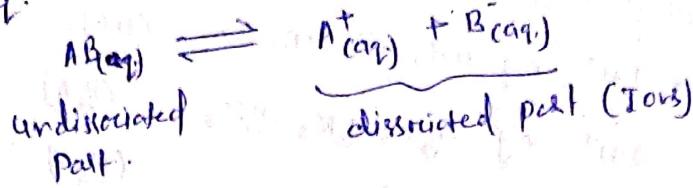


Ionic equilibrium (for Ionic Rxn)

①

Eq. establish b/w dissociated part (i.e. ions) & undissociated part is known as Ionic eq.



Classification of Sub :-

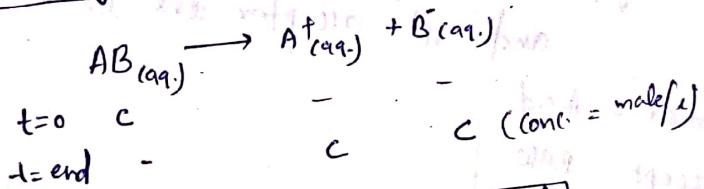
(i) Electrolyte :- which dissociates into component ions.
(Ionic bond or polar covalent Bond) ex. NaCl, HCl

(ii) Non electrolyte :- which does not dissociate into its component ions.
(Non polar C.B.)

Ex: Urea, glucose, sucrose.

Classification of electrolytes :- on the basis of degree of dissociation electrolytes are classified into two categories

① Strong Electrolyte (SE) :- electrolytes which are 100% ionize ($\alpha = 1$)



$$[\text{Ion}] = \text{c} \text{ mol/l}$$

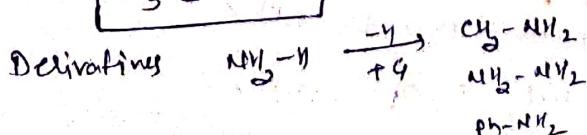
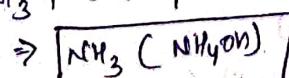
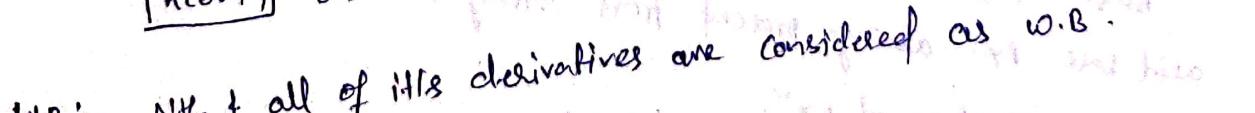
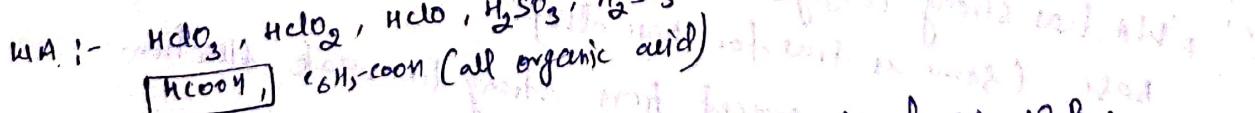
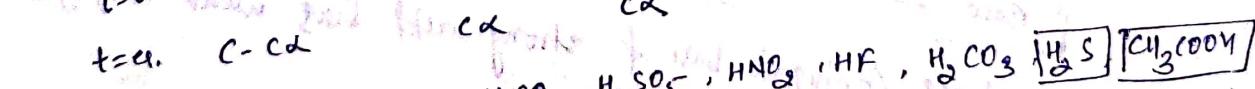
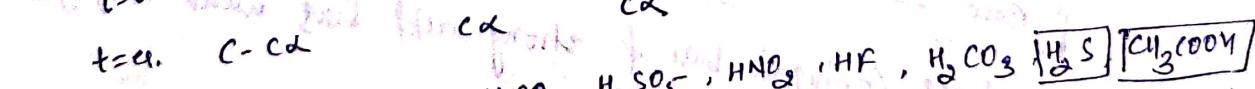
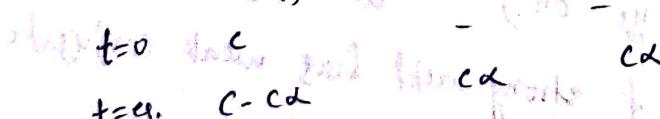
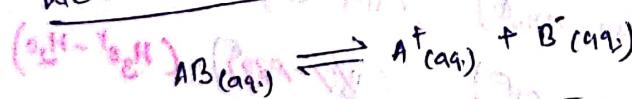
SA :- HClO_4 , H_2SO_4 , HNO_3 , H_2S , HBr , HCl

SB :- NaOH , KOH , RbOH , CsOH , $(\text{CaOn})_2$, Sr(OH)_2 , Ba(OH)_2

Salt :- NaCl (SASB), CH_3COO^- (WASB)

NH_4^+ (SAWB), $\text{CH}_3\text{COONH}_4$ (WAWB)

② Weak electrolyte (WE) :- electrolytes which are negligible dissociated into their component ions in aq. soln. $\alpha < 1$ (Unknown)



Theories related to acid & base :-

1. Arrhenius acid-base Theory :-

AN → Any substance which give H^+ ion in water is known as Arr. acid.

Monobasic/Monoprotic - $1H^+$ e.g. HCl, HF, HBr etc. (HA)

Dibasic/ Diprotic - $2H^+$ e.g. H_2S , H_3PO_4 , H_2CO_3 etc. (H₂A)

Tribasic/Triprotic - $3H^+$ e.g. H_3PO_4 (H₃A)

AB → Any substance which give OH^- in water is known as Arr. base.

Monoaacidic - $1OH^-$ e.g. NaOH, KOH, NH₄OH (BOH)

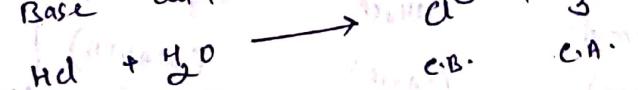
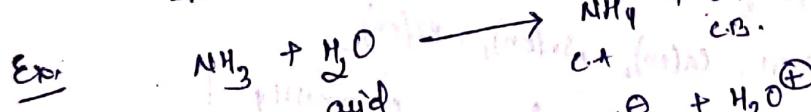
Diacidic - $2OH^-$ e.g. Mg(OH)₂, Zn(OH)₂, Fe(OH)₂, Ca(OH)₂ [B(OH)₂]

Triacidic - $3OH^-$ e.g. Al(OH)₃, Fe(OH)₃ [B(OH)₃]

according to this theory H^+ donor are acid and H^+ acceptor are Base.

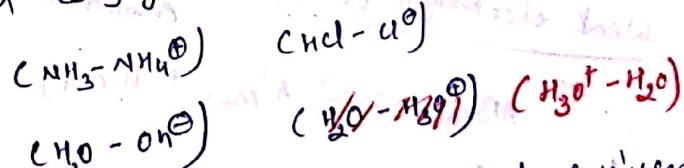
2. Bronsted-Lowry theory :-

H^+ donor - Acid
 H^+ accept - Base



Conjugate acid-base pair; - acid-base pair having difference of one H^+ ion is known conjugate acid-base pair.

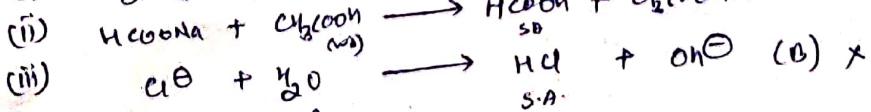
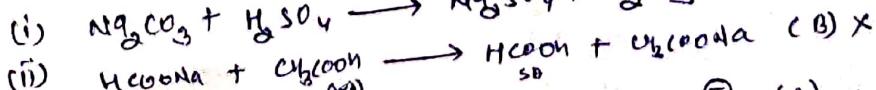
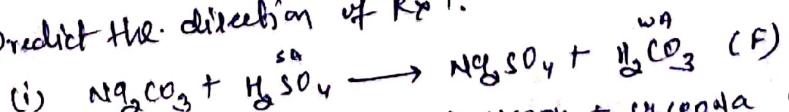
Acid $\xrightarrow{-H^+} C.B.$
Base $\xrightarrow{+H^+} C.A.$

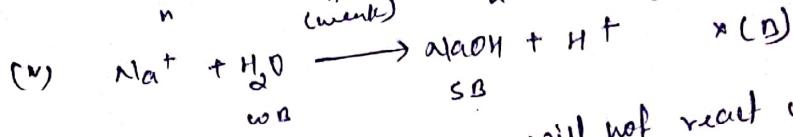
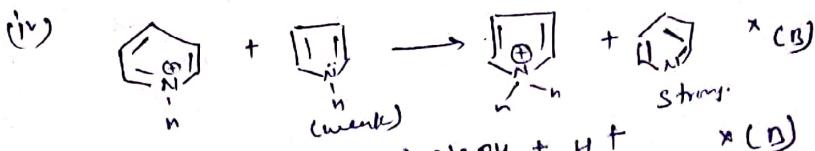


Note:- WA has strong conjugate base of strong acid has weak conjugate base. (same is true for base also)

2. acid-base Rxn always proceed from strong to weak direction.

Q. Predict the direction of Rxn.

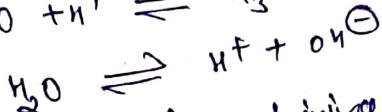
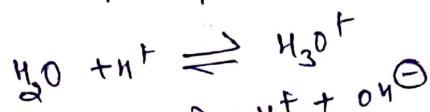




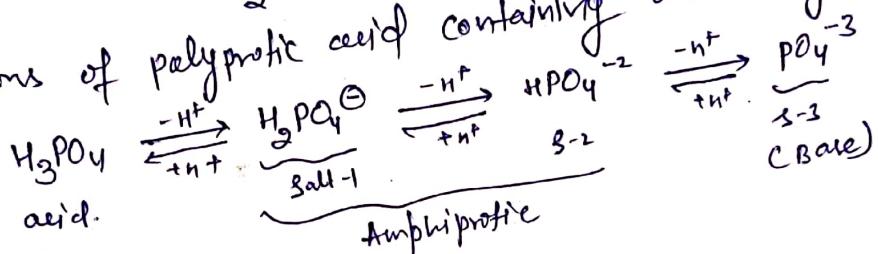
\Rightarrow Counter Ions of S.A. & S.B. will not react with water i.e. they do not undergo any hydrolysis.

Amphiprotic Substance :- Substance which can donate as well as accept H⁺ i.e. proton is known as amphiprotic sub.

(3 प्रकार दिए गए)



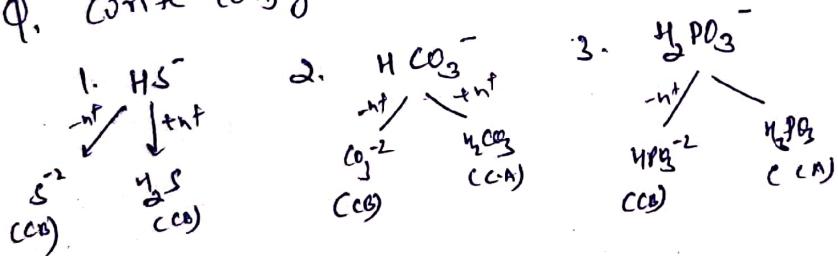
\Rightarrow anions of polyprotic acid containing acidic hydrogen are amphiprotic



$\Rightarrow \text{H}_n\text{A}$ (polyprotic acid) \Rightarrow salt = n
Basicity = n \Rightarrow amphiprotic form = n - 1

acidic salt = n - 1
(containing acidic H)

Q. Write conjugate acid & base of the following.



\Rightarrow 3. Lewis acid-base Theory :-

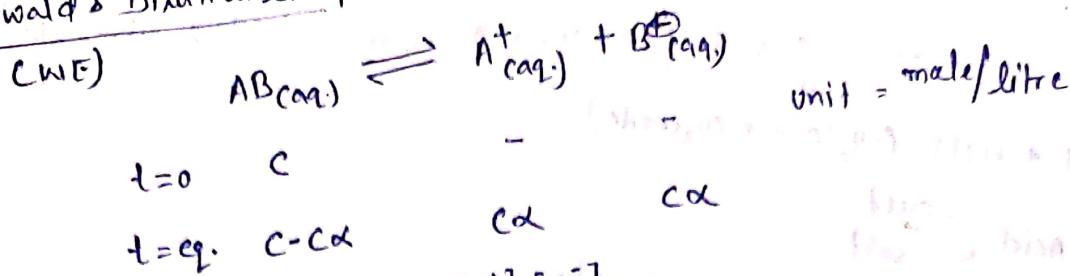
Lewis acid is lone pair acceptor ex. valent orbital, (+ve) charge

Lewis Base is lone pair donor.

Ex. NH_3 & their derivatives, CN^- , ON^- , SO_4^{2-}

Ostwald's Dilution law :-

(3)



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

K_i is Ionisation constant of weak electrolyte whose numerical value will be given in the problem. and it changes only & only with temp.

$$K_i = \frac{\alpha \cdot \alpha}{c(1-\alpha)}$$

$$K_i = \frac{c\alpha^2}{1-\alpha}$$

K_i & c = known.

α = unknown

Since α is negligible w.r.t. to one so $(1-\alpha) \approx 1$

$$\alpha = \sqrt{\frac{K_i}{c}}$$

$$\left\{ \begin{array}{l} \alpha = 5 \times 10^{-3} \\ \text{Max value } (\alpha) = 0.05 \\ (\text{ST formula } \alpha) \end{array} \right.$$

Factors affecting α :-

W.E. $\alpha \ll 1$ (Sufficiently given % at weak E.F. & less E.F. strong E.F.)

(i) Nature of solute :-

S.E. $\alpha = 1$

(ii) Nature of solvent :- solvent should be polar in nature of its dielectric constant should be high. water satisfies both of these properties hence treated as universal solvent.

(iii) Concentration of electrolyte :- always 100% dissociated at all concentration

Q) SE :- S.E. are always

$$\boxed{\alpha = 1}$$

Ans:-

(b) WE :- $\boxed{\alpha \propto \frac{1}{c}}$ $c \uparrow \alpha \downarrow$ $\left\{ \begin{array}{l} 0.1 \text{M} \\ 0.01 \text{M} \\ (\text{less}) \end{array} \right.$

at infinite dilution ($c \rightarrow 0$) then $c \rightarrow 0, \alpha \rightarrow 1$

⇒ at infinite dilution each & every electrolyte is strong electrolyte.

(iv) Temp. :- on increasing temp. K_i as well as speed of Ions increases due to which α increases.

$$T \uparrow \alpha \uparrow$$



$$\text{pOH} = -\log[\text{OH}^-] = 10^{-y}$$

$$[\text{OH}^-] = 10^{-\text{pOH}}$$

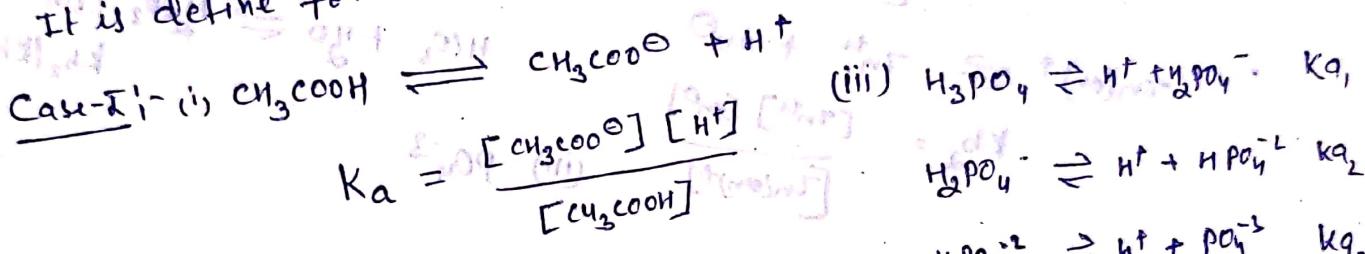
$$\text{pH} = -\log[\text{H}^+] = \text{pOH}$$

$$\text{pH} = 14 - \text{pOH}$$

K_a & K_b

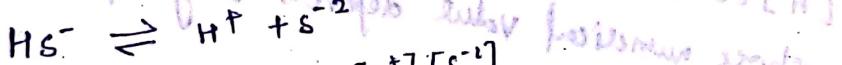
K_a = acid dissociation constant

It is defined for acids and cations.



$$K_{a_1} = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]}$$

first stage pKa $\Rightarrow K_{a_1} > K_{a_2} > K_{a_3}$ for any polyprotic acid.



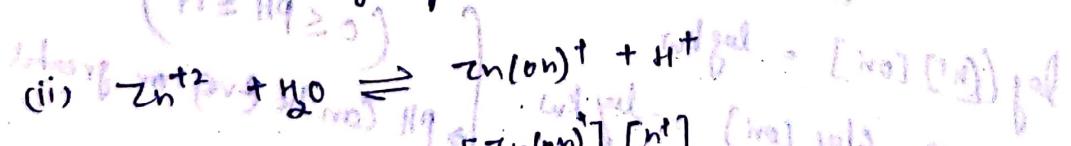
$$K_{a_2} = \frac{[\text{H}^+][\text{S}^{2-}]}{[\text{HS}^-]}$$

Case-II :- Cations.

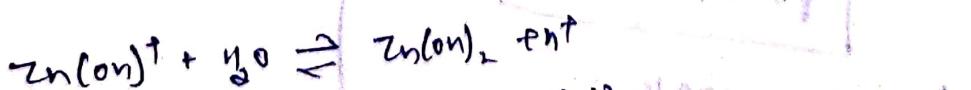


$$(K_a)_{\text{NH}_4^+} \text{ or } (K_b)_{\text{NH}_4^+} = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]}$$

(Hydrolysis constant)



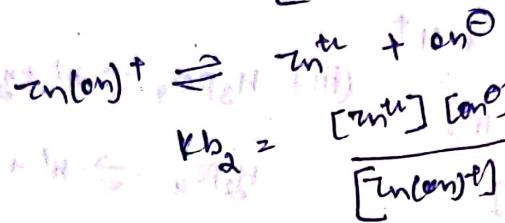
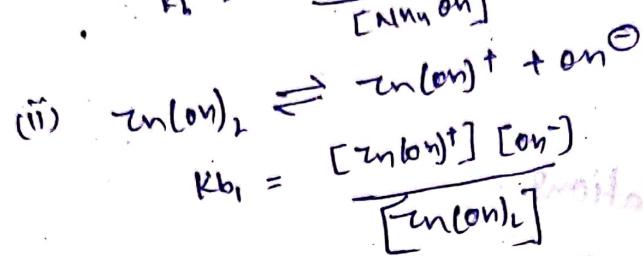
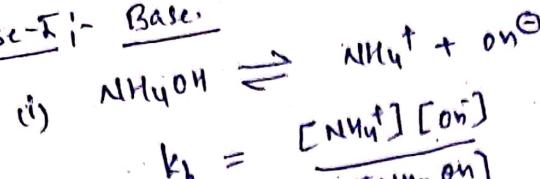
$$K_a \text{ or } K_{\text{H}_2\text{Zn}} = \frac{[\text{Zn(OH)}^+][\text{H}^+]}{[\text{Zn}^{2+}]}$$



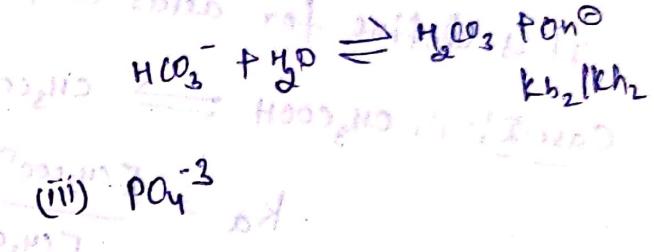
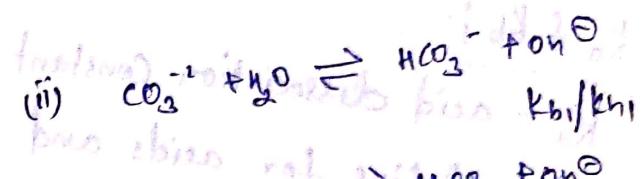
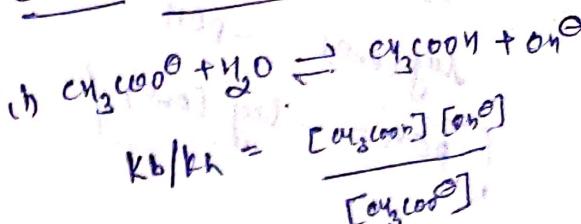
$$(K_a)_2 \text{ or } K_{\text{H}_2\text{Zn}} = \frac{[\text{Zn(OH)}_2][\text{H}^+]}{[\text{Zn(OH)}^+]}$$

K_b = Base dissociation constant
→ defined for bases and anion.

Case-I i- Base:

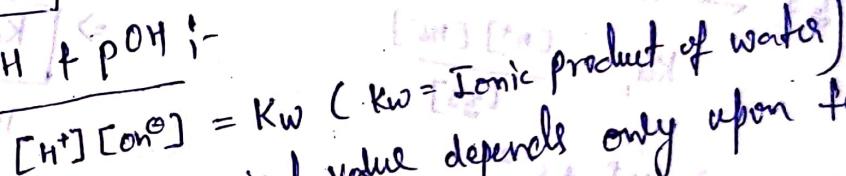


Case-II Anions:



$$\boxed{K_b > K_{b_2}}$$

⇒ Relation b/w pH & pOH :-



K_w is a constant whose numerical value depends only upon temp.

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

$$pK_w = -\log K_w$$

$$\text{at } 25^\circ\text{C} \quad pK_w = -\log 10^{-14}$$

$$\boxed{pK_w = 14}$$

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

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

$$\boxed{\text{pH} + \text{pOH} = pK_w}$$

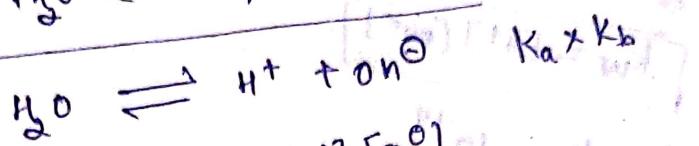
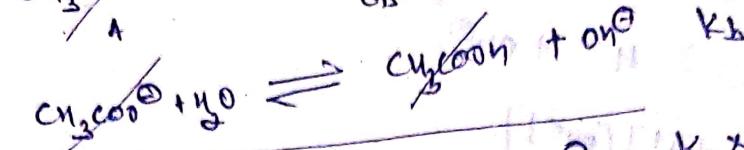
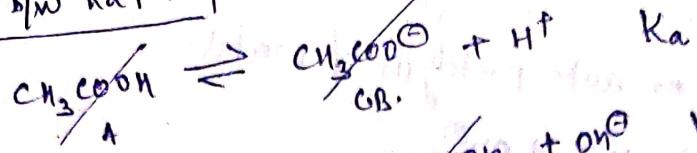
$$(0 \leq \text{pH} \leq 14)$$

⇒ pH can be even or greater than 14.

at 25°C or 298K

$$\boxed{\text{pH} + \text{pOH} = 14}$$

Relation b/w K_a & K_b



$$K_a \times K_b = [\text{H}^+] [\text{OH}^-] \quad \text{at } 25^\circ\text{C}$$

$$(K_a)_a \times (K_b)_a = K_w$$

$$(K_a)_b \times (K_b)_b = K_w$$

$$pK_a + pK_b = pK_w$$

$$pK_a = -\log K_a \quad (K_a \propto \frac{1}{pK_w})$$

K_a = high pK_a = low \Rightarrow acid = strong

K_a = low pK_a = high \Rightarrow acid = weak

$$pK_b = -\log K_b \quad (K_b \propto \frac{1}{pK_w})$$

K_b = high pK_b = low \Rightarrow base = strong

K_b = low pK_b = high \Rightarrow base = weak

$K_a > 1 \Rightarrow$ acid strong.

Properties of water :-

① Acid-Base nature :- @ water can be treated as Arrhenius as well as Brønsted acid and in terms of base it is

Arrhenius, Brønsted and Lewis base.

