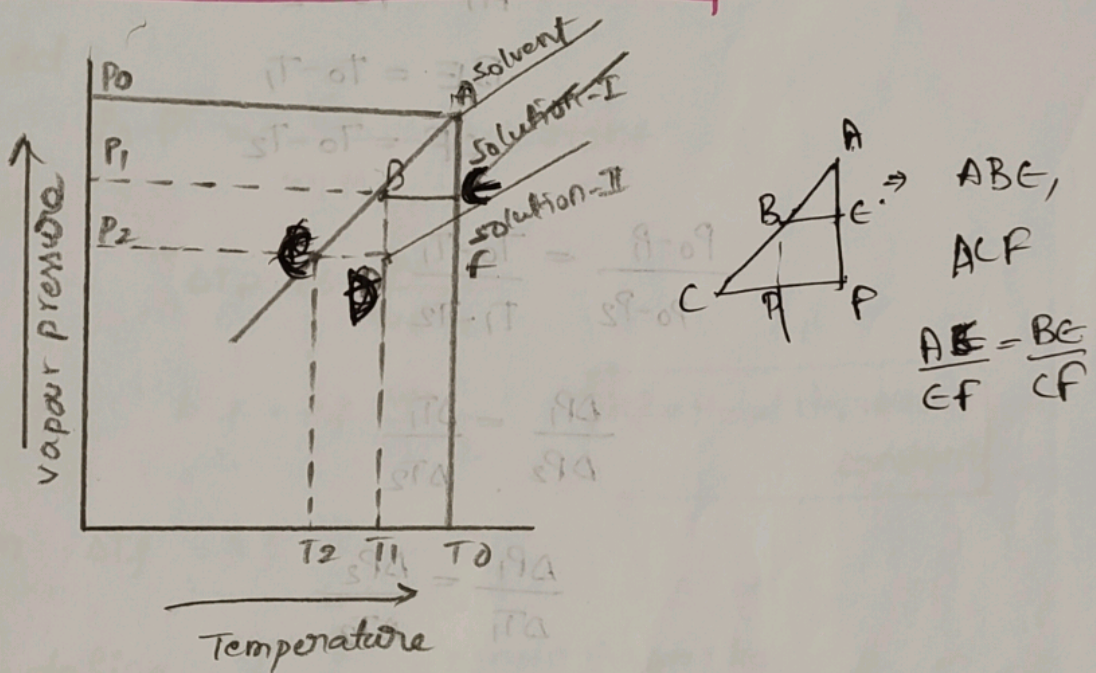
Study the freezing point curves, consider the solvent. solution-I solution-II. The vapour pressure and Temperature curves of this systems are as shown in the graph. from the graph point A represents the equilibirium b/w solid and liquid of pure solvent. Similarly the points B & C represents the freezing points of solution-I & solution-II. Let us consider P_0, P_1, P_2 are the vapour pressures of pure solvent, solution-I & solution-II.

similarly T_0, T_1, T_2 are the freezing points of solvent, solution-I, solution-II.

* For a very dilute solutions BE and CF are parallel line. Hence the triangles ABE & ACF are equal triangles.

$$\triangle ABE = \triangle ACF$$

Then $\dfrac{AE}{AF} = \dfrac{BE}{CF}$

from graph,

$$AE = P_0 - P_1$$
$$AF = P_0 - P_2$$
$$BE = T_0 - T_1$$
$$CF = T_0 - T_2$$

$$\dfrac{P_0 - P_1}{P_0 - P_2} = \dfrac{T_0 - T_1}{T_1 - T_2}$$

$$\dfrac{\Delta P_1}{\Delta P_2} = \dfrac{\Delta T_1}{\Delta T_2}$$

$$\dfrac{\Delta P_1}{\Delta T_1} = \dfrac{\Delta P_2}{\Delta T_2}$$

$\therefore \dfrac{\Delta P}{\Delta T} = $ constant $\qquad \therefore \boxed{\Delta T_f \propto P_0 - P}$

The temperature in freezing point is directly proportion to lowering of vapour pressure!

