

Ionic Equilibrium

pH Scale

$$pH = -\log [H^+]$$

$$pOH = -\log [OH^-]$$

Again, $K_w = [H^+][OH^-] = 10^{-7} \times 10^{-7} = 10^{-14}$ at 298 K

ie $pK_w = pH + pOH = 14$

Also, the pH scale is usually reported for values between 0 and 14

For acidic solution, $pH < 7$

For basic solution, $pH > 7$

For neutral solution, $pH = 7$

pH of some common substances;

Lime water; $pH = 10.5$

Milk of Magnesia; $pH = 10$

Egg white, sea water; $pH = 7.8$

Blood = 7.3 - 7.5

Saliva = 6.5 - 7.5

Urine = 5.5 - 7.5

Milk = 6.8

Beer = 4 - 5

Black Coffee = 5

Lemon Juice = 2.2 - 2.4

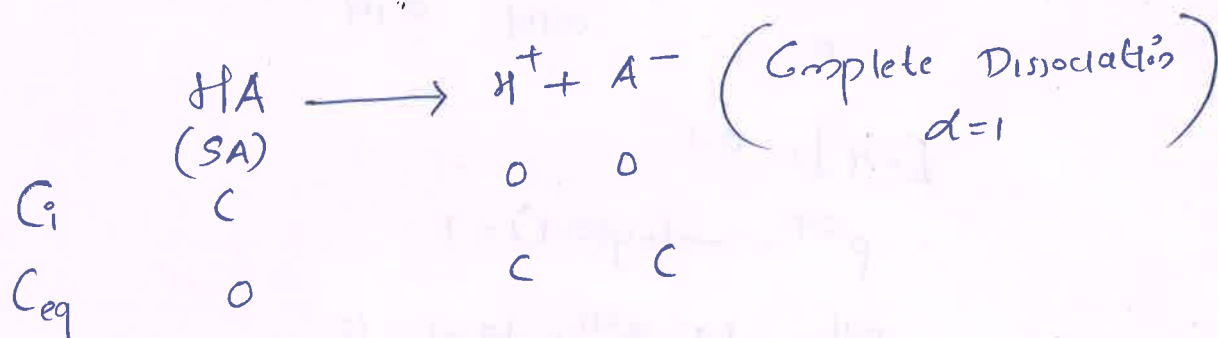
Gastric Juice = 1 - 3

Calculation of pH

2

Type 1

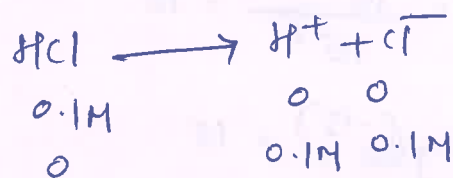
pH of Aqueous solutions of SA or SB



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

Q-01

pH of 0.1M HCl solution

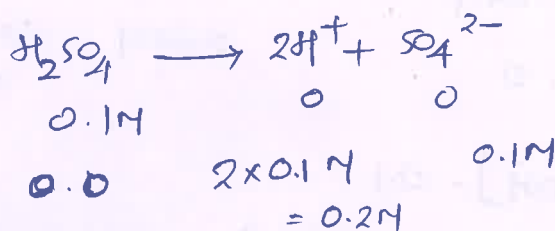


$$[\text{H}^+] = 0.1\text{M}$$

$$\therefore \text{pH} = -\log [0.1] = 1$$

Q-02

pH of 0.1M H_2SO_4 solution

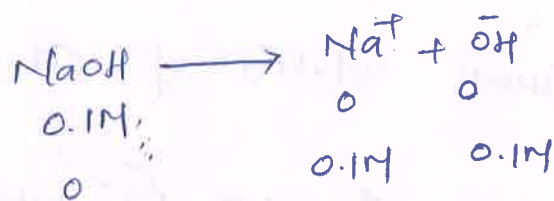


$$[\text{H}^+] = 0.2\text{M}$$

$$\therefore \text{pH} = -\log (0.2) = 0.7$$

Q-03

pH of 0.1M NaOH solution



$$[\text{OH}^-] = 0.1$$

$$\therefore p^{\text{OH}} = -\log(0.1) = 1$$

$$\therefore \text{pH} = 14 - p^{\text{OH}} = 14 - 1 = 13$$

OR

$$[\text{OH}^-] = 0.1$$

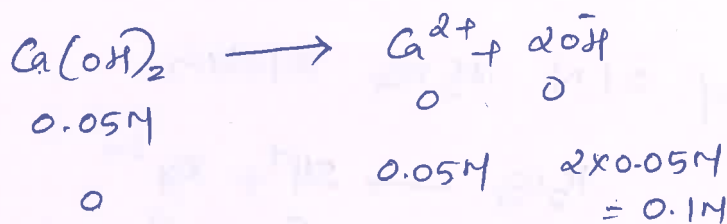
$$[\text{H}^+][\text{OH}^-] = 10^{-14} = K_w$$

