

Liquid Solution

Solution \rightarrow It is homogeneous mixture of two or more components

eg, air, sugar solⁿ, cold drink, etc.

Solution = Solute + solvent

• Classification of solⁿ \rightarrow

A] On the basis of no. of components :

1] Binary solⁿ : 1 solute + 1 solvent

2] Ternary solⁿ : 2 solute + 1 solvent

3] Quaternary solⁿ : 3 solute + 1 solvent

B] On the basis of Phases of solute & solvent :

1] Solid solution,

solute	solvent
Solid	Solid
liquid	Solid
gas	Solid

eg,
Brass - alloy
Hg - Na (sod amalgam)
 H_2 in Pd

2] liquid solution,

Solid	Liquid
liquid	liquid

NaCl (aq.)
 C_2H_5OH (l) in water

gas liquid $O_2(g)$ in water

3) Gaseous solution,

solid	gas	amphor in $N_2(g)$
liquid	gas	chloroform in $N_2(g)$
gas	gas	$O_2 + N_2$ (air)

* Solubility: It is maximum amt. of substance which can be dissolved in specified amt. of solvent at a given temp.

• Factors affecting Solubility:

- 1) Nature of solute & solvent
- 2) Temperature
- 3) Pressure

1) Solubility of solid in liquid:

• Effect of Temp.: Solu. changes on changing temp.

If $\Delta H \geq 0 \Rightarrow$ Endothermic \Rightarrow Sol. \uparrow on $\uparrow T$

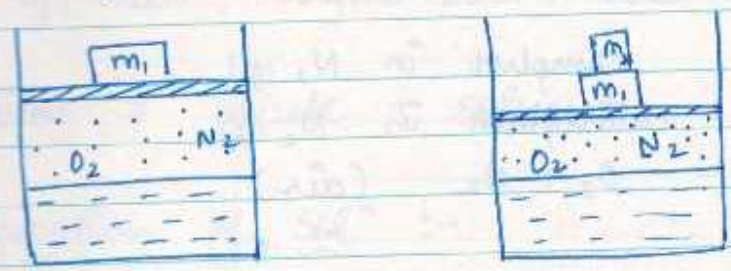
$\Delta H < 0 \Rightarrow$ Exothermic \Rightarrow Sol. \downarrow on $\uparrow T$

• Effect of Pressure: Pressure has negligible effect on solubility of solid in liquid coz both are almost incompressible

Liquid Solutions

Solubility of gas in liquid :

Effect of Pressure : on ↑ P, sol. of gas in liq. ↑



Henry's law :

Partial pressure of gas is directly proportional to mole fraction of gas in liquid solⁿ.

$$P_{\text{gas}} \propto X_g$$

$$P_{\text{gas}} = K_H X_{\text{gas}} = K_H \frac{n_{\text{g(aq.)}}}{n_{\text{g(aq.)}} + n_{\text{solvent}}}$$

where,

- $P_g \rightarrow$ Partial pressure of gas
- $X_g \rightarrow$ mole fraction of gas in liquid solⁿ
- $K_H \rightarrow$ Henry's constant

Henry's constant (K_H) depends on

- i) Nature of gas & solvent
- ii) Temp. : generally on ↑ temp. $K_H \uparrow$

Henry's law is applicable only for highly dilute solution.

$$P = K_H X$$

$$P = K_H \times \frac{n_B}{n_A + n_B} \rightarrow 0$$

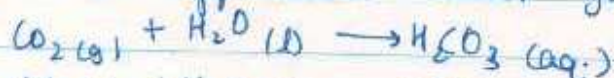
$$P \approx K_H \times \frac{n_B}{n_A} \approx K_H \times \frac{n_B}{W_A} \times 10^3 \times \frac{M_A}{10^3}$$

$$P = K_H \times \frac{M \times M_A}{1000}$$

• limitations of Henry's law :

- applicable only for dilute solutions.

- It is not applicable when gas combines with solid



- If gas dissociates after dissolution then this law cannot be applied.



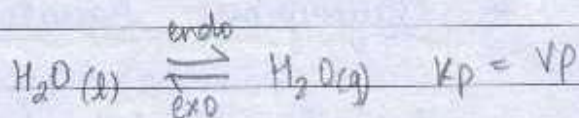
Q. If $\text{N}_2(\text{g})$ is bubbled thru water at 293 K, how many mm of gas would dissolve in water (1L) assume N_2 exerts a pressure of 1 bar.

Given : $K_H = 75 \text{ k bar}$ at 293 K

$\frac{40}{3 \times 10^3}$

$$\rightarrow 1 = \frac{75 \times 28 \times x}{1000} \quad \text{IL}$$

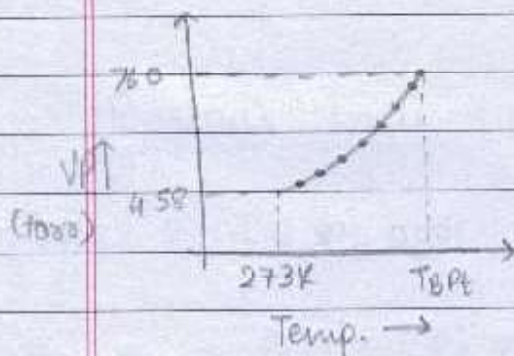
$$x = \frac{1}{75 \times 28} = \frac{1}{2100}$$

* Vapour Pressure :->

As T ↑ K ↑ VP ↑



It is the pressure exerted by vapours of a liquid when liquid & its vapours are in equilibrium.

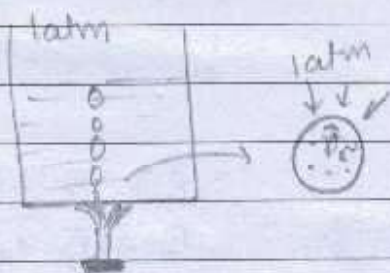


VP of a given liq. can be changed only by changing temperature.

* Boiling Point :->

It is the temp. at which VP of liq. becomes equal to external pressure.

At BP, KE of gaseous particles will be same as KE of liquid phase particles.



* Claapeyron equation :

$$\ln \frac{VP_2}{VP_1} = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Q. For a liquid normal BP is -173°C . Then at 2 atm pressure its BP should be nearly —

$$\rightarrow \ln 2 = \frac{200}{2} \left(\frac{1}{100} - \frac{1}{x} \right)$$

$$\Rightarrow \frac{1.4}{200} = \frac{x-100}{100x}$$

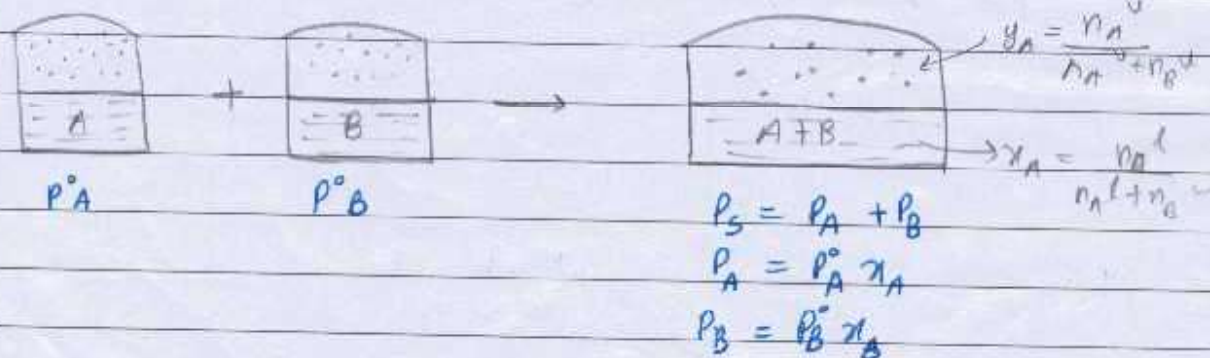
$$\Rightarrow 1.4x = 2x - 200 = x = \frac{2000}{6} = \frac{1000}{3} \text{ K}$$

* Binary Solutions \Rightarrow

1] VP of liquid in liquid :

- Rault's law :

Accⁿ to it the partial VP of each component is directly proportional to mole fraction of that component in liq. solⁿ.



$$P_A \propto x_A$$

$$P_A = P_A^\circ x_A$$

$$P_B = P_B^\circ x_B$$

$$P_s = P_A^\circ x_A + P_B^\circ x_B$$

$$P_s = (P_A^\circ - P_B^\circ) x_A + P_B^\circ$$

where,

$P_A^\circ, P_B^\circ \rightarrow$ VP of pure A & B resp.

$P_A, P_B \rightarrow$ Partial VP of A & B

$x_A, x_B \rightarrow$ mol fraction of A in liq. solution

$P_s \rightarrow$ VP of solⁿ.

- Dalton's law :

$$P_A = y_A P_s$$

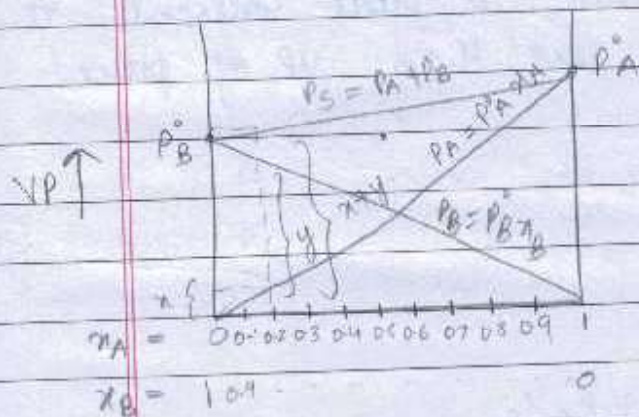
$$y_A = \frac{P_A}{P_s} = \frac{P_A^\circ x_A}{P_A^\circ x_A + P_B^\circ x_B} \quad (\text{same for } y_B)$$

$$P_s = P_B^\circ + x_A (P_A^\circ - P_B^\circ)$$

$$\downarrow \quad \downarrow \quad \downarrow$$

$$c \quad + \quad x \quad (m)$$

$$P_A^\circ > P_B^\circ$$



Note : The solutions which obey Raoult's law are called ideal solutions.

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- Equilibrium approximation :

Accⁿ to it, initial moles of components will be equal to moles of components in liq. solⁿ & we will neglect moles of components vapourised.

Q. Find VP of mixture obtained by mixing 2 mol of benzene and 5 mole of toluene at 30°C.
(Given: VP of Benzene & toluene are 20 & 30 torr)
Also find the mole fraction of benzene & toluene in vapor phase at eq.

$$\rightarrow P_s = P_A + P_B = \frac{190}{7} \text{ torr}$$

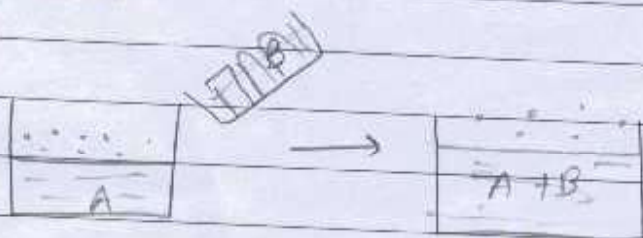
$$P_A = 20 \times \frac{2}{7}$$

$$P_B = 30 \times \frac{5}{7}$$

$$y_A = \frac{P_A}{P_s} = \frac{4}{19} \quad \& \quad y_B = \frac{15}{19}$$

2] VP of solid in liquid :-

On addⁿ of non volatile solute in pure solvent, VP of resulting solⁿ will be less than VP of pure solvent.



$$P_s = P_A^{\circ} x_A + P_B^{\circ} x_B$$

$$P_s = P_A^{\circ} x_A \quad (\because P_B^{\circ} = 0 \text{ (as B is non vol.)})$$

$$P_s < P_A^{\circ}$$

$$V_p \text{ Sol} < V_p \text{ of solvent}$$

8. The VP of benzene at certain temp. is 640 torr. A non volatile non electrolyte solute having mass 2.175 g is added to 39 g benzene. Now VP of sol is 600 torr. Find molar mass of solute.

$$\rightarrow \frac{640}{600} = \frac{640 \times 0.5}{0.5+x} \Rightarrow \frac{15}{16} = \frac{0.5}{0.5+x}$$

$$\Rightarrow 7.5 + 15x = 8 \quad \frac{15}{8} = \frac{1}{0.5+x}$$

$$x = \frac{5}{150} = \frac{1}{30}$$

$$\frac{2.175}{g} = \frac{1}{30} \Rightarrow M_{\text{solute}} = 65.25$$

* Classification of Solⁿ on the basis of behaviour:

i) Ideal Solution :->

- These are the solutions which follow Raoult's law.
- Force of interaction b/w AA, BB & AB are approximately same.



$$F_{A-A} \\ P_A^*$$

≈

$$F_{B-B} \\ P_B^*$$

≈

$$F_{A-B}$$

$$P_S = P_A + P_B$$

$$P_A = P_A^* x_A$$

$$P_B = P_B^* x_B$$

} Raoult's law

• Thermodynamic parameters:

$$\Delta_{\text{mix}} G < 0$$

$$\Delta_{\text{mix}} H = 0$$

$$\Delta_{\text{mix}} S > 0$$

$$\Delta_{\text{mix}} V = 0$$

Examples :

- benzene + toluene
- ethyl bromide + ethyl iodide
- ethyl alcohol + methyl alcohol
- chlorobenzene + bromobenzene
- n-butyl chloride + n-butyl bromide

P_s v/s x_A

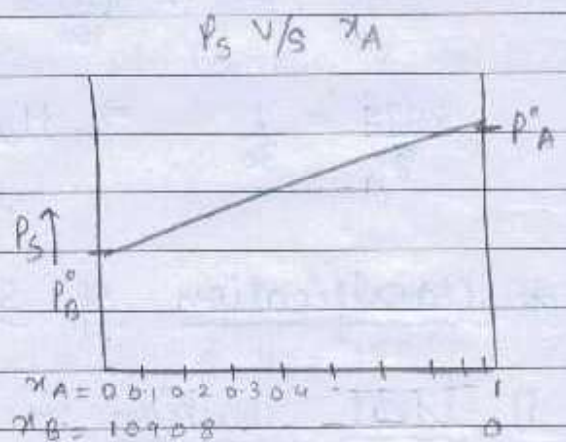
We assume $P_A^\circ > P_B^\circ$

$$P_s = P_A^\circ x_A + P_B^\circ x_B$$

$$P_s = P_A^\circ x_A + P_B^\circ (1 - x_A)$$

$$P_s = P_B^\circ + x_A (P_A^\circ - P_B^\circ)$$

$$y = c + mx$$



P_s v/s x_B

We assume $P_A^\circ > P_B^\circ$

$$P_s = P_A^\circ x_A + P_B^\circ x_B$$

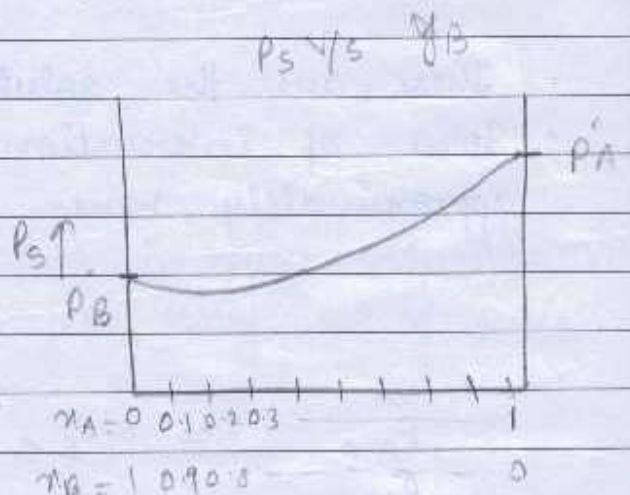
$$P_s = P_A^\circ (1 - x_B) + P_B^\circ x_B$$

$$P_s = P_A^\circ + x_B (P_B^\circ - P_A^\circ)$$

$$y = c + mx$$

$$P_s = \frac{P_A^\circ P_B^\circ}{P_A^\circ - y_A (P_A^\circ - P_B^\circ)}$$

$$P_s = \frac{P_A^\circ P_B^\circ}{P_A^\circ - y_A (P_A^\circ - P_B^\circ)}$$



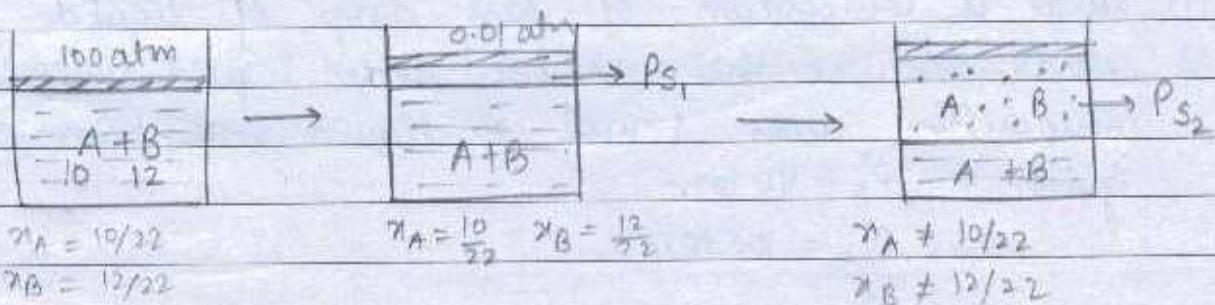
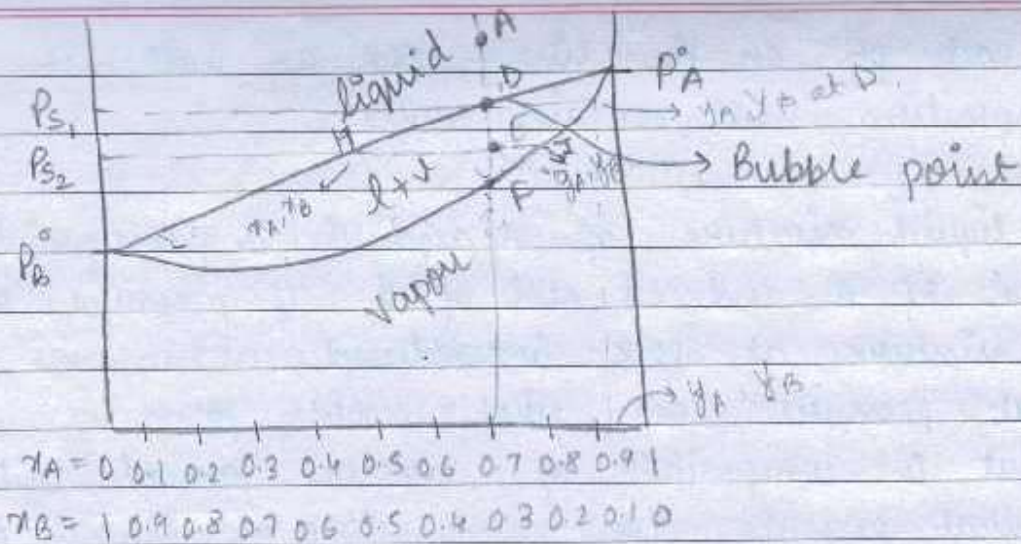
overall
mole fraction

$$x_A = \frac{n_A(\text{Total})}{n_{\text{Total}}} = \frac{n_A^l + n_A^g}{n_A^l + n_A^g + n_B^l + n_B^g}$$

$$y_A = \frac{n_A^g}{n_A^g + n_B^g}$$

$$x_B = \frac{n_B(\text{Total})}{n_{\text{Total}}} = \frac{n_B^l + n_B^g}{n_A^l + n_A^g + n_B^l + n_B^g}$$

$$y_B = \frac{n_B^g}{n_A^g + n_B^g}$$



- At pt. A only liq. exists
- When we further lower the pressure then at pt. D first drop of liq. will evaporate. This is also called bubble pt. At this pt. only small amt. of liq. has been evaporated.
- When we further lower the pressure till pt. E considerable amt. of liquid has been evaporated.
- When we further lower the pressure till F, at F last drop of liq. will be left.

Here,

$$y_A = x_{AI}$$

$$y_B = x_{BI}$$

- line ADEF is called isopleth. Here overall composition will remain same.
- HEI is called tie line whose end points give composition of two different phases.

at each pt. on tie line, liq. as well as vapour composition will remain same.