Determination of Molecular weight of solute from depre in freezing point :-

From the graph, we know th...

$$\Delta T_f \propto P_0 - P \rightarrow ①$$

From raoult's law

$$\frac{P_0 - P}{P_0} = \frac{W_2 M_1}{W_1 M_2} \rightarrow ②$$

$$P_0 - P = \frac{W_2 M_1}{W_1 M_2} \times P_0$$

from ① & ②

$$\Delta T_f = \frac{W_2 M_1}{W_1 M_2} \times P_0$$

The product of $M_1 P_0$ remains constant, when the same solvent is used

$$P_0 - P = \frac{W_2}{W_1 M_2} \times constant$$

$$\Delta T_P \propto \frac{W_2}{W_1 M_2}$$

$$\Delta T_f = k_f \frac{W_2}{W_1 M_2}$$ $\boxed{k_f = \text{Molal depression}\\ \qquad\qquad \text{constant}}$

Then $\Delta T_f = k_f \dfrac{W_2}{W_1 M_2}$

to define it $\dfrac{W_1}{M_2} = 1 \, mole$ & $w_1 = 1 \, kg$
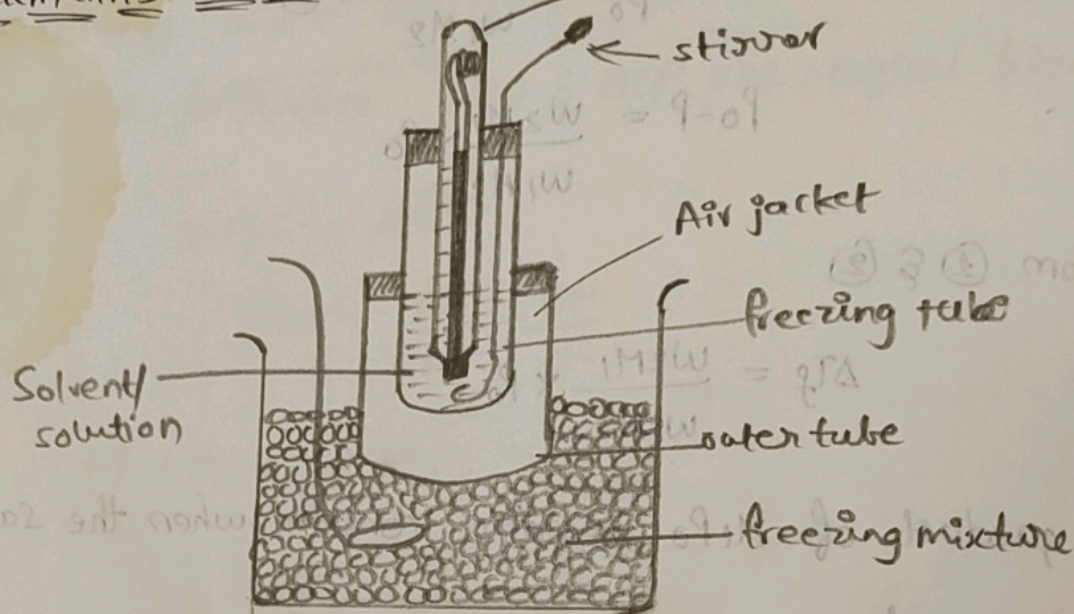
Then $\boxed{\Delta T_f = k_f}$

$$\therefore M_2 = \frac{k_f W_2}{W_1 \Delta T_f}$$

If the weight of the solvent is given in gms.

then, $\boxed{M_2 = k_f \cdot \dfrac{W_2 \times 1000}{W_1 \times \Delta T_f}}$

(d)

Determination of Freezing point depression:

Beckmann's method :-

The diagram labels: Beckmann's thermometer, stirrer, Air jacket, freezing tube, water tube, freezing mixture, Solvent/solution

The inner freezing tube fitted with a beckmann thermometer and a platinum stirrer. The outer glass tube which is fitted the inner freezing tube, leaving an air space btw them. A glass jar containing a suitable freezing mixture whose F.P is about 5°C lower than that of the pure solvent.

Take a known weight of the pure solvent in the freezing tube, and suspended the thermometer in the freezing tube. Report the F.P of a pure solvent. Now, add non-volatile solute to the solvent and Report the F.P of solution. The difference between them is called depression in F.P.