$$\therefore [\text{H}^+] = \frac{10^{-14}}{10^{-1}} = 10^{-13}$$

$$\therefore \text{pH} = -\log(10^{-13}) = 13$$

Q-04

pH of 0.05M $\text{Ca}(\text{OH})_2$ solution



$$[\text{OH}^-] = 0.1$$

$$\therefore p^{\text{OH}} = -\log(10^{-1}) = 1$$

$$\therefore \text{pH} = 14 - p^{\text{OH}} = 14 - 1 = 13$$

OR

$$\text{Use } [\text{H}^+][\text{OH}^-] = 10^{-14} = K_w$$

Type-2

pH of very dilute solution of SA or SB

For very dilute SA,

$$[H^+]_{total} = [H^+]_{acid} + [H^+]_{water}$$

Here, $[H^+]_{water} = 10^{-7} M$ at 298 K

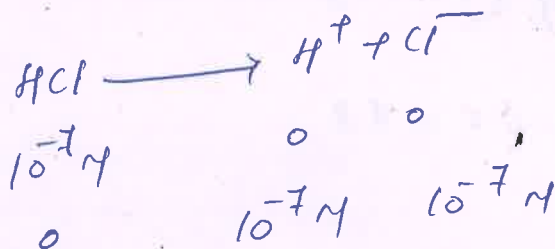
For very dilute SB,

$$[OH^-]_{total} = [OH^-]_{base} + [OH^-]_{water}$$

Here, $[OH^-]_{water} = 10^{-7} M$ at 298 K

Q-05

pH of $10^{-7} M$ HCl solution



$$pH = -\log(10^{-7}) = 7 \quad (\text{wrong because HCl solution is acidic})$$

\therefore pH should be less than 7

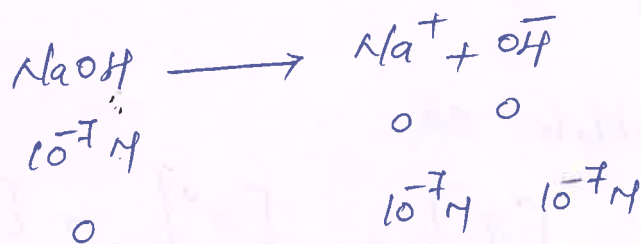
Here,

$$\begin{aligned}
 [H^+]_{total} &= [H^+]_{HCl} + [H^+]_{H_2O} \\
 &= 10^{-7} + 10^{-7} = 2 \times 10^{-7} M
 \end{aligned}$$

$$pH = -\log(2 \times 10^{-7}) = 6.7$$

Q-06

pH of $10^{-7}M$ NaOH solution



$$pOH = -\log[\text{OH}^-] = -\log(10^{-7}) = 7$$

$$\therefore pH = 14 - pOH = 14 - 7 = 7 \quad \left(\text{wrong because NaOH solution is basic} \right. \\ \left. \therefore pH \text{ should be more than } 7 \right)$$

Here,

$$\begin{aligned} [\text{OH}^-]_{\text{total}} &= [\text{OH}^-]_{\text{NaOH}} + [\text{OH}^-]_{\text{H}_2\text{O}} \\ &= 10^{-7} + 10^{-7} = 2 \times 10^{-7}M \end{aligned}$$