② Molar Concentration :-

$$\text{Molarity} = \frac{\text{moles}}{\text{volume}}$$

$$m = 1000 \times 1 \\ = 1000 \text{ gm}$$

$$m = \frac{1000}{18} = 55.5$$

$$[\text{H}_2\text{O}] = \frac{55.5}{1000}$$

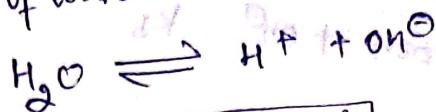
$$[\text{H}_2\text{O}] = 55.5 \text{ M}$$

$$d = 1 \text{ gm/ml}$$



③ Ionic product of water:-

or
self ionisation of water or auto-protolysis of water.



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

$$T = 25^\circ\text{C} \quad K_w = 10^{-14}$$

$$\rho K_w = 14$$

$$(T < 25^\circ\text{C})$$

$$K_w < 10^{-14}$$

$$\rho K_w > 14$$

$$(T > 25^\circ\text{C})$$

$$K_w > 10^{-14}$$

$$\rho K_w < 14$$

Note:- ① In any aq. soln. (acidic, basic or neutral) product of conc. of H^+ and OH^- i.e. Ionic product (Kw) of water always remains constant.

②

$[\text{H}^+] = [\text{OH}^-]$ = Neutral solution. ($\text{pH} = \text{pOH}$)

$[\text{H}^+] > [\text{OH}^-]$ = Acidic ($\text{pH} < \text{pOH}$)

$[\text{H}^+] < [\text{OH}^-]$ = Basic ($\text{pH} > \text{pOH}$)

③ Pure water is always neutral at all temp.

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

Q. pH of water will higher at which temp. (4°C or 25°C)

$$\text{Sol: } T = 25^\circ\text{C}, K_w = 10^{-14} \quad [\text{H}^+] = \sqrt{10^{-14}} = 10^{-7} \Rightarrow \text{pH} = 7.$$

$$\text{Ans: } T = 4^\circ\text{C} \quad K_w < 10^{-14} \quad [\text{H}^+] < 10^{-7}; \quad \text{pH} > 7$$

Q. what will be the nature of the salt changing pH = 6.2. (temp. will depend on it)

④ K_a or K_b of water:-

$$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$$

$$K_a \text{ or } K_b = \frac{[\text{H}^+] [\text{OH}^-]}{[\text{H}_2\text{O}]}$$

$$K_a \text{ or } K_b = \frac{K_w}{55.5}$$

$$T = 25^\circ\text{C} \quad K_a / K_b = \frac{10^{-14}}{55.5} \Rightarrow K_a / K_b = 1.8 \times 10^{-16}$$

Q. Cal. degree of dissociation of water at 25°C .

$$\text{Soln: } [\text{H}^+] = c\alpha \quad \left\{ \begin{array}{l} T = 25^{\circ}\text{C} \\ K_w = 10^{-14} \end{array} \right.$$

$$\Rightarrow 10^{-7} = 55.5 \times \alpha \quad [\text{H}^+] = \sqrt{10^{-14}} = 10^{-7}$$

$$\alpha = \frac{10^{-7}}{55.5}$$

$$\alpha = 1.8 \times 10^{-9}$$

$$\alpha = 1.8 \times 10^{-7} \%$$

Q. at 90°C degree of dissociation of water is 1.8×10^{-6} v. cal.

$$\begin{aligned} \text{pH} &= 6. \\ \text{pH} &= 6.5 \\ \text{pH} &= 5.5 \end{aligned}$$

$$\text{Soln: i) } \alpha = 1.8 \times 10^{-6} \%$$

$$\alpha = 1.8 \times 10^{-8}$$

$$[\text{H}^+] = [\text{OH}^-] = c\alpha = (55.5 \times 1.8) \times 10^{-8}$$

$$[\text{H}^+] = [\text{OH}^-] = 10^{-6} \Rightarrow \text{pH} = 6$$

$$K_w = 10^{-12}$$

$$K_a = \frac{10^{-12}}{55.5} = 1.8 \times 10^{-14}$$

$$\text{ii) pH} = 6 \text{ (Neutral)}$$

$$\text{pH} = 6.5 \text{ (basic)}$$

$$\text{pH} = 5.5 \text{ (acidic)}$$

$$\text{at } 90^{\circ}\text{C} \quad \boxed{\text{pH} + \text{pOH} = 12}$$

for this question

pH calculation for different types of solution :-

Case-I:- Acidic solution:- (acid is dissolved in water) (i) strong Acid (ii) Mixture of SA & WA (iii) weak Acid (iv) Mixture of WA + SA (C.C.I.E.)

(v) Mix. of WA + OA (vi) Polyprotic acid (single / WA / SA) (C.C.I.E.)

Case-II:- Basic solution:- (base is dissolved in water) (i) SB (ii) Mix. of SB (iii) WB (iv) Mix. of WB + SB (C.C.I.E.)

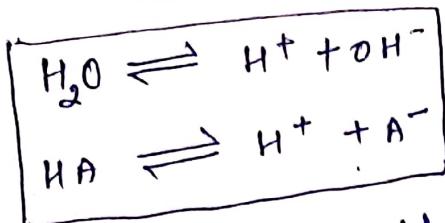
Case-III:- Acid and Base are dissolved in water (Rxn)



Part-1:- acid & base are equal \Rightarrow salt (salt hydrolysis)

Part-2:- acid & base are not equal.

Case-I :- Acid is dissolved in water :-



Source of H^+ \rightarrow acid + water

source of $\text{OH}^- \rightarrow$ water.

$$[\text{H}^+] > [\text{OH}^-]$$

$$\textcircled{1} \text{ strong Acid} : \quad ([\text{H}^+]_{\text{water}})_{\text{constant}} = 10^{-7} \text{ M} \quad (\text{at } 25^\circ\text{C})$$

HCl 0.1 N HCl

(SA)

$$\begin{array}{l} 10^{-2} \text{ M HCl} \quad \text{H}^+ \text{ due to} \\ \text{water} \\ \text{neglect contribution from water} \end{array}$$

$$10^{-4} \text{ M HCl}$$

{ same for bases for OH^- from water }

$$10^{-5} \text{ M "}$$

$$10^{-6} \text{ M "}$$

upto 10^{-7} M " acid + water. on contribution

$$10^{-8} \text{ M "}$$

10^{-9} M " exact water.

\Rightarrow In aqueous solution of strong Acid all the H^+ ions are produced by strong acid unless the solution is very dilute ($< 10^{-6} \text{ N}$)

Q. Cal. pH of (i) 10^{-1} M HCl (ii) 10^{-3} N HNO_3 (iii) $10^{-5} \text{ N H}_2\text{SO}_4$ [Ans. (i) $[\text{H}^+] = 10^{-1} \text{ M}$, (ii) $[\text{H}^+] = 10^{-3} \text{ M}$, (iii) $[\text{H}^+] = 10^{-5} \text{ M}$] (iv) $\text{pH} = 5 - \log 2$ (v) $\text{pH} = 4.7$

(Ans. (i) $\text{pH} = 1$, (ii) $\text{pH} = 3$, (iii) $\text{pH} = 5$, (iv) $\text{pH} = 4.7$)

Q. Cal. weight of H_2SO_4 which should be dissolved in 1000 ml of water to change its pH by 4 units.

Given: $(\text{pH})_f = 7 - 4 = 3$
 $(\text{pH})_i = 7$
 $[\text{H}^+]_f = 10^{-3} \text{ M}$ (due to H_2SO_4)

$$[\text{H}_2\text{SO}_4] = \frac{10^{-3}}{2} \text{ M/l.}$$

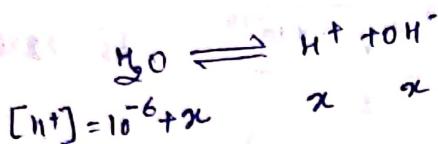
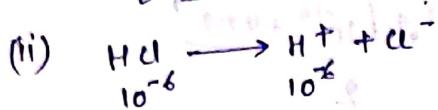
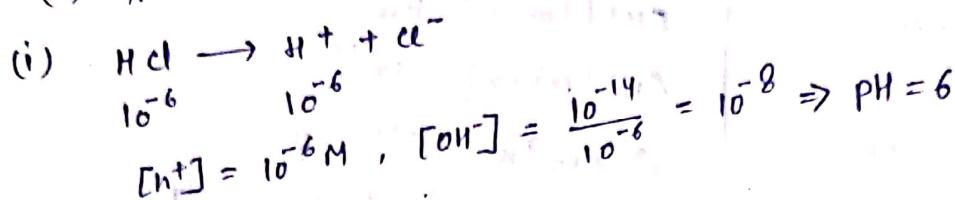
$$V = 10^3 \text{ l.} \Rightarrow n = M \times V = \frac{10^{-3}}{2} \times 10^3 = \frac{1}{2}$$

$$W = \frac{1}{2} \times 98 = 49 \text{ gm.}$$



Q. Cal. $[H^+]$, $[OH^-]$, pH in 10^{-6} M HCl solution.

- (i) neglect H^+ due to water.
- (ii) consider H^+ due to water.
- (iii) % error.



$$[OH^-] = x$$

$$[H^+] [OH^-] = K_w \Rightarrow (10^{-6} + x)(x) = 10^{-14}$$

$$\Rightarrow x^2 + 10^{-6}x - 10^{-14} = 0$$

$$\Rightarrow x = \frac{-10^{-6} \pm \sqrt{10^{-12} + 4 \times 10^{-14}}}{2} \quad \left\{ x = \frac{-b \pm \sqrt{b^2 + 4ac}}{2a} \right.$$

neglecting $[H^+]$ from the product

$$= \frac{-10^{-6} + \sqrt{1.04 \times 10^{-12}}}{2}$$

$$x = \frac{-10^{-6} + 1.02 \times 10^{-6}}{2}$$

$$x = 0.01 \times 10^{-6} = 10^{-8}$$

$$[OH^-] = 10^{-8}, [H^+] = 1.01 \times 10^{-6}$$

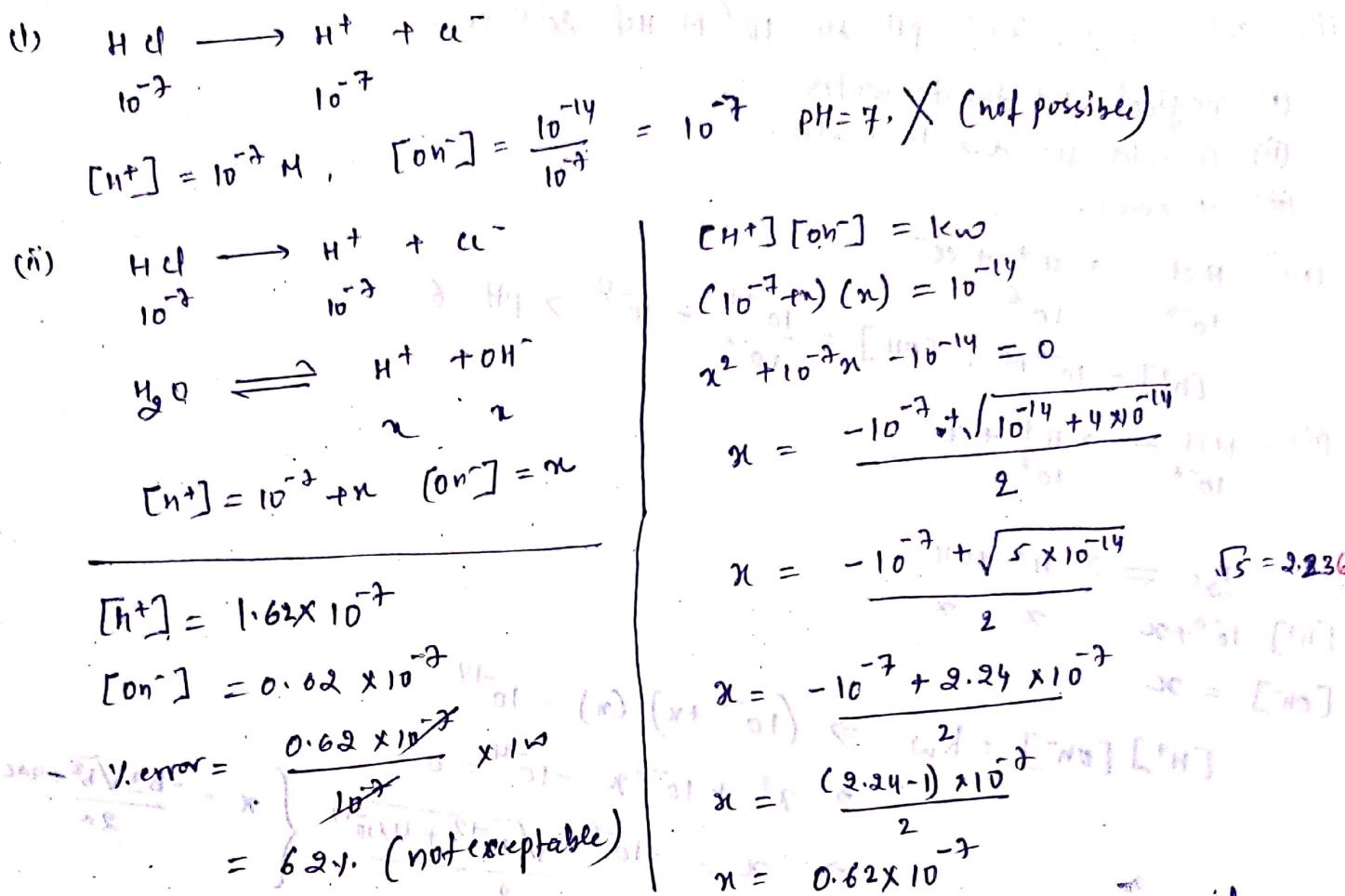
(iii) % error :- $\% \text{ error} = \frac{\text{change} \times 100}{\text{Initial}}$

$$= \frac{0.01 \times 10^{-6}}{10^{-6}} \times 100$$

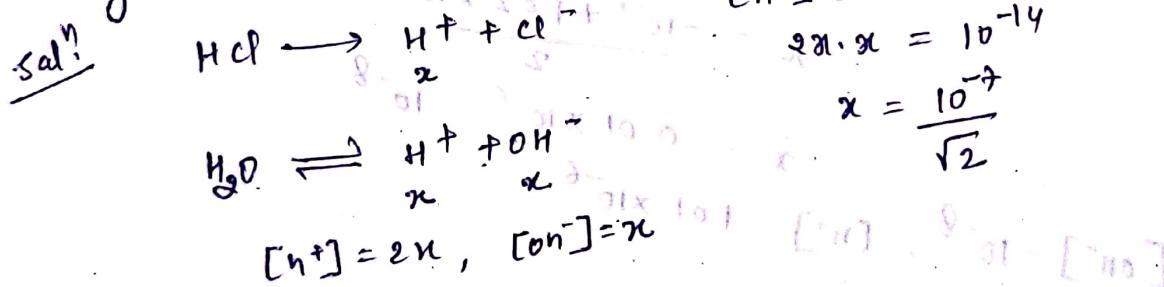
$$= 1.0\%$$

Q. Cal. $[H^+]$, $[OH^-]$ & pH in 10^{-7} M HCl solution

- (i) neglect H^+ due to water.
- (ii) consider H^+ due to water.
- (iii) % error.



Q. Calc. $[\text{HCl}]$ at which $[\text{H}^+]$ produced by HCl and $[\text{H}^+]$ produced by water are equal.



Imp. chart:

$[\text{HCl}]$	Source of H^+	$[\text{H}^+]$	pH
10^{-6}	HCl	10^{-6} M	6
10^{-7}	$\text{HCl} + \text{H}_2\text{O}$	$1.62 \times 10^{-7} \text{ M}$	6.79
10^{-8}	$\text{HCl} + \text{H}_2\text{O}$	$1.05 \times 10^{-8} \text{ M}$	6.97
10^{-9}	H_2O	10^{-9} M	7

Q. Cal. change in pH when 1 ml of 10^{-5} M HCl solution is diluted to 1000 ml

$$\text{Soln: } M_1 V_1 = M_2 V_2 \quad (\text{dilution formula})$$

$$(\text{pH})_1 = 10^{-5} \text{ M HCl} \quad [\text{H}^+] = 10^{-5} \quad \text{pH} = 5$$

$$M_1 V_1 = M_2 V_2$$

$$10^{-5} \times 1 = M_2 \times 10^3$$

$$M_2 = 10^{-8}$$

$$(\text{pH})_2 = 10^{-8} \text{ M HCl}, \quad [\text{H}^+] = 10^{-8} \quad \text{pH} = 8$$

$$\Delta \text{pH} = 3$$

$$\text{pH} = 6.97 \quad (\text{chart fit})$$

$$\Delta \text{pH} = 1.97$$

② Mix. of strong Acid i.e. In Aqueous solution of mix. of S.A. all the H^+ ion are produced by strong acids unless one of the given acid is very dilute.

$$[\text{H}^+] = \frac{\sum M_i V_i}{\sum V_i} \quad [\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = 10^{-14}$$

Q. cal. $[\text{H}^+]$, $[\text{OH}^-]$ and pH of a solution obtained by

Mixing 200 ml of 0.1 M HCl and 800 ml of 0.05 M H_2SO_4 .

$$\text{Soln: } 200 \text{ ml of } 0.1 \text{ M HCl} + 800 \text{ ml of } 0.05 \text{ M } \text{H}_2\text{SO}_4$$

$$[\text{H}^+] = \frac{0.1 \times 200 + 0.05 \times 800}{200 + 800} = \frac{100}{1000} = 0.1$$

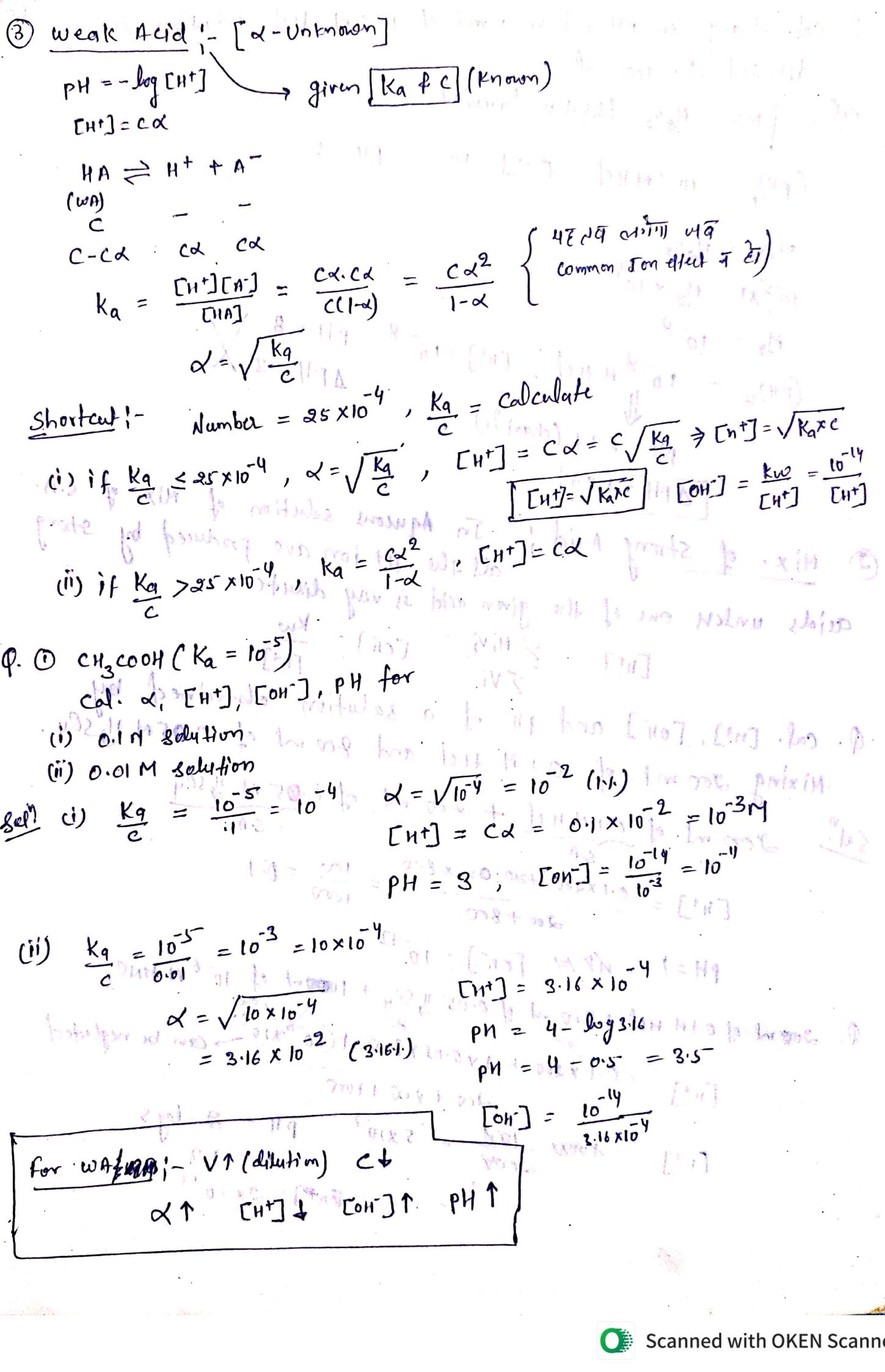
$$\text{pH} = 1 \text{ M}, \quad \text{H}^+/\text{OH}^- = 10^{-13}$$

Q. 200 ml of 0.1 M HCl + 800 ml of 0.05 M SO_4^{2-} + 1000 ml of 10^{-6} M HNO_3

$$[\text{H}^+] = \frac{(0.1 \times 200) + (8 \times 0.05 \times 800) + (10^{-6} \times 10^3)}{200 + 800 + 1000}$$

$$[\text{H}^+] = \frac{100 + 640 + 10^{-3}}{2000} = 5 \times 10^{-2} \quad \text{pH} = 2 - \log 5$$

$$[\text{H}^+] = 2 \times 10^{-3}$$



② 0.01 M CH_3COOH ($K_a \approx 1.25 \times 10^{-5}$) ⑨

Cal. α , $[\text{H}^+]$, $[\text{OH}^-]$, $[\text{CH}_3\text{COO}^-]$

$$\text{Soln: } \frac{K_a}{c} = \frac{1.25 \times 10^{-5}}{10^{-2}} = 1.25 = \frac{5}{4}$$

$$K_a = \frac{c\alpha^2}{(1-\alpha)} \Rightarrow \frac{K_a}{c} = \frac{\alpha^2}{1-\alpha} \Rightarrow \frac{5}{4} = \frac{\alpha^2}{1-\alpha}$$

$$\Rightarrow 4\alpha^2 + 5\alpha - 5 = 0$$

$$\alpha = \frac{-5 \pm \sqrt{25+80}}{8}$$

$$\alpha = \frac{5.2}{8}$$

$$\alpha = 0.65 (65\%)$$

$$[\text{H}^+] = [\text{CH}_3\text{COO}^-] = c\alpha \\ = 0.65 \times 10^{-2} \\ = 6.5 \times 10^{-3}$$

$$[\text{OH}^-] = \frac{10^{-14}}{6.5 \times 10^{-3}}$$

③ $c = 10^{-3} \text{ M}$, $\alpha = 0.1$, K_a & pH = ?

$$[\text{H}^+] = c\alpha = 10^{-4} \text{ M} \quad \text{pH} = 4$$

$$K_a = \frac{c\alpha^2}{1-\alpha} = \frac{10^{-3} \times (0.1)^2}{1-0.1} = \frac{1}{9} \times 10^{-5} = \frac{10}{9} \times 10^{-5} \\ = 1.11 \times 10^{-5}$$

$$④ K_a = 2.5 \times 10^{-5}$$

$$[\text{H}^+] = 4 \times 10^{-5}$$

$$c, \alpha = ?$$

$$K_a = \frac{c\alpha^2}{1-\alpha}$$

$$K_a = \frac{[\text{H}^+] \alpha}{1-\alpha}$$

$$2.5 \times 10^{-5} = 4 \times 10^{-5} \times \frac{\alpha}{1-\alpha}$$

$$\frac{10}{4} = \frac{4\alpha}{1-\alpha} \Rightarrow 10 - 10\alpha = 16\alpha$$

$$\alpha = \frac{10}{26} = \frac{5}{13} = 0.4 (40\%)$$

$$[\text{H}^+] = c\alpha$$

$$4 \times 10^{-5} = c \times 0.4$$

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

Q. Cal. amount of formic acid ($K_a = 2 \times 10^{-4}$) which should be dissolved in 10 L of water to obtain a solution having pH 3.7.