PROBLEMS

Ex: 1) 0.750gr of a compound A dissolved in 25gr. of the solvent lowered the F.P of the solvent by 0.502°C. calculate the m.wt of the substance. The molecular depression constant of the solvent is 50.2°C per 10gr of the solvent.

w= 0.750gr ΔTf =0.502°C   W= 25gr

kf =50.2°C pec 100gr

mw= 100 X kf X W / ΔTf X W

mw=?

= 100 X 50.2 X 0.750 / 0.502 X 25

$$\boxed{mw = 300}$$

calculate the FoP of 1% solution of Glucose in water, given t molal depression constant for water is 1.84 k.mole⁻¹.

w= 1gr   W =99gr.

mw=180   kf = 1.84.

$$ΔTf = \left(\frac{1}{A}\right) \frac{1000 \cdot kf \cdot w}{mw \times W}$$

= 1000 X 1.84 X 1 / 180 X 99.

= 0.1032°C.

freezing of the solution = F.no.of solvent − ΔTf

= 0 − 0.1032°C

= −0.1032°C.

Abnormal behaviour of Solutions:-

Since, the colligative properties of solutions depend on the no.of solute particles present in solution and not on their nature, colligative properties of the solutes which undergo dissosciation in solution would be higher than expected for the non-electrolytes.

Vant Hoff factor(i) :- " It can be defined as the ratio of observed colligative property to normal colligative propert

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

(or)

$$i = \frac{\text{Normal molecular weight}}{\text{observed molecular weight.}}$$

Van't Hoff factor and Degree of Association :- The degree association of a substance is defined as the fraction o the total no.of molecules of the substance which exist a associated molecules.

Initial no.of moles $A' \rightleftharpoons \left[°A\right]_n^{2TA}$
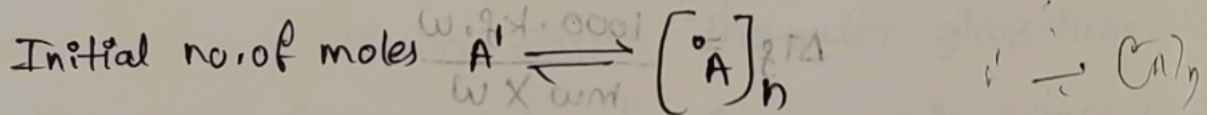
No.of moles after association $1 - \alpha + \dfrac{\alpha}{n}$

Total no.of moles after association $= 1 - \alpha + \dfrac{\alpha}{n}$

Van't Hoff factor (i) $= \dfrac{\text{observed colligative effect}}{\text{Normal colligative effect}}$

$$i = \frac{1 - \alpha + \dfrac{\alpha}{n}}{1}$$

$$i = 1 - \alpha + \dfrac{\alpha}{n}$$

$$i = 1 - \alpha\left[1 - \dfrac{1}{n}\right]$$

$$\alpha = \frac{1 - i}{1 - \dfrac{1}{n}}$$

rty9 The degree of dissociation of a substance is defined as the fraction of the total no. of molecules which dissociate in the solution into simpler molecules.

1 mole of an electrolyte gives n number of ions.

ω = degree of dissosciation.

No. of undissociated molecules of the electrolyte = $1-\omega$

No. of ions produced due to dissociation = $n\omega$

∴ Total no. of particles after dissosciation = $1-\omega + n\omega$

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

$i = \dfrac{1-\omega + n\omega}{1}$

$i-1 = \omega(n-1)$

$\omega = \dfrac{i-1}{n-1}$

$i = 1-\alpha + n\alpha$

$i = 1-\alpha(1-n)$

$i-1 = \alpha(n-1)$

$\alpha = \dfrac{i-1}{n-1}$

SHORT QUESTIONS

01) state and explain the Raoult's law.

2) what is vant Hoff's factor and explain.

3.) Explain about the abnormal colligative properties.

4) Explain about determination of depression of freezing point by Beckmann's method.

5.) How can you determine the osmatic pressure by Berkeley-artley's method.

LONG QUESTIONS

(01) Derive an expression for depression of freezing point.

(02) Derive an equation for elevation of boiling point.