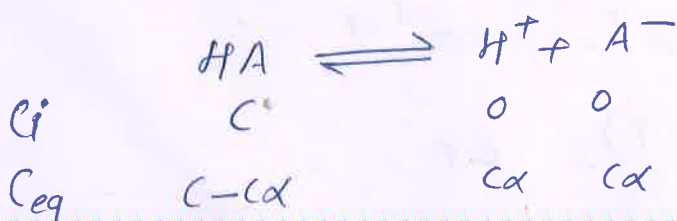
$$pOH = -\log(2 \times 10^{-7}) = 6.7$$

$$\therefore pH = 14 - 6.7 = 7.3$$

Type-3

pH of aqueous solution of WA or WB

Consider a weak acid HA ($\alpha < 1$)



$$\therefore \text{Dissociation Constant, } K_a = \frac{[H^+][A^-]}{[HA]}$$

$$= \frac{c\alpha \cdot c\alpha}{c - c\alpha}$$

$$K_a = \frac{c\alpha^2}{1 - \alpha} \Rightarrow \text{Ostwald Dilution Law}$$

If $\alpha \ll 1$; $1 - \alpha \approx 1$, then

$$K_a = c\alpha^2$$

$$\therefore \alpha = \sqrt{\frac{K_a}{c}}$$

$$pH = -\log [H^+] = -\log c\alpha$$

$$= -\log \left(\sqrt{\frac{K_a}{c}} \right)$$

$$= -\log \sqrt{K_a \cdot c} = -\log (K_a \cdot c)^{1/2}$$

$$= -\frac{1}{2} [\log K_a + \log c]$$

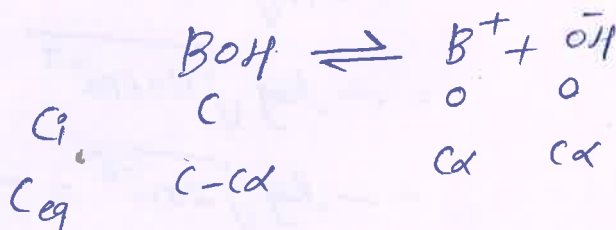
$$= \frac{1}{2} [-\log K_a - \log c]$$

$$\text{Since } pK_a = -\log K_a,$$

$$pH = \frac{1}{2} [pK_a - \log c]$$

As $K_a \uparrow$ $pK_a \downarrow$, acidic character \uparrow

Similarly Consider a weak base BOH



Dissociation Constant, $K_b = \frac{c\alpha^2}{1-\alpha} \Rightarrow$ Ostwald Dilution Law

$$\text{Also, } K_b \approx c\alpha^2 \\ \alpha = \sqrt{K_b/c}$$

$$pOH = -\log [OH^-] = -\log c\alpha \\ = -\log c \sqrt{\frac{K_b}{c}}$$

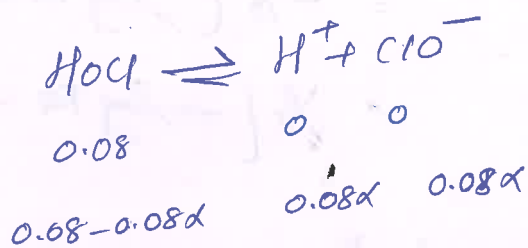
$$\text{ie } pOH = \frac{1}{2} [pK_b - \log c]$$

As $K_b \uparrow$ $pK_b \downarrow$,
basic character \uparrow

$$\text{or } pH = 14 - \frac{1}{2} [pK_b - \log c]$$

Q-07

pH of 0.08M HCl soln if its $K_a = 2.5 \times 10^{-5}$



$$\begin{aligned} pH &= -\log [H^+] = -\log 0.08\alpha \\ &= -\log \sqrt{K_a \cdot 0.08} \\ &= -\log \sqrt{2.5 \times 10^{-5} \times 8 \times 10^{-2}} \\ &= -\log \sqrt{20 \times 10^{-7}} \\ &= -\log \sqrt{2 \times 10^{-6}} = -\frac{1}{2} [\log 2 + \log 10^{-6}] \\ &= 2.85 \end{aligned}$$

OR

$$\begin{aligned}
 \text{pH} &= \frac{1}{2} [\text{p}K_a - \log c] \\
 &= \frac{1}{2} [4.6 - \log 0.08] \\
 &= \frac{1}{2} [4.6 - \log 8 \times 10^{-2}] \\
 &= \frac{1}{2} [4.6 - \log 8 - \log 10^{-2}] \\
 &= \frac{1}{2} [4.6 - 3 \times 0.3 + 2] \\
 &= 2.85
 \end{aligned}$$

$$\begin{aligned}
 \text{p}K_a &= -\log 2.5 \times 10^{-5} \\
 &= -\log 25 \times 10^{-6} \\
 &= 6 - \log 25 \\
 &= 6 - 2 \times 0.7 \\
 &= 6 - 1.4 \\
 &= 4.6
 \end{aligned}$$