Q. A liquid mixture of A and B is composed of 1 mol of A and 1 mol of B. If pressure over the mixture at 300K is reduced, at

- i) what pressure does first bubble form
- ii) what is composition of vapours formed initially
- iii) at what pressure does last drop of liquid disappear
- iv) what is composition of last drop of liquid
- v) what will be the pressure and liquid vapor composition when 1 mol of liquid has been evaporated : $P_B^\circ = 40 \text{ torr}$
 $P_A^\circ = 100 \text{ torr}$.

$$\rightarrow \text{i) } P_s = P_A + P_B \\ = 0.5 \times 40 + 0.5 \times 100 = 70 \text{ torr}$$

$$\text{ii) } y_A = \frac{P_A}{P_s} = \frac{50}{70}$$

$$y_B = \frac{P_B}{P_s} = \frac{20}{70}$$

$$\text{iii) } P_s = \frac{40 \times 100}{100 - \frac{1}{2}(60)} = \frac{4000}{7} \text{ torr}$$

$$\text{iv) } \text{Ans. } \text{Ans } \frac{4}{14}, \frac{10}{14}$$

$$\text{v) } P_s = P_A^\circ x_A + P_B^\circ x_B \quad \text{Ans } \frac{1}{2} + \frac{5}{7} \quad \frac{17}{28} ; \frac{11}{28}$$
$$\frac{440}{28} + \frac{1700}{28}$$

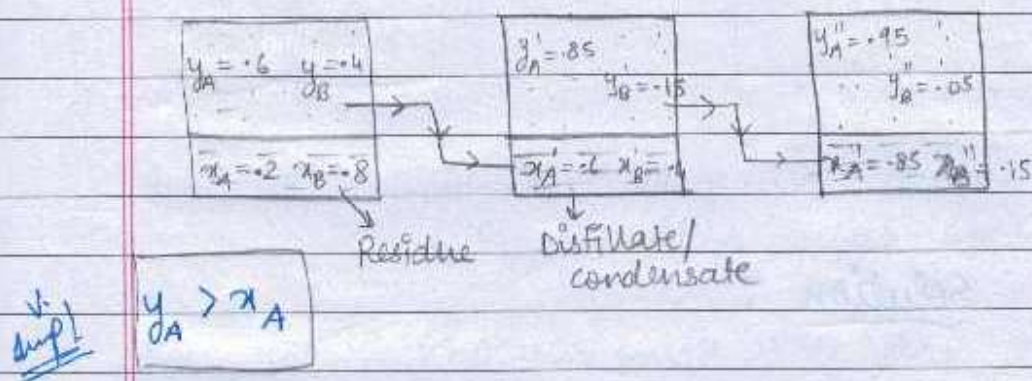
* Fractional Distillation :

It is process of separation of two liquids having diff. boiling points.

- 1] At constant temperature
- 2] At constant pressure

• At constant temperature :->

Vapours will be richer in the component which is more volatile.



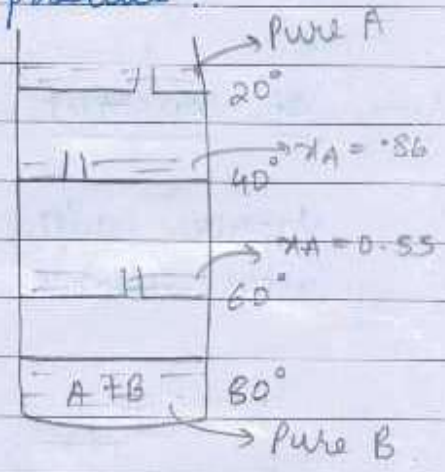
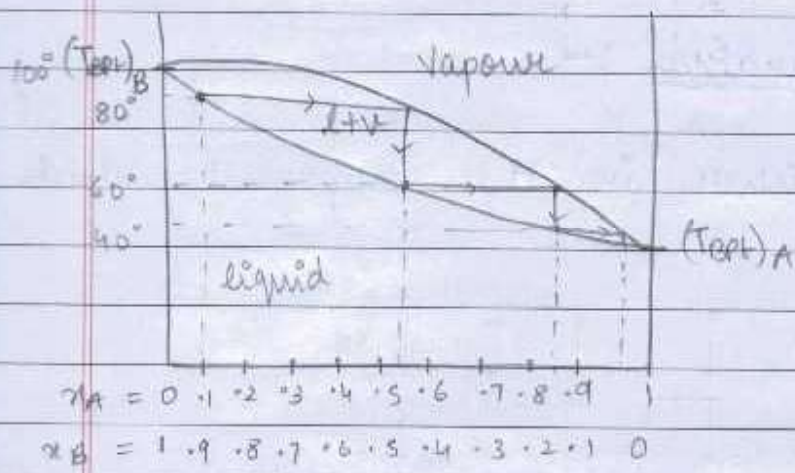
Q. A solution is prepared by mixing 12 mole benzene and 8 mole toluene. If vapours over this solⁿ were removed & condensed & again brought to same temp. then what would be the mole fraction of benzene & toluene in vapour state.

$$\begin{aligned}
 \rightarrow x_B &= \frac{3}{5} & y_B &= \frac{162}{198} = x'_B & y'_B &= \frac{P_B}{P_S} = \frac{243}{261} & 2/19 \\
 x_T &= \frac{2}{5} & y_T &= \frac{36}{198} = x'_T & y'_T &= \frac{P_T}{P_S} = \frac{18}{261} & 2/19
 \end{aligned}$$

$\frac{2430}{2610} = \frac{11}{11}$

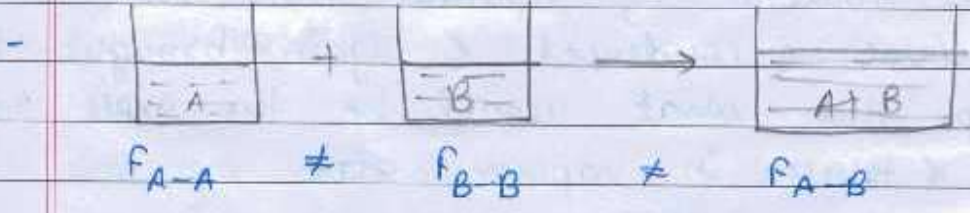
At constant Pressure :

Suppose we take a mixture having composition $x_A = .1 \ \& \ x_B = .9$. As we \uparrow temp. from 80°C to 100°C the vapours formed will be richer in more volatile component, however, residue will become richer in less volatile product.



ii] Non-ideal Solution :

- The solutions which do not follow Raoult's law are called non-ideal solutions.



-
$$P_s = P_A + P_B \quad \checkmark$$

$$P_A \neq P_A^\circ x_A$$

$$P_B \neq P_B^\circ x_B$$

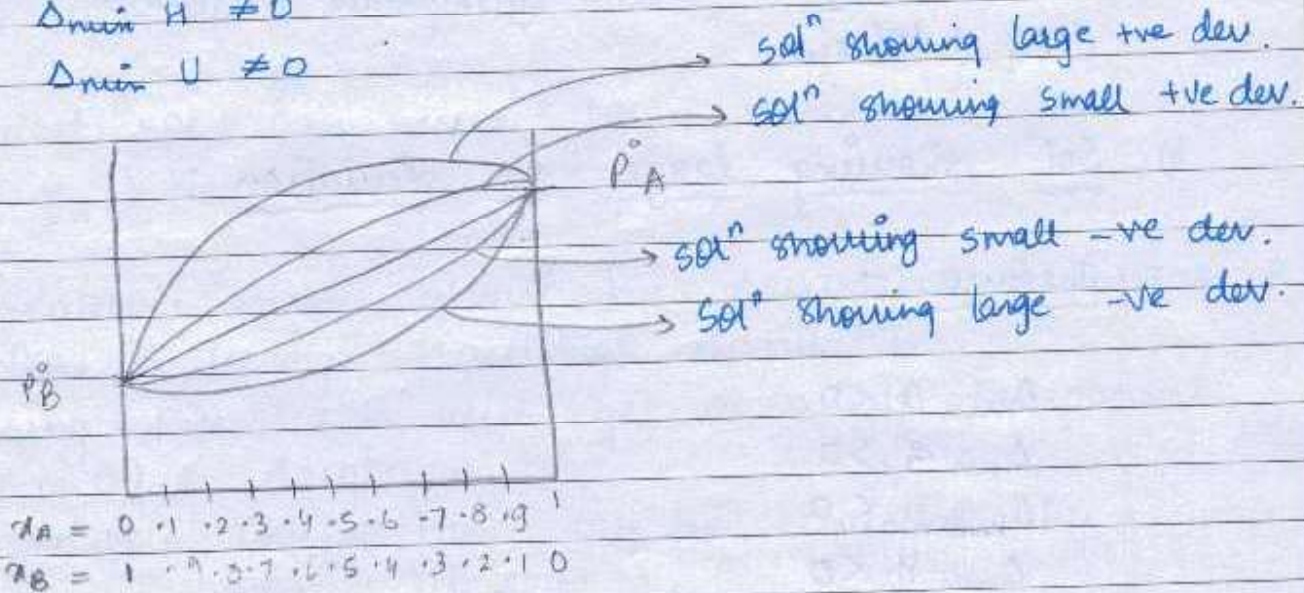
- Thermodynamics :

$$\Delta_{mix} G < 0$$

$$\Delta_{mix} S > 0$$

$$\Delta_{mix} H \neq 0$$

$$\Delta_{mix} U \neq 0$$



For solⁿ showing large +ve deviation
 $(VP)_{sol} > (P^0)_A$ (at some comp.)

For solⁿ showing small +ve dev.
 $P_B \leq (VP)_s \leq P_A^0$

- A solⁿ is said to be showing +ve deviation if its VP is greater than expected from ideal behaviour.

- Force of attⁿ b/w A-B will be weaker than A-A or B-B.

$$P_s = P_A + P_B$$

$$P_A > P_A^0 x_A$$

$$P_B > P_B^0 x_B$$

$$\Delta_{mix} G < 0$$

$$\Delta_{mix} H > 0$$

$$\Delta_{mix} S > 0$$

$$\Delta_{mix} U > 0$$

- lq,

acetone + ethanol	CCl ₄ + CH ₃ OH
water + ethanol	water + methanol
acetone + benzene	CCl ₄ + CHCl ₃
acetone + CS ₂	cyclohexane + ethanol
CCl ₄ + toluene	

b) Solⁿ showing large -ve deviation :

- Thermo. →

$$\Delta_{\text{mix}} G < 0$$

$$\Delta_{\text{mix}} S > 0$$

$$\Delta_{\text{mix}} V < 0$$

$$\Delta_{\text{mix}} H < 0$$

- $P_S = P_A + P_B$
 $P_A < P_A^0 \chi_A$
 $P_B < P_B^0 \chi_B$

- lq,

acetone + aniline	CH ₃ OH + CH ₃ COOH
chloroform + diethyl ether	acetic acid + pyridine
chloroform + benzene	H ₂ O + HNO ₃
water + HCl	acetone + chloroform

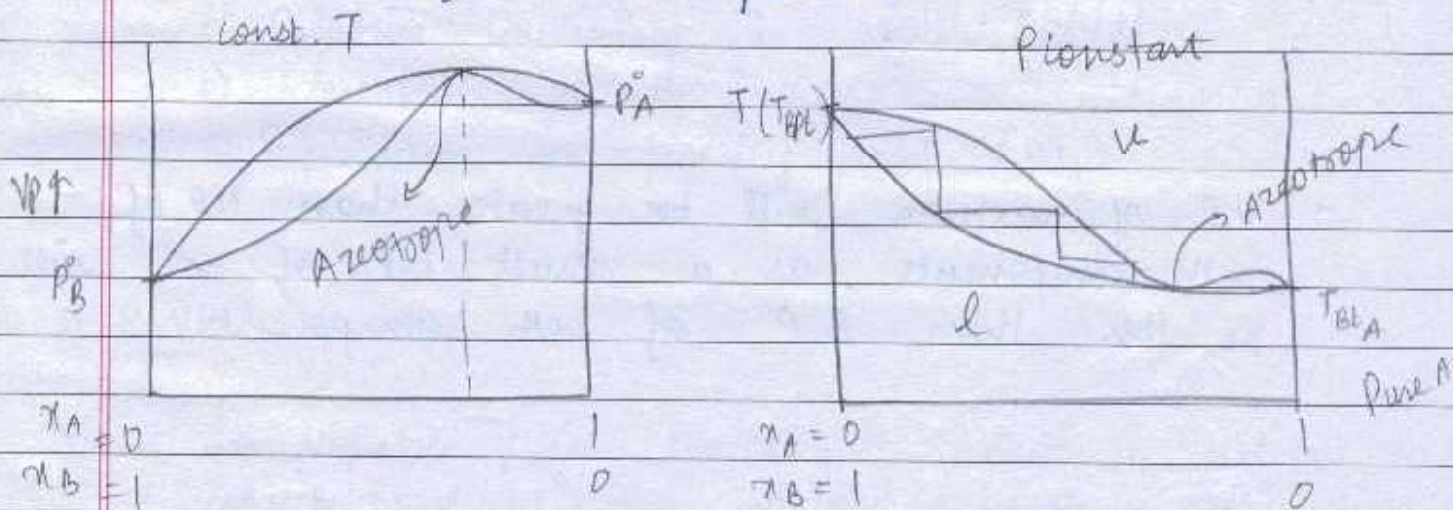
- All mineral acids show -ve deviation

* Azeotrope :

It is a solⁿ which boils like a pure liquid & it will have same composition in vapour state as well as in liquid state.

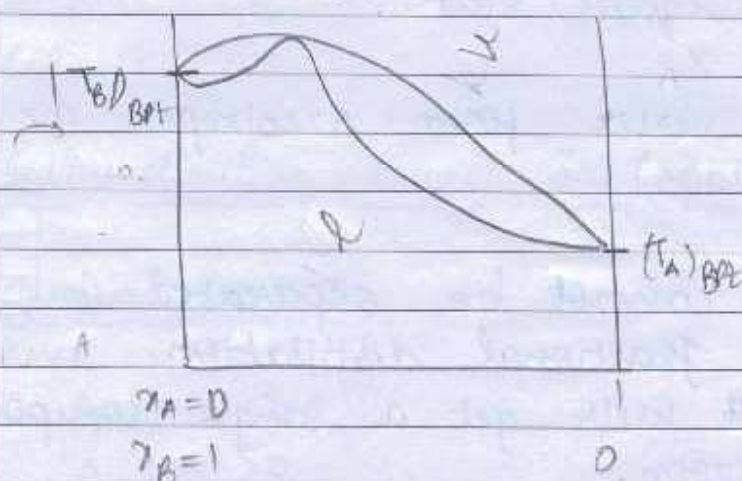
* Ideal solⁿ can never form Azeotrope coz $y_A = x_A$
 $y_A > x_A$ (always)

- azeotropic min. cannot be separated in Pure A & Pure B using fractional distillation.
- Using F.D. ~~will~~ will get a single component (A or B) & Azeotrope.
- Azeotropic composition can be changed by changing ext. pressure
- Types of Azeotrope :
 - i) min. boiling azeotrope
 - ii) max. boiling azeotrope
- min. b.a. are obt. from a solⁿ showing +ve deviation
- These azeotropic mixtures will have lower BPs than both of its components.



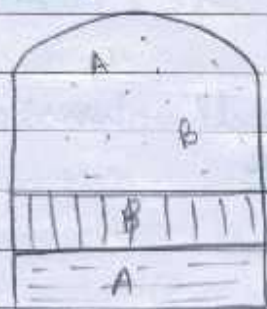
ii) Max. boiling azeotrope :

- Max. b.p. are obt. from a solⁿ showing +ve deviation.



* Raoult's law for solⁿ containing two immiscible liquids :

- When two immiscible liquids are mixed then V.P is given by,



$$\begin{aligned}
 P_s &= P_A + P_B \\
 &= P_A^0 x_A + P_B^0 x_B \\
 &= P_A^0 + P_B^0
 \end{aligned}$$

- V.P. of mixture will be greater than V.P. of both components, as a result B.P. of solⁿ will be less than B.P. of both components

- This solⁿ will boil only when v.p. of solⁿ (P_s) becomes equal to external pressure.
v.p. of mixture (P_s) will remain constant irrespective of proportion in which A & B are mixed.

$$P_A^{\circ} = n_A^v \frac{RT}{V}$$

$$P_B^{\circ} = n_B^v \frac{RT}{V}$$

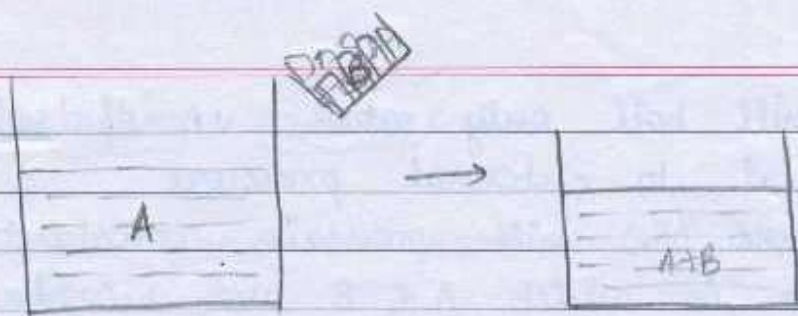
$$\frac{P_A^{\circ}}{P_B^{\circ}} = \frac{n_A^v}{n_B^v} = \frac{w_A}{w_B} \times \frac{M_B}{M_A}$$

* Colligative (to collect) Properties :->

- These are the prop which depend on no. of solute particles present in the solⁿ. These do not depend upon nature of particle.
- However, colligative prop. may change on changing solvent.
- Colligative prop. are defined only for non-volatile solute particles and these are additive in nature.
- There are 4 colligative prop:
 - a) Relative lowering in VP (RLVP)
 - b) Elevation of BP (ΔT_B)
 - c) Depression in freezing point (ΔT_f)
 - d) Osmotic pressure (π)

1] RLVP :

- If non volatile / non electrolyte solute is added to a volatile solvent then VP of resulting solⁿ will ↓ coz some of the SA will be occupied by solute.



$$P_A^0 = 100 \text{ torr}$$

$$P_s = 95 \text{ torr}$$

$$P_s = P_A^0 x_A + P_B^0 x_B^0$$

$$\begin{aligned} \text{Lowering in VP} &= P_A^0 - P_s = P_A^0 x_B \\ \text{Relative lowering in VP} &= \frac{P_A^0 - P_s}{P_A^0} = x_B \end{aligned}$$

if solⁿ is highly dilute,

$$\frac{P_A^0 - P_s}{P_A^0} = \frac{n_B}{n_A + n_B} \approx \frac{n_B}{n_A} = \frac{n_B}{w_A} \times 10^3 \times \frac{M_A}{10^3} \rightarrow \text{approx}$$

$$\Rightarrow \boxed{\frac{P_A^0 - P_s}{P_A^0} \approx \frac{n_B}{n_A} \approx \frac{m M_A}{10^3}}$$

$$\begin{aligned} P_s &= P_A^0 x_A \\ \frac{1}{x_A} &= \frac{n_A + n_B}{n_A} = \frac{P_A^0}{P_s} \end{aligned}$$

$$\boxed{\frac{P_A^0 - P_s}{P_s} = \frac{n_B}{n_A} = \frac{m M_A}{10^3}} \rightarrow \text{Exact}$$

↓
NOT RLVP

- If more than one non volatile solutes are present,

$$P_s = P_A^0 x_A + P_B^0 x_B + P_C^0 x_C + \dots$$

$x_1, x_2, x_3 \rightarrow$ mole fraction of solute 1, 2 & 3
 $M_A \rightarrow$ Molar mass of solvent
 $m \rightarrow$ molality

→ Till now we have considered non volatile, non electrolyte solutes.

In case of electrolytes due to association/dissociation colligative properties of solution will be different from expected values, such CP are called abnormal or experimental colligative prop. To account for association or dissociation Vant Hoff factor (i) is defined.