Soln:

$$\text{pH} = 3.7 = -\log [\text{H}^+]$$

$$[\text{H}^+] = 10^{-3.7} = 10^{-4} \times 10^{0.3}$$

$$[\text{H}^+] = 2 \times 10^{-4}$$

$$K_a = [\text{H}^+] \cdot \frac{\alpha}{1-\alpha}$$

$$2 \times 10^{-4} = 2 \times 10^{-4} \cdot \frac{\alpha}{1-\alpha}$$

$$\alpha = \frac{1}{2} (50\%)$$

Q. Cal. amount of water which should be added in 300 ml of 0.1 M acetic acid soln ($K_a = 10^{-5}$). soln. To double it's
(i) α & (ii) P_H -double.

Soln: 300 ml of 0.1 M CH_3COOH ($K_a \neq 10^{-5}$)

$$\alpha_1 = \sqrt{10^{-4}} \quad \text{pH}_1 = 3, [\text{H}^+] = \sqrt{10^{-5} \times 10^{-1}} = \sqrt{10^{-6}} = 10^{-3}$$

$$= 10^{-2} (\text{H})$$

(i) α -double. Dilution

$$\alpha_2 = 2 \times 10^{-2} (\alpha_1)$$

$$M_1 V_1 = M_2 V_2$$

$$K_a = \frac{C_1 \alpha_1^2}{(1-\alpha_1)} = \frac{S_2 \alpha_2^2}{(1-\alpha_2)}$$

$$0.1 \times (10^{-2})^2 = S_2 \times (2 \times 10^{-2})$$

$$S_2 = \frac{0.1}{4}$$

f(ii) $\text{pH}_2 = 6, [\text{H}^+] = 10^{-6}$

$$10^{-5} = 10^{-6} \times \frac{\alpha}{1-\alpha}$$

$$10 \times 10^{-6} = 10^{-6} \times \frac{\alpha}{1-\alpha}$$

$$\alpha = \frac{10}{11}$$

$$[\text{H}^+] = C\alpha$$

$$10^{-6} = C \times \frac{10}{11} \Rightarrow C = 11 \times 10^{-7}$$

$$[\text{H}^+] = C\alpha$$

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

$$C = 4 \times 10^{-4} \text{ M/l}$$

$$W = C \times V \times M$$

$$= 4 \times 10^{-4} \times 10 \times 45$$

$$= 180 \times 10^{-3}$$

$$W = 0.18 \text{ gm}$$

$$0.1 \times 300 = \frac{0.1}{4} \times V_2$$

$$V_2 = 1200 \text{ ml}$$

$$V_w = 1200 - 300$$

$$= 900 \text{ ml}$$

$$0.1 \times 300 = 11 \times 10^{-7} \times V_2$$

$$30 = \frac{11}{10^7} \times V_2$$

(4) Mix. of SA and WA; - common Ion = H^+ , C.I.E = WA (Q4) 10

$$K_a = \frac{c\alpha^2}{1-\alpha} \text{ (not applicable here)}$$

$$K_a = \frac{[H^+] [A^-]}{[HA]}$$

Assumptions involved are (i) Common Ion (H^+) will be produced only because of SA and contribution from WA is negligible.

(ii) In presence of SA dissociation of WA is almost negligible.

$$\begin{aligned} [H^+] &= [H^+]_{SA} \\ WA \rightarrow [HA]_{initial} &= [HA]_{eq.} \end{aligned}$$

Q. Cal. $[H^+]$, $[CH_3COO^-]$, $[OH^-]$, α , pH of a solution containing 0.1M CH_3COOH ($K_a = 10^{-5}$) and 0.1M HCl (SA).

$$\begin{aligned} \text{Soln: } [H^+] &= 0.1 \\ pH &= 1 \\ [OH^-] &= \frac{10^{-14}}{0.1} \\ &= 10^{-13} \end{aligned}$$

$$\begin{aligned} K_a &= \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \\ 10^{-5} &= \frac{(0.1)(0.1)}{0.1} \\ \alpha &= 10^{-4} \end{aligned}$$

$$\begin{aligned} [CH_3COO^-] &= 0.1 \times 10^{-4} \\ &= 10^{-5} \end{aligned}$$

Q. Cal. pH of a solution containing 0.1M HA ($K_a = 10^{-7}$) and 0.05M H_2SO_4 .

$$\begin{aligned} \text{Soln: } [H^+] &= 0.05 \times 2 = 0.1 \\ pH &= 1 \end{aligned}$$

(iii) also cal. $[A^-]$

$$\begin{aligned} K_a &= \frac{[H^+][A^-]}{[HA]} \\ 10^{-7} &= \frac{0.1 \times 0.1 \times \alpha}{0.1} \\ \alpha &= 10^{-6} \end{aligned}$$

$$\begin{aligned} [A^-] &= c\alpha \\ &= 0.1 \times 10^{-6} \\ &= 10^{-7} \end{aligned}$$

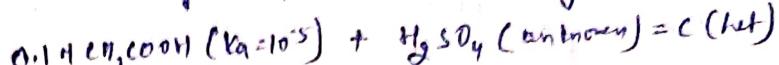
Q. How much H_2SO_4 (in gm) must be added in 500 ml of 0.1 M CH_3COOH ($K_a = 10^{-5}$) to change its degree of dissociation by 200 times.

$$\text{Soln} \quad W = C \times M \times V \\ = C \times 98 \times \frac{1}{2}$$

$$W = 49C$$

$$W = 49 \times 0.1 \text{ gm}$$

$$W = 4.9 \text{ gm}$$



$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$10^{-5} = \frac{(0.1) \times 2c}{(0.1)}$$

$$10^{-5} = \frac{(0.1) \times \frac{10^{-2}}{200} \times 2c}{0.1}$$

$$(d)_{CH_3COOH \text{ dilute}} = \sqrt{10^{-4}} = 10^{-2}$$

$$(d)_{CH_3COOH \text{ (with 2c)}} = \frac{10^{-2}}{200}$$

$$c = 0.1$$

Q. 500 ml of 0.1 M H_2COOH ($K_{ac} = 10^{-4}$) is mixed with 1500 ml of 0.05 M H_2SO_4 . Cal. pH of final solution.

Sol?

$$[H^+] = 2 \times 0.05 \\ = 0.1$$

$$pH = 1 \times \frac{1}{2} \quad (\text{wrong})$$

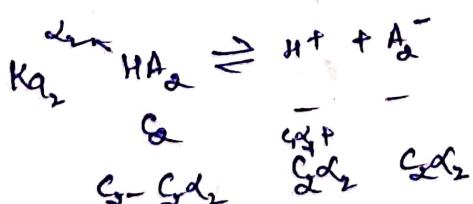
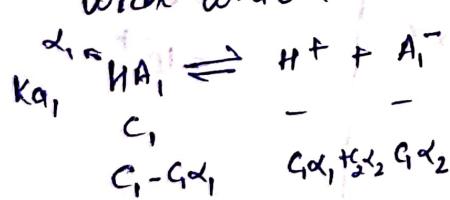
$$[H^+] = 2 \times \frac{15}{400} = \frac{15}{200} = \frac{15}{2} \times 10^{-2}$$

$$pH = 2 - \log \frac{15}{2}$$

$$M_1 V_1 = M_2 V_2 \\ 0.05 \times 500 = M_2 \times 2000 \\ M_2 = \frac{0.05}{4} = \frac{15}{400}$$

Case (ii):- Mix. of WA (WA + WA) :-

Common ion effect, in this case C.I.E. will operate on both weak acid and effect will be more on the electrolyte which is more weaker.



$$HA_1 \rightleftharpoons K_{a_1} = \frac{[H^+][A_1^-]}{[HA_1]} = \frac{(C_1 \alpha_1 + C_2 \alpha_2)(\alpha_1 \alpha_2)}{C_1(1-\alpha_1)^2} \quad (1)$$

$$HA_2 \rightleftharpoons K_{a_2} = \frac{[H^+][A_2^-]}{[HA_2]} = \frac{(C_1 \alpha_1 + C_2 \alpha_2)(\alpha_1 \alpha_2)}{C_2(1-\alpha_2)^2} \quad (2)$$

(1) \div (2)

$$\frac{K_{a_1}}{K_{a_2}} = \frac{\alpha_1}{\alpha_2}$$

$$\Rightarrow \alpha_1 = \frac{K_{a_1}}{K_{a_2}} \times \alpha_2$$

(11)

Putting in ① $K_{a_1} = \left(c_1 \cdot \frac{K_{a_1}}{K_{a_2}} \alpha_2 + c_2 \alpha_1 \right) \times \frac{K_{a_1}}{K_{a_2}} \times \alpha_2$

$$1 = \frac{(c_1 K_{a_1} + c_2 K_{a_2})}{K_{a_2}} \times \frac{\alpha_2^2}{K_{a_2}}$$

$$\boxed{\alpha_2 = \frac{K_{a_2}}{\sqrt{c_1 K_{a_1} + c_2 K_{a_2}}}}$$

$$\alpha_1 = \frac{K_{a_1}}{K_{a_2}} \times \frac{K_{a_2}}{\sqrt{c_1 K_{a_1} + c_2 K_{a_2}}}$$

$$\boxed{\alpha_1 = \frac{K_{a_1}}{\sqrt{c_1 K_{a_1} + c_2 K_{a_2}}}}$$

$$[H^+] = c_1 \alpha_1 + c_2 \alpha_2$$

$$[H^+] = c_1 \cdot \frac{K_{a_1}}{\sqrt{c_1 K_{a_1} + c_2 K_{a_2}}} + c_2 \cdot \frac{K_{a_2}}{\sqrt{c_1 K_{a_1} + c_2 K_{a_2}}}$$

$$\boxed{[H^+] = \sqrt{c_1 K_{a_1} + c_2 K_{a_2}}}$$

$$\boxed{[H^+] = \sqrt{\sum K_{a_i} c_i}} \quad (\text{general}) \quad (\text{sqrt of sum of acid eq})$$

if water is consider.

$$\boxed{[H^+] = \sqrt{\sum K_{a_i} c_i + K_w}}$$

Q. 0.1M HA, ($K_a = 10^{-5}$) + 0.2M HA_2 ($K_a = 4 \times 10^{-5}$)

Cal. $[H^+]$, $[A^-]$, $[A_2^-]$, $[OH^-]$ in solution.

Soln.

$$\begin{aligned} [H^+] &= \sqrt{0.1 \times 10^{-5} + 0.2 \times 4 \times 10^{-5}} \\ &= \sqrt{10^{-6} + 8 \times 10^{-6}} = 3 \times 10^{-3} \end{aligned}$$

$$[OH^-] = \frac{10^{-14}}{3 \times 10^{-3}}$$

$$HA_1 \Rightarrow 10^{-5} = \frac{3 \times 10^{-3} \times [A_1^-]}{0.1} \Rightarrow [A_1^-] = \frac{10^{-3}}{3}$$

$$HA_2 \Rightarrow 4 \times 10^{-5} = \frac{3 \times 10^{-3} \times [A_2^-]}{0.2} \Rightarrow [A_2^-] = \frac{0}{3} \times 10^{-3}$$

Q. 0.1M $HA_1 (K_a = 10^{-5}) + 0.2M HA_2 (K_a = 4 \times 10^{-9})$

Cal. $[H^+]$, $[A_1^-]$, $[A_2^-]$, $[OH^-]$ in soln.

Soln. $[H^+] = \sqrt{0.1 \times 10^{-5} + 0.2 \times 4 \times 10^{-9}} = \sqrt{10^{-6} + 8 \times 10^{-10}} \text{ (neglect)} \\ = 10^{-3} \quad (\text{C.E.F will operate only on } HA_2)$

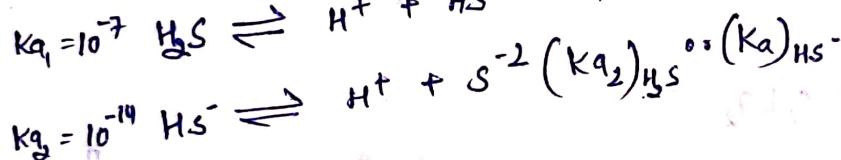
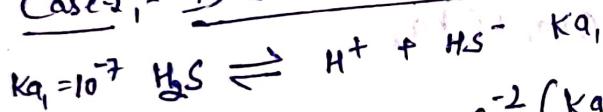
$$HA_1 \Rightarrow \frac{10^{-3} \times [A_1^-]}{0.1} \Rightarrow [A_1^-] = 10^{-3}$$

$$HA_2 \Rightarrow \frac{10^{-3} \times [A_2^-]}{0.2} \Rightarrow [A_2^-] = 8 \times 10^{-7}$$

$$[OH^-] = \frac{10^{-14}}{10^{-3}} = 10^{-11}$$

Case-II:- Polyprotic acid :-

Case-I:- Dibasic acid



$$K_a_1 > K_a_2$$

Note:- ① In aq. soln of polyprotic acid H^+ ion will be produced mainly because of first step and C.E.F. will operate on all the remaining steps.

Q. Cal. $[H^+]$, $[HS^-]$ and $[S^{2-}]$ in 0.1M H_2S solution ($K_a_1 = 10^{-7}$, $K_a_2 = 10^{-14}$)

Soln. $[H^+] = \sqrt{K_a_1 \times C} = \sqrt{10^{-8}} = 10^{-4}, \quad pH = 4$

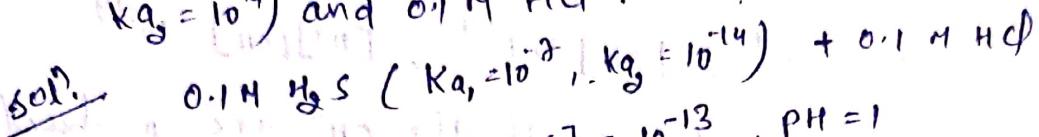
$$[OH^-] = \frac{10^{-14}}{10^{-4}} = 10^{-10}$$

$$K_a_1 = \frac{[H^+][HS^-]}{[H_2S]} \Rightarrow 10^{-7} = \frac{10^{-4} \times [HS^-]}{0.1} \Rightarrow [HS^-] = 10^{-4}$$

$$K_a_2 = \frac{[H^+][S^{2-}]}{[HS^-]} \Rightarrow 10^{-14} = \frac{10^{-4} [S^{2-}]}{10^{-4}} \Rightarrow [S^{2-}] = 10^{-14}$$

Note:- in mixture of weak polyprotic acid and strong acid H^+ will produce salt by SA and $Cd \cdot E$ will operate on all steps of polyprotic acid.

Q. Cal. $[H^+]$, $[HS^-]$, $[S^{2-}]$ in a solⁿ containing 0.1 M H_2S ($K_{a_1} = 10^{-7}$, $K_{a_2} = 10^{-14}$) and 0.1 M HCl.

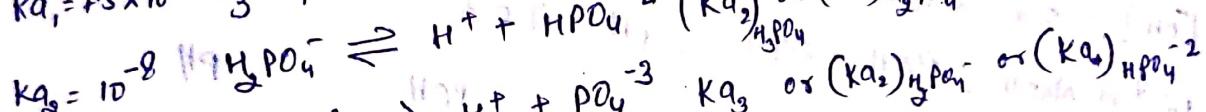
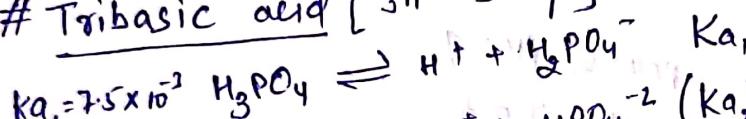


$$[H^+] = 0.1 \text{ M}, [OH^-] = 10^{-13}, pH = 1$$

$$K_{a_1} = \frac{[H^+] [HS^-]}{[H_2S]} \Rightarrow 10^{-7} = \frac{0.1 \times [HS^-]}{0.1} \Rightarrow [HS^-] = 10^{-7}$$

$$K_{a_2} = \frac{[H^+] [S^{2-}]}{[HS^-]} \Rightarrow 10^{-14} = \frac{0.1 \times [S^{2-}]}{10^{-7}} \Rightarrow [S^{2-}] = 10^{-20}$$

Tribasic acid [3 H^+ - 3 steps]



Q. Cal. $[H^+]$, $[OH^-]$, $[H_2PO_4^-]$, $[HPO_4^{2-}]$, $[PO_4^{3-}]$ and $[H_3PO_4]$ in a solⁿ containing 0.1 M H_3PO_4 .

Soln.

$$\frac{K_{a_1}}{C} = \frac{7.5 \times 10^{-3}}{0.1} = 750 \times 10^{-4}$$

$$\frac{K_{a_2}}{C} = \frac{\alpha^2}{1-\alpha} \Rightarrow \frac{750\alpha^2}{10000\alpha} = \frac{\alpha^2}{(1-\alpha)}$$

$$\Rightarrow 40\alpha^2 + 3\alpha - 3 = 0$$

$$\alpha = \frac{-3 \pm \sqrt{9 + 480}}{80}$$

$$\alpha = \frac{-3 + \sqrt{489}}{80}$$

$$\alpha = \frac{-3 + 22}{80}$$

$$\alpha = \frac{19}{80} = 0.25 (25\%)$$

$$[H^+] = [H_2PO_4^-] = Cd = 0.25 \times 0.1 = 2.5 \times 10^{-2}$$

$$[OH^-] = \frac{10^{-14}}{2.5 \times 10^{-2}} = 4 \times 10^{-13}$$

$$[H_3PO_4] = 0.1 (1 - 0.25) = 0.075$$

$$K_{a_2} = \frac{[H^+] [HPO_4^{2-}]}{[H_2PO_4^-]}$$

$$10^{-8} = \frac{2.5 \times 10^{-2} [HPO_4^{2-}]}{2.5 \times 10^{-2}}$$

$$[HPO_4^{2-}] = 10^{-8}$$

$$K_{a_3} \Rightarrow 10^{-13} = \frac{[H^+] [PO_4^{3-}]}{[HPO_4^{2-}]}$$

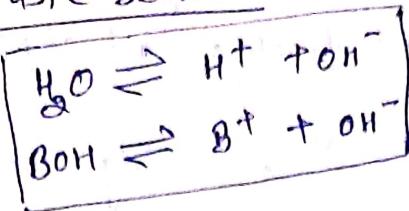
$$10^{-13} = \frac{2.5 \times 10^{-2} [PO_4^{3-}]}{10^{-8}}$$

$$[PO_4^{3-}] = 4 \times 10^{-20}$$



Case-II :- Basic solution. (Base is dissolved in water)

Part-II



Common Ion = OH^-

source of OH^- = $\text{H}_2\text{O} + \text{B}(\text{OH})_3$

source of H^+ = H_2O

$$[\text{H}^+] < [\text{OH}^-]$$

$$\text{at } T = 25^\circ\text{C} \quad [\text{H}^+] < 10^{-7}, \quad [\text{OH}^-] > 10^{-7}, \quad [\text{H}^+][\text{OH}^-] = 10^{-14}$$

Case-II :- strong Base is in ap. salt of S.B all the OH^- are produced from S.B unless the solution is very dilute ($< 10^{-6}\text{ M}$)

Q. Cal. pH of following (i) 10^{-2} M NaOH
(ii) $5 \times 10^{-6}\text{ M Ca(OH)}_2$
(iii) 10^{-8} M NaOH

Salt (i) $[\text{OH}^-] = 10^{-2}$
 $\text{pOH} = 2, \text{pH} = 12$

(ii) $[\text{OH}^-] = 2 \times 5 \times 10^{-6} = 10^{-5}, \text{pOH} = 5, \text{pH} = 9$

(iii) $10^{-8}\text{ M NaOH}, \text{pOH} = 6.97, \text{pH} = 7.03$

<u>[NaOH]</u>	<u>Source of OH⁻</u>	<u>[\text{OH}^-]</u>	<u>pOH</u>
10^{-6}	NaOH only	10^{-6}	6
10^{-2}	NaOH + H_2O	1.62×10^{-2}	6.79
10^{-8}	NaOH + H_2O	1.05×10^{-7}	7.03
10^{-9}	H_2O only	10^{-9}	7

Case-II :- Mix. of SB :- All OH^- will be produced by SB unless one of the given base is very dilute.

$$[\text{OH}^-] = \frac{\sum M_i V_i}{\sum V_i}, \quad [\text{H}^+] = \frac{K_w}{[\text{OH}^-]}$$

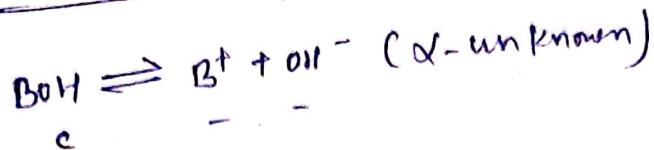
Q. Cal. pH of a solution obtained by mixing 200 ml of 10^{-2} M NaOH , 80 ml of $5 \times 10^{-3}\text{ M Ca(OH)}_2$ and 4 l of water.

Salt $[\text{OH}^-] = \frac{10^{-2} \times 200 + 2 \times 5 \times 10^{-3} \times 80}{200 + 80 + 4000} = \frac{2 + 8}{5000} = \frac{10}{5000} = 2 \times 10^{-3}$

$$\text{pOH} = 3 - \log 2 = 2.7 \quad \text{pH} = 11.3$$

(13)

Case-III weak Base: $K_b \neq C$ - known



$$C - \alpha \quad \alpha \quad \alpha$$
$$K_b = \frac{[B^+] [OH^-]}{[B]_0} = \frac{\alpha^2}{1-\alpha}$$

$$\frac{K_b}{C} = \text{Ratio}, \quad \text{No.} = 25 \times 10^{-14}$$

$$\textcircled{1} \quad \text{if } \frac{K_b}{C} \leq 25 \times 10^{-14} \quad \alpha = \sqrt{\frac{K_b}{C}}, \quad [OH^-] = \alpha = C \sqrt{\frac{K_b}{C}}$$

$$\textcircled{2} \quad \text{if } \frac{K_b}{C} > 25 \times 10^{-14} \quad K_b = \frac{\alpha^2}{1-\alpha}, \quad [OH^-] = \alpha, \quad [H^+] = \frac{10^{-14}}{[OH^-]}$$

Q. NH_4OH ($K_b = 10^{-5}$)

Cal. pH of 0.1 M, NH_4OH solution

$$\text{Soln: } C = 0.1 \quad \frac{K_b}{C} = 10^{-4} \quad [OH^-] = \sqrt{10^{-5} \times 0.1} = 10^{-3} \quad pOH = 3 \\ pH = 11$$

Q. How much CH_3NH_2 ($K_b = 10^{-4}$) should be dissolved in 5 l of water such that final soln contains 5×10^{-11} moles of H^+ ion.

$$\text{Soln: } CH_3-NH_2 + H_2O \rightleftharpoons CH_3-NH_3^+ + OH^-$$
$$[H^+] = \frac{5 \times 10^{-11}}{5} = 10^{-11}, \quad [OH^-] = 10^{-3}$$
$$K_b = 10^{-4} \quad M = C V M \\ = 11 \times 10^3 \times 5 \times 31 \\ = 1.815 \text{ gm.}$$
$$K_a = \frac{[H^+] \alpha}{1-\alpha}, \quad K_b = \frac{[OH^-] \alpha}{1-\alpha}$$
$$10^{-4} = \frac{10^{-3} \cdot \alpha}{1-\alpha} \quad \alpha = \frac{1}{11}$$
$$[OH^-] = C \alpha \quad 10^{-3} = C \times \frac{1}{11} \\ C = 11 \times 10^{-3}$$

Case-IV Mix. of SB + WB.

$$C. S. = OH^-$$

$$\boxed{K_b = \frac{\alpha^2}{1-\alpha}}$$

$$(i) [OH^-] = [OH^-]_{SB}$$

$$(ii) [WB]_{\text{initially}} = [WB]_{\text{eq.}}$$

$$(iii) [B^+]_{WB} = \alpha$$

$$(iv) K_b = \frac{[B^+] [OH^-]}{[B]_0}$$

Q. How much NaOH should be added in 500 ml of 0.1 M NH_4OH ($K_b = 10^{-5}$) solution such that $[NH_4^+]$ equals to 10^{-5} mole/litre.

$$\begin{aligned}
 \text{Soln: } W &= C V M \\
 &= C \times \frac{1}{2} \times 40 \\
 W &= 20 \text{ g} \\
 W &= 20 \times 0.1 \\
 &= 2 \text{ gm}
 \end{aligned}
 \quad
 \begin{aligned}
 0.1 \text{ M } \text{NH}_4\text{OH} + \text{NaOH} \\
 K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} \\
 10^{-5} = \frac{10^{-5} \times [\text{OH}^-]}{0.1} \\
 [\text{OH}^-] = 0.1, c = 0.1
 \end{aligned}$$

Case-ii:- Mix. of WBi:- $[\text{OH}^-] = \sqrt{K_b c_1 + K_b c_2}$

Q. Cal. pH of a solution obtained by mix. 500 ml of 0.4M B_2OH ($K_b = 10^{-3}$) and 1500 ml of 0.6M $\frac{0.6}{3} \text{B}_2\text{OH}$ ($K_b = 4 \times 10^{-7}$)

$$\text{Soln: } \text{B}_2\text{OH} \Rightarrow 0.4 \times 500 = \text{H}_2 \times 2000 \Rightarrow \text{H}_2 = 0.1$$

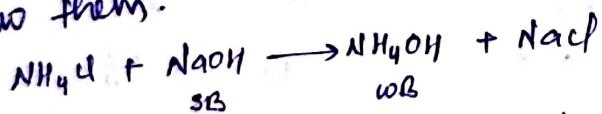
$$\text{B}_2\text{OH} \Rightarrow \frac{0.6}{3} \times 1500 = \text{H}_2 \times 2000 \Rightarrow \text{H}_2 = 0.2$$

$$\begin{aligned}
 [\text{OH}^-] &= \sqrt{10^{-3} \times 0.1 + 4 \times 10^{-7} \times 0.2} \\
 &= \sqrt{10^{-8} + 8 \times 10^{-8}} = \sqrt{9 \times 10^{-8}} = 3 \times 10^{-4}
 \end{aligned}$$

$$\text{pOH} = 4 - \log 3 = 4 - 0.48 = 3.52$$

$$\text{pH} = 10.48$$

Part-III:- Acid and Base are mixed together.
whenever acid and base are mixed together always write first
Rxn b/w them.