Q-08

pH of 0.004M Hydrazine solution if its K_b is 9×10^{-7}

$$\begin{aligned}
 \text{pH} &= -\log \alpha = -\log \sqrt{K_b \cdot c} \\
 &= \frac{1}{2} [-\log K_b - \log c]
 \end{aligned}$$

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

$$\text{pH} = 14 - \frac{1}{2} [\text{p}K_b - \log c]$$

$$= 14 - \frac{1}{2} [6.04 - \log(4 \times 10^{-3})]$$

$$= 14 - \frac{1}{2} [6.04 - \log 4 - \log 10^{-3}]$$

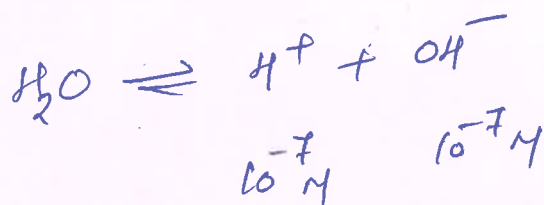
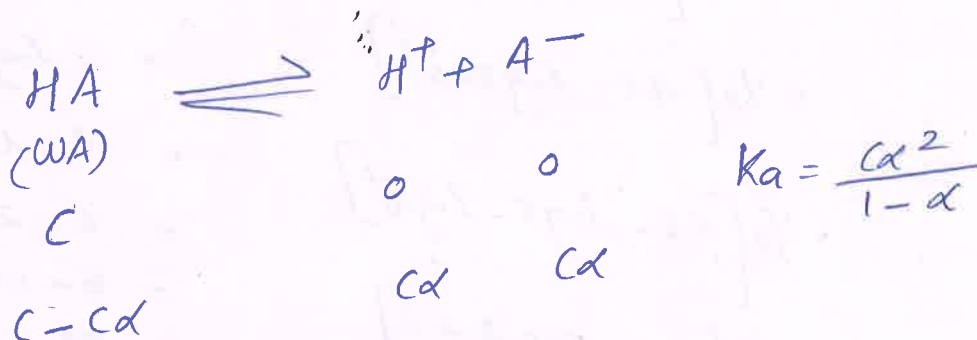
$$= 14 - \frac{1}{2} [6.04 - 0.6 + 3]$$

$$= 9.78$$

$$\begin{aligned}
 \text{p}K_b &= -\log K_b \\
 &= -\log 9 \times 10^{-7} \\
 &= 7 - 2 \times 0.48 \\
 &= 7 - 0.96 \\
 &= 6.04
 \end{aligned}$$

Type - A

pH of very dilute aqueous solution of WA or WB



$$[\text{H}^+]_{\text{total}} = [\text{H}^+]_{\text{acid}} + [\text{H}^+]_{\text{H}_2\text{O}}$$

But during dilution, α increases \therefore we can't neglect α

$$[\text{H}^+]_{\text{total}} = C\alpha + 10^{-7}$$

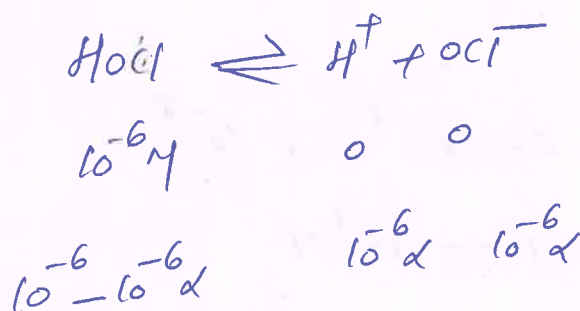
$$[\text{H}^+]_{\text{acid}} = C\alpha \quad \Rightarrow \quad K_a = \frac{C\alpha^2}{1-\alpha}$$

Solve for α

$$\text{Then } \text{pH} = -\log [\text{H}^+]_{\text{total}}$$

Q-02

pH of 10^{-6} M HOCl if its K_a is 10^{-8} .



$$\text{pH} = -\log \alpha = -\log(10^{-6} \alpha)$$

$$= -\log \sqrt{K_a \cdot 10^{-6}} = -\log \sqrt{10^{-8} \times 10^{-6}}$$

$= 7$ (wrong because HOCl soln is acidic)