• Vant Hoff factor (i) \rightarrow It is mathematically defined as

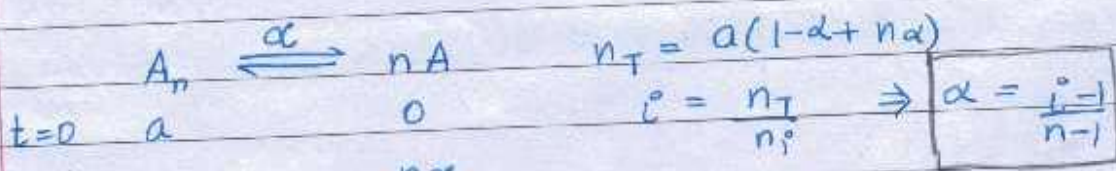
$$i = \frac{\text{Final moles after ass/diss.}}{\text{Initial moles}} = \frac{\text{Theo. Molar mass}}{\text{observed molar mass}}$$

$$= \frac{\text{Obs. CP}}{\text{Th. CP}} = \frac{\Delta T_f}{T \cdot \Delta T_f} = \frac{\Delta T_f}{T \cdot \frac{\Delta T_f}{K}} = \frac{\Delta T_f \cdot K}{T \cdot \Delta T_f}$$

only for highly dilute solⁿ

• Calculation of Vant Hoff factor:

a) For dissociation,



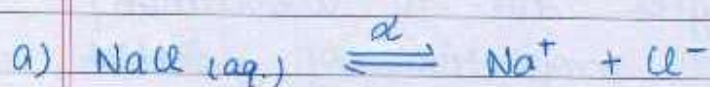


$$t=0 \quad a$$

$$t=t \quad a-2\alpha \quad \frac{3\alpha}{2} \quad n_T = a \left(1 - \alpha + \frac{3\alpha}{2}\right)$$

Q. Calculate 'i' for:

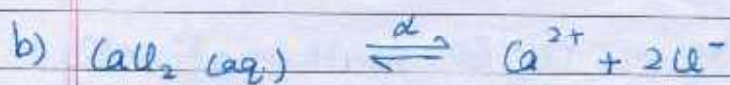
if $\alpha=1$



$$t=0 \quad a$$

$$a - \alpha \alpha \quad \alpha \alpha \quad \alpha \alpha$$

$$\therefore i = \frac{\alpha(1+\alpha)}{\alpha} \quad 2$$



$$t=0 \quad a$$

$$a - \alpha \alpha \quad \alpha \alpha \quad 2\alpha \alpha$$

$$\therefore i = 1 + 2\alpha \quad 3$$



$$i = 1 + 3\alpha \quad 4$$

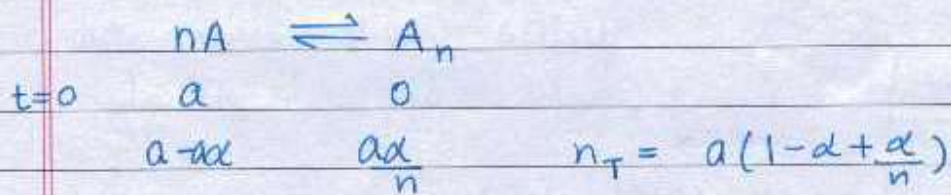


$$t=0 \quad a$$

$$i = 1 + 4\alpha \quad 5$$

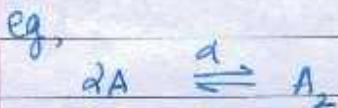
Note: Generally if an electrolyte is given and nothing is mentioned, then take $\alpha = 1$.
For association, α is given.

b) For Association:



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

$i < 1$ for association



$$i = 1 - \alpha + \frac{\alpha}{2}$$

g. Find VP of solⁿ obtained by dissolving 30g of glucose in 360g of water at 25°C. Given VP of pure water at 25°C is 21 torr.

a) Also find RLVP.

$$\rightarrow \frac{P_A - P_s}{P_s} = \frac{n_B}{n_A} \Rightarrow \frac{21 - P_s}{P_s} = \frac{1/6}{20} = \frac{1}{120}$$

$$RLVP = P_s$$

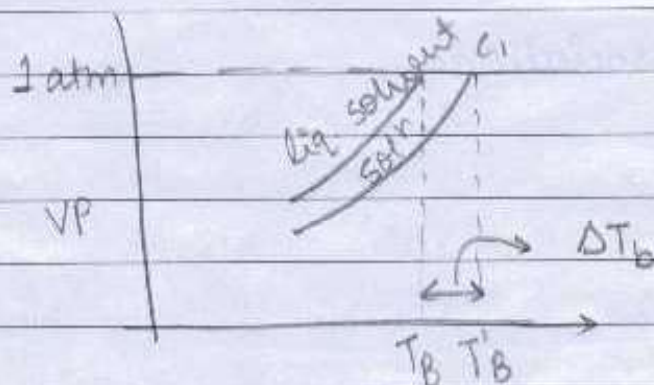
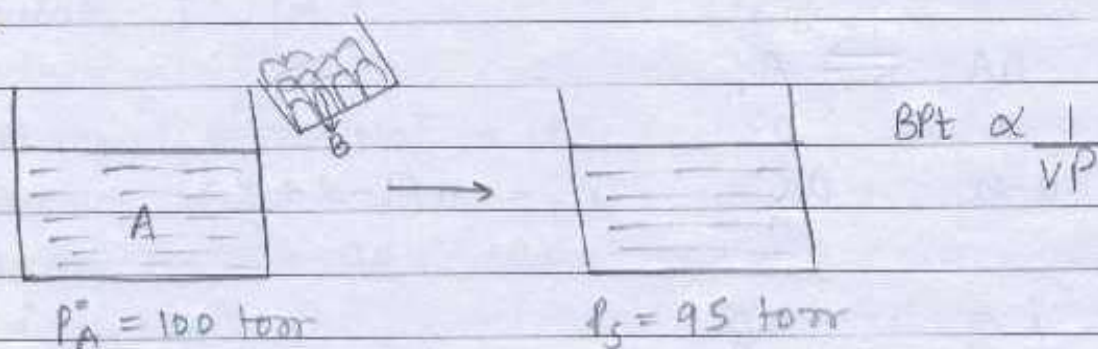
2,

$$\frac{21 - P_s}{P_s} = \frac{1}{200} \in RLVP = \frac{0.1}{20.1} \quad \text{② Find } P_s \text{ \& RLVP if } \alpha = 2$$

$$P_s = 1.4 P_s$$

2) Elevation in Boiling Point \Rightarrow

When we non volatile solute to a volatile solvent, VP will \downarrow as a result BP will \uparrow and this increase in BP is called elevation in BP.



$\Delta T_b = T'_b - T_b =$ elevation in boiling point
for non volatile non electrolyte solutes

$$\Delta T_b \propto m$$

$$\Delta T_b = K_b m$$

where,

$m \rightarrow$ molality

$K_b \rightarrow$ Ebullioscopic constant

K_b is characteristic constant of solvent and its value is independent of temperature.

For more than one solute,

$$\Delta T_b = \Delta T_{b_1} + \Delta T_{b_2} + \dots$$

$$\Delta T_b = K_b m_1 + K_b m_2 + \dots$$

$$= K_b (m_1 + m_2 + \dots)$$

If solute is an electrolyte

$$\Delta T_b = i K_b m$$

For more than solute

$$\Delta T_b = K_b (i_1 m_1 + i_2 m_2 + \dots)$$

$$K_b = \frac{RT_b^2}{1000 L_v} = \frac{RT_b^2 \times M(\text{g/mol})}{1000 \times \Delta_{\text{vap}} H}$$

$L_v \rightarrow$ latent heat of vap. (energy/g)

$\Delta_{\text{vap}} H \rightarrow$ enthalpy of vap. (energy/mol)

$T_b =$ Boiling point of solvent (in K)

$M \rightarrow$ Molar mass of solvent (in g/mol)

Q. Calculate K_b for water ($L_v = 540 \text{ cal/g}$)

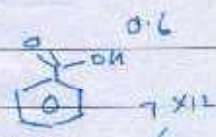
$$\rightarrow K_b = \frac{2 \times (373)^2}{1000 \times 540} = 0.5 \text{ K kg mol}^{-1}$$

Q. A solⁿ of 122g of benzoic acid in 1000g benzene shows a bpt elevation of 1.4°C assuming that solute dimerises to extent of 80%. Calculate BPT of benzene ($\Delta_{\text{vap}} H_B = 7.8 \text{ kcal/mol}$)

$$\rightarrow 1 \text{ mol.} \quad ; \quad \text{b} \quad \text{273K} \quad \text{1.4} = \frac{2 \times \frac{78}{122} \times T^2}{1000 \times 7800} \times \frac{73.2}{1000}$$

$$\frac{1}{3} = \frac{2 \times T^2 \times 78}{1000 \times \frac{7800}{100}}$$

$$\frac{700 \times 1000}{6} = T^2$$



Q. 1L of aq. solⁿ of urea having density 1.06 g/ml is found to have $\Delta T_b = 0.5^\circ\text{C}$. If temp. of this solⁿ increases to 101.5°C , then calculate amt. of water which must have gone in vapor state upto this point. ($K_b(\text{H}_2\text{O}) = 0.5 \text{ K kg mol}^{-1}$)

$$\rightarrow 0.5 = 0.5 \times m \Rightarrow m = 1 \quad \frac{1060}{1000} \left[\frac{1000}{3} \right] 101$$

60 gm urea 1000 gm

$3 = m$

Note :

A pure solvent gets evaporated completely at its boiling pt. while if we take a solⁿ containing non volatile solute & a volatile solvent then on \uparrow temp. its Bpt will \uparrow coz solvent particles will evaporate as a result, molality will increase.

• Determination of K_b :

$$\ln \frac{VP_2}{VP_1} = \frac{\Delta_{\text{vap}} H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Assume $\Delta_{\text{vap}} H_{\text{sol}^n} = \Delta_{\text{vap}} H_{\text{solvent}}$

$$\Rightarrow \ln \frac{P_A}{P_s} = \frac{\Delta_{\text{vap}} H}{R} \left(\frac{1}{T_b} - \frac{1}{T_b'} \right)$$

$$\Rightarrow - \ln \frac{P_s}{P_A} = \frac{\Delta_{\text{vap}} H}{R} \left(\frac{\Delta T_b}{T_b^2} \right) \quad \{ T_b' \approx T_b \}$$

$$\Rightarrow - \ln(1 - x_B) = \frac{\Delta_{\text{vap}} H}{R} \times \frac{\Delta T_b}{T_b^2}$$

$$\Rightarrow \frac{m \times M_A}{1000} = x_B \approx \frac{\Delta H}{R} \times \frac{\Delta T_b}{T_b^2}$$

$$\therefore \Delta T_b = \frac{RT_b^2 M_A}{1000 \times \Delta_{\text{vap}} H} \times m$$

$$\Delta T_b = K_b \times m$$

3] Depression in Freezing point :
(ΔT_f)

Freezing Pt : Temp. at which VP of substance in liquid phase becomes equal to VP in solid phase.

A solⁿ will freeze when its VP becomes equal to vapour pressure of pure solid solvent.

$$\Delta T_f = T_f - T_f' = \text{Depression in F.Pt.}$$

For non volatile, non electrolyte solute,

$$\Delta T_f \propto m$$

$$\Delta T_f = K_f m$$

where,

$m \rightarrow$ molality

$K_f \rightarrow$ cryoscopic constant

K_f is characteristic constant of solvent & its value is independent of temp.

unit of $K_f \rightarrow K \text{ kg mol}^{-1}$

For more than one solute,

$$\Delta T_f = K_f (m_1 + m_2 + \dots)$$

If solute is an electrolyte,

$$\Delta T_f = i K_f m$$

For more than one solute

$$\Delta T_f = K_f (i_1 m_1 + i_2 m_2 + \dots)$$

$$K_f = \frac{RT_f^2}{1000 L_f} = \frac{RT_f^2 \times M_A}{1000 \times \Delta_{\text{fus}} H}$$

$L_f \rightarrow$ latent heat of fusion (energy/g)

$\Delta_{\text{fus}} H \rightarrow$ ~~latent~~ ^{enthalpy} heat of fusion (energy/mol)

$T_f \rightarrow$ Freezing Pt. of solvent

$M_A \rightarrow$ Molar mass of solvent

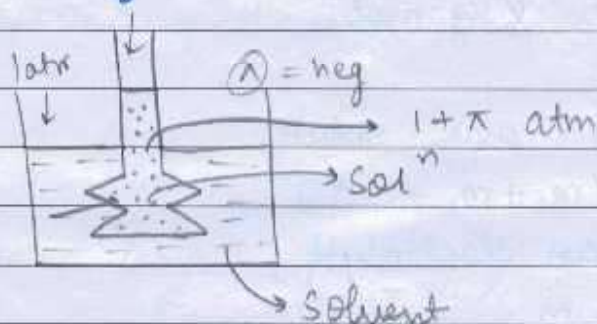
- Q. Calculate the amount of sucrose in moles that must be dissolved in 500g of water so that diff in Ppt & Bpt becomes 10°C .
 $K_b = 0.52$, $K_f = 1.86$

(11) $M_{22} O_{12}$

$$\begin{aligned} \rightarrow x &= 0.52 \times 2n & ; & \quad y = 1.86 \times 2n \\ 10 &= 2.38 \times 2n & \Rightarrow & \quad n = \frac{10}{2.38} = \frac{200}{238} \end{aligned}$$

4] Osmotic Pressure :

- Osmosis \Rightarrow It is a phenomena of movement of solvent particles from low conc. solⁿ (w.r.t solute) to high conc. solⁿ



- Osmotic pressure (π): It is the pressure corresp. to height 'h'.

$$\pi = h \rho g$$

h \rightarrow height of column of liq. solⁿ

ρ \rightarrow density of solⁿ

g \rightarrow accⁿ due to gravity.

It is the pressure that should be applied ~~to~~ on higher conc. solⁿ in order to just prevent osmosis.

If,

Applied pressure $>$ Osmotic pressure

then,

Reverse osmosis: If pressure app. is greater than osmotic P then solvent particles will start moving from higher conc. solⁿ (w.r.t. solute) to lower conc. solⁿ.

eg,

Desalination of sea water.

- Van't Hoff law:

For non volatile, non electrolyte solute,

$$\pi \propto C$$

$$\pi = CRT$$

where,

π \rightarrow osmotic pressure

C \rightarrow molarity

R \rightarrow gas constant

T \rightarrow Temp. (in K)

If solute is electrolyte,

$$\pi = iCRT$$

$i \rightarrow$ vant Hoff factor

For more than one solute,

$$\pi = RT (i_1 C_1 + i_2 C_2 + \dots)$$

This colligative property is independent of nature of solvent.

• Isotonic Solution :

2 solⁿ are said to be isotonic if they have same osmotic pressure at same temp.

$$\begin{aligned} \pi_A &= \pi_B \\ i_A C_A &= i_B C_B \end{aligned}$$

• Hypertonic & Hypotonic Solution :

A solⁿ 'A' is said to be hypertonic w.r.t 'B' if,

$$\pi_A > \pi_B \text{ (at same temp.)}$$

Here 'B' is said to be hypotonic w.r.t 'A'

Q. Which of the following solution is isotonic, hypertonic or hypotonic w.r.t. 0.1M $AlCl_3$

- | | | | |
|----|------|------------------|-----------|
| A) | 0.1M | $K_4 [Fe(CN)_6]$ | hyper |
| B) | 0.1M | $NaCl$ | hypo |
| C) | 0.2M | KCl | Iso |
| d) | 0.4M | Urea | hypotonic |
| e) | 0.1M | $FeCl_3$ | Iso |

Q. Calculate π of 0.1M urea solution at 300K (in atm)

$$\rightarrow \pi_{\text{urea}} = 0.1 \times 0.0821 \times 300 = 2.463 \text{ atm}$$

Q. 200 ml of 0.2M urea is mixed with 300 ml of 0.3M glucose at 300K. Find π .

$$\rightarrow \pi = \frac{40}{500} \times RT + \frac{90}{500} RT = \frac{13}{50} RT$$

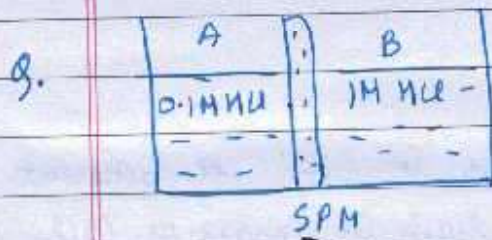
Q. A solⁿ having 0.1M NaCl, 0.2M Na₂SO₄ & 0.5M KA ($\alpha=0.2$). Find π at 300K.

$$\rightarrow \pi = RT(0.1 \times 1/1 \times 2 + 0.2 \times 1/1 \times 3 + 0.5 \times 1.2)$$

Q. If 200 ml of 0.2M BaCl₂ solⁿ is mixed with 500 ml of 0.1M Na₂SO₄ solⁿ. Calculate π of resulting solⁿ at 300K.

$$\rightarrow \begin{matrix} 2Cl^-, 2Na^+ \\ 10mm & 50mm \end{matrix}$$

$$\pi = RT(9/70)$$



- On which side we have to apply osmotic P to stop osm.
- How much osmotic pressure we have to apply?

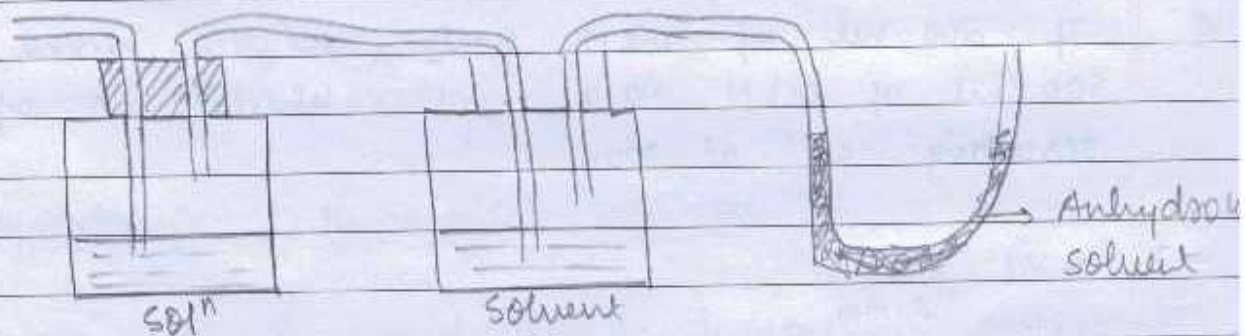
- On B
- $\pi = 0.9 \times 300 R$

* Imperimental determination of colligative Prop. :->

1) Ostwald Walker Dynamic Method :->

It is used to determine relative lowering in VP. In this method, a fixed amount of dry air is passed thru first a solⁿ & then thru a solvent. The loss in wt. of solⁿ & solvent is calculated.

When air is passed thru solⁿ it takes up amt. of vapours which is proportional to VP of solⁿ & when it is passed thru pure solvent it takes up amt. of vapours which is proportional to difference in VP of solution and solvent.



$$w_1 \propto P_s$$

$$w_2 \propto P_A^\circ - P_s$$

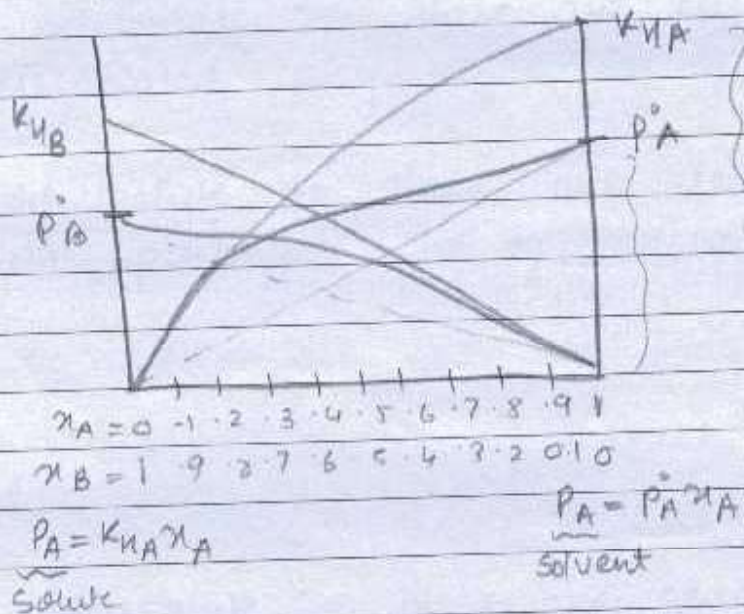
$$w_1 + w_2 \propto P_A^\circ$$

$$RLVP = \frac{P_A^\circ - P_s}{P_A^\circ} = \frac{w_2}{w_1 + w_2} = \frac{\text{loss in wt. of solvent}}{\text{gain in mass of CaCl}_2}$$

• Relationship between Henry's law & Raoult's law :-

A solⁿ cannot be described by Raoult's law over all compositions. Such solutions are called non-ideal solutions.

Henry's law is applicable for solute while Raoult's law is applicable for solvent.



For ideal solⁿ $K_{HA} = P_A^0$

1/8/18

Ionic Equilibrium

* Electrolyte : These are substances which on dissolution in suitable solvent produces ions. Electrolytes are of two types :

i) Strong } on the basis of extent of dissolution
ii) Weak }

A) Strong Electrolyte \Rightarrow These are electrolytes which get dissociated completely. For eg, NaCl , HCl , etc.

B) Weak Electrolyte \Rightarrow These are electrolytes which dissociate partially. For eg, CH_3COOH , NH_4OH , etc.

i) True } on the basis of nature
ii) Potential }

A) True Electrolyte \Rightarrow These are generally ionic compounds which contain ions in their pure state. For eg, NaCl , CaCl_2

B) Potential Electrolytes : These are electrolytes which do not contain ions in their pure state but they can produce ions if dissolved in suitable solvents. For eg, CH_3COOH .

* ACIDS and BASES \Rightarrow

In 1810, Davy proposed that 'H' was essential part of acid.

- Acids are substances which are sour in taste and can turn blue litmus into red.

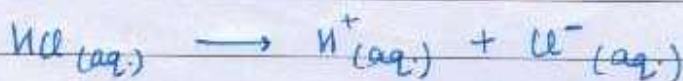
Acid: latin word (Acidus) → sour in taste

- Bases are bitter in taste and can turn red litmus into blue.
- Water soluble bases are called alkali.
Alkali: al-kali (arabic word) → Ashes of plants

A) Arrhenius Theory (1880-90):

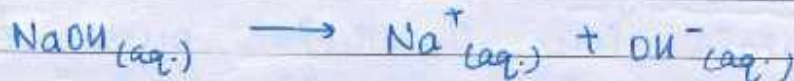
- * Acids: These are the substances which can lose H^+ in water.

eg,



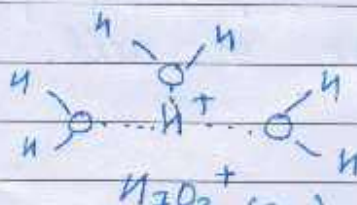
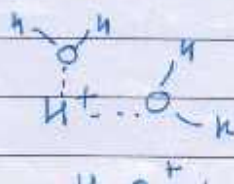
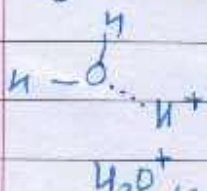
- * Bases: These are the substances which lose OH^- in water.

eg,

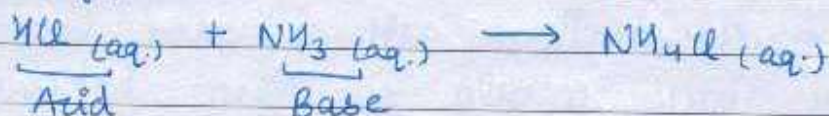


Drawbacks:

- i) Due to very ↑ +ve charge density, H^+ cannot exist isolatedly in water. It can exist only in hydrated form as shown.