Note:- In general whenever in eq. two components having no common
Ion b/w them are giving given always think of possibility
of Rxn b/w them.

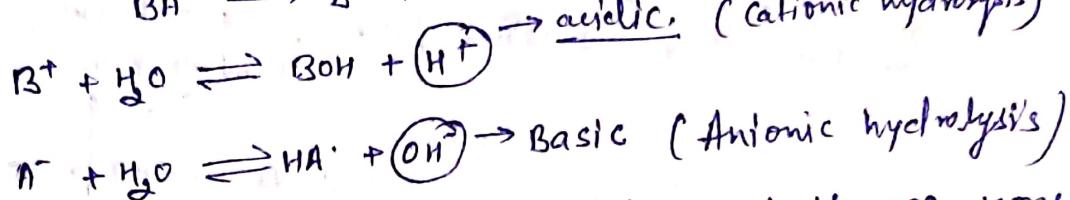
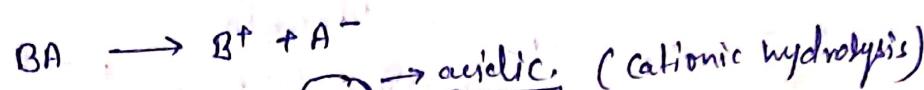
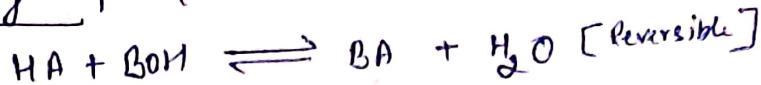


Case-I:- when acid + Base are in equal proportion (salt hydrolysis)

if acid + Base are mixed in equal proportion i.e. both are
L.R. then our final soln contains only salt so it will be a
case of salt hydrolysis.

Salt Hydrolysis :- (water Reactant in it will act as solvent in it)

(14)



phenomenon of interaction of cation or anion or both or none of the salt with water to produce acidic, basic or neutral solution is known as salt hydrolysis. $HA + BOH \rightleftharpoons BA + H_2O \quad [\text{Reversible}]$

Forward direction $\Rightarrow ABN$ [Extent - More] (Acid-base Neutralization)

Backward direction $\Rightarrow SH$ [Less] (salt hydrolysis)

$K_{ABN} = \frac{1}{K_h}$ (SH is endothermic process) (Neutralization = exo)

Case-I: Strong Acid and strong Base. ($SASB$):

SA $[H_1V_1] - H^+$, millimoles of $H^+ = H_1V_1 = a$

SB $[H_2V_2] - OH^-$, millimoles of $OH^- = H_2V_2 = b$

Case I $a = b$

Case-II

$a > b$

Case-II $b > a$

Neutral. (salt) $\Rightarrow SH$

Acidic

$$\text{Source} \quad SA - [H^+] = \frac{a-b}{V_1+V_2}$$

Basic

$$SB \rightarrow [OH^-] = \frac{b-a}{V_1+V_2}$$

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

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

Q. 200 ml of 0.1 M HCl is mixed with 300 ml of 0.1 M NaOH cal pH of the final solution.

$$a = H_1V_1 = 0.1 \times 200 = 20$$

$$b = H_2V_2 = 0.1 \times 300 = 30$$

$$[OH^-] = \frac{30-20}{500} = \frac{10}{500} = 2 \times 10^{-3}$$

$$Poh = 3 - \log 2 = 2.7$$

$$pH = 11.3$$

Q. Cal. Volume of 0.1 M NaOH which should be added in 300 ml of HCl solution having pH = 2 to change its pH by 2 units.

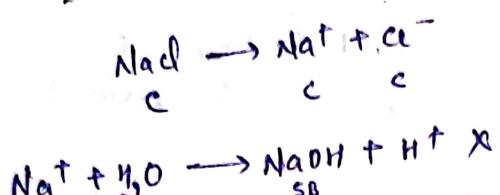
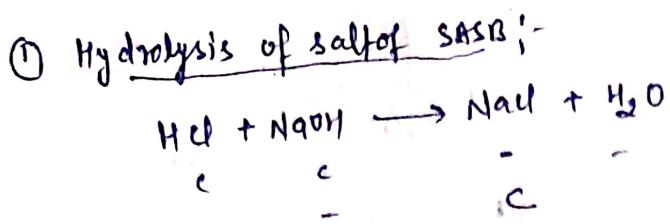
$$\begin{aligned} \text{Soln.} \quad & 300 \text{ ml of HCl soln} \\ & pH = 2 \quad [H^+] = 10^{-2} \\ & \text{(acidic)} \\ & a = H_1V_1 = 10^2 \times 300 \\ & = 3000 \end{aligned}$$

$$pH = 2 + 2 = 4 \quad (\text{acidic}), \quad b = V \times 0.1$$

$$[H^+] = \frac{a-b}{V_1+V_2} \quad b = 0.1V$$

$$10^{-4} = \frac{3000 - 0.1V}{300 + V} \Rightarrow 0.03 + 10^{-4}V = 3 - 0.1V$$





(No hydrolysis) Neutral, pH = 7

Source of H⁺ or OH⁻ \Rightarrow water.

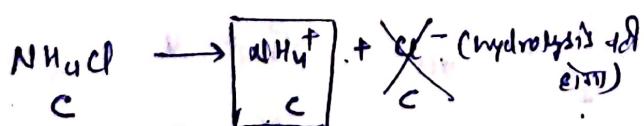
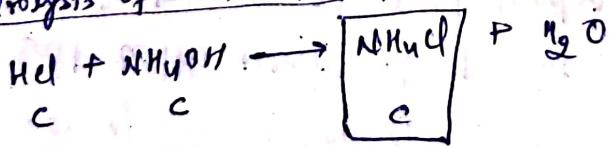
Anions which will not hydrolyse $\Rightarrow \text{ClO}_4^-, \text{SO}_4^{2-}, \text{NO}_3^-, \text{Cl}^-, \text{Br}^-, \text{I}^-$

Cations which will not hydrolyse $\Rightarrow \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+, \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}$

Q. Which of the following salts undergo hydrolysis. also identify the ion undergoing hydrolysis and nature of aqueous soln.

- | | | |
|--|---|---|
| ① <u>CaSO_4</u>
(No hydrolysis)
Neutral. | ⑤ <u>HCOONa</u>
AH , Basic C | ⑧ <u>$\text{Sr}(\text{NO}_3)_2$</u>
NO_3^- |
| ② <u>CH_3COONa</u>
Anionic Hyd., Basic C | ⑥ <u>$\text{CH}_3\text{NH}_3^+ \text{Cl}^-$</u>
CH_3 , A | ⑨ <u>$\text{CH}_3\text{COONH}_4$</u>
$(\text{C}+\text{A})\text{H}$, Neutral. |
| ③ <u>NH_4^+</u>
Cationic Hyd., Acidic. | ⑦ <u>$\text{CH}_3\text{NH}_3^+ \text{Br}^-$</u>
CH_3 , A | ⑩ <u>KI</u>
(No Hyd.) Neutral. |
| ④ <u>NaClO_4</u>
(No Hyd.) Neutral | | |

② Hydrolysis of salt SA + BOB :-



CH₄, Acidic pH < 7

① general hydrolysis Rxn :-



$$\text{Hydrolysis constant } K_h = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]} \quad \text{--- (1)}$$

$$(K_a)_{\text{NH}_4^+} \times (K_b)_{\text{NNH}_3^+} = K_w$$

(15)

② Relation b/w K_h , K_w , K_b :-

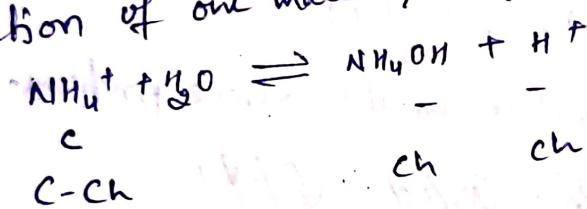
$$K_w = [H^+] [OH^-] \quad \text{--- (1)}$$

$$K_b = \frac{[NNH_3^+] [OH^-]}{[NNH_2ON]} \quad \text{--- (2)}$$

$$\text{Q + S} \quad \frac{K_w}{K_b} = \frac{[NNH_2ON]}{[NNH_3^+] [H^+]}$$

formula:
$$\frac{K_w}{K_b} = K_h \quad \text{--- (a)}$$

③ Relation b/w K_h & h :- $h \Rightarrow$ degree of hydrolysis f. defined as fraction of one mole hydrolysed.



$$K_h = \frac{ch \times ch}{c(c-h)} \Rightarrow K_h = \frac{ch^2}{(1-h)} \quad \left\{ \text{Ratio } \frac{K_h}{c} = ? \right\}$$

$$\text{if } h \leq 5\%, \quad 1-h \approx 1, \quad K_h = ch^2 \quad h = \sqrt{K_h/c}$$

④ Derivation of pH :- $[H^+] = c \times h$

$$= c \times \sqrt{\frac{K_h}{c}} = \sqrt{K_h \times c}$$

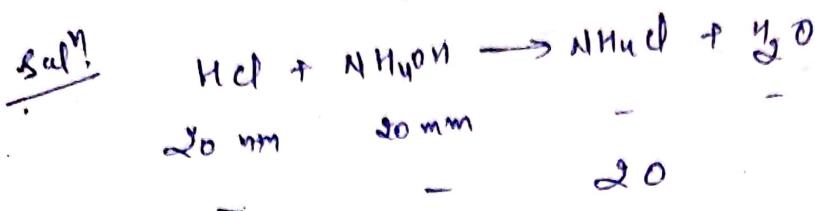
$$[H^+] = \sqrt{\frac{K_w \times c}{K_b}}$$

$$\log [H^+] = \frac{1}{2} [\log K_w - \log K_b + \log c]$$

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

$$\text{pH} = \frac{1}{2} [\text{p}K_w - \text{p}K_b - \log c]$$

Q. Cal. pH of a salt obtained by mixing 200 ml of 0.1 M NH_4OH ($K_b = 10^{-5}$) and 200 ml of 0.1 M HCl.



$$[\text{NH}_4^+] = \frac{20}{400} = \frac{1}{20}$$

$$[\text{NH}_4^+] = \frac{1}{20}$$

$$\text{pH} = \frac{1}{2} [\text{pK}_w - \text{pK}_b - \log c] \quad \begin{matrix} \text{sum concentration} \\ \text{hydrolysis effect} \end{matrix}$$

$$= \frac{1}{2} [14 - 5 - \log \frac{1}{20}]$$

$$= \frac{10.3}{2} = 5.15 \text{ (acidic)}$$

Q. also cal. K_h & h of salt produced in the above problem.

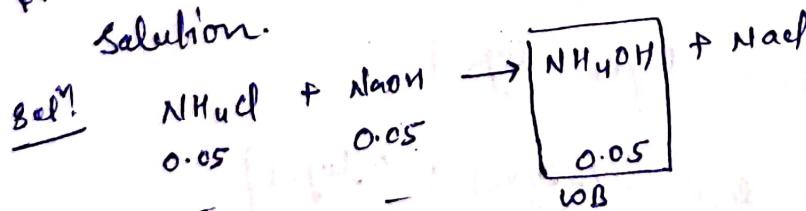
salt: $K_h = \frac{10^{-14}}{10^{-5}} = 10^{-9}$ $K_h = \sqrt{K_w K_b} = \sqrt{\frac{10^{-14}}{2}} = 1.4 \times 10^{-7}$

$$h = \sqrt{\frac{K_h}{c}} = \sqrt{\frac{10^{-9}}{1/20}} = \sqrt{\frac{20 \times 10^{-9}}{1/2 \times 10^{-7}}} = 1.4 \times 10^{-4}$$

Q. also cal. equilibrium constant of the Rxn b/w HCl and NH_4OH

salt: K_{RN} $= \frac{1}{K_h} = 10^9$

Q. cal. the change in pH when 0.05 M NaOH is added to the above solution.



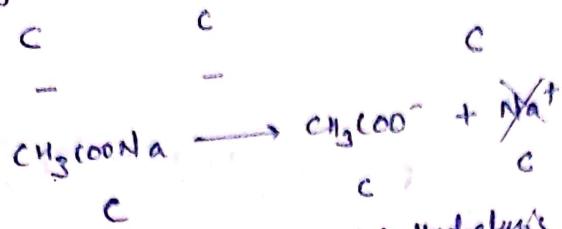
$$\frac{K_b}{c} = \frac{10^{-5}}{0.05} = 200 \times 10^{-4}$$

$$K_b = \frac{c\alpha^2}{1-\alpha}, [\text{OH}^-] = C\alpha, [\text{H}^+] = \frac{10^{-14}}{[\text{OH}^-]}$$

$$\text{pOH}, \text{pH} = ?$$

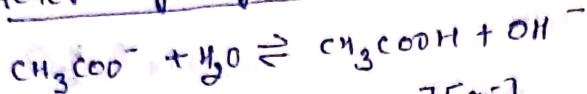
$$\text{change in pH} = ?$$

(3) Hydrolysis of salt of WA and SB:-



Anionic Hydrolysis
Basic, pH > 7

(1) General hydrolysis Rxn:-



$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} \quad \text{--- (1)}$$

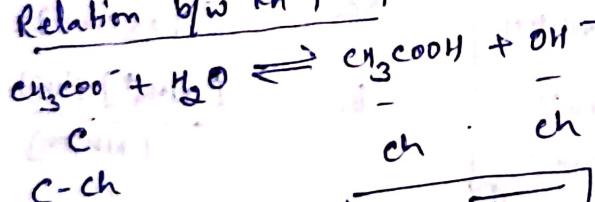
(2) Relation b/w K_h , K_w , K_a

$$K_w = [\text{OH}^-][\text{H}^+] \quad \text{--- (2)}$$

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} \quad \text{--- (3)}$$

$$(2) \div (3) \Rightarrow \boxed{\frac{K_w}{K_a} = K_h}$$

(3) Relation b/w K_h & h :-



$$K_h = \frac{ch^2}{1-h} \Rightarrow \boxed{h = \sqrt{\frac{K_h}{c}}}$$

(4) Derivation of PH:-

$$[\text{OH}^-] = ch \Rightarrow c \times \sqrt{\frac{K_h}{c}} = \sqrt{K_h \times c}$$

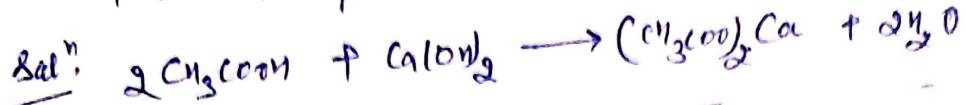
$$[\text{OH}^-] = \sqrt{\frac{K_w \times c}{K_a}} \Rightarrow [\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{K_w}{\sqrt{\frac{K_w \times c}{K_a}}} = \sqrt{\frac{K_w \times K_a}{c}}$$

$$\boxed{[\text{H}^+] = \sqrt{\frac{K_w \times K_a}{c}}}$$

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

$$\boxed{\text{PH} = \frac{1}{2} [\text{PK}_w + \text{PK}_a + \log c]}$$

Q. Cal. pH of a salt obtained by mixing 20 ml of 0.1 M Acetic acid ($K_a = 10^{-5}$) and 50 ml of 0.2 M calcium hydroxide ($\text{Ca}(\text{OH})_2$).



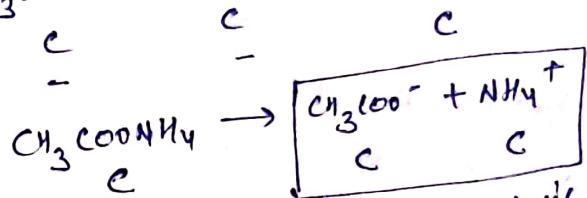
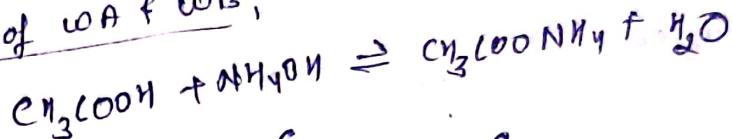
$$\begin{array}{ccc} \text{mili} & 20 & 10 \\ \text{molar} & - & - \\ & - & 10 \end{array}$$

$$[(\text{CH}_3\text{COO})_2\text{Ca}] = \frac{10}{250} = \frac{1}{25}$$

$$[\text{CH}_3\text{COO}^-] = 2 \times \frac{1}{25} = \frac{2}{25}$$

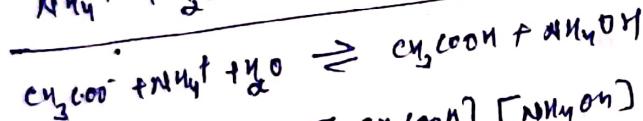
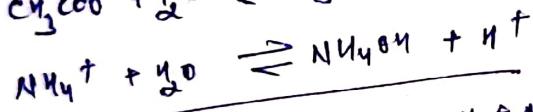
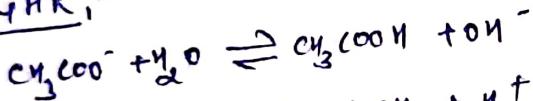
$$\text{pH} = \frac{1}{2} [14 + 5 + \log \frac{2}{25}]$$

④ Hydrolysis of salt of HA & OB^- :



(C+A) Hydrolysis.
A/B/Neutral.

⑤ GHR:-



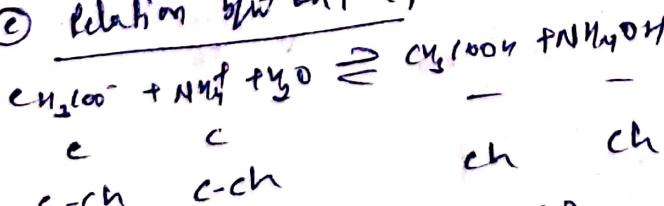
$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{NH}_4\text{OH}]}{[\text{CH}_3\text{COO}^-][\text{NH}_4^+]}$$

⑥ $\div 3 \times 4$

$$\boxed{\frac{K_w}{K_a \times K_b} = K_h} \quad \leftarrow (\text{a})$$

large.

⑦ Relation b/w K_h & K_i :-



$$K_h = \frac{ch \times ch}{c(1-h)(1-h)} = \frac{h^2}{(1-h)^2} \quad \boxed{\text{(b)}}$$

der of. pH:-

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

$$K_a = \frac{c(1-h) \times h^2}{ch}$$

$$[H^+] = K_a \times \frac{h}{1-h}$$

$$[H^+] = K_a \times \sqrt{K_w}$$

$$[H^+] = K_a \times \sqrt{\frac{K_w}{K_a \times K_b}}$$

$$[H^+] = \sqrt{\frac{K_w \times K_a}{K_b}}$$



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

$$\boxed{\text{pH} = \frac{1}{2} [PK_w + PK_a - PK_b]}$$

Q. $\text{CH}_3\text{COONH}_4$ ($K_a = 10^{-5}$, $K_b = 10^{-5}$)

$$PK_a = 5, \quad PK_b = 5$$

$$\text{pH} = \frac{1}{2} [14] = 7 \text{ (Neutral)}$$

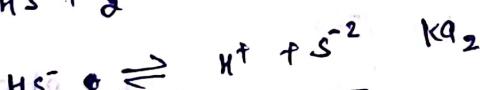
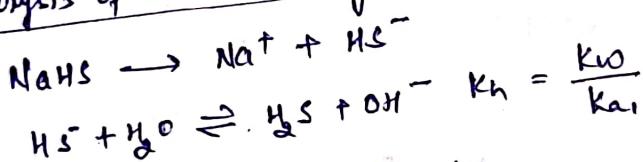
Q. HCOONH_4 ($K_a = 10^{-4}$, $K_b = 10^{-5}$)

$$PK_a = 4, \quad PK_b = 5$$

$$\text{pH} = \frac{1}{2} [14 + 4 - 5] = \frac{13}{2} = 6.5 \text{ (acidic)}$$

Note:- degree of dissociation and pH of solution of salt of weak acid & weak base does not depend upon concentration i.e. it is independent from dilution.

(5) Hydrolysis of salt containing Amphiprotic Anion:-



$$\boxed{\text{pH} = \frac{PK_{a_1} + PK_{a_2}}{2}} \quad (\text{conc. independent})$$

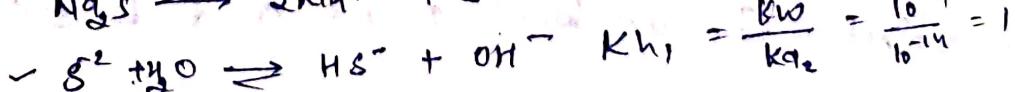
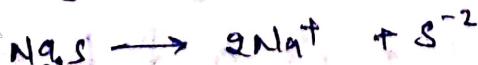
Ex: NaHCO_3 , NaHSO_3 , Na_2HPO_4 , Na_2HPo_4 .

Q. Calc. pH of 0.1 M NaHS solution ($K_{a_1} = 10^{-7}$, $K_{a_2} = 10^{-14}$)

$$\text{pH} = \frac{PK_{a_1} + PK_{a_2}}{2} = \frac{7 + 14}{2} = 10.5$$

(6) Hydrolysis of salt containing polyvalent anion:-

Ex: Na_2S , Na_2CO_3 , Na_3PO_4 , Na_2SO_3



Q. $\text{CH}_3\text{CH}_2\text{NH}_2\text{COONH}_4$ ($K_a = 10^{-6}$, $K_b = 10^{-5}$)

$$PK_a = 6, \quad PK_b = 5$$

$$\text{pH} = \frac{1}{2} [14 + 6 - 5]$$

$$= 7.5 \text{ (Basic)}$$

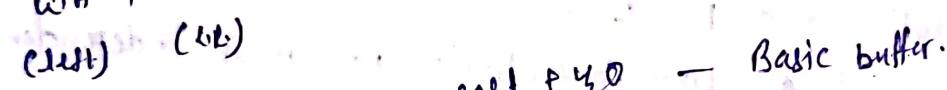
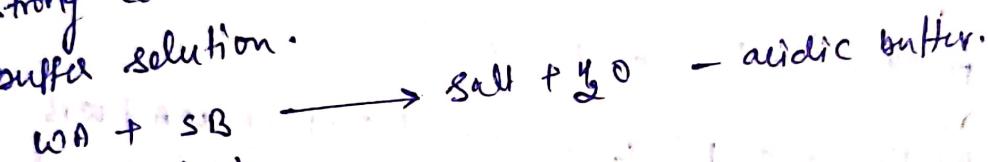
Q. Cal. pH of 0.1 M Na_2S solution.

$$K_{\text{b}} = \frac{c\text{H}^2}{(1-\text{H})} \Rightarrow 1 = \frac{0.1\text{H}^2}{(1-\text{H})} \Rightarrow \text{H}^2 + 10\text{H} - 10 = 0$$

$$\text{H} = \frac{-10 \pm \sqrt{100+40}}{2} = \frac{1.8}{2} = 0.9 \text{ (approx.)}$$

$$[\text{OH}^-] = \text{cH} = 9 \times 10^{-7}, \text{pOH} = 2 - \log 9 = 1.04, \text{pH} = 12.96$$

Part-II: Case-II: when amount (eq.) of acid & base are unequal then any one component will be finished and other will be remained in the solution. when $w_A \neq w_B$ remaining in the solution after the Rxn with their strong counter part then that type of solution is known as buffer solution.