\therefore pH should be less than 7

$$[\text{H}^+]_{\text{total}} = [\text{H}^+]_{\text{HOCl}} + [\text{H}^+]_{\text{H}_2\text{O}}$$

For dilute solution, α can't be neglected

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

$$10^{-8} = \frac{10^{-6} \alpha^2}{1-\alpha}$$

$$(1-\alpha)10^{-2} = \alpha^2$$

$$\alpha^2 + 10^{-2} \alpha - 10^{-2} = 0$$

$$\alpha = \frac{-10^{-2} \pm \sqrt{(10^{-2})^2 - 4 \times 1 \times (-10^{-2})}}{2 \times 1} = 0.005$$

$$\begin{aligned}
 [H^+]_{H_2O} &= \alpha \\
 &= 10^{-6} \times 0.095 \\
 &= 0.95 \times 10^{-7} \text{ M}
 \end{aligned}$$

$$\begin{aligned}
 [H^+]_{\text{total}} &= 0.95 \times 10^{-7} + 10^{-7} \\
 &= 1.95 \times 10^{-7} \text{ M}
 \end{aligned}$$

$$\begin{aligned}
 \text{pH} &= -\log(1.95 \times 10^{-7}) \\
 &= 6.7
 \end{aligned}$$

Type 5

pH of mixture of aqueous solution of two SA OR two SB

a) Acid + acid

$$[H^+] = \frac{N_{H^+ \text{ mix}}}{V_{\text{mix}}}$$

b) Base + base

$$[OH^-] = \frac{N_{OH^- \text{ mix}}}{V_{\text{mix}}}$$

c) Acid + base \Rightarrow neutralization

$$M_{H^+} \text{ OR } M_{OH^-} = \frac{N_{H^+ \text{ OR } OH^- \text{ left after neutralization}}}{V_{\text{total}}}$$

Q-10

pH of a mixture of 400 mL of solution with $pH=3$ and 100 mL of solution with $pH=4$

$pH=3$ & $pH=4 \Rightarrow$ Both are acidic solns

$$pH=3 \Rightarrow [H^+] = 10^{-3}$$

$$pH=4 \Rightarrow [H^+] = 10^{-4}$$

$$M_{H^+} = \frac{M_1V_1 + M_2V_2}{V_1 + V_2} = \frac{10^{-3} \times 400 + 10^{-4} \times 100}{500}$$

$$= \frac{0.4 + 0.01}{500} = \frac{0.41}{500}$$

$$= \frac{41 \times 10^{-2}}{500} = \frac{41}{5} \times 10^{-4} = 8.2 \times 10^{-4}$$

$$pH = -\log [8.2 \times 10^{-4}]$$

$$= 4 - \log 8.2 = 4 - 0.91 = 3.09 \approx 3.1$$

Q-11

pH of a mixture of equal volumes of two solutions with $pH=4$ and $pH=10$

$$pH=4 \Rightarrow \text{acidic}$$

$$pH=10 \Rightarrow \text{Basic}$$

\therefore Neutralization occurs

$$pH = 4 \Rightarrow [H^+] = 10^{-4}$$

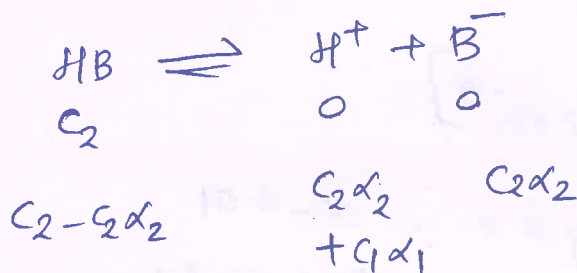
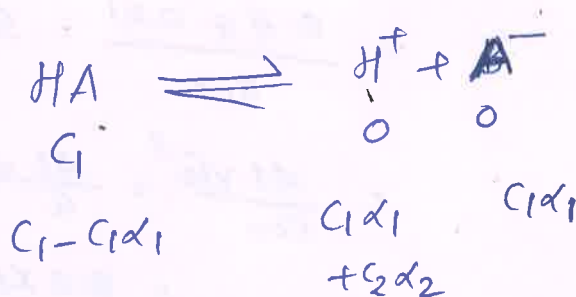
$$pH = 10 \Rightarrow [H^+] = 10^{-10} \Rightarrow [OH^-] = 10^{-4}$$