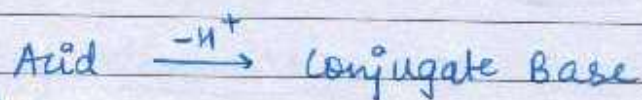
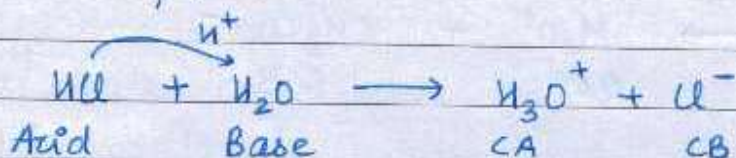
ii) There are certain bases which do not have OH^-
For eg,



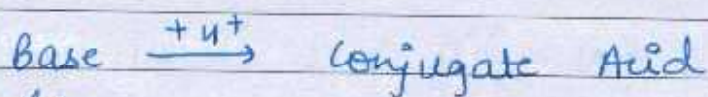
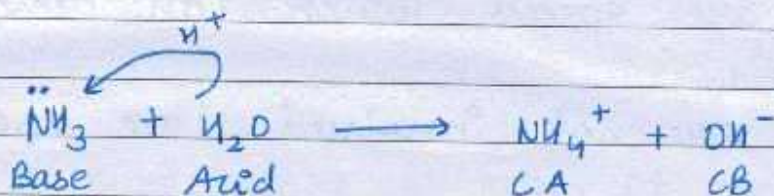
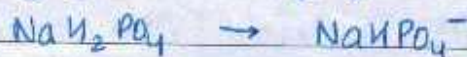
B) Bronsted Lowry Concept (1923):

* Acids: These are the substances which can donate a proton

* Bases: These are substances which can accept a proton.

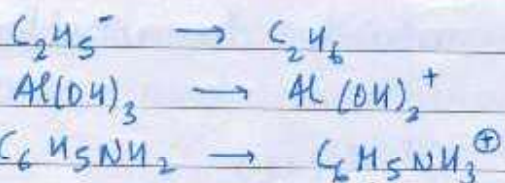


eg,

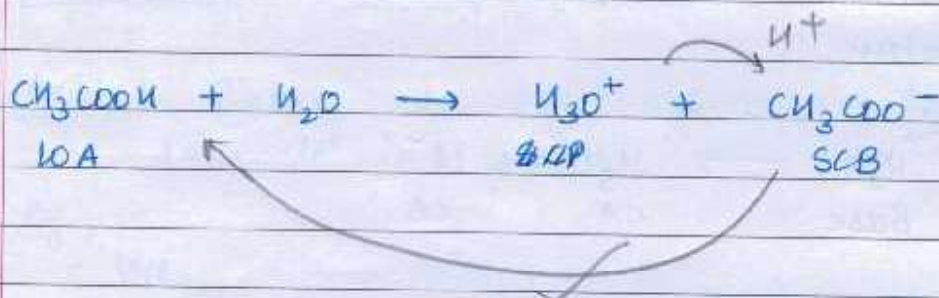
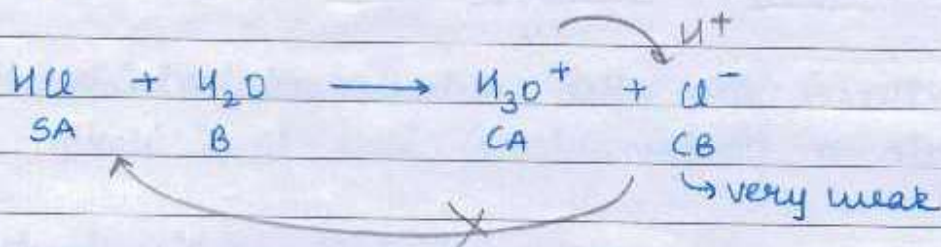


eg,



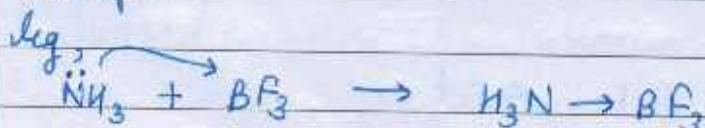


- A strong acid will have weak conjugate base and a weak acid will have strong conjugate base.



c) Lewis Concept (1923) :

- * Acids : These are species which can accept e^- pair.
 - * Bases : These are species which can donate an e^- pair.
- when protons are not involved, we use this concept.



Q. True / False

- 1) Bronsted base is also a Lewis base. **T**
- 2) Bronsted acid is also a Lewis acid. **F**

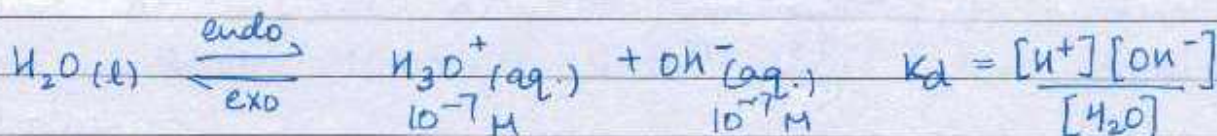
* p^H scale :

p^H → Puissance of hydrogen → Power of hydrogen

$$\begin{aligned}
 p^H &= -\log [H^+] & \leftarrow & p^H = -\log a_{H^+} \\
 p^{OH} &= -\log [OH^-] & & \text{For dilute sol}^n \\
 p^{K_a} &= -\log K_a & & a_{H^+} = [H^+] \\
 p^X &= -\log X
 \end{aligned}$$

- p^H scale can have values -ve or greater than 14.
This scale is useful for dilute solutions only.

* Self dissociation or Auto ionisation of water :



$$K_w = K_d [H_2O] = [H^+][OH^-]$$

↓
dissociation constant [H₂O] = 55.55 M

55 mol → 10⁻⁷ mol
out of 10²⁴ molecules
only 2 molecules of
H₂O are dissociated

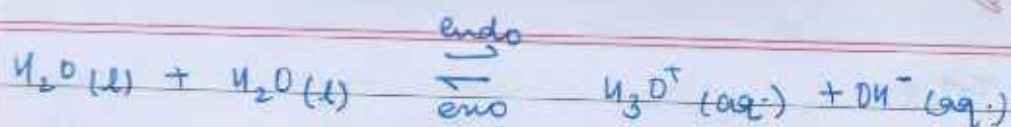
Q. If pure water is taken at 25°C (K_w = 10⁻¹⁴). Then calculate

a) [H₃O⁺], [OH⁻], p^H & p^{OH}

$$\begin{array}{cccc}
 \downarrow & \downarrow & \downarrow & \downarrow \\
 10^{-7} M & 10^{-7} M & 7 & 7
 \end{array}$$

b) If 0.1 mol of HCl is mixed with 1 L of water

- i) [H₃O⁺] [OH⁻] ii) 10⁻⁷ M
- 10⁻¹ M 10⁻⁷ M iii) 1, 7



$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

$$\text{At } 25^\circ\text{C}, K_w = 10^{-14}$$

$$p^{\text{H}} = p^{\text{OH}} = 7 \text{ (neutral)}$$

If

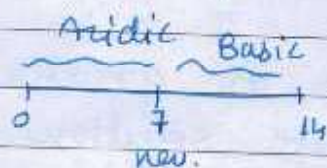
$$[\text{H}_3\text{O}^+] > [\text{OH}^-] \Rightarrow \text{Acidic}$$

$$[\text{H}_3\text{O}^+] < [\text{OH}^-] \Rightarrow \text{Basic}$$

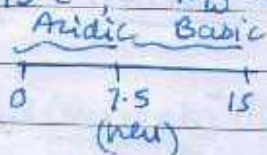
$$[\text{H}_3\text{O}^+] = [\text{OH}^-] \Rightarrow \text{neutral}$$

$$-\log K_w = -\log [\text{H}^+] = -\log [\text{OH}^-]$$

$$p^{K_w} = p^{\text{H}} + p^{\text{OH}} = 14$$

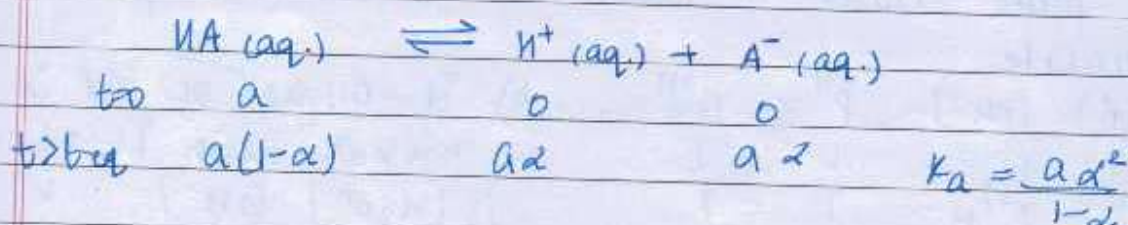


$$\text{At } 15^\circ\text{C}, K_w = 10^{-15}$$



• Arrhenius Theory :

Accⁿ to it, in case of weak electrolytes, there is always a dynamic equilibrium b/w dissociated and undissociated electrolyte.



if $\alpha \ll 1$ $\Rightarrow ka = a\alpha^2 \Rightarrow \alpha = \sqrt{\frac{ka}{c}}$
(0.05)

- if $\frac{ka}{c} \leq 10^{-3} \Rightarrow \alpha \ll 1 \Rightarrow$ we can neglect ' α '

if $\frac{ka}{c} > 10^{-3} \Rightarrow$ we can't neglect ' α '

• Factors affecting degree of dissociation \Rightarrow

- i) Nature of solute & solvent
- ii) Concentration
- iii) Temperature
- iv) Common ion effect

- Conc. :

$$\alpha \propto \frac{1}{\sqrt{c}} \quad (\text{for dilute sol}^n) \\ (\text{weak})$$

• Ostwald dilution law : As dilution \uparrow , $\alpha \uparrow$ and at infinite dilution, $\alpha \approx 1$, it means even a weak electrolyte will behave like strong electrolyte.

- Temp. :

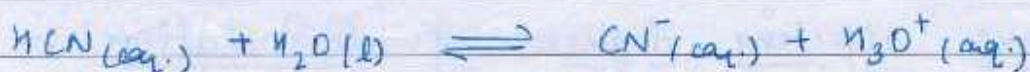
dissociation is an endothermic process. So on \uparrow temp., $\alpha \uparrow$.

- Common ion effect :

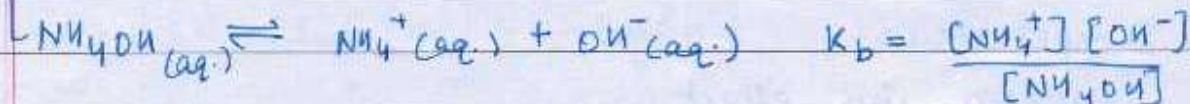
If a mixture of strong & weak electrolyte having at least one common ion is taken then, α of

* Dissociation constants of Acids & Bases:

For acids,

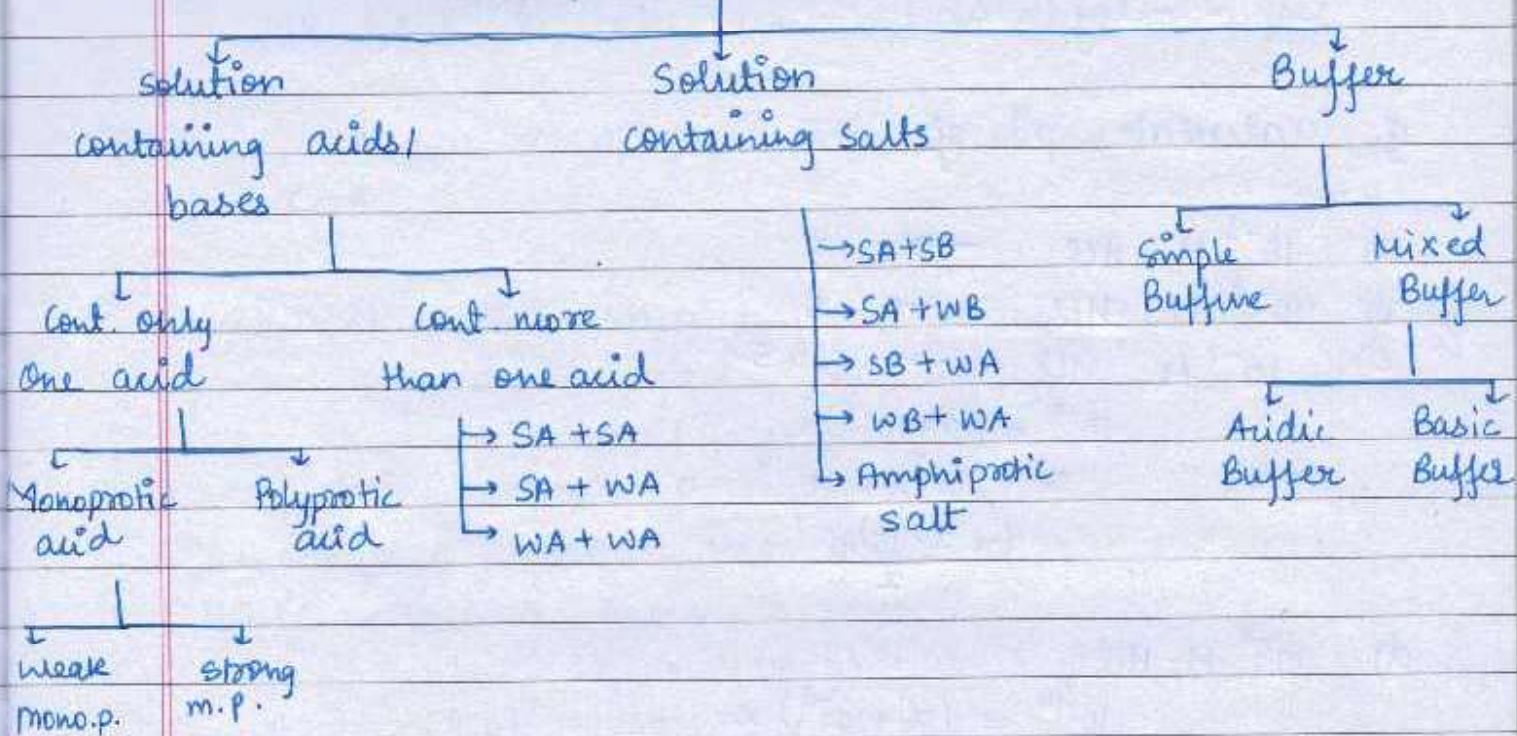


(Same)



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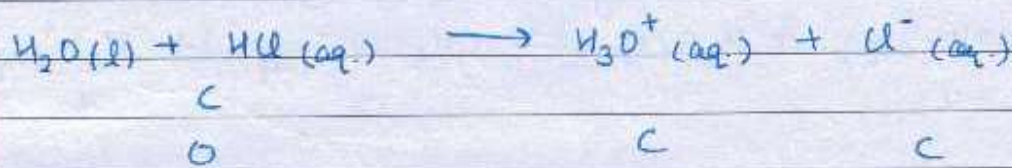
p^H Calculation



* p^H of solution containing strong monoprotic acid :->

Case I : If $C > 10^{-6}$ M

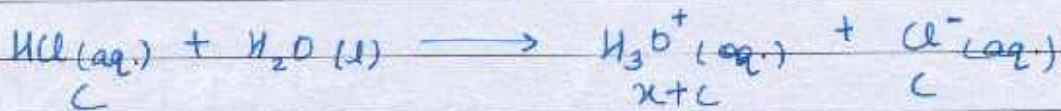
Then we can neglect $[H_3O^+]$ due to water



$$\begin{aligned}
 [H_3O^+] &= C \\
 p^H &= -\log C
 \end{aligned}$$

Case II : If $C \leq 10^{-6}$ M

we have to take conc. due to water



$$[\text{H}_3\text{O}^+] = x + c$$

$$p^{\text{H}} = -\log(x + c)$$

g. Calculate p^{H} of

a) $10^{-3} \text{ M HCl} \rightarrow 3$

b) $10^{-5} \text{ M HCl} \rightarrow 5$

c) $10^{-7} \text{ M HCl}, \rightarrow 6.45$

$$10^{-4} = (x + 10^{-7})x$$

$$x^2 + 10^{-7}x - 10^{-4} = 0$$

$$\frac{(-1 \pm \sqrt{5})10^{-7}}{2}$$

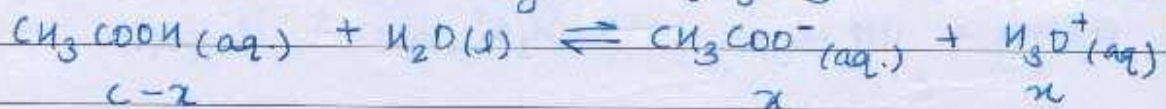
d) 10^{-8} M HCl

$$10^{-4} = (x + 10^{-8})x$$

$$x^2 + 10^{-8}x - 10^{-4} = 0$$

$$\frac{(-10^{-8} \pm 2)10^{-7}}{2}$$

Case III: If $c > 10^{-6} \text{ M}$ & $K_{\text{a}}c > 10^{-12}$
then we can neglect $[\text{H}_3\text{O}^+]$ due to water



If,

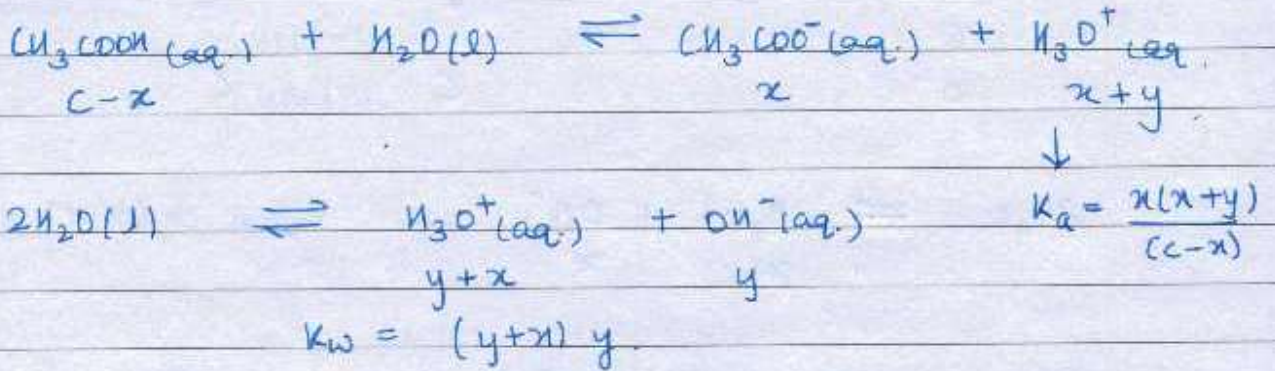
$$\frac{K_{\text{a}}}{c} < 10^{-3} \Rightarrow K_{\text{a}} = \frac{x^2}{c-x} \Rightarrow x = \sqrt{K_{\text{a}}c}$$

$$[\text{H}_3\text{O}^+] = x = \sqrt{K_{\text{a}}c}$$

$$p^{\text{H}} = -\frac{1}{2} \log K_{\text{a}}c = \frac{1}{2} (p^{\text{K}_{\text{a}}} - \log c)$$

Case IV : If $c > 10^{-6} M$ & $K_a c < 10^{-12}$

We have to take contribution due to water



$$[\text{H}_3\text{O}^+] = y+x = \sqrt{K_a c}$$

if $\frac{K_a}{c} < 10^{-3} \Rightarrow K_a c = x(x+y)$

$$K_w = y(x+y)$$

$$[\text{H}_3\text{O}^+] = x+y = \sqrt{K_w + K_a c}$$

$$p^H = -\log [\text{H}_3\text{O}^+] = -\log \sqrt{K_w + K_a c}$$

9. Calculate p^H of

a) 0.1M CH_3COOH

b) $10^{-4} M \text{CH}_3\text{COOH}$ at $25^\circ C$

Given $K_a (\text{CH}_3\text{COOH}) = 10^{-5}$

* $\frac{K_a}{c} < 10^{-3}$

$$\frac{-10^{-5} \pm \sqrt{41 \cdot 10^{-5}}}{2} \rightarrow \frac{10^{-10} + 410}{2}$$

$$x^2 - 10^{-9} + x \cdot 10^{-5}$$

$$5.4 \cdot 10^{-5}$$

$$2.7 \cdot 10^{-5}$$

$$-\log 2.7 + 5$$

a $\rightarrow K_a c = 10^{-6}$

$$p^H = \frac{-1}{2} \log 10^{-6} = 3$$

b $\rightarrow K_a c = 10^{-9}$

$$p^H = \frac{+1}{2} (9) \approx 4.5 \text{ or } 4.5$$

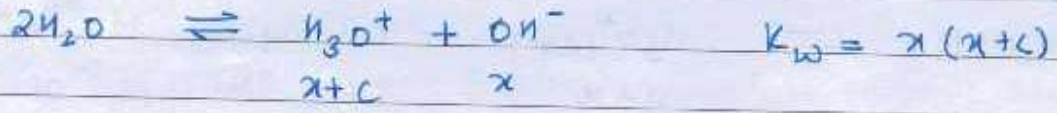
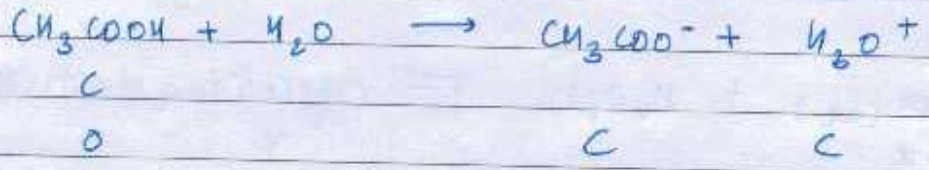
c) $10^{-4} M \text{HCN}$ ($K_a = 10^{-10}$)

$\rightarrow p^H = \frac{-1}{2} \log (10^{-10} + 10^{-14})$

$$= 7 - \frac{1}{2} (10 + 0.3)$$

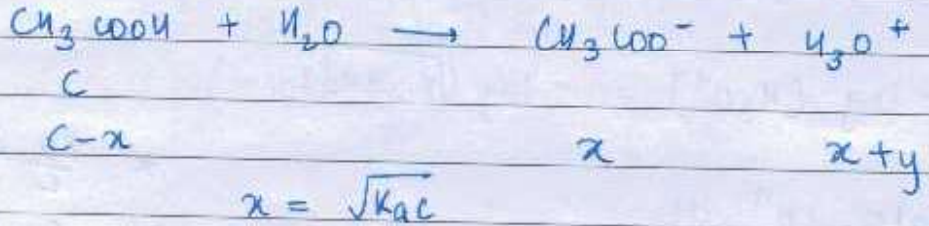
$$= \boxed{6.85}$$

Case V : If $C < 10^{-6}$ & $K_a > C \Rightarrow \alpha = 1$



here, weak acid will behave like strong acid.