Buffer Solution:-

Q. what is pH of 1L of pure water.

$$\text{pH} = 7$$

Q. 1L of pure water $\xrightarrow{0.365 \text{ gm HCl}}$ $[\text{HCl}] = \frac{0.365/36.5}{1} = 10^{-2}$ $[\text{H}^+] = 10^{-2}, \text{pH} = 2$

$$\Delta \text{pH} = 5.$$

Q. 1L of pure water $\xrightarrow{0.4 \text{ gm NaOH (BaK)}}$ $[\text{NaOH}] = \frac{0.4/40}{1} = 10^{-2}$ $[\text{OH}^-] = 10^{-2}, \text{pH} = 12, \Delta \text{pH} = 5$

Defn:- A solution whose pH does not change on the addition of small amount of acid or base or by dilution is known as buffer solution.

Buffer solution contain both acidic and basic part.

② Properties of Buffer Solution:-

- ① It has a constant pH.
- ② pH does not change on dilution.
- ③ pH does not change on standing for long.
- ④ pH does not change (slightly change) by the addition of small amount of acid or base.

⑤ Buffer Range:- Range of a buffer solution over which it is effective. (pH \neq change on dilution)

⑥ Buffer Action:- Action of buffer solution on the addition of small amount of acid or base by which it resists the change in pH.

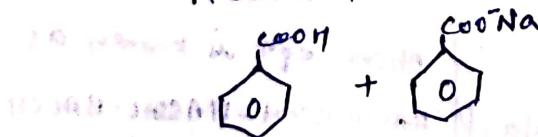
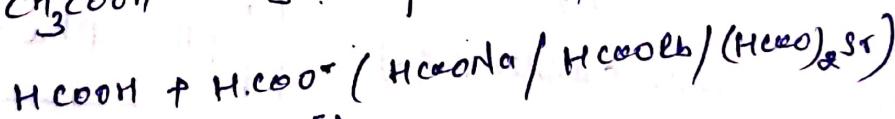
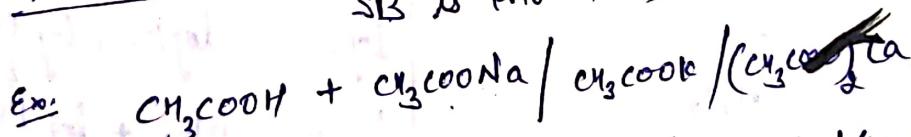
⑦ Types of Buffer Solution:-

① Simple Buffer:- 1 component

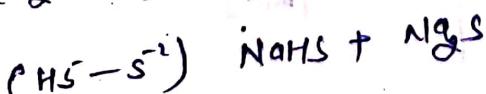
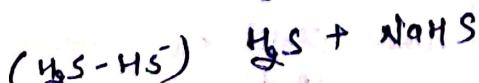
Ex: salt of weak
 CH_3COONa (salt hydrolysis)

② Mixed Buffer:- 2 components

(i) Acidic Buffer:- A solution containing WA and its salt with SB is known as acidic Buffer.



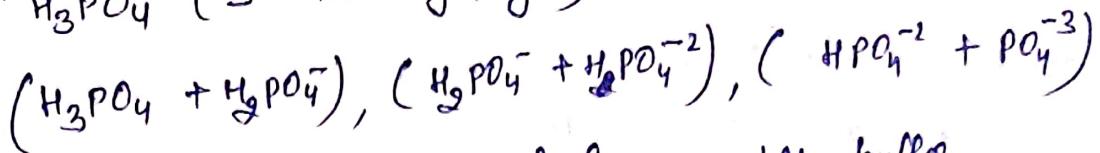
$\text{HS} - 2$ (acidic hydrogen)



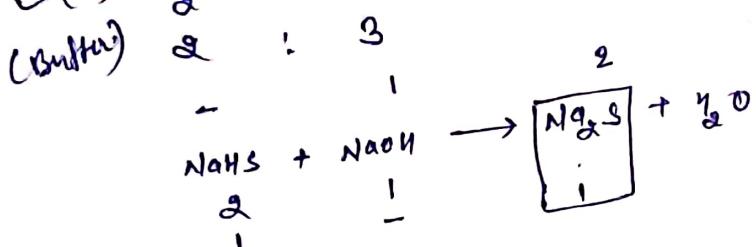
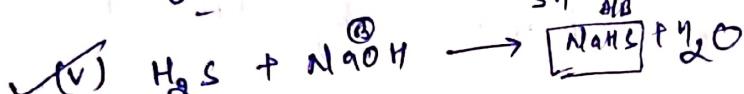
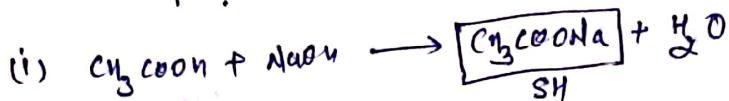
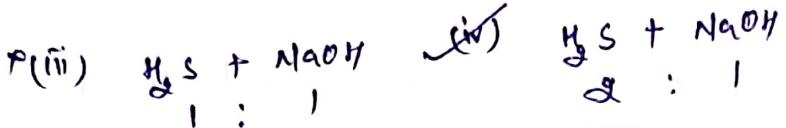
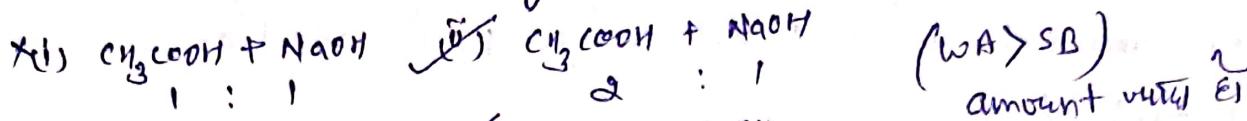
Acid + CB.

Buffer (acidic)

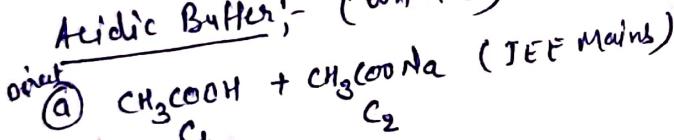
Ex: H_3PO_4 (3 acidic Hydrogen)



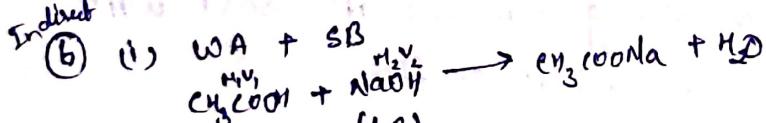
Q. which of the following will form acidic buffer.



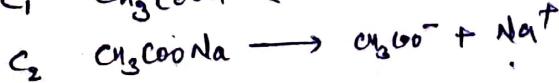
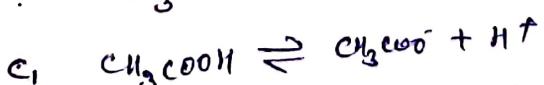
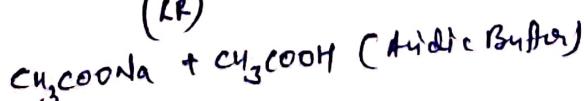
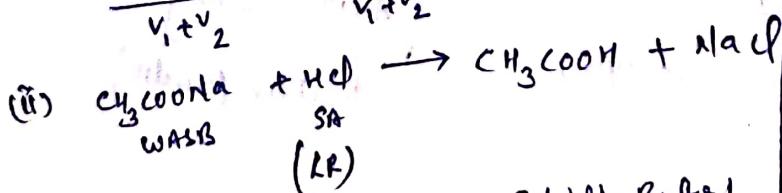
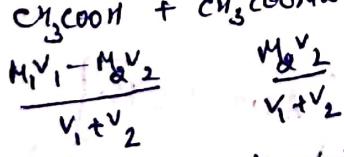
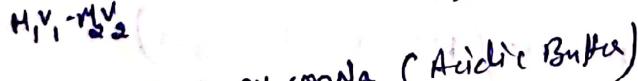
Acidic Buffer:- ($\text{wA} + \text{cB}$)



direct



三



$$R_a = \frac{[Cu_3(COON)]^n}{[Cu_3(COON)]} \rightarrow [Cu_3(COON)]$$

$$[H^+] = \frac{K_a [CH_3COO^-]}{[CH_3COOH] \rightarrow [salt]}$$

$$-\log(n^+) = -\log K_a + \log \frac{[\text{Acid}]}{[\text{salt}]}$$

$$pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

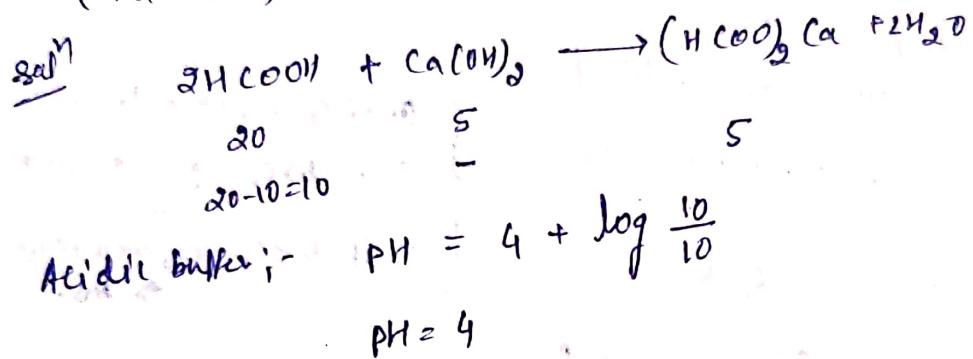
Above eqn is known as HENDERSON-HASSELBALCH equation for acidic buffer and it is applicable

when $\frac{[\text{salt}]}{[\text{Acid}]} \leq 10$

Q. Cal. pH of a salt containing 0.1M CH_3COO^- ($K_a = 10^{-5}$) and 0.2M CH_3COONa . (17)

$$\text{salt? } \text{pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]} \\ = 5 + \log \frac{0.2}{0.1} = 5 + 0.3 = 5.3$$

(Q) Cal. pH of a salt obtained by mixing 20 ml of 0.1M HCOOH ($K_a = 10^{-4}$) and 50 ml of 0.1M Ca(OH)_2 .



Buffer Range:-

Min. pH:- $\frac{[S]}{[A]} = \frac{1}{10} \Rightarrow (\text{pH})_{\min} = \text{pK}_a + \log \frac{1}{10}$

$$(\text{pH})_{\min} = \text{pK}_a - 1$$

Max. pH:- $\frac{[S]}{[A]} = 10 \Rightarrow (\text{pH})_{\max} = \text{pK}_a + \log 10$

$$(\text{pH})_{\max} = \text{pK}_a + 1$$

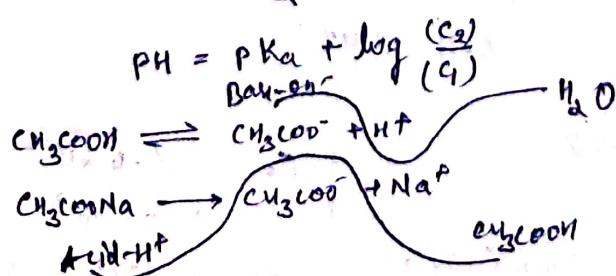
$$\boxed{\text{pK}_a - 1 \leq \text{B.R.} \leq \text{pK}_a + 1}$$

Best Buffer:- A Buffer salt whose resistance for change in pH is max.

is known as best buffer $\frac{[S]}{[A]} = 1$

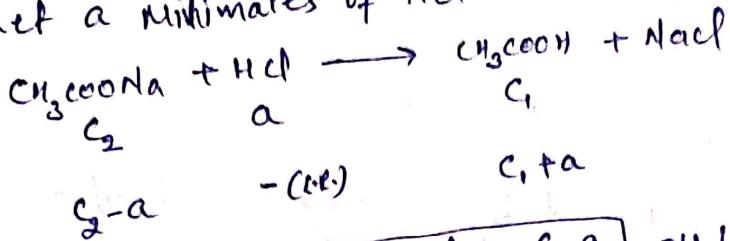
$$\boxed{\text{pH} = \text{pK}_a}$$

Buffer Action:- $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$ (original buffer)



① Strong Acid (SA) is added :-

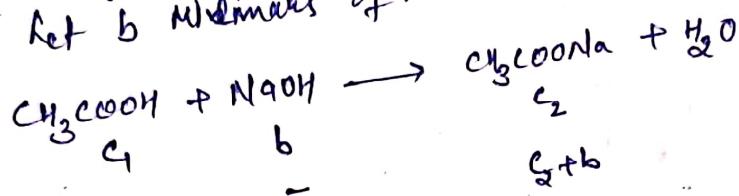
Let a millimoles of HCl are added.



$$\boxed{\text{pH} = \text{pK}_a + \log \frac{c_2-a}{c_1+a}} \quad \text{pH} \uparrow (\text{effect anti } \text{EII})$$

② Strong base is added

Let b millimoles of NaOH are added



$$\boxed{\text{pH} = \text{pK}_a + \log \frac{(c_2+b)}{(c_1-b)}} \quad \text{pH} \uparrow$$

- ① if $c_2 = b$, $\text{CH}_3\text{COONa} \Rightarrow \text{SB}$
- ② if $b > c_2$, $\frac{\text{NaOH} + \text{CH}_3\text{COONa}}{\text{SB}}$
- ③ if $b < c_2$, $\text{CH}_3\text{COONa} + \text{CH}_3\text{COOH} \Rightarrow \text{AB}$.

Q. 12 gm of CH_3COOH and 82 gm of CH_3COONa are dissolved in 1 l of water. $(\text{K}_a)_{\text{CH}_3\text{COOH}} = 10^{-5}$

④ Cal. pH of resulting sol?

⑤ change in pH when 3.65 gm of HCl are added $n_{\text{HCl}} = \frac{3.65}{36.5} = 0.1$

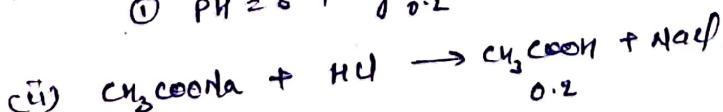
⑥ change in pH when 7.3 gm of HCl $n_{\text{HCl}} = \frac{7.3}{36.5} = 0.2$

⑦ change in pH when 10.95 gm $n_{\text{HCl}} = 0.3$

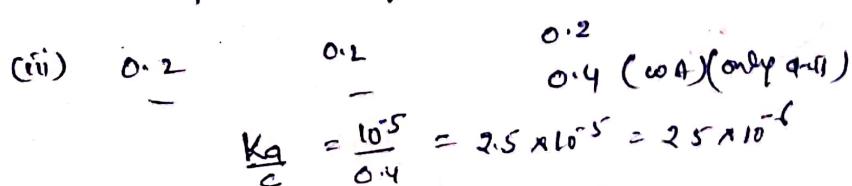
⑧ change in pH when 0.1 gm NaOH $n_{\text{NaOH}} = 0.001$

Ans. $n_{\text{AA}} = \frac{12}{60} = 0.2$, $n_{\text{SA}} = \frac{16.4}{82} = 0.2$

$$\text{① } \text{pH} = 5 + \log \frac{0.2}{0.2} = 5$$



$$\text{② } \text{pH} = 5 + \log \frac{0.1}{0.3} = 4.52$$

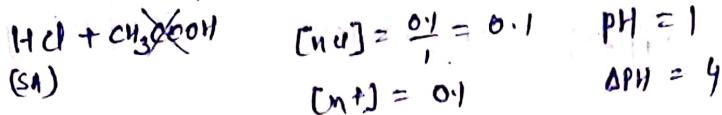


$$[\text{H}^+] = \sqrt{2.5 \times 10^{-6}} = 2 \times 10^{-3}$$

$$\text{pH} = 3 - \log 2 = 2.7$$

$$\Delta \text{pH} = 2.3$$

(iv) 0.2 0.3 0.2
- 0.1 0.4



$$(V) \quad \text{CH}_3\text{COOH} + \text{NaOH} \longrightarrow \text{CH}_3\text{COONa} + \frac{1}{2}\text{O}_2$$

0.2	0.1	0.2
0.1	-	0.3

$$pH = 5 + \log \frac{0.3}{0.1} = 5.48$$

Basic Buffer: - (weak salt)

④ Direct: $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$

⑥ Indirect :- (i) $\text{HCl} + \text{NH}_3 \rightarrow \text{NH}_4\text{Cl}$ (L.R.) B.B.

(ii) $\boxed{\text{NH}_2\text{C}_6\text{H}_4\text{CH}_3} + \text{NaOH}_{\text{aq}} \rightarrow \boxed{\text{NH}_2\text{C}_6\text{H}_4\text{CH}_2\text{OH}}_{\text{aq}} + \text{NaCl}$

$$\text{C.I.E.} \quad \begin{cases} \text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^- \\ \text{NH}_4\text{I} \rightleftharpoons \text{NH}_4^+ + \text{I}^- \end{cases}$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$

$$[OH^-] = K_b \times \frac{[NH_4OH]}{[NH_4^+]} \rightarrow [Base] \rightarrow [Salt]$$

$$-\log [OH^-] = -\log K_b + (-\log \frac{[Base]}{[Conc]})$$

$$pOH = pK_b + \log \frac{[\text{salt}]}{[\text{Base}]}$$

Henderson eqⁿ

$$\frac{1}{10} \leq \frac{[e]}{[E]} \leq 10$$

Q. Cal. pH of a solⁿ containing 0.1 M
~~Ammonium~~ and 0.2 M $(\text{NH}_4)_2\text{SO}_4$

$$(k_b)_{\text{N}_2\text{O}_4} = 10^5$$

Salt.

Basic Buffer.

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{salt}]}{[\text{Base}]}$$

$$= 5 + \log \frac{0.4}{0.1}$$

$$= 5 + \log 4$$

$$= 5.6$$

$$\text{pH} = 8.4$$

Buffer Range:-

$$(P_{\theta n})_{\min} \frac{[S]}{[E]} = \frac{1}{10}$$

$$(P_{\text{on}})_{\min} = P_{\text{thr}}^{-1}$$

$$(P_{ON})_{max} \Rightarrow \frac{[S]}{[CrS]} = 10$$

$$(P\Theta h)_{\max} = P\kappa_b + 1$$

$$\underline{\text{Best Buffer}}: - \frac{[S]}{[NS]} = 1$$

$$P_{OH} = P_{OB}$$

Solubility and Solubility product :-

Types of salt :-

(a) Highly soluble salt :- (HS^2) salts which are completely soluble in water. Solubility - High

All NO_3^- are water soluble.

All compounds of Na^+ / K^+ / Rb^+ / Cs^+ / NH_4^+ are water soluble.

(b) Sparingly soluble salt :- (S^2) salts which are insoluble in water. Solubility - Negligible

ex. AgCl , AgBr , AgF , All PO_4^{3-} , S^{2-} .

white yellow yellow
light dark

PPT - Sparingly soluble salt

Do not form PPT - HS^2

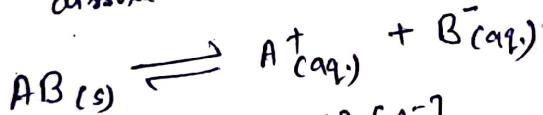
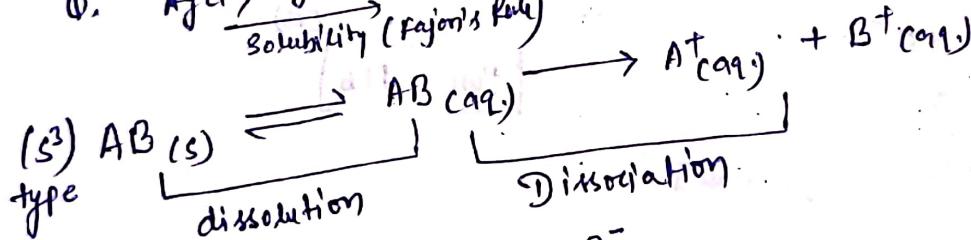
Q. Which of following is soluble

~~Iract~~ AgCl (Insoluble)

~~Soluble~~ AgF (Comparison)

Q. $\text{AgCl} > \text{AgBr} > \text{AgF}$

$\xrightarrow{\text{Solubility (Fajan's Rule)}}$



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

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

$$\boxed{K_{\text{sp}} = [\text{A}^+][\text{B}^-]}$$

where K_{sp} is a constant known as solubility product constant it is defined for sparingly soluble salts. It's value will change only

Value will be given in the problem and only with temp.

Solubility :- It is defined for Saturated solution and defined as max. mass of solute which can be dissolved in 100 gm

of water to form Saturated solution.

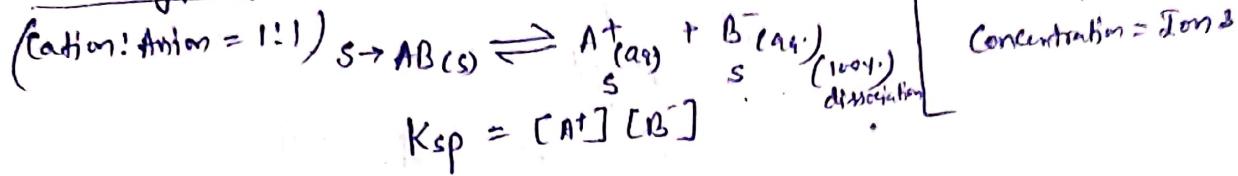
For K_{sp} solubility is expressed as mole/litre.

\Rightarrow For K_{sp} solubility is expressed as mole/litre.