Since n_{H^+} and n_{OH^-} are equal, neutralisation is complete

$$\therefore pH = 7$$

Type-6

pH of a mixture of two WA or two WAB solutions



H^+ is a common ion

$$\therefore [H^+] \uparrow$$

So according to Le Chatelier's principle, dissociation of weak acids ↓

$$K_{a1} = \frac{(C_1\alpha_1 + C_2\alpha_2)(C_1\alpha_1)}{C_1(1-\alpha_1)} \approx \frac{(C_1\alpha_1 + C_2\alpha_2)(C_1\alpha_1)}{C_1} \quad \text{--- (1)}$$

$$K_{a2} = \frac{(C_1\alpha_1 + C_2\alpha_2)(C_2\alpha_2)}{C_2(1-\alpha_2)} \approx \frac{(C_1\alpha_1 + C_2\alpha_2)(C_2\alpha_2)}{C_2} \quad \text{--- (2)}$$

α changes for both acids but individual α decreases

$$\therefore 1 - \alpha_1 \approx 1 \\ 1 - \alpha_2 \approx 1$$

From ①

$$K_{a1}C_1 = (C_1\alpha_1 + C_2\alpha_2)(C_1\alpha_1)$$

From ②

$$K_{a2}C_2 = (C_1\alpha_1 + C_2\alpha_2)(C_2\alpha_2)$$

$$\text{So } K_{a1}C_1 + K_{a2}C_2 = (C_1\alpha_1 + C_2\alpha_2)^2 = [H^+]^2$$

$$[H^+] = \sqrt{K_{a1}C_1 + K_{a2}C_2}$$

$$\text{Also } [OH^-] = \sqrt{K_{b1}C_1 + K_{b2}C_2}$$

Q-12

pH of a solution containing 0.1 M acetic acid ($K_a = 2 \times 10^{-5}$)
and 0.2 M phenol ($K_a = 10^{-10}$)

$$[H^+] = \sqrt{K_{a1}C_1 + K_{a2}C_2}$$

$$= \sqrt{2 \times 10^{-5} \times 0.1 + 10^{-10} \times 0.2}$$

$$= \sqrt{2 \times 10^{-6} + 2 \times 10^{-11}}$$

$$= \sqrt{2 \times 10^{-6} [1 + 10^{-5}]}$$

$$\approx \sqrt{2 \times 10^{-6}} = 1.414 \times 10^{-3}$$

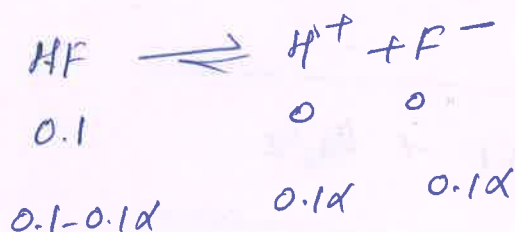
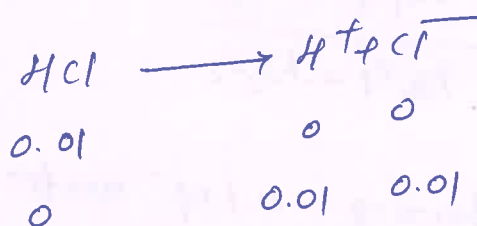
$$\begin{aligned} \text{pH} &= -\log(1.414 \times 10^{-3}) = 3 - \log 1.414 \\ &= 3 - 0.15 \\ &= 2.85 \end{aligned}$$

Type 7

pH of a solution obtained by mixing w + s

Q-13

pH of solution obtained by mixing 10 mL of a 0.01M HCl with 90 mL 0.1M HF solution at 25°C (K_a of HF is 5×10^{-4})

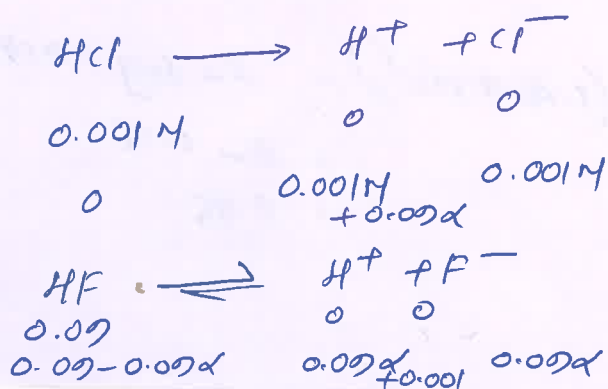


But on mixing $[\text{HCl}] = \frac{n}{V} = \frac{MV}{V_{\text{total}}} = \frac{0.01 \times 10}{10 + 90}$

$$= \frac{0.1}{100} = 10^{-3} \text{ M}$$

$$[\text{HF}] = \frac{n}{V} = \frac{MV}{V_{\text{total}}} = \frac{0.1 \times 90}{100} = 9 \times 10^{-2} \text{ M}$$