Case VI : If $C < 10^{-6}$ & $K_a < C$ ($\alpha < 1$)



$$\left. \begin{array}{l} K_w = (x+y)y \\ K_a = \frac{x(x+y)}{C-x} \end{array} \right\} \text{add.}$$

Q. Calculate p^H of 10^{-8} M CH_3COOH ($K_a = 10^{-5}$)

$$\begin{aligned} \rightarrow p^H &= 10^{-14} = \frac{x(x+10^{-8})}{10^{-8} + 4 \times 10^{-14}} = 2 \times 10^{-7} \\ &= \frac{-10^{-8} + 2 \times 10^{-7}}{2} = 0.95 \times 10^{-7} \end{aligned}$$

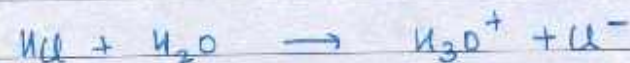
$$\begin{aligned} p^H &= -\log 10.5 \times 10^{-8} + 8 \\ &= 6.98 \end{aligned}$$

* p^H of a solution containing more than one acids:

Case I : SA + SA

$$[HCl] = C_1$$

$$[HBr] = C_2$$



C_1

0

$C_1 + C_1$ C_1



C_2

0

$C_2 + C_1$ C_2

$$[H_3O^+] = C_1 + C_2$$

$$\therefore p^H = -\log(C_1 + C_2)$$

Case II : SA + WA

$$[HCl] = C_1$$

$$[CH_3COOH] = C_2, \quad K_a$$



C_1

C_1

C_1



$C_2 - x$

x

$x + C_1$

$$\frac{(C_1 + x)x}{C_2 - x} = K_a$$

$$K_w = (x + y)y$$

Case III : WA + WA

$$[HCN] = C_1, \quad K_{a1}$$

$$[CH_3COOH] = C_2, \quad K_{a2}$$

$$K_{a1} = \frac{x(x+y)}{C_1 - x}$$

$$K_{a2} = \frac{y(x+y)}{C_2 - x}$$

Q. Calculate p^H of a sol. containing 1M CH_3COOH ($K_a = 10^{-5}$) & $10^{-3} M$ HCl

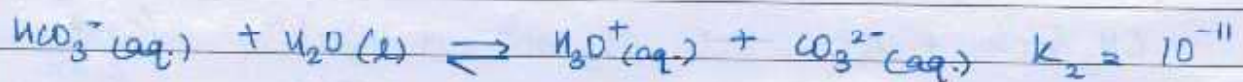
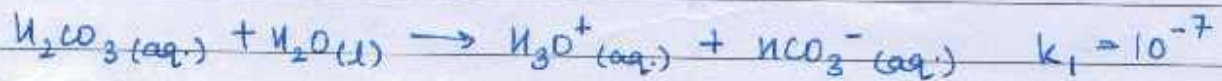
$$\begin{aligned} \rightarrow p^H &= -\log(10^{-3} + x) & x &= \frac{\sqrt{K_a C}}{10^{-3} \times \sqrt{10}} \\ &= -\log(4.2 \times 10^{-3}) \\ &= 3 - \log 4.2 \approx 2.4 \end{aligned}$$

Note: We can solve a problem without considering contribution of water if p^H comes out to be 6 to 8, it means we are wrong. We have to take contribution due to water.

* Polyprotic acids:

These are acids which contain more than one protons. For eg, H_2CO_3 , H_2SO_4 , H_3PO_4 , etc.

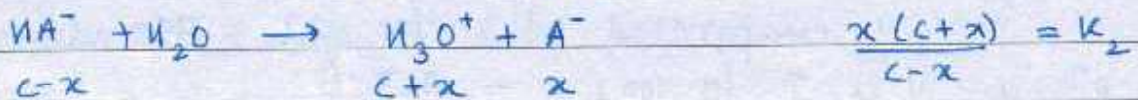
- Successive dissociation constants of polyprotic acids decreases by $10^4 - 10^6$



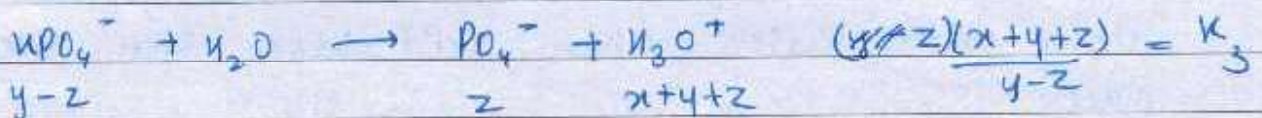
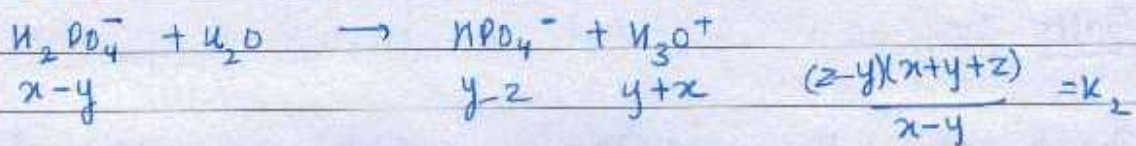
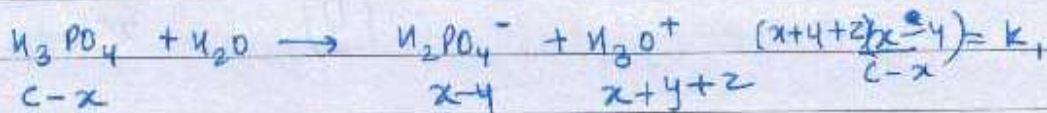
p^H Calculation:

Case I: If K_1 and K_2 are very large
 $[H_2A] = C$

Case II : if k_1 is very large but not k_2
 $[H_2A] = C$



Case III : if $k_1, k_2 \ll k_3$ are all very small
 $[H_3PO_4] = C$



We know,

$$k_1 \gg k_2 \gg k_3$$

$$x \gg y \gg z$$

$$[H_3O^+] = x+y+z \approx x$$

$$k_1 = \frac{x^2}{C-x}$$

$$k_2 = y$$

$$k_3 = \frac{x \times z}{y}$$

$$[H_3PO_4] = C-x$$

$$[H_2PO_4^-] = x-y \approx x$$

$$[HPO_4^{2-}] = y-z \approx y$$

$$[PO_4^{3-}] \approx z$$

H^+ mainly comes from 1st step so if only p^H is asked then we need to write only 1st step.

$$\frac{-\log K_a}{2}$$

$$\frac{2.55 \times 10^{-3}}{10^{-4}}$$

8. 1 mol of weak acid HA is added to water to produce 1L solⁿ [$K_a(\text{HA}) = 10^{-4} \text{ M}$] calculate
- Its pH = 2
 - Vol. of H_2O added to double its p^{H} = 9999 L
 - Vol. of H_2O added to double $[\text{OH}^-]$ = 3L
 - " " " evaporated " $[\text{H}_3\text{O}^+]$ = 999 ml
 - p^{H} if V is \uparrow to 100 L = 3.6
 - " " " " " " 10^7 L = 5.5
 - Change in p^{H} if 2L of 0.01 M NaCl is added

$$10^{-2} + 10^{-2} = 2 \times 10^{-2}$$

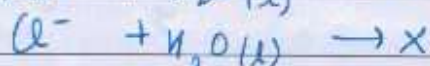
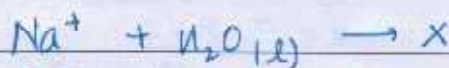
$$= 1.95$$

$$2 - 1.95 = 0.05$$

0

* Salts :->

These are the substances which are formed along with water when acid-base rxn takes place.



Types of salt

- Neutral salt (SA + SB)
- Acidic salt (SA + WOB)
- Basic salt (WA + WB)

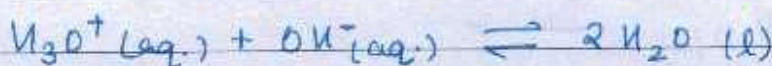
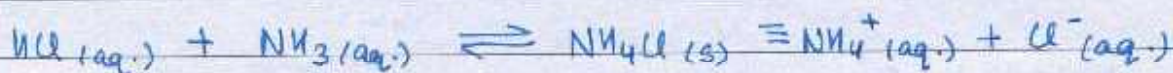
- Neutral salt :

Neutral salts are formed when strong acid reacts with strong base.

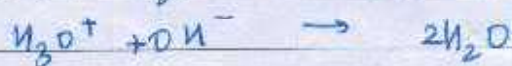
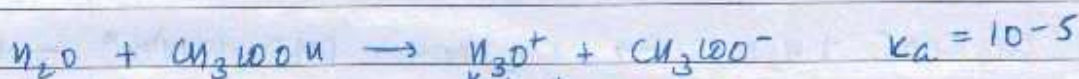
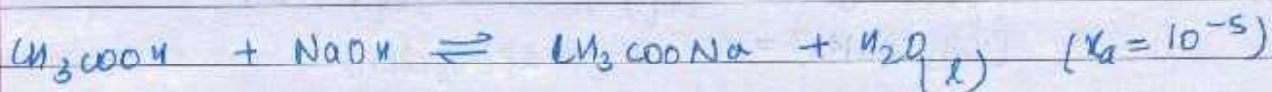
eg, NaCl, KCl, etc.

Here source of H^+ & OH^- is water.

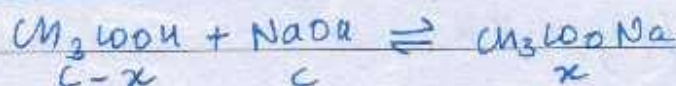
- Acidic salt :



- Basic salt :



$$K = \frac{1}{K_w} = 10^{14}$$



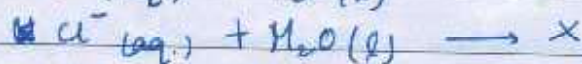
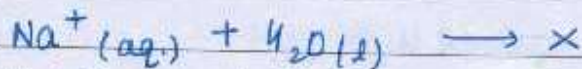
$$\frac{1}{K_{AT}} = K_{AT}$$

- Hydrolysis : This is phenomena of interaction of cation & anion of a solute with water to produce acidic / basic solⁿ. It is reverse of neutralisation so it will be endothermic.

Note : From above two cases it is clear that in acid-base rxn if one of them is strong then rxn will be almost completed.

* p^H calculation of salts :

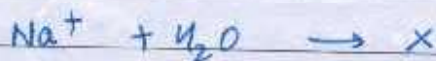
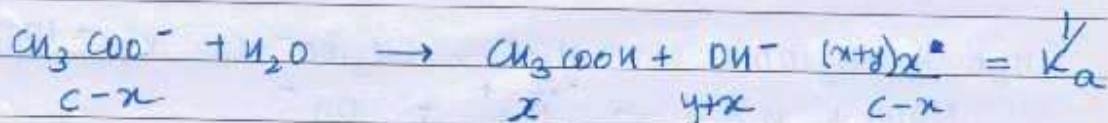
Case I : For neutral salts
eg, NaCl, KCl, etc.



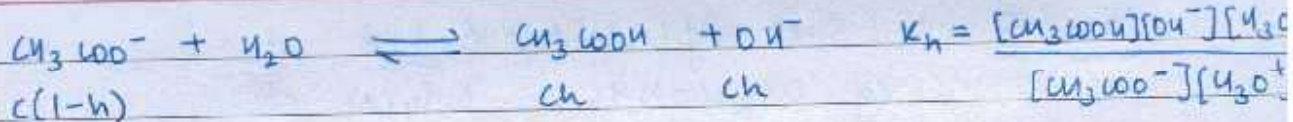
$p^H = 7$ all $[H_3O^+] \in [OH^-]$ will be due to water only.

Case II : For Basic Salt

eg, CH_3COONa (aq.), $NaCN$ (aq.), etc.
 $[CH_3COONa] = c$ $K_a(CH_3COOH)$



$$(x+y)y = K_w$$



$$= \frac{K_w}{K_a} = \frac{ch^2}{1-h}$$

$$\text{if } \frac{K_h}{c} < 10^{-3} \Rightarrow \frac{K_w c}{K_a} = c^2 h^2 = [\text{OH}^-]^2$$

$$-\log [\text{H}_3\text{O}^+] = -\frac{1}{2} (\log K_w + \log K_a - \log c)$$

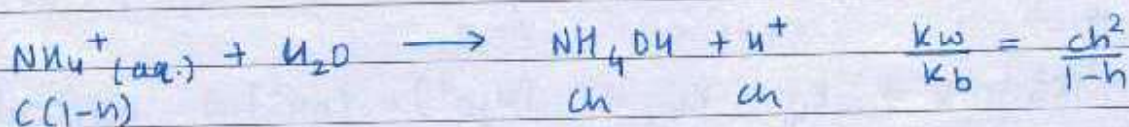
$$p^H = \frac{1}{2} (p^{K_w} + p^{K_a} + \log c)$$

Case III: For acidic salt

eg, $\text{NH}_4^+ \text{Cl}^-$, $\text{RNH}_3^+ \text{Cl}^-$

$$[\text{NH}_4\text{Cl}] = c \quad K_b(\text{NH}_3)$$

$$p^H = \frac{1}{2} (p^{K_w} - p^{K_b} + \log c)$$



$$\text{if } \frac{K_h}{c} < 10^{-3} \Rightarrow c^2 h^2 = \frac{K_w c}{K_b} = [\text{H}_3\text{O}^+]^2$$

$h \rightarrow$ degree of hydrolysis

$K_h \rightarrow$ hydrolysis constant

Q. Calculate h , K_h & p^H of 0.25 M NaCN $h = \frac{1}{50}$
 $K_a(\text{HCN}) = 10^{-10}$

$$\rightarrow p^H = \frac{-1}{2} (-14 - 10 - \log 25 - \log 10^{-2})$$

$$= 11 + \frac{1}{2} \log 5 = 11.6$$

$$K_h = 10^{-4}$$

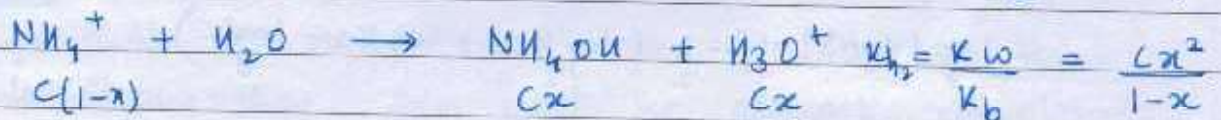
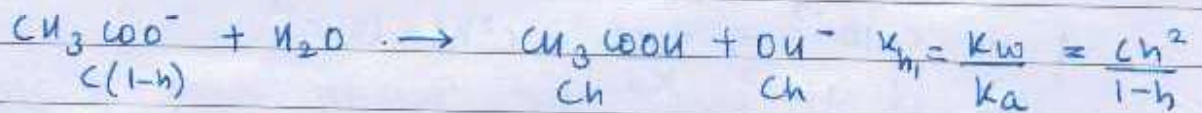
$$\frac{25 \times 10^{-2} \times h^2}{1-h} = 10^{-4}$$

$$\frac{h^2}{1-h} = \frac{1}{2500}$$

$$1 \pm 10^{-2} \quad 2500h^2 + h - 1 = 0$$

Case IV : Salt of WA & WB
 eg $\text{CH}_3\text{COONH}_4$, NH_4CN , etc.

$$[\text{CH}_3\text{COONH}_4] = c \quad K_a, K_b$$

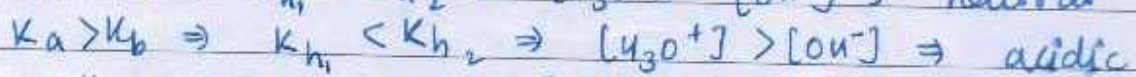
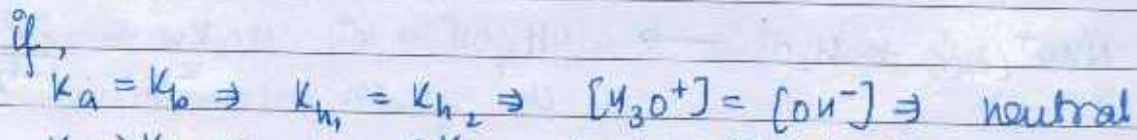


$$K = \frac{K_w}{K_a K_b} = \frac{(c h)^2}{(c(1-h))^2}$$

$$\frac{h}{1-h} = \sqrt{\frac{K_w}{K_a K_b}}$$

- Here, 'h' changes only on changing temp.

if,



We Assume,

$$h_1 = h_2 \Rightarrow [\text{CH}_3\text{COOH}] = [\text{NH}_3] \quad \& \quad [\text{CH}_3\text{COO}^-] = [\text{NH}_4^+]$$

But $[\text{H}_3\text{O}^+] \neq [\text{OH}^-]$

$$\frac{K_b}{K_a} = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} \times \frac{[\text{NH}_4^+]}{[\text{NH}_3][\text{H}_3\text{O}^+]}$$

$$= \frac{K_w}{[\text{H}_3\text{O}^+]^2} \Rightarrow [\text{H}_3\text{O}^+] = \sqrt{\frac{K_w K_a}{K_b}}$$

$$p^H = \frac{1}{2} (p^{K_w} + p^{K_a} - p^{K_b})$$

- For conjugate Acid / Base pair \Rightarrow

$$K_a(\text{HF}) \times K_b(\text{F}^-) = K_w$$

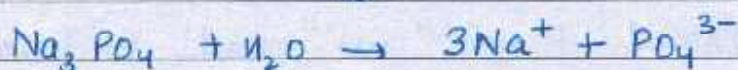
- * p^- of a solution containing polyvalent ions \Rightarrow

eg, Na_3PO_4 (aq.), Na_2CO_3 (aq.), Na_2SO_4 (aq.), etc.

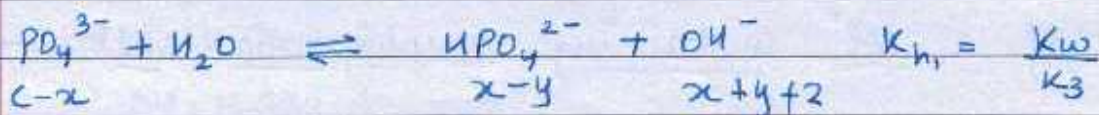
$$[\text{Na}_3\text{PO}_4] = c \quad K_1, K_2, K_3$$



\Downarrow



$$\begin{array}{ccc} c & 0 & 0 \\ 0 & 3c & 3c \end{array}$$

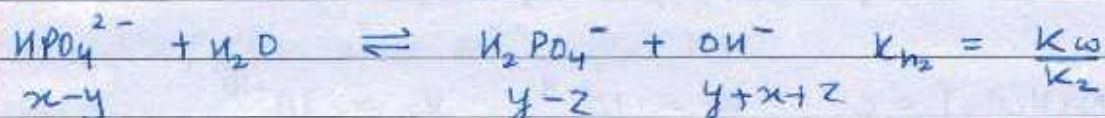


$$c-x$$

$$x-y$$

$$x+y+z$$

$$= \frac{[\text{HPO}_4^{2-}][\text{OH}^-][\text{H}_3\text{O}^+]}{[\text{PO}_4^{3-}][\text{H}_3\text{O}^+]}$$

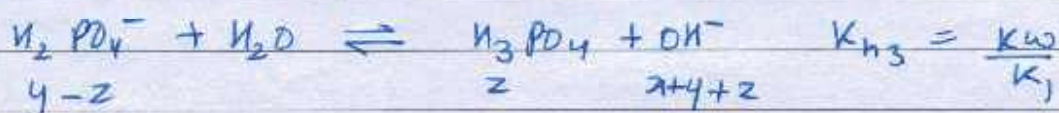


$$x-y$$

$$y-z$$

$$y+x+z$$

$$= \frac{[\text{H}_2\text{PO}_4^-][\text{OH}^-][\text{H}_3\text{O}^+]}{[\text{HPO}_4^{2-}][\text{H}_3\text{O}^+]}$$



$$y-z$$

$$z$$

$$x+y+z$$

We know,

$$K_1 \gg K_2 \gg K_3$$

$$x \gg y \gg z$$

$$K_{h1} = \frac{x^2}{c-x} ; K_{h2} = y ; K_{h3} = \frac{z x}{y}$$

$$[OH^-] = x + y + z \approx x$$

$$[PO_4^{3-}] = c - x$$

$$[HPO_4^{2-}] = x - y \approx x$$

$$[H_2PO_4^-] = y - z \approx y$$

$$[H_3PO_4] = z$$

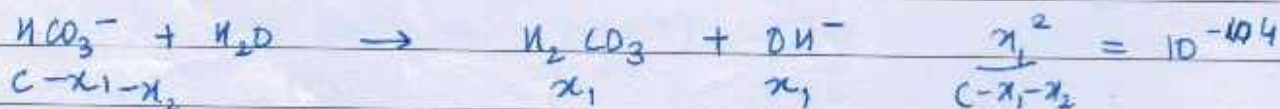
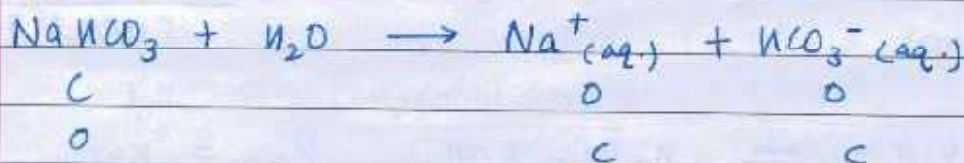
If only p^H is asked then we need to write hydrolysis of only 1st step.