Relation b/w K_{sp} and S for diff. types of salt

(21)

① 1:1 type of salt :- (AB type)

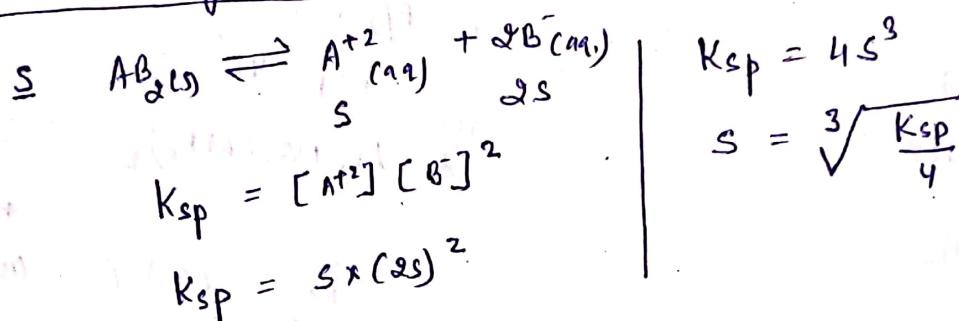


$$K_{sp} = s \times s$$

$$s = \sqrt{K_{sp}}$$

Ex: AgCl, AgBr, AgI, BaSO₄, Al₂SiO₅, AlN

② 1:2 or 2:1 type of salt :- (AB₂ or A₂B)

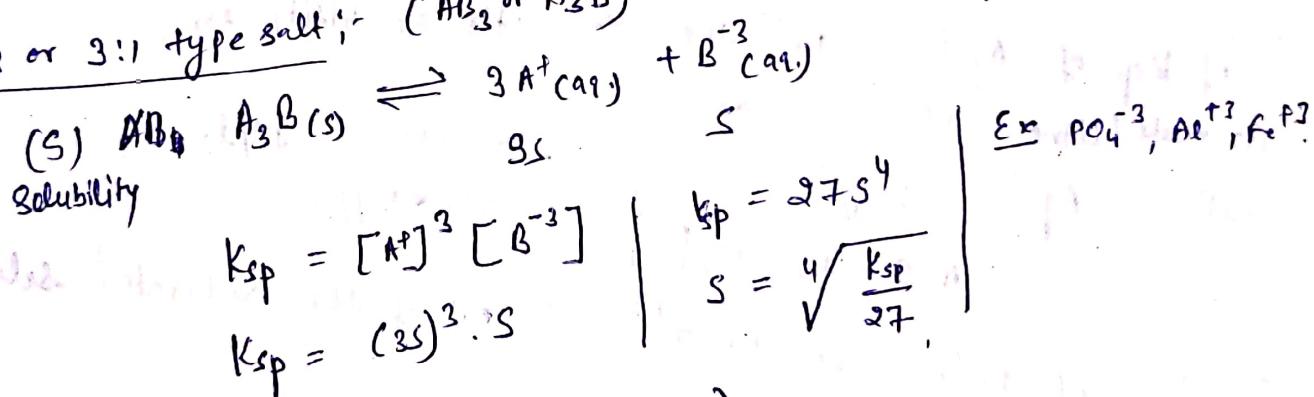


$$K_{sp} = 4s^3$$

$$s = \sqrt[3]{\frac{K_{sp}}{4}}$$

Ex: Ag₂CrO₄, MgCl₂, ZnCl₂

③ 1:3 or 3:1 type salt :- (AB₃ or A₃B)

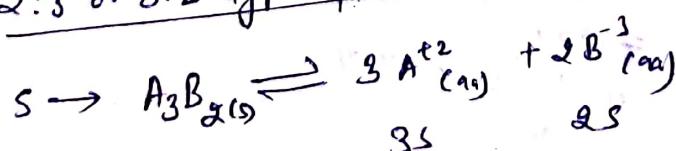


$$K_{sp} = 27s^4$$

$$s = \sqrt[4]{\frac{K_{sp}}{27}}$$

Ex: PO₄⁻³, Al⁺³, Fe⁺³

④ 2:3 or 3:2 type of salt :- (A₂B₃ or A₃B₂)



$$K_{sp} = [A^{+2}]^3[B^{-3}]^2$$

$$K_{sp} = (3s)^3(2s)^2$$

$$= 27s^3 \times 4s^2$$

$$K_{sp} = 108s^5$$

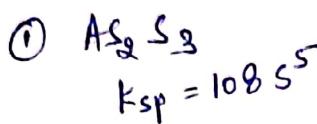
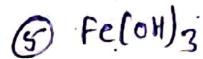
$$s = \sqrt[5]{\frac{K_{sp}}{108}}$$

(5) $A_x B_y$ type of salt:-

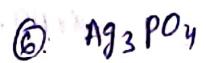
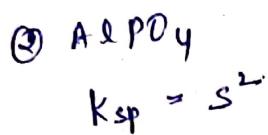
$$K_{sp} = x^x \cdot y^y \cdot s^{x+y}$$

$$s = \sqrt[x+y]{\frac{K_{sp}}{x^x \cdot y^y}}$$

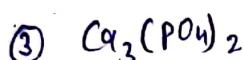
Q. write expression of K_{sp} in terms of 's' for following :-



$$K_{sp} = 27 s^4$$



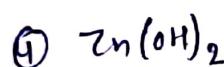
$$K_{sp} = 27 s^4$$



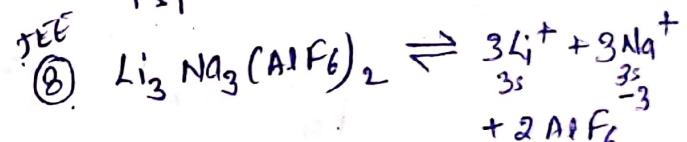
$$K_{sp} = 108 s^5$$



$$K_{sp} = 4s^3$$



$$K_{sp} = 4s^3$$



$$K_{sp} = (3s)^3 (3s)^3 (2s)^2 (2s)$$

$$K_{sp} = 2916 s^8$$

Q. if K_{sp} of AgCl is 10^{-10} then calc. its solubility in

(1) mole/litre (2) gm/litre.

$$(ii), 10^{-5} \times 143.5 \text{ gm/l.}$$

Soln. $\text{AgCl} \quad s = \sqrt{10^{-10}}$ (i) $s = 10^{-5} \text{ mol/l}$

$$[\text{Cl}^-] = 2s$$

$$= 2 \times 10^{-5}$$

$$\text{pOH} = 4 - \log 2 = 3.7$$

$$\text{pH} = 11.3$$

Q. K_{sp} of Fe(OH)_2 is 4×10^{-12} calc. pH of the saturated solution

of Fe(OH)_2 .

Soln. $K_{sp} = 4s^3$
 $4 \times 10^{-12} = 4s^3$
 $s = 10^{-4}$

Q. K_{sp} of water is 4×10^{-8} calc. volume of water in litre

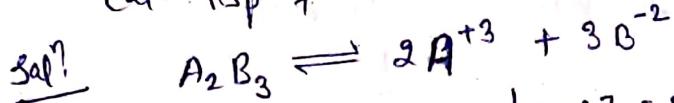
Q. K_{sp} of BaSO_4 is 4×10^{-8} calc. volume of water in litre needed to dissolve 4.66 gm of BaSO_4 ($M=233$)

Soln. $s = \sqrt{4 \times 10^{-8}} = 2 \times 10^{-4} \text{ mol/l} = 2 \times 233 \times 10^{-4} \text{ gm/l} = 4.66 \times 10^{-2} \text{ gm/l}$
 $1 \text{ l} = 4.66 \times 10^{-2} \text{ gm} \Rightarrow 4.66 \text{ gm} = \frac{1 \times 4.66}{4.66 \times 10^{-2}} = 100 \text{ l.} \quad \left\{ \begin{array}{l} W = C M V \\ 1 \text{ l} \end{array} \right\}$



Q. Conc. of A^{+3} in a saturated soln of A_2B_3 salt is $2 \times 10^{-4} \text{ m/l}$ (22)

Cal. K_{sp} of the salt.



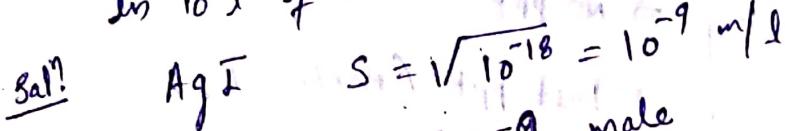
$$K_{sp} = 108 S^5, \quad [A^{+3}] = 2 \times 10^{-4}$$

$$K_{sp} = 108 \times (10^{-4})^5 \quad 2S = 2 \times 10^{-4}$$

$$K_{sp} = 1.08 \times 10^{-18} \quad S = 10^{-4}$$

K_{sp} = cal. Mass of AgI which can be dissolved

Q. K_{sp} of AgI is 10^{-18} . Cal. Mass of AgI which can be dissolved in 10 l of water to make a saturated solution of AgI .



$$1 \text{ l} = 10^{-3} \text{ mole}$$

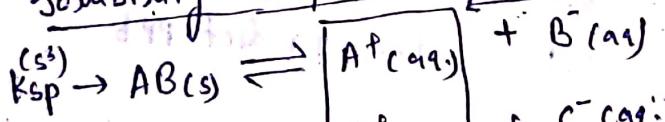
$$10^{-3} = 10^{-8} \text{ mole}$$

$$W = 10^{-9} \times 235 \times 10$$

$$W = 2.35 \times 10^{-6} \text{ gm}$$

$$W = 2.35 \mu\text{gm}$$

Solubility in presence of a Common Ion:-



C.C.I.E. (BETWEEN CONC. OF COMMON ION AND SOLUBILITY)

$$K_{sp} = [A^+] [B^-]$$

$$K_{sp} = (C) \times [B^-]$$

Q. K_{sp} of $AgCl$ is 10^{-10} . Cal His solubility in

① pure water

$$S = \sqrt{10^{-10}}$$

$$S_1 = 10^{-5}$$

$$S_2 = 0.5 \times 10^{-10}$$

$$10^{-10} = [Ag^+] \times (0.5)$$

$$S_3 = 2 \times 10^{-10}$$

$$S_4 = 10^{-10}$$

$$S_1 > S_2 > S_3 > S_4$$

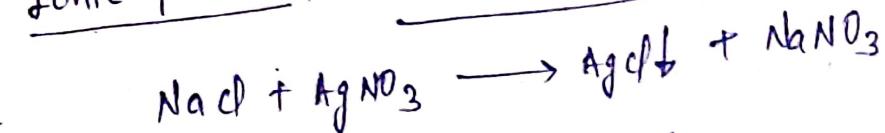
Note:- Higher is the conc. of common ion less will be the solubility.

$$S_1 > S_2 > S_3 > S_4$$

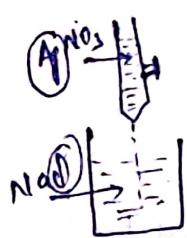
$$\textcircled{1} 0.5M \text{ AgNO}_3 \quad \textcircled{2} 0.5M \text{ NaCl}_2 \\ 10^{-10} = (0.5) [Cr] \quad S_1 = 2 \times 10^{-10} \\ [Ag^+] = 10^{-10} \quad S_2 = 10^{-10}$$



Ionic Product; - (Condition of PPT)

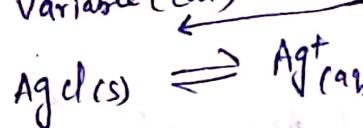


$$(K_{\text{sp}})_{\text{AgCl}}$$



$$K_{\text{ip}} = [\text{Ag}^+] [\text{Cl}^-]$$

Variable (cal.)



(white ppt)

fix = constant
(given)

K_{ip} is as like K in
chemical eq.

product of conc. of ions is known as Ionic product.

Condition of PPT:- ① if $K_{\text{ip}} < K_{\text{sp}} \Rightarrow$ No ppt

② if $K_{\text{ip}} = K_{\text{sp}} \Rightarrow$ Just ppt. (Max/Min)

③ if $K_{\text{ip}} > K_{\text{sp}} \Rightarrow$ ppt will form.

Q. 10^{-4} M AgNO_3 is mixed, 10^{-5} M NaCl if K_{sp} of AgCl is 10^{-10}
then predict ppt. of AgCl will form or not.

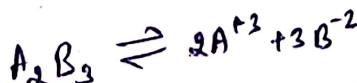
Soln:

$\text{AgNO}_3 - 10^{-4}$ M	$K_{\text{ip}} = [\text{Ag}^+] [\text{Cl}^-]$	
$\text{NaCl} - 10^{-5}$ M	$= 10^{-4} \times 10^{-5} = 10^{-9} > K_{\text{sp}}$	(ppt will form)

Q. 200 ml of 10^{-2} M $\text{A}_2(\text{SO}_4)_3$ and 300 ml of 10^{-3} M Na_2B are mixed together. if K_{sp} of A_2B_3 is 10^{-20} then predict ppt of A_2B_3 will form or not.

Soln:

$\text{A}_2(\text{SO}_4)_3 \Rightarrow \frac{M_1 V_1}{M_2 V_2} = \frac{M_1}{M_2} \times \frac{V_1}{V_2}$	$[\text{A}^{+2}] = 2 \times \frac{2}{3} \times 10^{-2}$	$[\text{Na}_2\text{B}] = \frac{3 \times 10^{-3}}{5 \times 2}$
$200 \times 10^{-2} = M_2 \times 5 \times 10^{-3}$	$= \frac{4}{3} \times 10^{-2}$	$= 6 \times 10^{-3}$
$M_2 = \frac{2}{3} \times 10^{-2}$	$[\text{A}^{+2}] = 8 \times 10^{-3}$	$[\text{B}^{2-}] = 6 \times 10^{-3}$



$$\begin{aligned}
 K_{\text{ip}} &= [\text{A}^{+2}]^2 \times [\text{B}^{2-}]^3 \\
 &= (8 \times 10^{-3})^2 (6 \times 10^{-3})^3 \\
 &= 64 \times 10^{-6} \times 216 \times 10^{-9} \\
 &= 64 \times 216 \times 10^{-15} \\
 &\quad \text{K}_{\text{ip}} > K_{\text{sp}} \quad (\text{Ppt will form})
 \end{aligned}$$

Q. Cal. the min. conc. of SO_4^{2-} ion required to ppt. BaSO_4 in a salt containing 10^{-4} mole of Ba^{2+} . (K_{sp}) _{BaSO_4} = 4×10^{-10} (23) 0

Soln: $K_{\text{ip}} = K_{\text{sp}}$ (just ppt) min/max.

$$\underline{\text{BaSO}_4} : [\text{Ba}^{2+}] = 10^{-4} \text{ mole/l}$$

$$[\text{Ba}^{2+}][\text{SO}_4^{2-}] = 4 \times 10^{-10}$$

$$10^{-4} \times [\text{SO}_4^{2-}] = 4 \times 10^{-10}$$

$$[\text{SO}_4^{2-}] = 4 \times 10^{-6} \text{ (min.)}$$

{ Min - to start ppt
Max - to prevent ppt

Q. How many gm of CaBr_2 (200) can be added to 250 ml of 0.01 M salt of AgNO_3 to just start the ppt of AgBr . (K_{sp}) _{AgBr} = 5×10^{-13}

Soln:

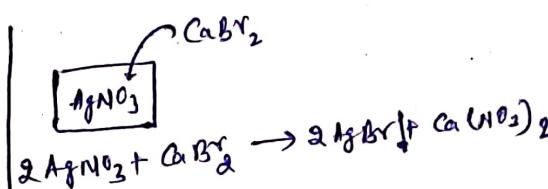
$$W = C \times V \times M$$

$$= C \times 250 \times \frac{1}{4}$$

$$W = 50C$$

$$W = \frac{25}{80} \times \frac{1}{4} \times 5 \times 10^{-11}$$

$$W = \frac{125}{32} \times 10^{-11} \text{ gm.}$$



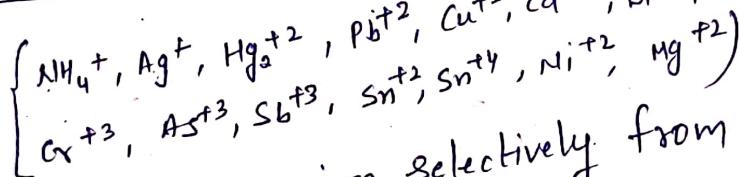
$$K_{\text{ip}} = K_{\text{sp}}$$

$$[\text{Ag}^+] [\text{Br}^-] = 5 \times 10^{-13}$$

$$0.04 [\text{Br}^-] = 5 \times 10^{-13}$$

$$[\text{Br}^-] = \frac{5}{4} \times 10^{-11}$$

Ques: Selective precipitation:- (Qualitative Analysis) or (salt Analysis)



To precipitate any ion selectively from a given solution containing more than one ion is known as selective precipitation.

Q. A solution is giving containing 0.1M Cl^- , 0.1M Br^- and 0.1M I^- . If AgNO_3 is gradually added in a container from a burette and K_{sp} of AgCl is 1.8×10^{-10} , K_{sp} of AgBr is 5×10^{-13} and K_{sp} of AgI is 5×10^{-18} then (i) cal. $[\text{Ag}^+]$ required to ppt AgCl , AgBr and AgI respectively.

$$\underline{\text{Soln: AgCl}} \quad [\text{Ag}^+] [\text{Cl}^-] = 1.8 \times 10^{-10}$$

$$[\text{Ag}^+] \cdot (0.1) = 1.8 \times 10^{-9}$$

$$[\text{Ag}^+] = 1.8 \times 10^{-9}$$

$$\begin{array}{l} \text{AgBr} \quad \text{Ag}^+(0.1) = 5 \times 10^{-13} \\ \quad [\text{Ag}^+] = 5 \times 10^{-12} \\ \text{AgI} \quad \text{Ag}^+(0.1) = 5 \times 10^{-18} \\ \quad [\text{Ag}^+] = 5 \times 10^{-16} \end{array}$$

(ii) which will ppt first $\text{AgCl}/\text{AgBr}/\text{AgI}$ to ppt.

Sol. AgI will ppt first because $[\text{Ag}^+]$ required is lowest.

(iii) Cal. % of I^- Ion ~~remaining~~ remaining when AgBr starts precipitating.

$$[\text{Ag}^+][\text{I}^-] = 5 \times 10^{-12}$$

$$(5 \times 10^{-2}) [\text{I}^-] = 5 \times 10^{-12}$$

$$[\text{I}^-] = 10^{-5} \text{ (remain)}$$

$$\% = \frac{10^{-5}}{0.1} \times 100 = 0.01\%$$

$$\boxed{\% \text{ ppt} = 99.99\%} \quad (\text{practically complete ppt})$$

(iv) Cal. % of Br^- precipitated when AgCl starts precipitating.

$$1.8 \times 10^{-9} \times [\text{Br}^-] = 5 \times 10^{-13}$$

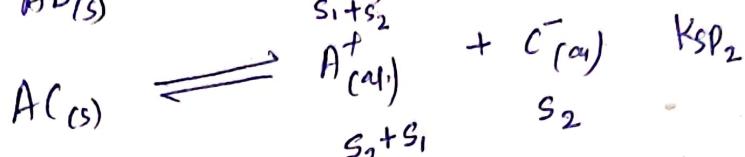
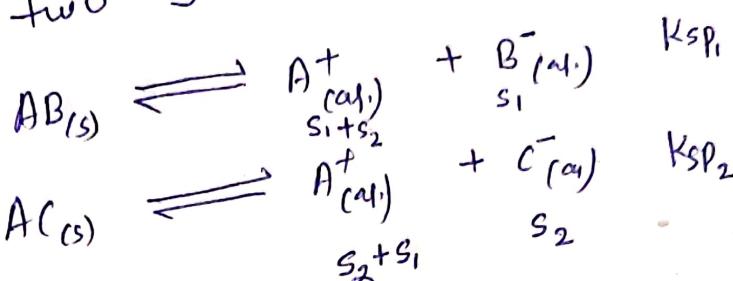
$$[\text{Br}^-] = \frac{5}{1.8} \times 10^{-4}$$

$$\% \text{ of } \text{Br}^- = \frac{5 \times 10^{-4}}{0.1} \times 100$$

$$\% \text{ of } \text{Br}^- = \frac{5}{18} = 0.3\%$$

Simultaneous solubility :- It is defined for a solution (24)

Containing two S^3



$$\text{For } AB_{(s)} \quad K_{SP_1} = [A^+] [B^-]$$

$$K_{SP_1} = (S_1 + S_2) \times S_1 \quad \text{--- (i)}$$

$$\text{For } AC_{(s)} \quad K_{SP_2} = [A^+] [C^-]$$

$$K_{SP_2} = (S_1 + S_2) \times S_2 \quad \text{--- (ii)}$$

(i) \div (ii)

$$\frac{K_{SP_1}}{K_{SP_2}} = \frac{S_1}{S_2}$$

Q. Cal. Simultaneous solubility of AgBr and AgCN. Also. cal $[Ag^+]$ ion
given K_{SP} of $AgCN = 10^{-12}$ & K_{SP} of $AgBr = 5 \times 10^{-13}$

Soln. $AgBr \quad 5 \times 10^{-13} = (S_1 + S_2) S_1 \quad \text{--- (i)}$

$AgCN \quad 10^{-12} = (S_1 + S_2) S_2 \quad \text{--- (ii)}$

$$\frac{5}{10} = \frac{S_1}{S_2}$$

$$S_2 = 2S_1$$

from eq. (ii)

$$10^{-12} = (S_1 + 2S_1) 2S_1$$

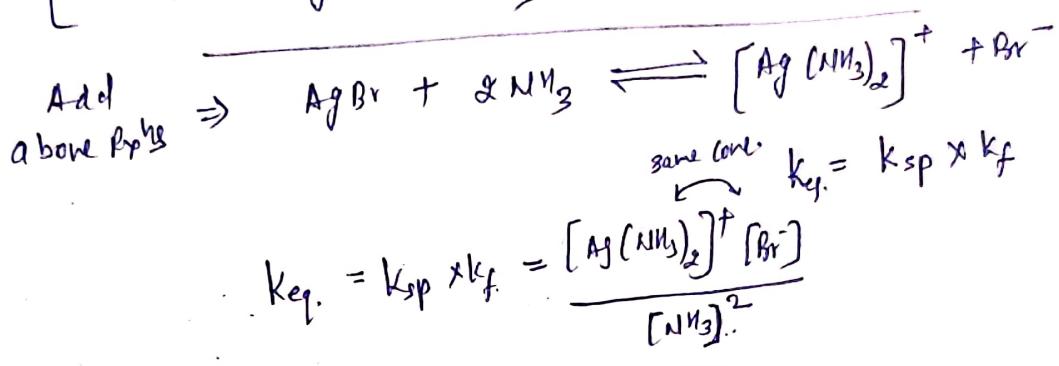
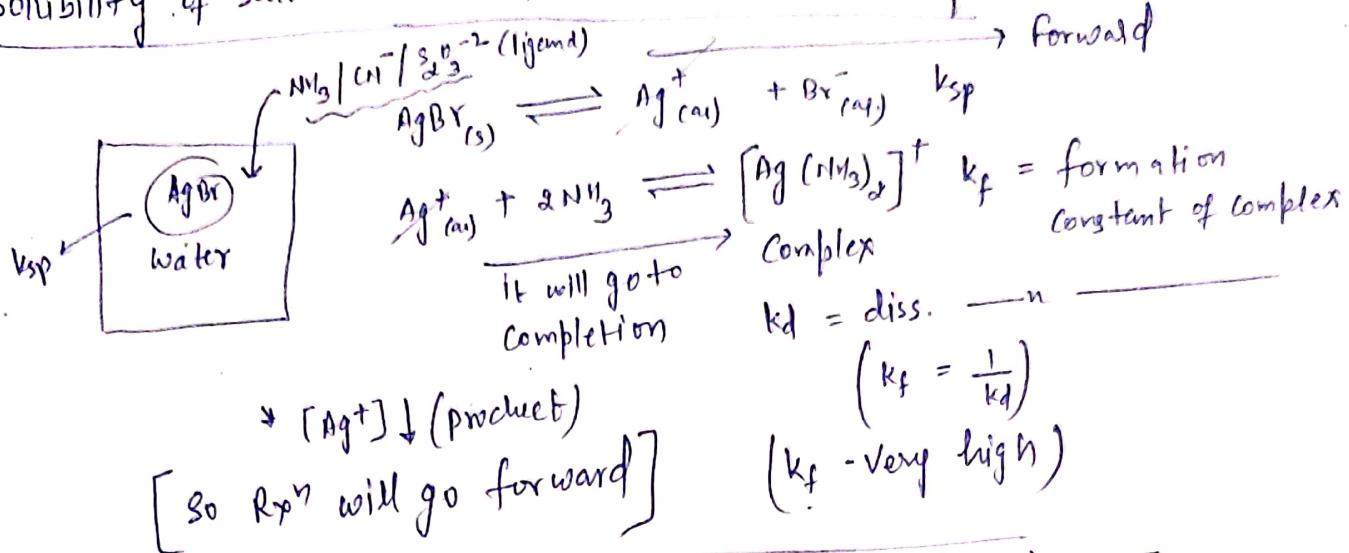
$$10^{-12} = 6S_1^2$$

$$S_1 = \frac{10^{-6}}{\sqrt{6}}$$

$$AgCN \Rightarrow S_2 = \sqrt{\frac{2}{3}} \times 10^{-6}$$

$$[Ag^+] = 10^{-6} \left(\frac{1}{\sqrt{6}} + \sqrt{\frac{2}{3}} \right)$$

Solubility of salt when complex formation occurs:-



$$K_{\text{sp}} \times k_f = \frac{s^2}{[\text{NH}_3]^2}$$

Note:- Due to complex formation solubility of salt drastically increases.