Now,



$$K_a = \frac{0.09\alpha (0.09\alpha + 0.001)}{0.09(1-\alpha)}$$

$$5 \times 10^{-4} = \frac{0.09\alpha^2 + 0.001\alpha}{1-\alpha}$$

$$0.09\alpha^2 + 0.001\alpha = 5 \times 10^{-4} - 5 \times 10^{-4}\alpha$$

$$0.09\alpha^2 + 0.001\alpha + 0.0005\alpha - 0.0005 = 0$$

$$0.09\alpha^2 + 0.0015\alpha - 0.0005 = 0$$

$$9\alpha^2 + 0.15\alpha - 0.05 = 0$$

$$900\alpha^2 + 15\alpha - 5 = 0$$

$$180\alpha^2 + 3\alpha - 1 = 0$$

$$\alpha = \frac{-3 \pm \sqrt{(3)^2 - 4 \times 180 \times -1}}{2 \times 180}$$

$$= \frac{-3 \pm \sqrt{9 + 720}}{360}$$

$$= \frac{-3 \pm 27}{360} = \frac{-3 + 27}{360} = \frac{24}{360} = 0.067$$

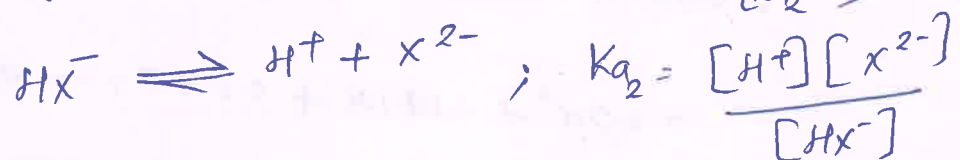
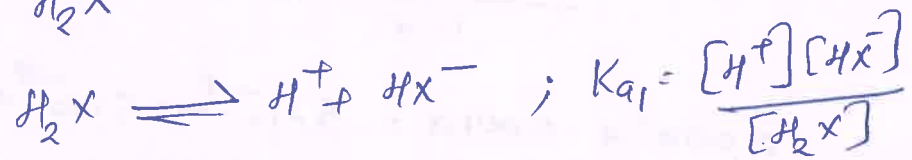
$$\begin{aligned} [H^+] &= 0.001 + 0.09\alpha = 0.001 + 0.09 \times 0.067 \\ &= 0.00703 \\ &\approx 0.007 = 7 \times 10^{-3} \end{aligned}$$

$$\begin{aligned} pH &= -\log[H^+] = -\log(7 \times 10^{-3}) = 3 - \log 7 \\ &= 3 - 0.84 = 2.16 \end{aligned}$$

Type 8

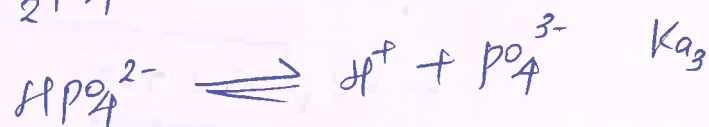
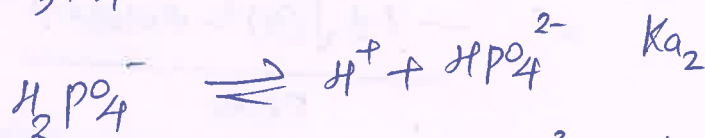
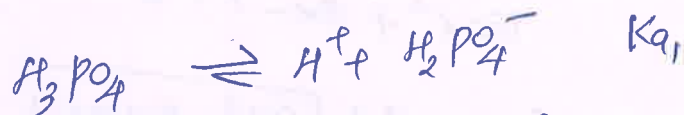
pH of aqueous solution of Diprotic & Polyprotic acids or bases