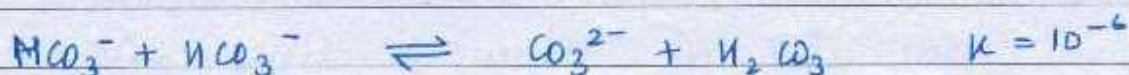
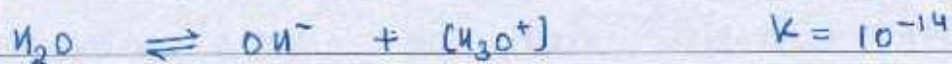
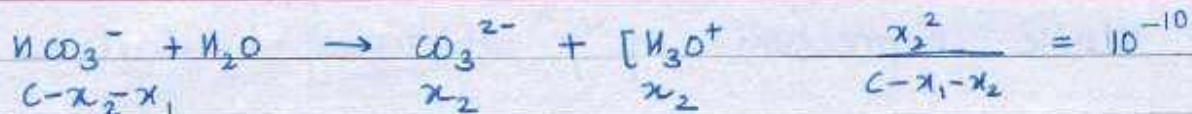
* p^H of a sol containing amphiprotic salt \Rightarrow

- Amphiprotic salts: They can accept as well as lose a proton.

eg, $NaHCO_3$, H_2PO_4 , Na_2HPO_4 , etc.

$$[NaHCO_3] = c \quad K_1 = 10^{-4} \quad K_2 = 10^{-10}$$





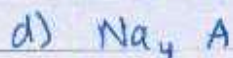
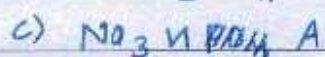
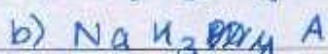
$$[\text{CO}_3^{2-}] \approx [\text{H}_2\text{CO}_3]$$

$$\frac{K_1 K_2}{K_w} = \frac{[\text{CO}_3^{2-}][\text{H}_3\text{O}^+]}{[\text{HCO}_3^-]} \times \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3][\text{OH}^-]}$$

$$K_1 K_2 = [\text{H}_3\text{O}^+]^2$$

$$\therefore p^H = \frac{1}{2} (p^{K_1} + p^{K_2})$$

Q. Write expression of p^H for



[Given : K_1, K_2, K_3, K_4 for H_4A]

$$\rightarrow \text{a) } \frac{1}{2} (p^{K_1} + p^{K_2} + p^{K_3} + p^{K_4})$$

$$\text{b) } \frac{1}{2} (p^{K_1} + p^{K_2})$$

$$\text{c) } \frac{1}{2} (p^{K_3} + p^{K_4})$$

$$\text{d) } \frac{K_w}{K_4} = \frac{x^2}{c-x}$$

Q. Write expression of p^H obtained by

i) 100 ml 0.1 M H_3PO_4 + 100 ml 0.1 M NaOH

ii) 100 ml 0.1 M H_3PO_4 + 200 ml 0.1 M NaOH

iii) 100 ml 0.1 M H_3PO_4 + 300 ml 0.1 M NaOH

iv) 100 ml 0.1 M H_3PO_4 + 400 ml 0.1 M NaOH

→ i) $NaH_2PO_4 \rightarrow \frac{1}{2} (p^{K_2} + p^{K_1})$

ii) $Na_2HPO_4 \rightarrow \frac{1}{2} (p^{K_3} + p^{K_2})$

iii) $Na_3PO_4 \rightarrow \frac{K_w}{K_3} = \frac{x^2}{c-x}$

iv) $12 - \log 2 = 11.7$

$\frac{K_w}{K_3} = \frac{x(x+1/50)}{(10-x)}$

n.w.

R.B. \Rightarrow 14 to 21, 37, 38

Ex. 1 \Rightarrow till 27.

3. DPP

26, 27

28, 29 \Rightarrow

R.B. \Rightarrow 36-41, 43, 44, 45, 46, 47, 48

• Mixed buffer :

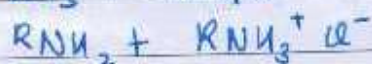
1) Acidic : It is mixture of weak acid and its conjugate base

eg,



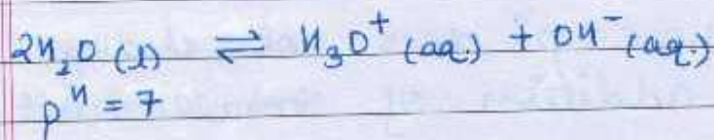
2) Basic : It is mixture of weak base and its conjugate acid

eg,



* Mechanism of Buffer Action :

- Suppose we take 1l of pure water at 25°C



If we add 0.1 mol of HCl to it

$$[\text{HCl}] = 0.1\text{M}$$

$$p^H = 1$$

$$\% \text{ change in } p^H = \frac{7-1}{7} \cong 85\%$$

- If we take a buffer of CH_3COOH & CH_3COONa

$$[\text{CH}_3\text{COOH}] = 1\text{M} \quad K_a = 10^{-5}$$

$$[\text{CH}_3\text{COONa}] = 1\text{M}$$

$$p^H = 5.$$

If we add 0.1 mol HCl to it

$$\frac{(1+x)/(0.1+x)}{(1-x)} = 10^{-5}$$

$$\Rightarrow 0.1 + 1.1x + x^2 = 10^{-5} - 10^{-5}x$$

$$\Rightarrow x^2 + 1.1x + 0.1 = 0$$

$$\frac{-1.1 \pm 0.9}{2}$$

$$p^H = 5 - \log \frac{11}{9} = 4.98$$

$$\% \text{ change in } p^H = \frac{5 - 4.98}{5} \times 100 = 0.4\%$$

In this case when we add HCl (strong acid) it reacts with conjugate base completely to form a weak acid (CH_3COOH) which cannot provide as much H^+ ions as would have been provided by HCl. (0.1M)

If we add 0.1 mol NaOH,



0.1M

1M

x

0.9M

1.1M

$$p^H = 5.02$$

* p^H calculation :-

A) For Acidic Buffer :

$$[\text{CH}_3\text{COOH}] = a \quad K_a$$

$$[\text{CH}_3\text{COONa}] = s$$



$$x \frac{(s+x)}{a-x} = K_a$$

Here we assume,

$$s \gg x$$

$$a \gg x$$

$$p^H = p^{K_a} + \log \frac{s}{a} \rightarrow \text{Henderson eq}^n.$$

B) For Basic Buffer :

$$[\text{NH}_3] = b \quad K_b$$

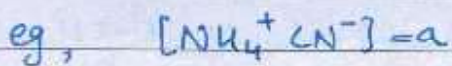
$$[\text{NH}_4^+] = s$$



$$\frac{x(s+x)}{b-x} = K_b \Rightarrow K_b = \frac{sx}{b}$$

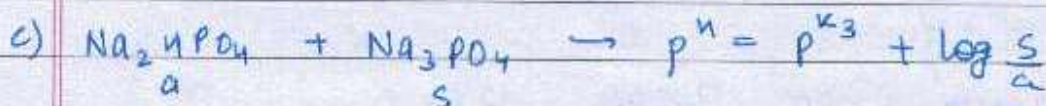
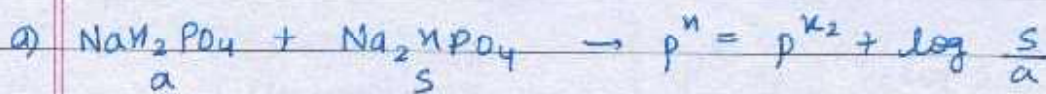
$$p^H = p^{K_w} - p^{K_b} - \log \frac{s}{b}$$

g) For simple Buffer:

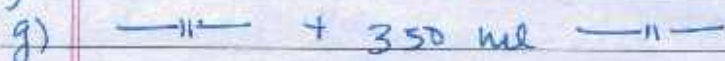
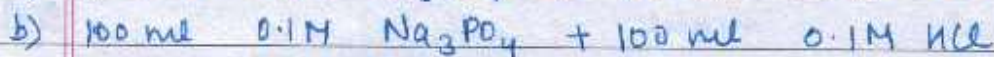
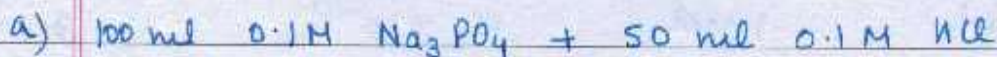


$$p^H = \frac{1}{2} (p^{K_w} + p^{K_a} - p^{K_b})$$

g. Write expression of p^H for



g. Write expression of p^H for a sol. obtained by



a $\rightarrow p^H = p^{K_3} + \log \frac{5}{5}$

b $\rightarrow p^H = \frac{1}{2} (p^{K_3} + p^{K_2})$

c $\rightarrow p^H = p^{K_2} + \log \frac{5}{5}$

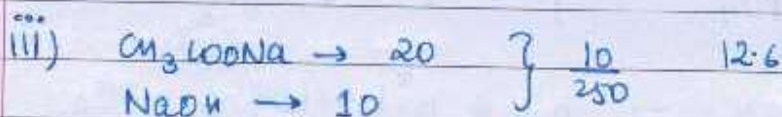
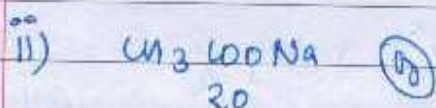
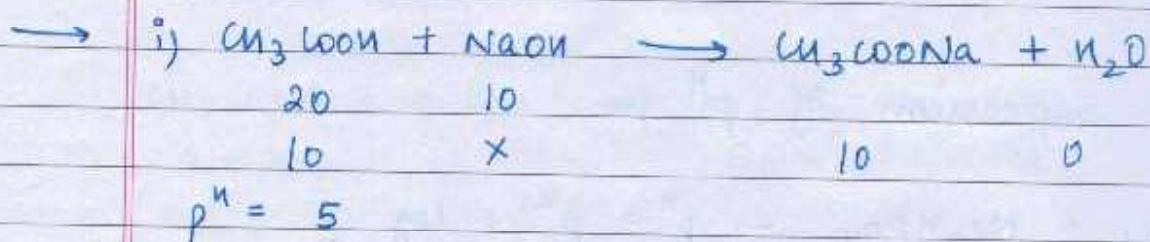
a $\rightarrow p^H = \frac{1}{2} (p^{K_2} + p^{K_1})$

e $\rightarrow p^H = p^{K_1} + 0$

f $\rightarrow p^H = \frac{1}{2} p^{K_1}$

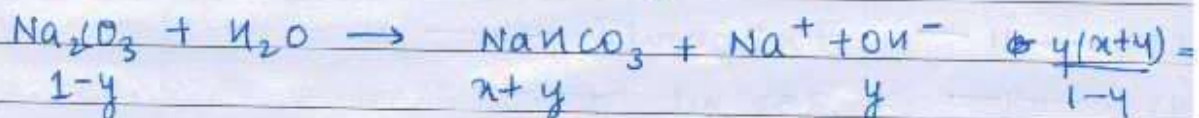
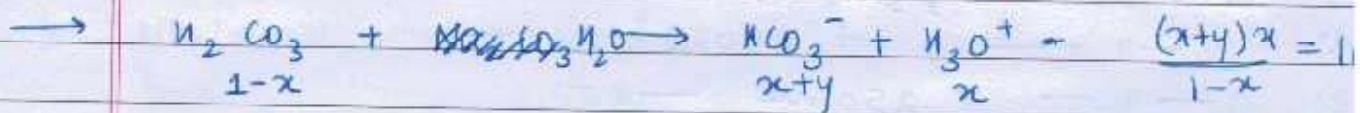
g \rightarrow

- Q. Calculate p^H of a solution obtained by mixing
- 100 ml of 0.2 M CH_3COOH + 50 ml of 0.2 M $NaOH$
 - 100 ml of 0.2 M CH_3COOH + 100 ml of 0.2 M $NaOH$
 - 100 ml of 0.2 M CH_3COOH + 150 ml of 0.2 M $NaOH$
- ($K_a(CH_3COOH) = 10^{-5}$)



- Q. Find p^H of solⁿ obtained by mixing

	H_2CO_3	Na_2CO_3		
a)	1 mol	1 mol	$K_1 = 10^{-6}$	6
b)	2 mol	1 mol	$K_2 = 10^{-10}$	7.6
c)	1 mol	2 mol		9.9



$xy = 10^{-14}$
 $10^{-6} \cdot 10^{-8}$ $\frac{1-x}{1-y} = 10^2$

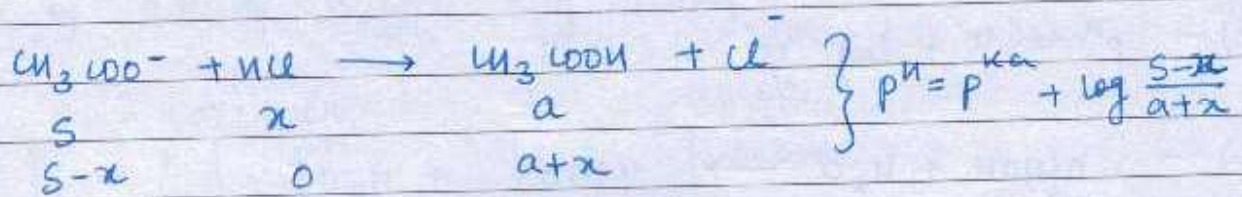
Conclusion : From above ques. it is clear that in an aq. solⁿ only conjugate acid-base pair can exist.

* Change in p^H of buffer :

1] Effect of addⁿ of SA/SB on p^H of buffer :

a) If we add x mol of HCl to 1 L Buffer

$$\left. \begin{array}{l} [CH_3COOH] = a \\ [CH_3COO^-] = s \end{array} \right\} p^H = p^{Ka} + \log \frac{s}{a}$$



b) If we add x mol of NaOH

$$p^H = p^{Ka} + \log \frac{s+x}{a-x}$$

2] Effect of Dilution :

If a buffer is diluted to a small extent then its p^H will not change.

But if it is diluted to a large extent then its p^H will change & we cannot apply formula.

Q. A buffer is prepared by mixing 1 mol of HCOOH with 1 mol of HCOONa in 1L solution. Calculate

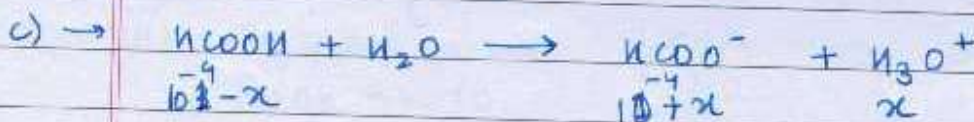
- a) p^H of sol. $K_a = 10^{-4}$
 b) p^H if it is diluted 10 times
 c) p^H if it is diluted 10^4 times
 d) p^H if $\frac{1}{3}$ mol of HCl are added to 1L of sol.
 e) p^H if $\frac{1}{3}$ mol of NaOH " " " " " "

a) $\rightarrow p^H = 4$

b) $\rightarrow p^H = 4$

d) $\rightarrow p^H = 4 + \log \frac{2/3}{4/3} = 3.7$

e) $\rightarrow p^H = 4 + \log \frac{4/3}{2/3} = 4.3$

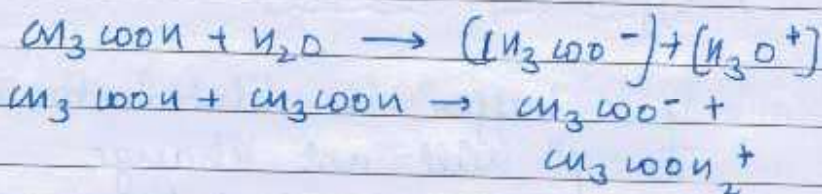
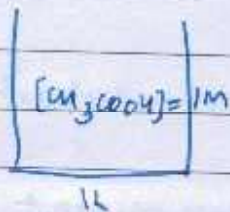


$$\frac{(10^{-4} + x)x}{10^{-4} - x} = 10^{-4}$$

$$2 \times 10^{-4} x + x^2 = 10^{-8}$$

$$x = \frac{10^{-4} - 2 \times 10^{-4} \pm 2\sqrt{2} \cdot 10^{-4}}{2}$$

eg,



Conditions for an effective Buffer,

- constituents of buffer should be present in large amount.

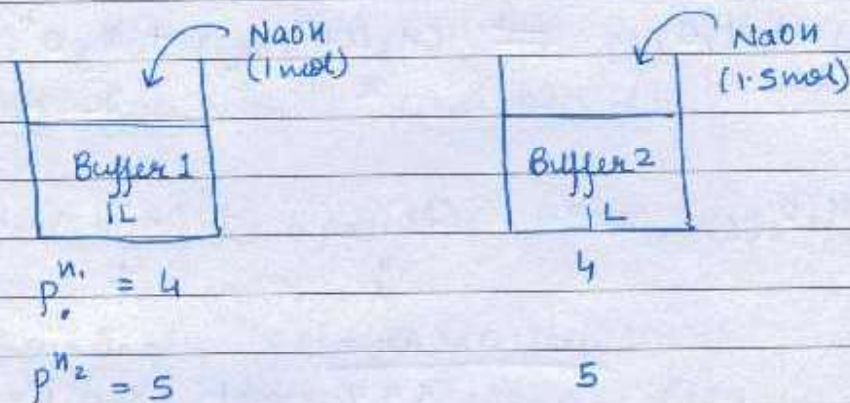
$$\frac{1}{10} \leq \frac{[\text{Salt}]}{[\text{Acid}]} \leq \frac{10}{1}$$

g. True / False

1) p^H of acidic buffer at 25°C must be less than 7
False.

• Buffer Capacity:

No. of moles of strong acid / base added to change p^H of 1L of buffer by unity.



$$BC = \frac{\text{no. of SA/SB added}}{\text{change in } p^H \text{ of buffer}}$$

$$[\text{Salt}] + [\text{acid}] = \text{constant}$$

$$a + s = c$$

no. of moles of H^+ / OH^- added = change in moles of salt

$$p^H = p^{K_a} + \log \frac{s}{a}$$

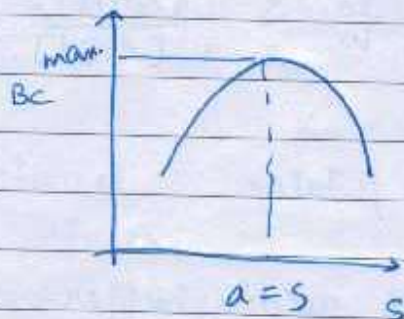
$$p^H = p^{K_a} + \log \frac{s}{c-s} \Rightarrow \frac{dp^H}{ds} = 0 + \frac{c/s \cdot c}{s(c-s)^2} = \frac{c}{s(c-s)^2}$$

$$Bc = \frac{ds}{dp^n} = \frac{Ds}{dp^n} = \frac{s(c-s)}{c}$$

$$\frac{d(Bc)}{ds} = c - 2s = 0$$

$$s = c/2$$

$$s = a = c/2$$



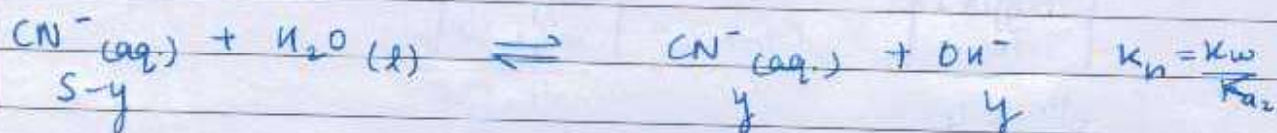
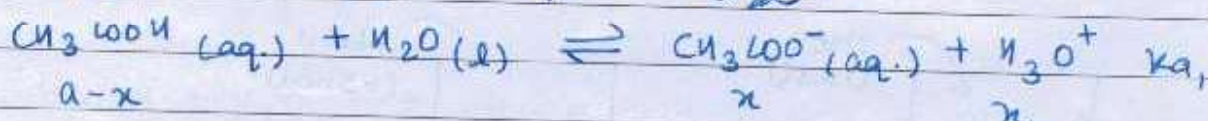
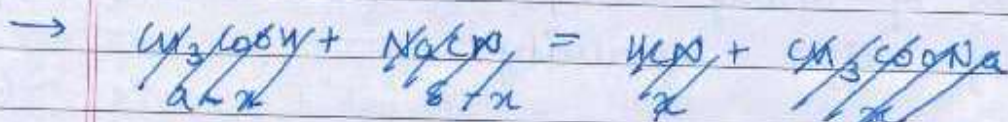
Q. Find p^n of

$$[CH_3COOH] = a$$

$$[NaCN] = s$$

$$K_a(CH_3COOH)$$

$$K_a(HCN)$$

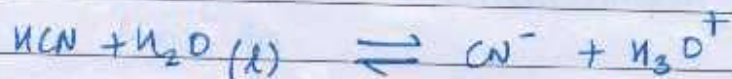


We assume,

$$x = y \quad \text{but} \quad [H_3O^+] = [OH^-]$$

$$\frac{K_{a1} K_{a2}}{K_w} = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} \times \frac{[CN^-]}{[HCN][OH^-]}$$

$$\Rightarrow K_{a1} K_{a2} = \frac{s}{a} \times [H_3O^+]^2$$



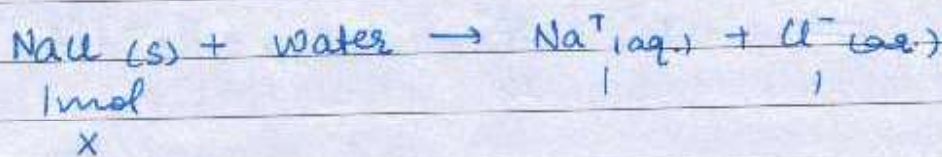
* Solubility & Solubility products :-

- Solubility : Maximum amt. of substance that can be dissolved in specified amt. of solvent at a given temp.