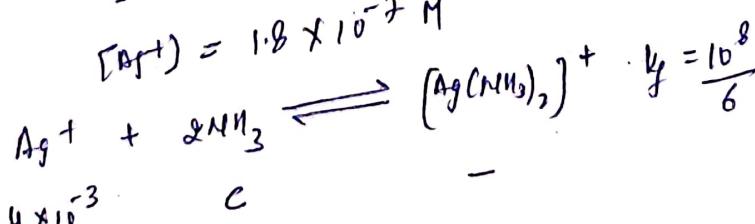
Q. What must be the conc. of aq. NH_3 which must be added to a soln containing $4 \times 10^{-3} \text{ M Ag}^+$ and 10^{-3} M Cl^- to prevent the ppt of AgCl

$$(K_{\text{sp}})_{\text{AgCl}} = 1.8 \times 10^{-10}, \quad (k_f)_{\text{Ag}(\text{NH}_3)_2^+} = \frac{10^8}{6}$$

soln $[\text{Ag}^+] [\text{Cl}^-] = 1.8 \times 10^{-10} \quad (K_{\text{sp}} = K_{\text{sp}})$

$$[\text{Ag}^+] \times 10^{-3} = 1.8 \times 10^{-10}$$

$$[\text{Ag}^+] = 1.8 \times 10^{-7} \text{ M}$$



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

$$C - 0.008$$

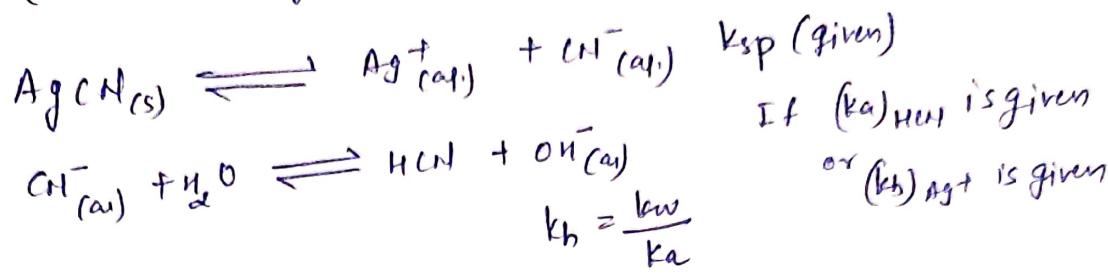
$$4 \times 10^{-3}$$

$$\frac{10^8}{C} = \frac{4 \times 10^{-3}}{1.8 \times 10^{-3} (C - 0.008)^2}$$

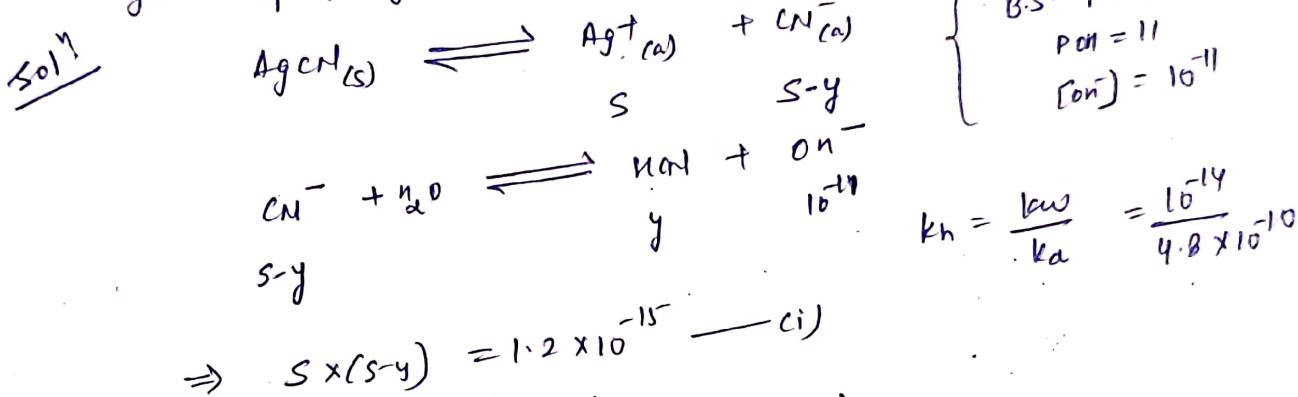
$$C = 0.04445 \text{ M}$$

Solubility of Salt in a Buffer Solution:- (when Hydrolysis occurs) In this case solubility of salt increases.

(25)



Q. Cal. solubility of AgCN in Buffer solution of pH = 3
given K_{sp} of AgCN = 1.2×10^{-15} , K_a of HCN is 4.8×10^{-10} .



$$\Rightarrow s \times (s-y) = 1.2 \times 10^{-15} \quad (\text{i})$$

$$\frac{y \times 10^{-11}}{(s-y)} = \frac{10^{-4}}{4.8} \quad (\text{ii})$$

$$(s-y) \times 10^{-11} = \frac{1.2}{4.8} \times 10^{-15}$$

$$sy = 2.5 \times 10^{-9}$$

from eq. (i)

$$s^2 - sy = 1.2 \times 10^{-15}$$

$$s^2 = 1.2 \times 10^{-15} + 2.5 \times 10^{-10}$$

$$s = 5 \times 10^{-5}$$

Titration :- A v/s B (chemical Rxn) ① N

↓
Unknown
concentration

known (standard \Rightarrow Titrant)
conc. solution

It is a method to know/cal. conc of a solution using a standard solution known as titrant
 → For a Rxn \Rightarrow End point or Equivalent point
 (we define)

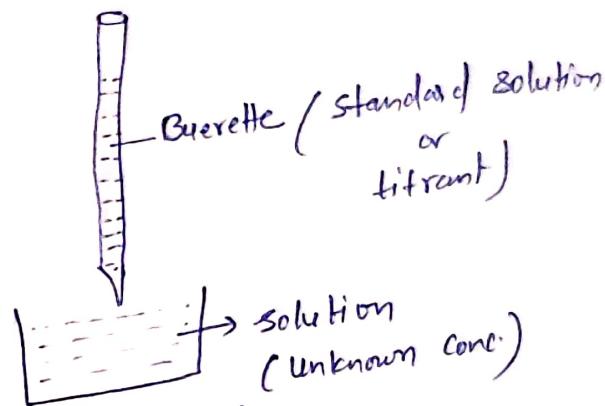
$$E_1 = E_2$$

Indicator \Rightarrow It ~~represents~~ shows end point by colour change

Acid - base titration :-

$$E_1 = E_2$$

$$N_1 V_1 = N_2 V_2 \text{ (end point)}$$



Case-I :- S.A. v/s S.B. (strong acid v/s s.B.)

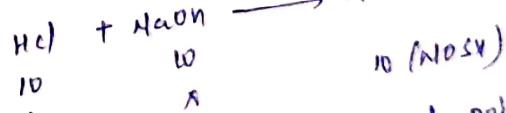
Ex: 100 ml of 0.1M HCl is taken. It is titrated against 0.1 M NaOH solution. cal. pH if volume of NaOH added is-

(i) 0 ml NaOH
 $t=0$ $\frac{[H^+]}{SA} = 0.1 \text{M}$ ($n_f = 1$)
 $N = 0.1 \times 1 = [H^+]$
 $pH = 1$

(ii) 50 ml NaOH
 millimoles of HCl = $100 \times 0.1 = 10$
 millimoles of NaOH = $50 \times 0.1 = 5$
 $HCl + NaOH \rightarrow NaCl + H_2O$
 $10 \quad 5 \text{ (ex)} \quad (Na) \quad (H_2O)$
 millimoles of HCl remaining = 5
 $[H^+] = \frac{5}{150} = \frac{1}{3} \times 10^{-1}$

$pH = 1 + \log 3 = 1.48$

(iii) 100 ml NaOH is added :-



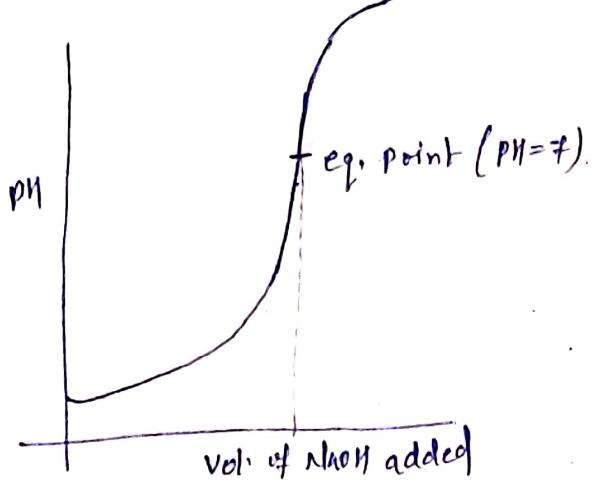
↓ end point or equivalent point

$$\Rightarrow pH = 7$$

(iv) 150 ml NaOH :-

$$HCl + NaOH \rightarrow NaCl + H_2O$$

10 mm 15 (10mm)
 LR 5
 $[NaOH] = \frac{5}{250} = \frac{1}{5} \times 10^{-1}$
 $[H^+] = \frac{1}{3} \times 10^{-1}$
 $pH = 1 + \log 5 = 1.7$ $pH = 12.3$



⇒ eq. point / end point \rightarrow close
pH drastically change (it's 7)
so graph vertical shift

Case-II :- WA v/s SB

Ex:- 100 ml of 0.1 M CH_3COOH is taken in a beaker gradually 0.1M NaOH is added. cal. pH when Vol. of NaOH is added is
(K_a of $\text{CH}_3\text{COOH} = 2 \times 10^{-5}$)

$$(i) \text{ 0 ml of NaOH: } [\text{CH}_3\text{COO}^-] = 0.1$$

$$\alpha = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{2 \times 10^{-5}}{0.1}} = \sqrt{2} \times 10^{-2} = \sqrt{2} \times 1. = \underline{1.414 \cdot 1} \text{ (correct)}$$

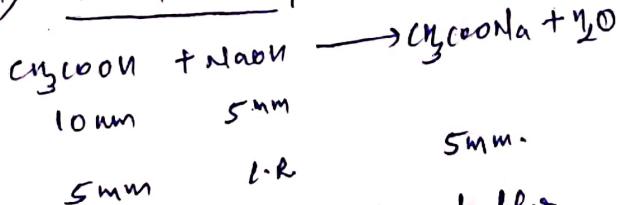
$$[\text{H}^+] = c\alpha = 0.1 \times \sqrt{2} \times 10^{-2}$$

$$[\text{H}^+] = \sqrt{2} \times 10^{-3}$$

$$\begin{aligned} \text{pH} &= 3 - \log \sqrt{2} \\ &= 3 - \frac{1}{2} \log 2 \\ &= 3 - \frac{1}{2} \times 0.3 \end{aligned}$$

$$\boxed{\text{pH} = 2.85}$$

$$(ii) \text{ 50 ml NaOH: }$$

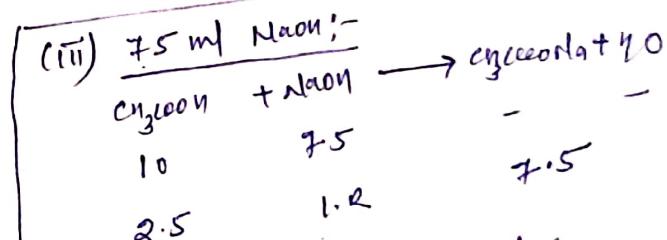


⇒ It becomes acidic buffer.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$\text{pH} = 5 - \log 2$$

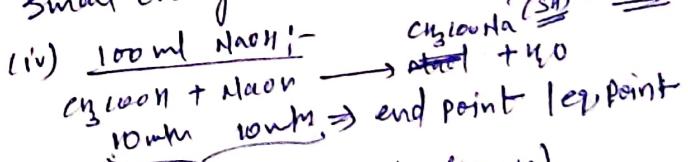
$$\boxed{\text{pH} = 4.7}$$



$$\begin{aligned} \text{pH} &= \text{p}K_a + \log \frac{7.5/4}{2.5/4} \\ &= 5 - \log 2 + \log 3 \\ &= 5 - 0.30 + 0.48 \end{aligned}$$

$$\boxed{\text{pH} = 5.18}$$

Small change due to buffer solution.

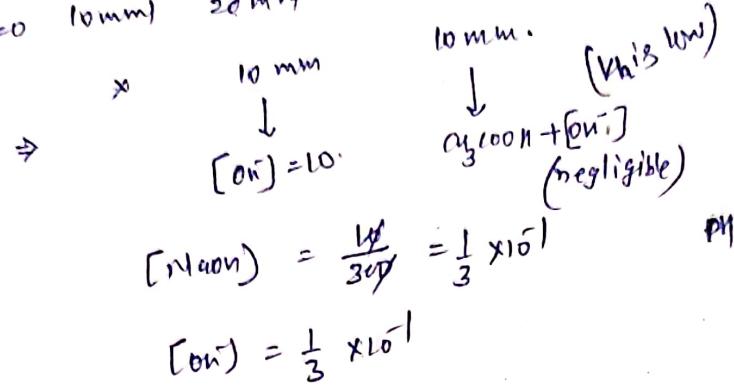
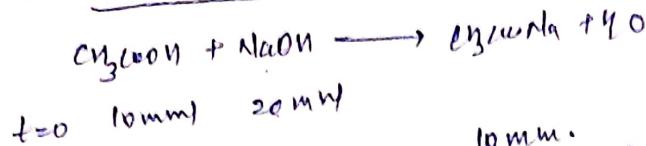


$$\Rightarrow \text{pH} = 7 \times \text{CH}_3\text{COONa (10 mm)} / (\text{WA} + \text{SB}) \text{ (pH} \neq 7)$$

$$[\text{CH}_3\text{COO}^-] = \frac{10}{20 \text{ mm}} = \frac{1}{2} \times 10^{-1}$$

$$\begin{aligned} \text{pH} &= \frac{1}{2} [14 + 5 - \log 2 + \log (1/2 \times 10^{-1})] \\ &= \frac{1}{2} [19 - \log 2 + \log 2 - 1] \\ &= \frac{1}{2} [18 - 2 \log 2] = 9 - 0.3 = \underline{\underline{8.7}} \end{aligned}$$

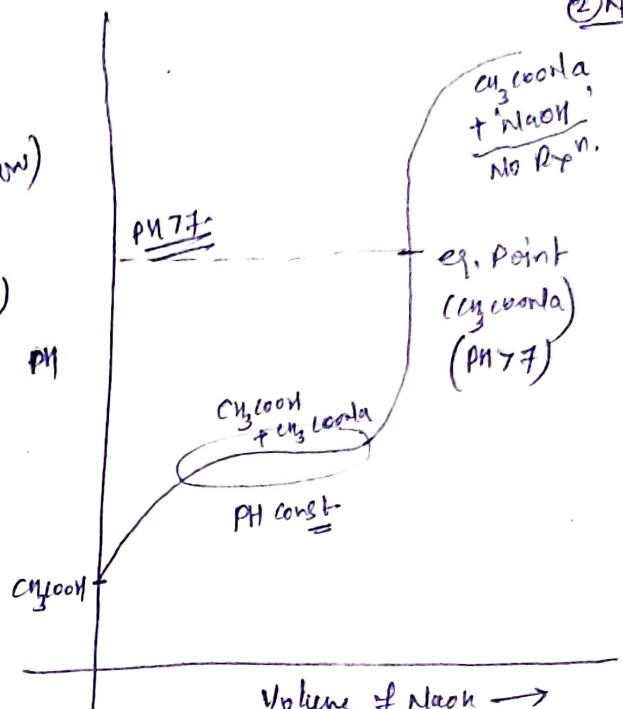
(V) 200ml NaOH is added :-



$$pOH = 1 + \log 3$$

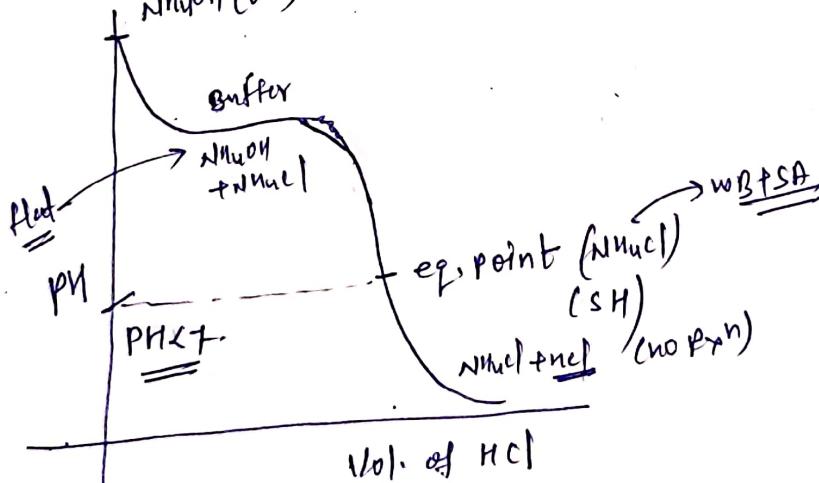
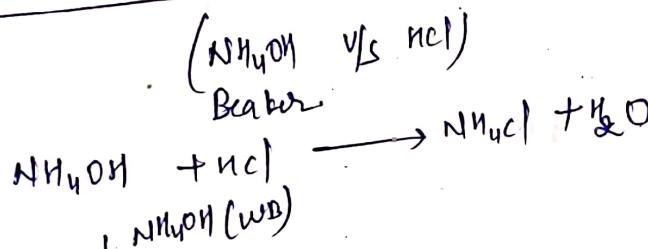
$$= 1.48$$

$$(pH = 12.52)$$



\Rightarrow pH vs Buffer Titration Curve
flat at eq. pt.

Case-III :- WB v/s SA



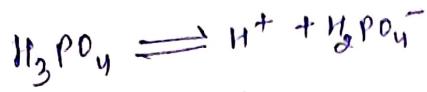
Q. 100ml of 0.1M H_3PO_4 is taken and gradually 0.1N NaOH is added

$$(K_{a_1} = 10^{-2}, K_{a_2} = 10^{-7}, K_{a_3} = 10^{-12})$$

Cal. pH when vol. of NaOH added is -

(i) 0 ml NaOH added :- $[\text{H}_3\text{PO}_4] = 0.1$ (Polyprotic A.)

$$K_{a_1} \gg K_{a_2} \gg K_{a_3} \quad \text{consider only 1st ionisation.}$$



$$K_{a_1} = \frac{C \alpha_1^2}{1 - \alpha_1}$$

$$\alpha_1 = \sqrt{\frac{K_{a_1}}{C}} = \sqrt{\frac{10^{-2}}{0.1}} > 10\% \\ (\text{wrong})$$

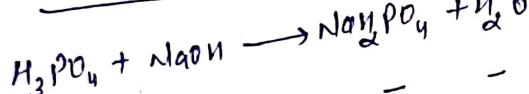
$$10^{-2} = \frac{0.1 \alpha_1^2}{1 - \alpha_1^2} \quad (\alpha_1 = 0.27)$$

$$[H^+] = C \alpha_1 \\ = 0.1 \times 0.27$$

$$(H^+) = 2.7 \times 10^{-3}$$

$$pH = 3 - \log 2.7$$

(b) 50 ml NaOH :-



+∞	10	5 (w)	-
⇒	5 (w)	x	(Conj. Base)

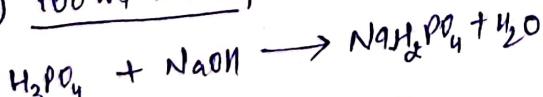
$$pH = pK_{a_1} + \log \frac{[H_2PO_4^-]}{[H_3PO_4]}$$

$$\boxed{pH = 2} \quad (\text{Buffer})$$

Max. buffer capacity

$$[\text{Acid}] = [\text{Conj. Base}]$$

(c) 100 ml NaOH :-



+∞	10mm	10mm	-
⇒	x	x	10mm.

$$\boxed{pH = \frac{pK_{a_1} + pK_{a_2}}{2}}$$

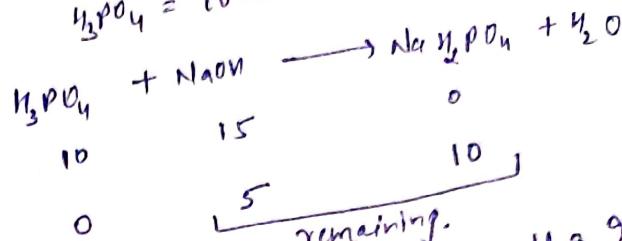
$$pH = \frac{2 + 7}{2}$$

$$pH = 4.5$$

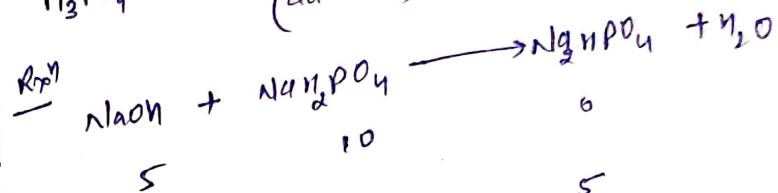
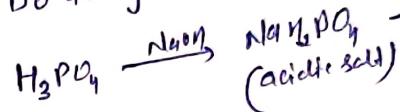
(d) 150 ml NaOH is added :-

$$NaOH = 15 \text{ mM}$$

$$H_3PO_4 = 10 \text{ mM}$$



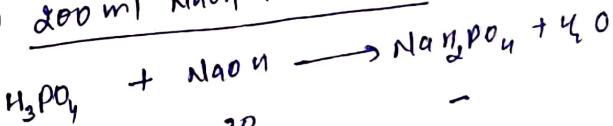
Do they react with each other?



$$pH = pK_{a_2} + \log \frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$$

$$\boxed{pH = 7}$$

(e) 200 ml NaOH is added :-



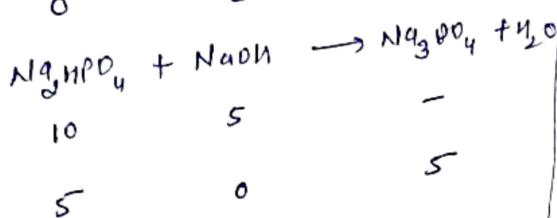
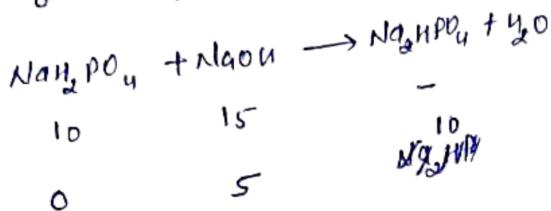
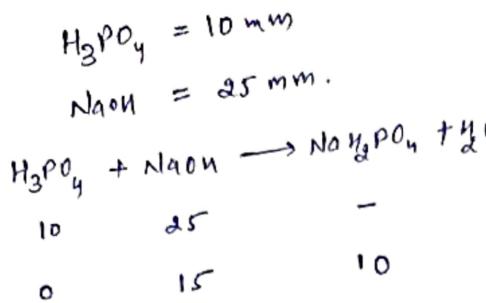
+∞	10	20	-
⇒	10	10	10
10	10	-	-
0	0	Na ₂ HPO ₄	Na ⁺ → HPO ₄ ²⁻

2nd (end point)
Equivalent point)

$$\boxed{pH = \frac{pK_{a_3} + pK_{a_2}}{2}}$$

$$pH = \frac{7 + 12}{2} = 9.5$$

(F) 250 ml NaOH is added :-

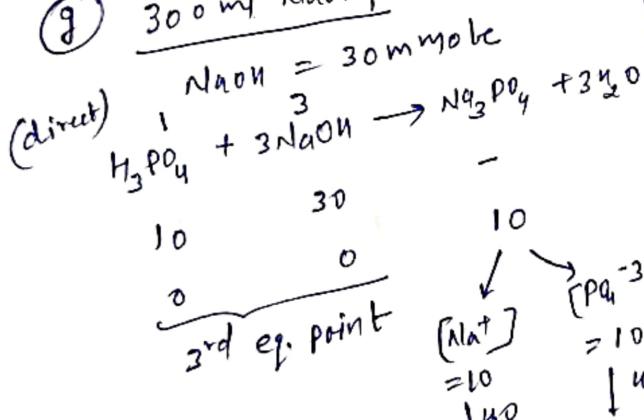


\Rightarrow Buffer

$$\text{pH} = \text{pK}_3 + \log \frac{[\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]}$$

$$\boxed{\text{pH} = 12}$$

(G) 300 ml NaOH :-



2nd eq. point

$$\begin{array}{c} [\text{Na}^+] = 10 \\ \downarrow 40 \\ x \end{array} \quad \begin{array}{c} [\text{PO}_4^{3-}] = 10 \\ \downarrow 40 \\ \text{PolyValent cation.} \end{array}$$