OR

It is maximum no. of moles of a substance which can be dissolved in 1L of solvent.

For ionic compounds



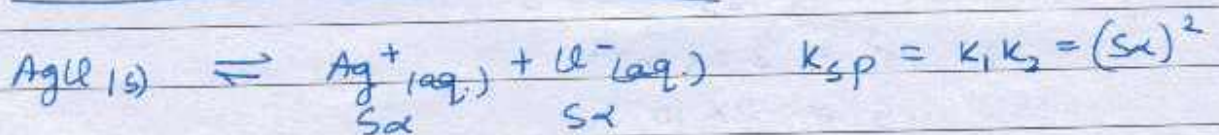
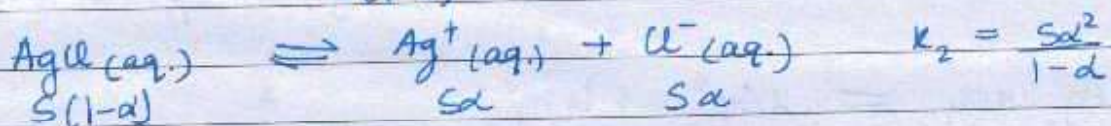
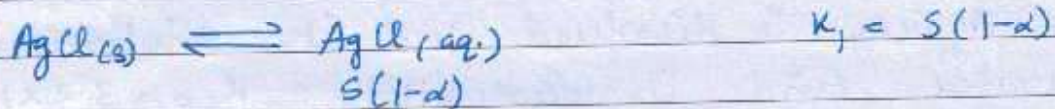
For non-ionic compounds



Sparingly Soluble salt :

eg, AgCl (s) , $\text{BaSO}_4 (\text{s})$, $\text{CaCO}_3 (\text{s})$

These are the substances which can dissolve to a very small extent.



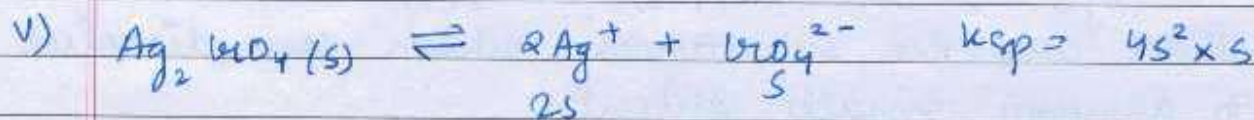
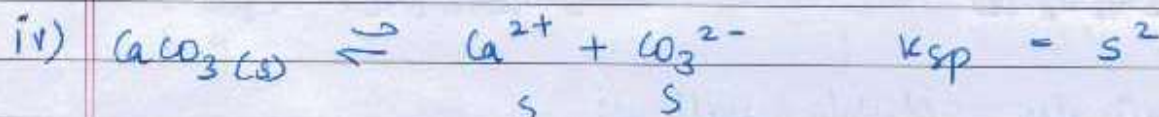
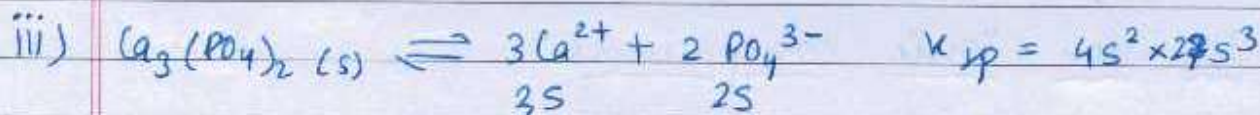
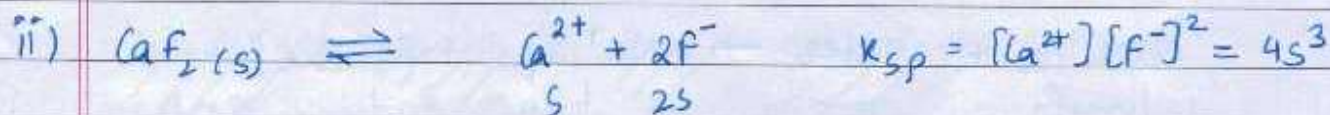
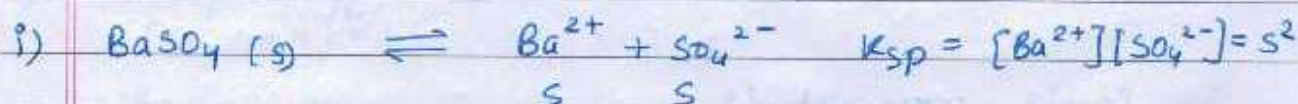
Due to very low solubility solⁿ will be considered infinitely dilute

$$\alpha \approx 1$$

$$K_{sp} = s^2 = [Ag^+]_{aq} [Cl^-]_{aq}$$

↓
solubility

Q. Write expression of K_{sp} for



Q. Solid Ag_2CrO_4 is dissolved and its solution is saturated. Find its solubility. $K_{sp} = 3.2 \times 10^{-11}$



$$\Rightarrow 4s^3 = 3.2 \times 10^{-11}$$

$$s = 2 \times 10^{-4}$$

Q. Calculate the solubility product of AgCl if its saturated solⁿ 1.435 mg per litre

$$\rightarrow M = 10^{-5}$$

$$K_{sp} = 10^{-10}$$

Q. Calculate K_{sp} of PbI_2 if its saturated solⁿ contains 10^{-4} M I^- ions.

$$\rightarrow \frac{1}{8} \times 10^{-4} \times 4 \times 10^{-8} = K_{sp} = \frac{1}{2} \times 10^{-12}$$

Q. A particular saturated solution of Ag_2CrO_4 has $[\text{Ag}^+] = 5 \times 10^{-5} \text{ M}$ & $[\text{CrO}_4^{2-}] = 4 \times 10^{-4} \text{ M}$. What is K_{sp} of Ag_2CrO_4 .

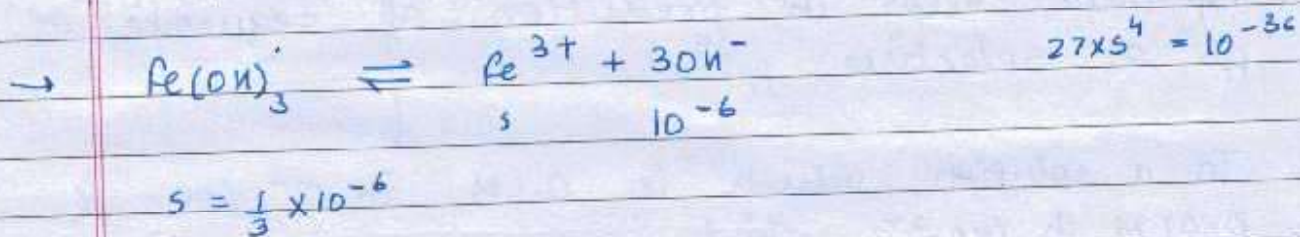
$$\rightarrow \frac{5 \times 10^{-5} \times 4 \times 25 \times 10^{-10}}{2.5 \times 10^{-13}} \quad / \quad \frac{2 \times 10^{-8}}{1 \times 10^{-13}} \quad \rightarrow \times$$

$$K_{sp} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}]$$

$$= 25 \times 10^{-10} \times 4 \times 10^{-4}$$

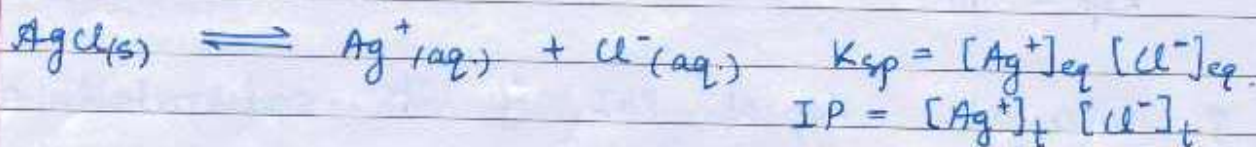
$$= 10^{-12}$$

Q. What is the solubility of $\text{Fe}(\text{OH})_3$ in aq. solⁿ if $p^H = 8$ $K_{sp} = 10^{-36}$



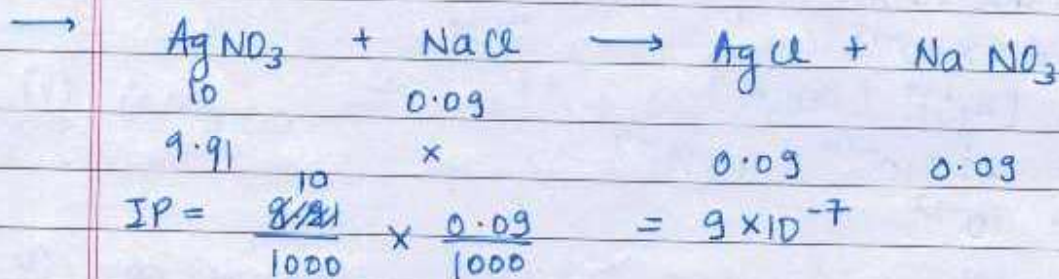
* Application of Solubility product (K_{sp}) :->

- With the help of K_{sp} data we can predict whether pptⁿ will take place or not.



- if $IP > K_{sp} \Rightarrow$ pptⁿ will take place
- if $IP < K_{sp} \Rightarrow$ no pptⁿ will take place
- if $K_{sp} = IP \Rightarrow$ solution is saturated.

Q. 100 ml of 0.1M AgNO_3 + 900 ml of 0.0001M NaCl are mixed. Will pptⁿ take place?
 $K_{sp} = 10^{-10}$



As $IP > K_{sp} \Rightarrow$ pptⁿ will take place.

- K_{sp} data helps in prediction of sequence of pptⁿ or selective pptⁿ.

Q. To a solution which is 0.1M in Cl^- ions & 0.01M in CrO_4^{2-} Find

- Sequence of precipitation
- conc. of already precipitating ion when other ion just starts pptⁿ when other ion
- % of already precipitating ion, just starts pptⁿ

d) Can 100% ion be precipitated.

$$K_{sp}(\text{AgCl}) = 10^{-10}$$

$$K_{sp}(\text{Ag}_2\text{CrO}_4) = 10^{-12}$$

a) $\rightarrow \text{Cl}^- > \text{CrO}_4^{2-}$

b) $\rightarrow 10^{-5}$

c) $\rightarrow 0.01\%$

d) $\rightarrow \text{No}$

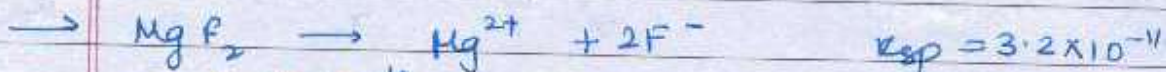
* Factors affecting solubility :

1) Common ion effect :

Q. Calculate solubility of MgF_2 ($K_{sp} = 3.2 \times 10^{-11}$)

a) in pure water

b) in 0.1M NaF

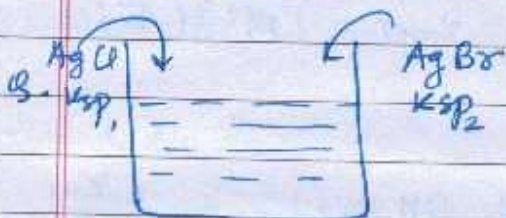


a) 2×10^{-4}

b) 3.2×10^{-9}

$$(2s+10^{-1})^2(s) = 3.2 \times 10^{-11}$$

due to common ion effect, sol. of sparingly soluble salt will decrease.



$$\rightarrow (s+x)x = K_{sp1}$$

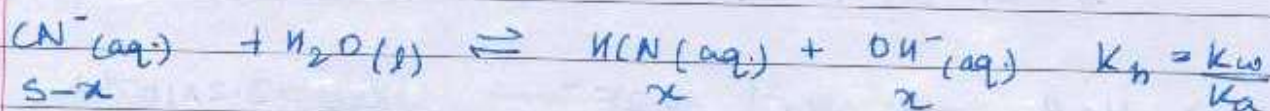
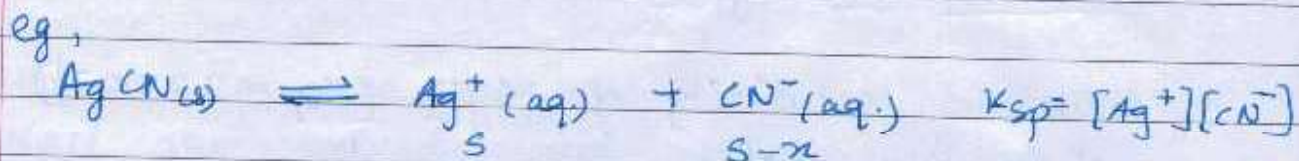
$$(s+x)s = K_{sp2}$$

2) Effect of hydrolysis :

due to hydrolysis, solubility will increase.

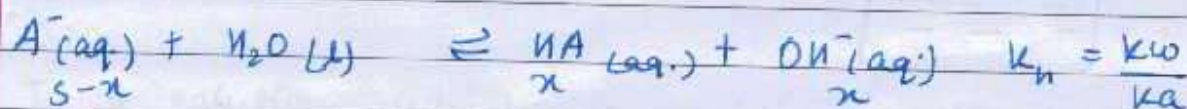
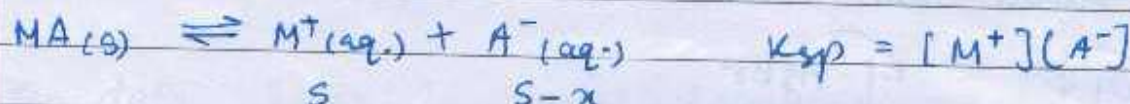
Note : In case if anion produced from sparingly soluble salt is conjugate base of weak acid \Rightarrow cation produced from salt is conjugate acid of weak base then hydrolysis will take place & solubility of salt will increase.

eg,



In above case solubility will \downarrow on \uparrow p^H .

In general,



$$\text{S.B.S } s = (s-x) + x$$

$$[\text{M}^+] = [\text{A}^-] + [\text{HA}]$$

$$= [\text{A}^-] \left(1 + \frac{K_w}{K_a} \right)$$

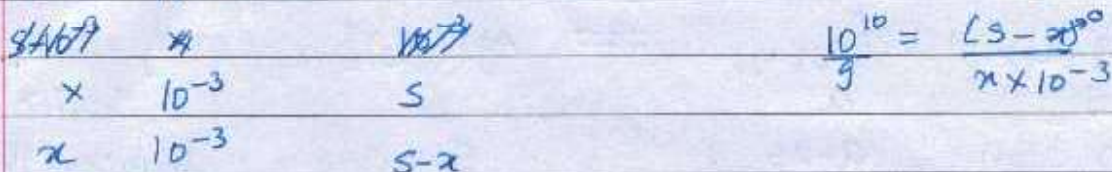
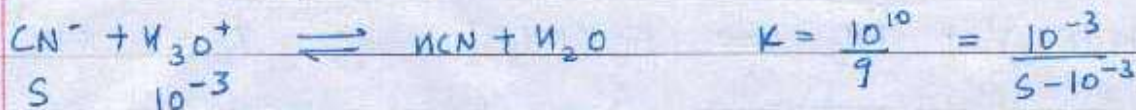
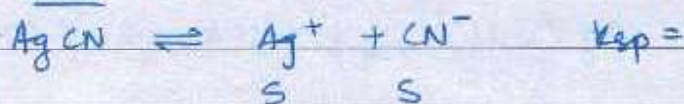
$$K_{sp} = \frac{[\text{M}^+][\text{A}^-]}{\left(1 + \frac{K_w}{K_a} \right)}$$

$$\Rightarrow S = \sqrt{K_{sp} \left(1 + \frac{[H_3O^+]}{K_a}\right)}$$

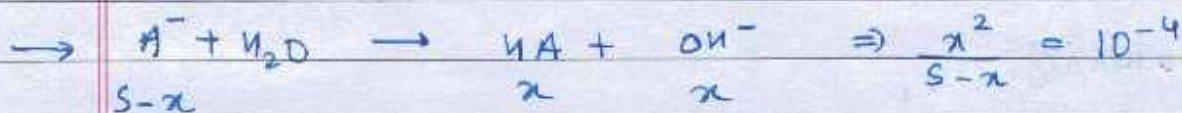
8. Calculate solubility of $AgCN$ ($K_{sp} = 4 \times 10^{-16}$) in buffer of $p^H = 3$ ($K_a(HCN) = 9 \times 10^{-10}$)

$$\rightarrow S = \sqrt{4 \times 10^{-16} \left(1 + \frac{10^{-3}}{9 \times 10^{-10}}\right)} = \frac{2}{3} 10^{-9/2}$$

M-II :



9. p^H of a saturated solⁿ of silver salt ($AgA(s)$) of monobasic acid (HA) is found to be 9. Find K_{sp} . (Given $K_a(HA) = 10^{-10}$)



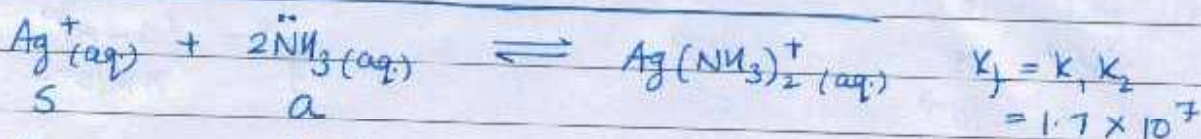
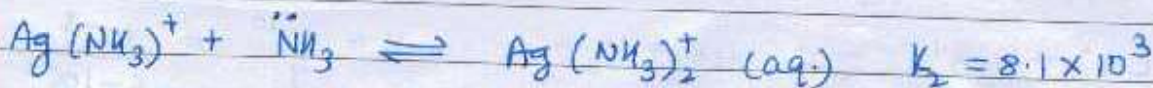
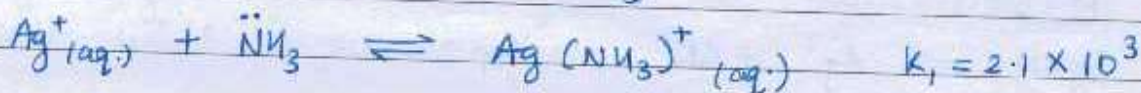
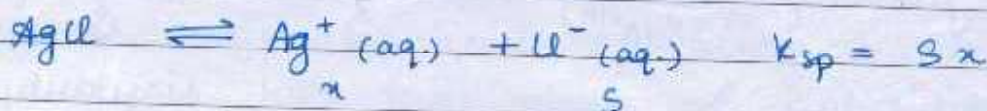
$$2 \times 10^{-4} = S$$

$$\frac{4 \times 10^{-8}}{11}$$

3) Effect of complex formation:

When sparingly soluble salts are dissolved in solution containing Lewis base then their solubility increases considerably

eg,



0	a - 2s	S
x	a - 2x + 2x	S - x

larger the value of K_f , more will be stability of complex

$$K_f = \frac{(S-x)}{x(a-2s+2x)^2} = \frac{S}{xa^2}$$

$$K_{instability} = \frac{1}{K_f}$$

Q. Calculate the solubility of $AgCl(s)$ in water ($K_{sp}(AgCl) = 10^{-10}$)

b) cal. the sol. of $AgCl$ in 2M NH_3 solⁿ.
 $K_f = 10^7$

→ a) 10^{-5}

b) $\frac{S^2}{a^2} = 10^{-3}$

c - 2x $10^{-3/2}$

8. What are conc of $\text{Ag}^+(\text{aq})$, $\text{Ag}(\text{NH}_3)^+(\text{aq})$, $\text{Ag}(\text{NH}_3)_2^+$ in solⁿ prepared by mixing 0.1 mol of AgNO_3 to 1 L 3.2 M $\text{NH}_3(\text{aq})$
- $K_1 = 2 \times 10^3$ $K_2 = 8 \times 10^3$ $K_f = 1.6 \times 10^6$

$$\rightarrow 1.6 \times 10^6 = \frac{0.1}{x \times (3.2)^2} \Rightarrow x = \frac{1}{1.6 \times 10^7 \times 10.24}$$

$$[\text{Ag}(\text{NH}_3)_2^{2+}] = 0.1 \text{ M}$$

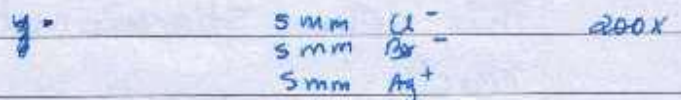
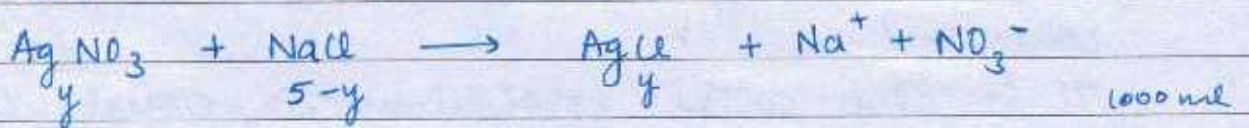
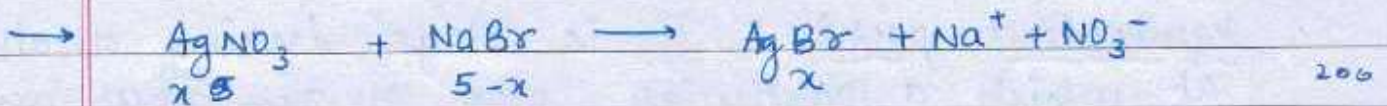
$$\frac{1}{1.6 \times 10^7 \times 3.2} \cdot 2 \times 10^3 = \frac{y}{x \cdot 5}$$

$$[\text{Ag}(\text{NH}_3)^+] = \frac{10^{-4}}{25.6}$$

9. 0.01 M, 500 ml AgNO_3 is mixed with 250 ml each NaBr & NaCl having molarity 0.02 M. Find $[\text{Br}^-]_{\text{eq}}$ & $[\text{Cl}^-]_{\text{eq}}$.

$$K_{sp}(\text{AgBr}) = 5 \times 10^{-13}$$

$$K_{sp}(\text{AgCl}) = 10^{-10}$$



$$[\text{Br}^-] = \frac{1}{200 \times 20}$$

$$\frac{5-x}{1000} = 200z$$

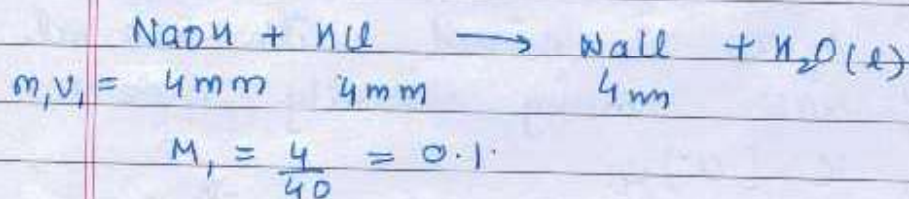
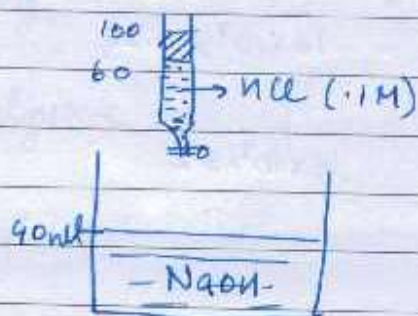
$$[\text{Cl}^-] = \frac{1}{20}$$

$$\frac{1}{200} - 200z = \frac{5-y}{1000} = z \quad ; \quad x+y=5$$

$$z =$$

* Indicator Theory :

- Titration : It is the process of determination of conc. of unknown solⁿ with the help of known solⁿ.



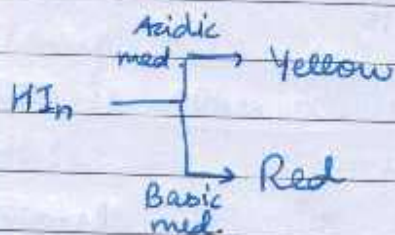
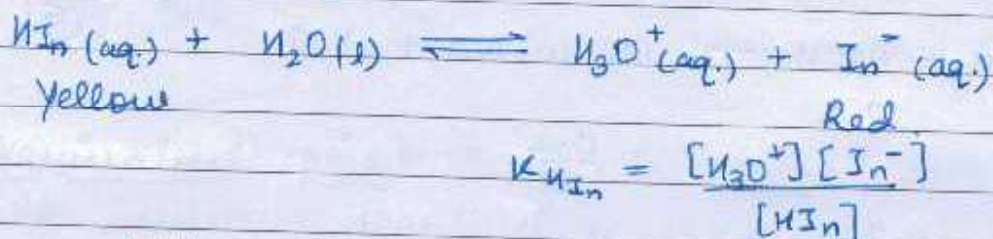
- Equivalent point : It is stage during titration at which a particular step of rxn has been completed.
It is also called stoichiometric point coz at this pt. stoichiometric amt. of reactant reacts
- End Point : It is the pt. at which all reactant has been consumed and there is no further scope for any rxn.
During titration there can be more than one equivalent points but there will be only one end point.

* Indicators :-

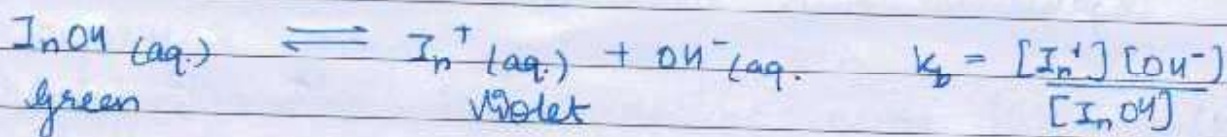
- These are the substances which exhibit diff. colours under diff. p^H range.
- Indicators are of two types :
 - i) acidic indicator (HIn)
 - ii) Basic indicator ($InOH$)

A) Acidic Indicator :

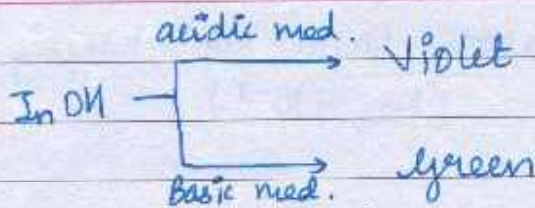
These are weak acids which exhibit diff. colours in dissociated form & undissociated form.



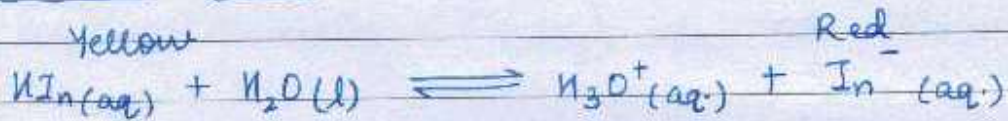
B) Basic Indicator :



It is a weak base which exhibits diff. colour in dissociated & undissociated form.



• Detection Ratio :



$t=0$	100	0	Y
$t=t_b$	90	10	Y
	60	40	O
	40	60	O
	10	90	R

$$K_{\text{In}} = \frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]}$$

$$\Rightarrow [\text{H}_3\text{O}^+] = K_{\text{In}} \frac{[\text{HIn}]}{[\text{In}^-]}$$

$$p^{\text{H}} = p^{\text{K}_{\text{In}}} + \log \frac{[\text{In}^-]}{[\text{HIn}]}$$

if $\frac{[\text{In}^-]}{[\text{HIn}]} \geq 10 \Rightarrow \% [\text{In}^-] \approx 91\% \Rightarrow \text{Red colour}$

if $\frac{[\text{In}^-]}{[\text{HIn}]} \leq \frac{1}{10} = 0.1 \Rightarrow \% [\text{HIn}] \approx 91\% \Rightarrow \text{Yellow}$

if $0.1 \leq \frac{[\text{In}^-]}{[\text{HIn}]} \leq 10 \Rightarrow \text{Transition range} \Rightarrow \text{Orange}$

• Transition range : This is the p^{H} range in which an indicator changes its colour

$$p^{\text{H}} = p^{\text{K}_{\text{In}}} + \log [\text{In}^-]$$

Case I: if we add an indicator to a solⁿ having
 $p^H = p^{K_{In}} - 1 \approx 2$ ($K_{In} = 10^{-3}$)

$$p^H = p^{K_{In}} + \log \frac{[In^-]}{[HIn]}$$

$\Rightarrow \% [HIn] = 91\% \Rightarrow$ Yellow colour

Case II: if we add an indicator to a solⁿ having
 $p^H = p^{K_{In}} + 1 \approx 4$

$$\frac{[In^-]}{[HIn]} = 10$$

$\Rightarrow \% [In^-] = 91\% \Rightarrow$ Red colour

9/10/1

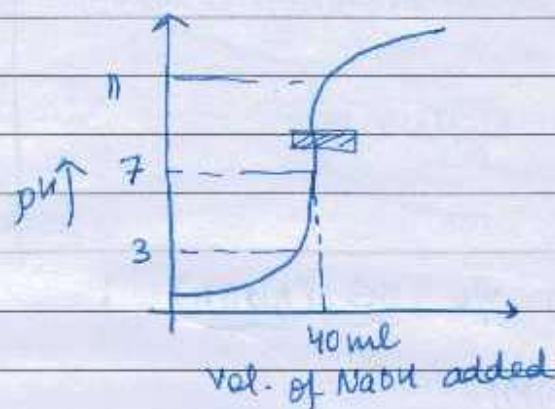
Sr. No.	Indicators	p^H range	color in acidic med.	color in basic med.
1.	Methyl Orange	3.1-4.4	Pink	Yellow
2.	Methyl Red	4.2-6.3	Red	Yellow
3.	litmus	5.5-7.5	Red	Blue
4.	Phenol Red	6.8-8.4	Yellow	Red
5.	Phenolphthaleine	8.5-10	Colourless	Pink
6.	Thymol Blue	1.2-2.8	Red	Yellow

* Types of Titration :

- i) SA v/s SB
- ii) WA v/s SB
- iii) SA v/s WB
- iv) SB v/s SA
- v) Polyprotic acid (H_2CO_3) v/s SB (NaOH)

A) SA v/s SB (Jump 3 to 11)

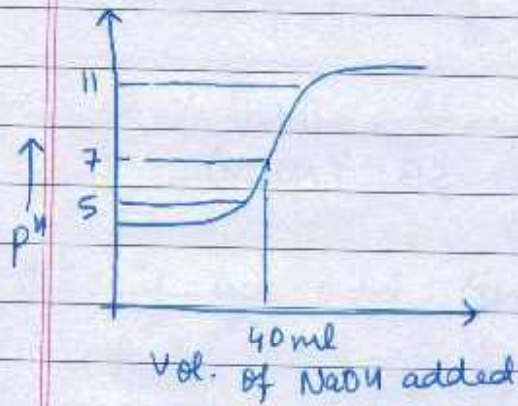
So. No.	Vol. of NaOH add.	Vol of sol ⁿ	mm of H ⁺	[H ⁺]	p ^H
1	0	40	4	0.1	1
2	10 ml	50	3	0.06	1.2
3	10 ml	60	2	2/60	1.5
4	10 ml	70	1	1/70	1.8
5	9 ml	79	0.1	0.1/79	2.3
6	1 ml	80	-	-	7
7	1 ml	81	[OH ⁻]=0.1	0.1/81	11



- we can use any indicator which lies on vertical line.
- For Best indicator
p^H at equivalent pt. = p^{K_I} of indicator.

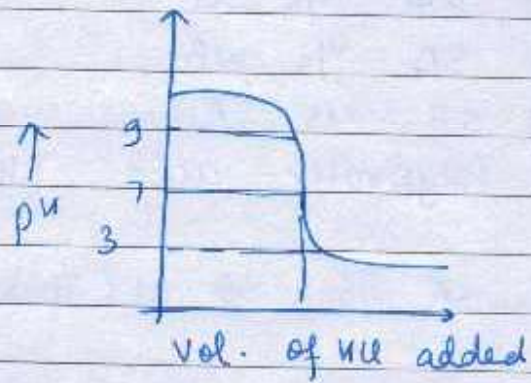
ii) WA v/s SB

(Jump 5 to 11)



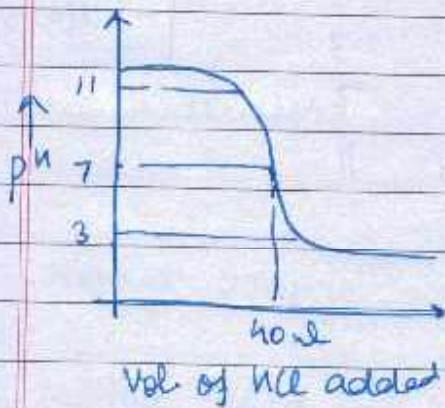
iv) WB v/s SA

(Jump 9 to 3)

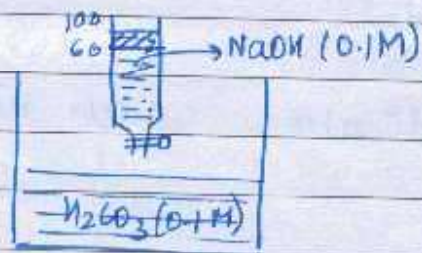


iii) SB v/s SA

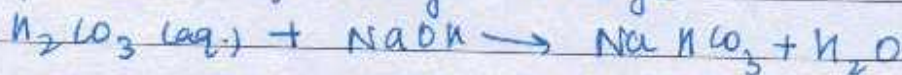
(Jump 11 to 3)



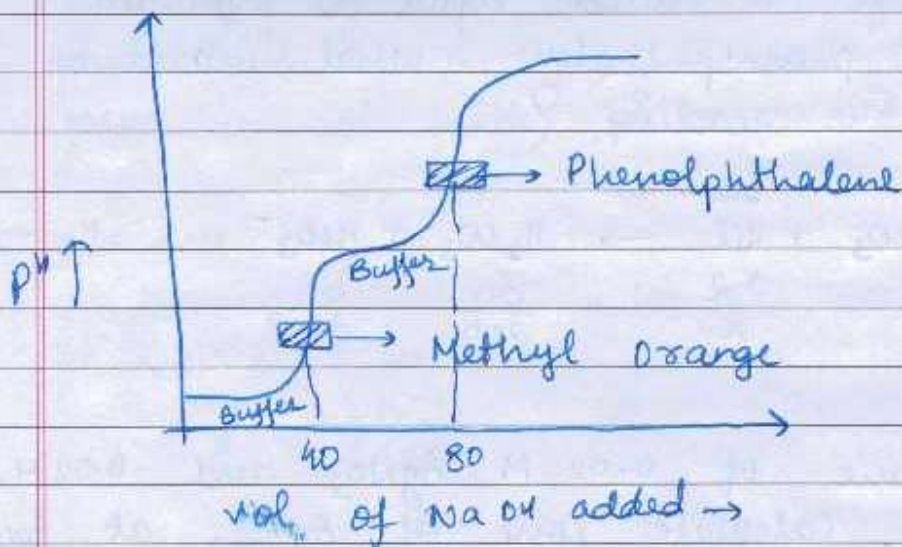
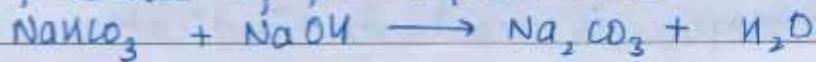
v) Polyprotic Acid (H₂CO₃) v/s SB (NaOH) :



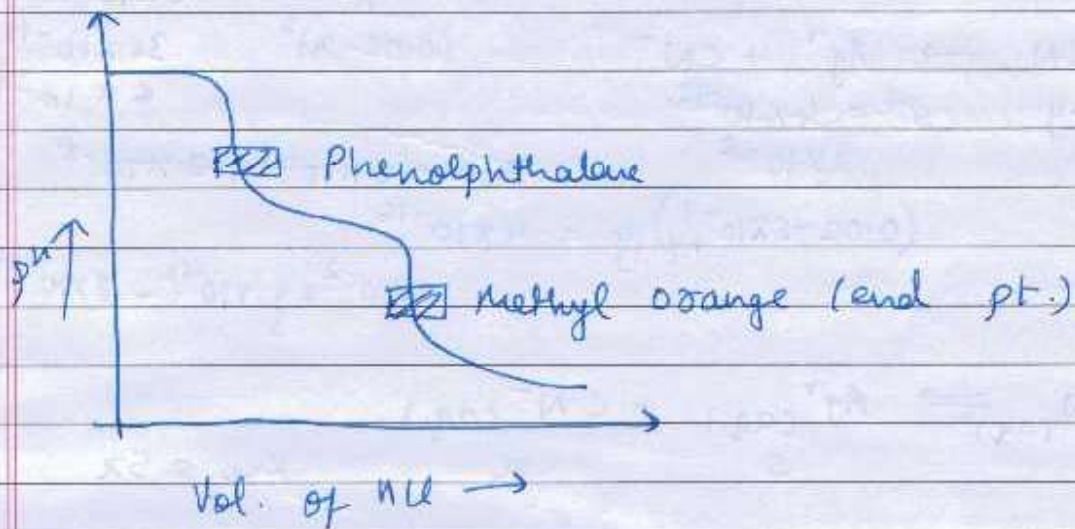
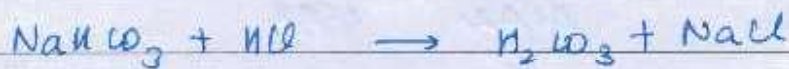
In presence of Methyl orange



In presence of phenolphthaleine

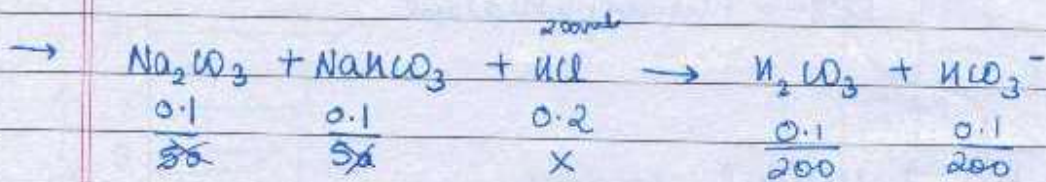


eg,

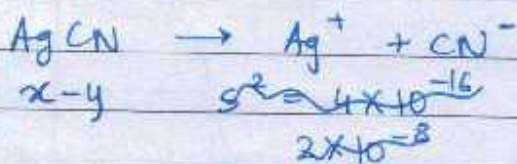
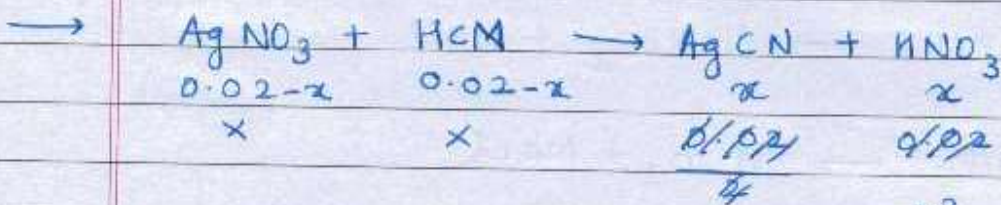


8. Water is added to a mixture containing 0.1 mol of Na_2CO_3 & NaHCO_3 each to make some solution. The solⁿ is titrated with 1M HCl. What will be the titre reading if
- a) Only phenolphthaleine is used as indicator

- b) Only methyl orange is used as indicator 300
- c) Methyl orange is added after I equivalent point with phenolphthaleine. What would be the change in reading? 20



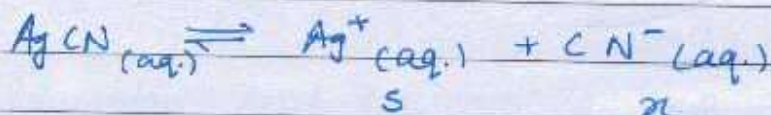
- Q. Equal volume of 0.02 M AgNO_3 and 0.02 M KCN were mixed. Calculate conc of Ag^+ at equilibrium. [Take $K_a(\text{HCN}) = 9 \times 10^{-10}$ $K_{sp}(\text{AgCN}) = 4 \times 10^{-16}$]



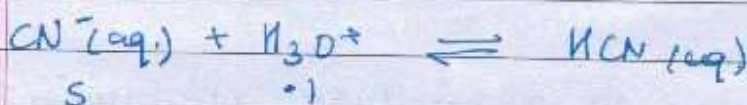
$$\begin{array}{l} x^2 = 9 \times 10^{-10} \\ (0.02-x)^2 = 36 \times 10^{-14} \\ 6 \times 10^{-7} \end{array}$$

$$0.02 - 6 \times 10^{-7} + 2 \times 10^{-8} \\ (0.02 - 6 \times 10^{-7} + 2 \times 10^{-8}) y = 4 \times 10^{-16}$$

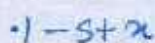
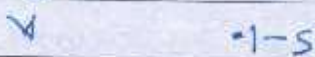
$$2 \times 10^{-2} \times \frac{1}{3} \times 10^{-12} = 8 \times 10^{-14}$$



$$K_{sp} = 5x$$



$$K = \frac{10^{-10}}{9} = \frac{S}{(-1)x}$$



8. For the acid indicator Thymol blue, p^H is 2 when half of the indicator is in unionised form. Find the % of indicator in unionised form in solⁿ with $[H^+] = 4 \times 10^{-3} M$

$$\rightarrow p^H = 2.4$$

$$2.4 = 2 + \log \frac{1}{2} \Rightarrow p^{H_{In}} = 2$$

$$2.4 = 2 + \log$$

$$\frac{1}{10} = \frac{[In^-]}{[HIn]}$$

Div.

$$0.4 = \log \frac{[In^-]}{[HIn]} = \frac{4}{10}$$

$$\% [In^-] = \frac{200}{7}$$