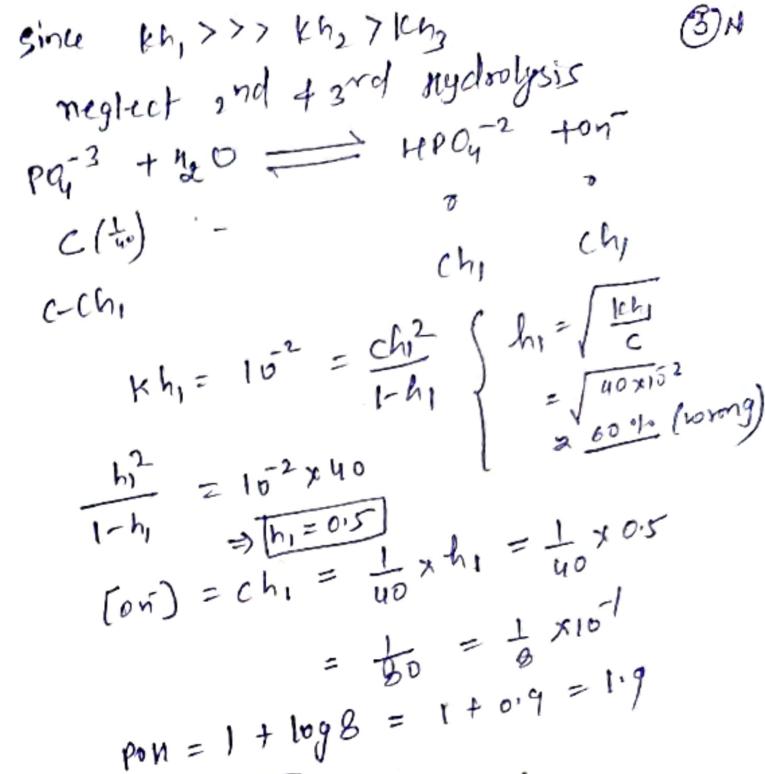
(3 step hydrolysis)

$$[\text{PO}_4^{3-}] = \frac{10}{V_T} = \frac{10}{40} = \frac{1}{40}$$

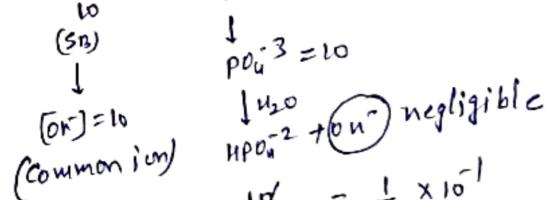
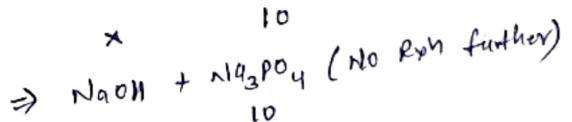
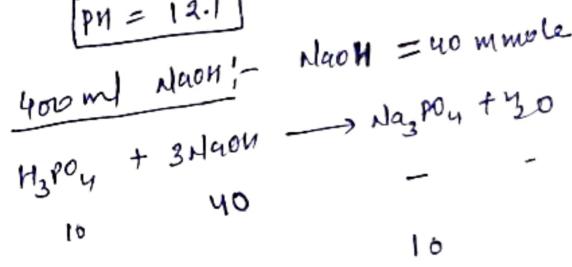
$$\text{Kh}_1 = \frac{k_w}{\text{Ka}_3} = 10^{-2}$$

$$\text{Kh}_2 = \frac{k_w}{\text{Ka}_2} = 10^{-7}$$

$$\text{Kh}_3 = \frac{k_w}{\text{Ka}_1} = 10^{-12}$$



(H)



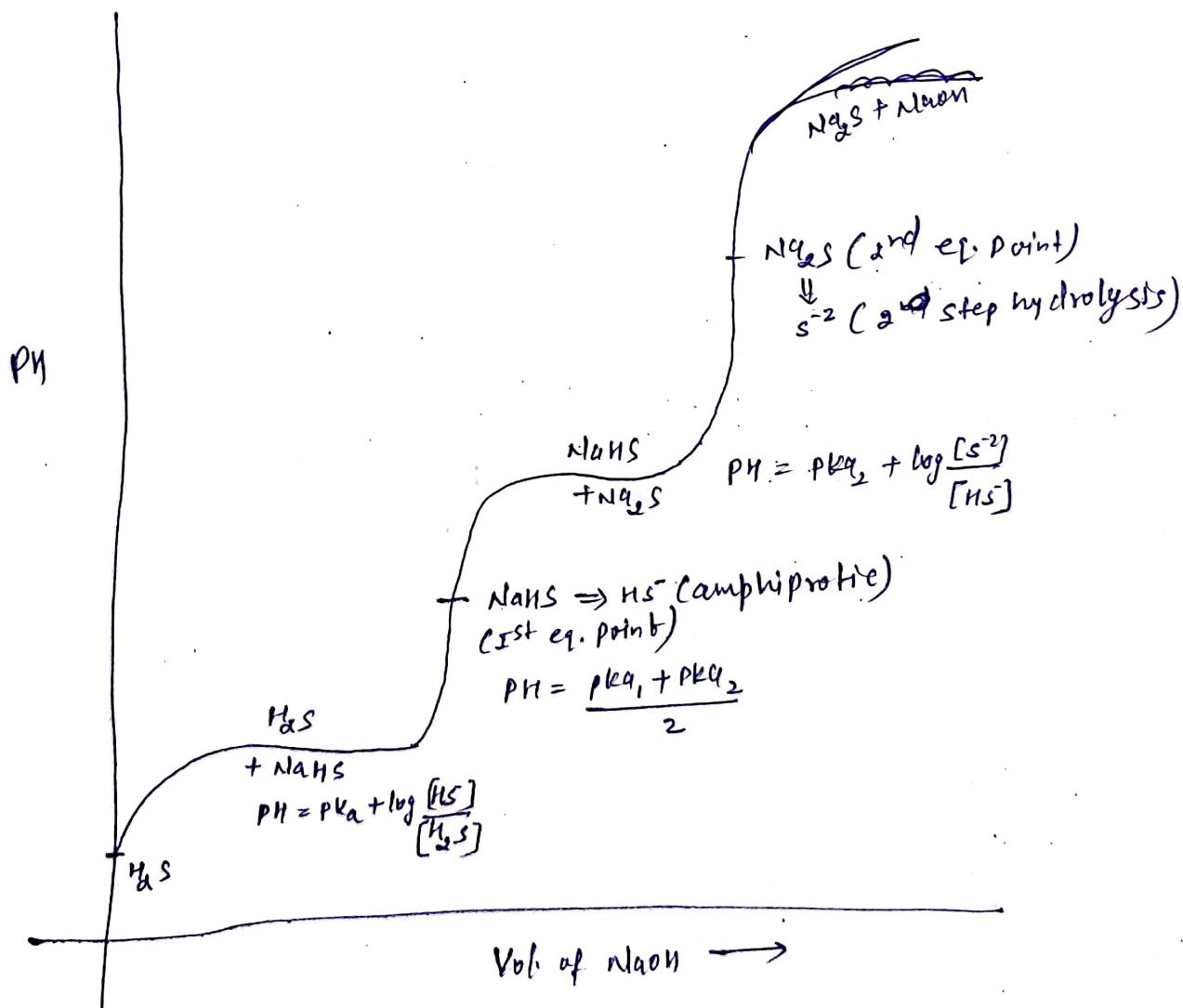
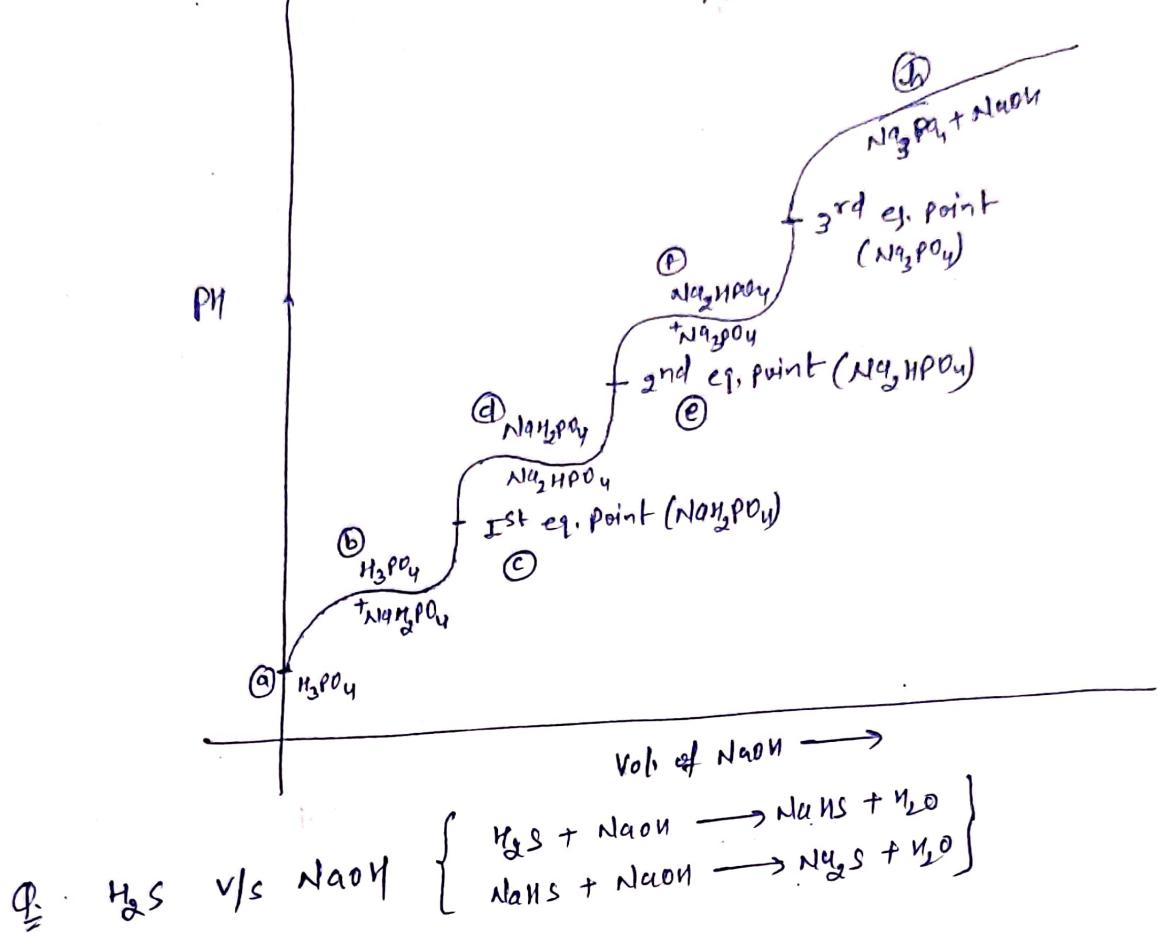
(common ion)

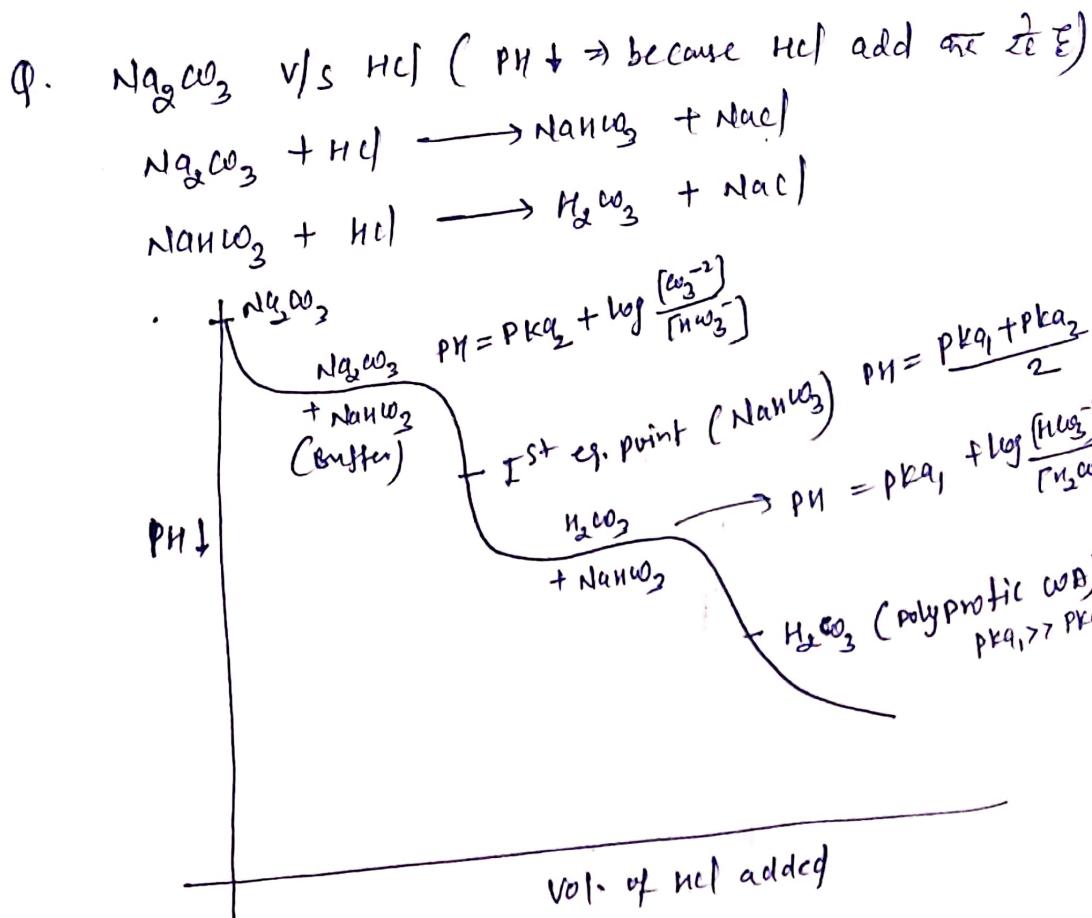
$$[\text{OH}^-] = \frac{10}{50} = \frac{1}{5} \times 10^{-1}$$

$$\text{pOH} = 1 + \log 5 = 1.7$$

$$\text{pH} = 14 - 1.7 = 12.3$$





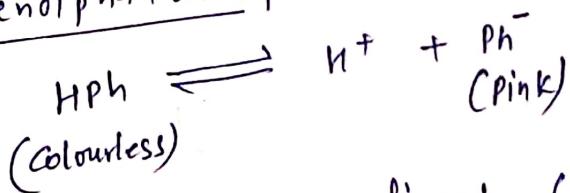


Indicator :- (Acid base titration)

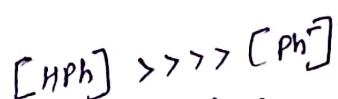
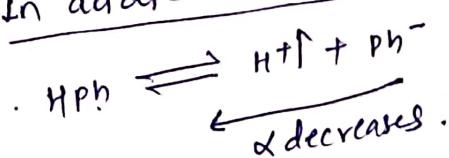
They are weak Acid or weak Base.

⇒ They are weak Acid or weak Base.

① phenolphthalein :- (HPH) (It is a w/w) (formula is complex) (Indicator used in very small amount)

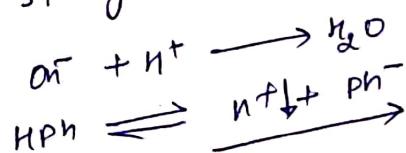


Case-I :- In acidic medium :- (H^+)

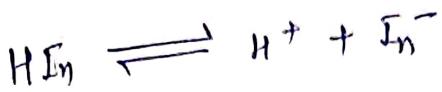


Soln: will be colourless.

Case-II :- In strong Basic medium (OH^-)



⇒ Soln. becomes pink in colour.



K_{IN} = K for indicator

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

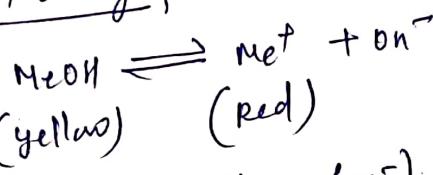
$$\log K_{IH} = \log [H^+] + \log \frac{[In^-]}{[HIn]}$$

$$PH = PK_{IN} + \log \frac{[In^-]}{[HIn]}$$

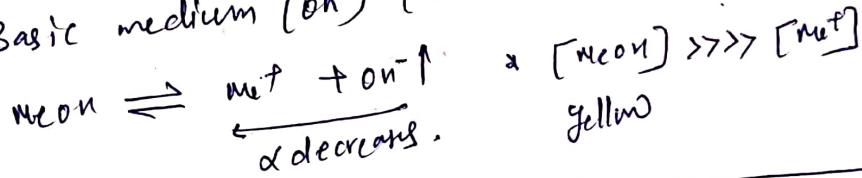
Ionised Part
unionsed part

If is suitable for SB v/s SA, SB v/s wB.

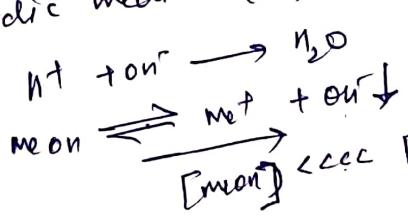
② Methyl orange:- (MeOH) (weak Base)



Case-I:- In Basic medium (OH^-) (It will show common ion effect)



Case-II:- In Acidic medium (H^+):-



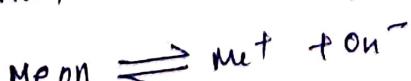
$$PH = -PK_{IN} + \log \frac{[Me^+]}{[MeOH]}$$

If is suitable for

SA v/s SB

SA v/s wB

pH Range \Rightarrow HPh (8.3 - 10.5)
 $MeOH \Rightarrow (3.2 - 4.5)$



$$K_{IH} = \frac{[Me^+] [OH^-]}{[MeOH]}$$

$$\log K_{IN} = \log [OH^-] + \log \frac{[Me^+]}{[MeOH]}$$

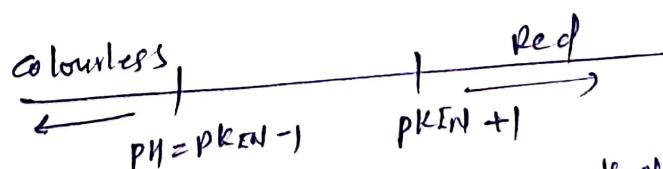
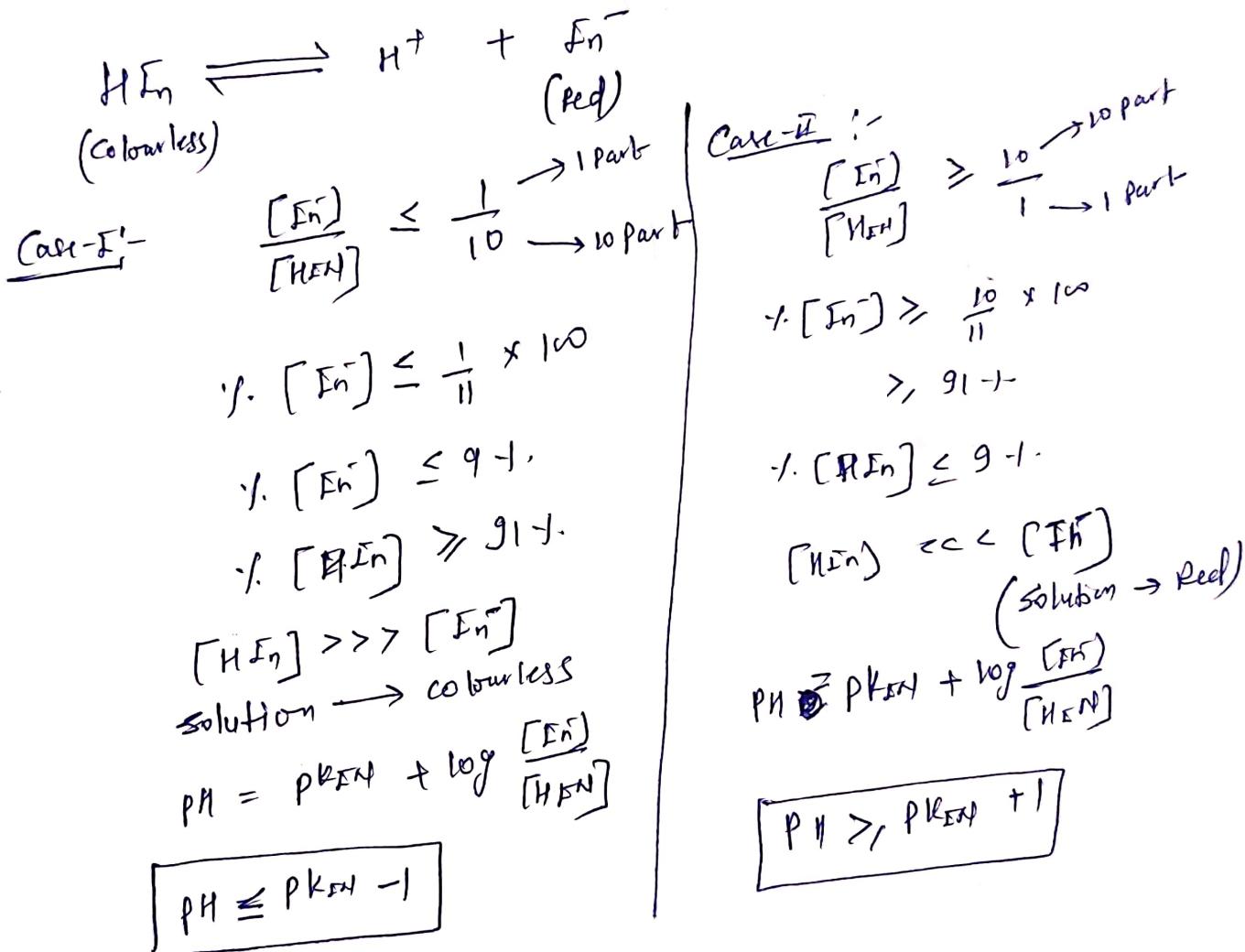
pH Range \Rightarrow Range in which colour change is shown

$$\text{pH Range} = \text{pK}_{\text{EN}} \pm 1$$



$$\text{pH Range} = 9 \pm 1$$

$$\Rightarrow \underline{8 \text{ to } 10}$$



change $= \text{pK}_{\text{EN}} - 1 \text{ to } \text{pK}_{\text{EN}} + 1$

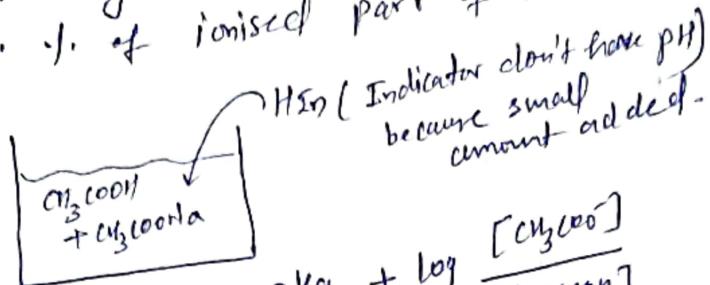
~~pH range~~ $\boxed{\text{pH Range} = \text{pK}_{\text{EN}} \pm 1}$

e.g. $\text{K}_{\text{EN}} = 10^{-9}$
 $\text{Range} \Rightarrow \underline{8 \text{ to } 10}$



Ex. In a solution conc. of CH_3COOH and CH_3COONa is 0.1M and 0.2M respectively. In this solution indicator HIn ($K_{\text{In}} = 10^{-6}$) is added. Calc. % of ionised part of indicator in solution (K_a for $\text{CH}_3\text{COOH} = 10^{-5}$)

Soln.



$$\text{pH} = \text{p}K_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$$\text{pH} = 5 - \log 2 + \log_{10} \frac{0.2}{0.1}$$

$$\text{pH} = 5 - \log 2 + \log 2$$

$\text{pH} = 5$

K_{In}

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

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

$$\gamma_{\text{In}^-} = \frac{1}{11} \times 100 \\ = 9.1\%$$

$$\left\{ \begin{array}{l} 5 = 6 + \log \frac{[\text{In}^-]}{[\text{HIn}]} \\ -1 = \log \frac{[\text{In}^-]}{[\text{HIn}]} \\ \log \frac{1}{10} = \log \frac{[\text{In}^-]}{[\text{HIn}]} \end{array} \right.$$