Consider H_2X



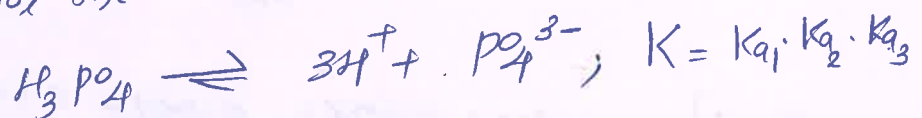
Here $K_{a1} > K_{a2}$ because second ionisation is very difficult

Eg. Consider H_3PO_4



Here $K_{a3} > K_{a2} > K_{a1}$

Also for the dissociation,



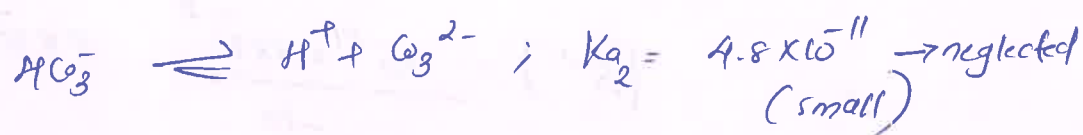
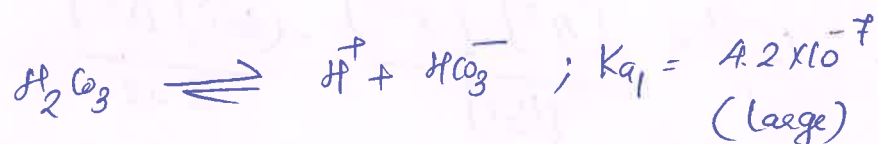
For most cases, contribution of higher order ionization to the total $[H^+]$ could be ignored

So pH will be determined considering only first

ionization reaction

Q-14

pH of an aqueous solution of carbonic acid if molar solubility of CO_2 in the given condition is 0.01
 $K_{a1} = 4.2 \times 10^{-7}$ and $K_{a2} = 4.8 \times 10^{-11}$



$$K_{a1} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

$$[\text{H}^+] = \alpha_1 = \sqrt{K_{a1} C} = \sqrt{4.2 \times 10^{-7} \times 0.01}$$

$$= \sqrt{4.2 \times 10^{-9}}$$

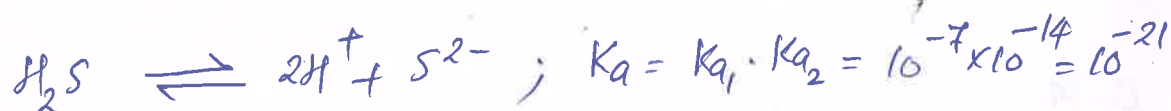
$$\text{pH} = -\log \sqrt{4.2 \times 10^{-9}}$$

$$= -\frac{1}{2} [\log 4.2 + \log 10^{-9}]$$

$$= -\frac{1}{2} [0.62 - 9] = 4.19$$

Q-15

Ionization constant of H_2S are $K_{a1} = 10^{-7}$ and $K_{a2} = 10^{-14}$.
 If molar solubility of H_2S is 0.03M, determine molar concentration of sulphide ion in a saturated solution of H_2S where $\text{pH} = 3$



$$K_a = \frac{[H^+]^2 [S^{2-}]}{[H_2S]}$$

$$10^{-21} = \frac{[H^+]^2 [S^{2-}]}{[H_2S]} = \frac{(10^{-5})^2 [S^{2-}]}{0.03}$$

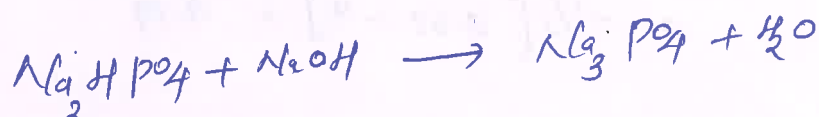
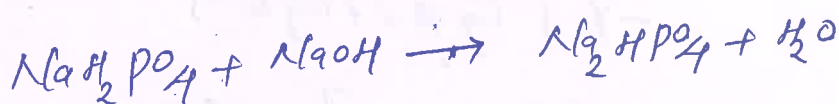
$$pH = 5 \\ [H^+] = 10^{-5} M$$

$$[S^{2-}] = \frac{10^{-21} \times 3 \times 10^{-2}}{10^{-10}} = 3 \times 10^{-13} M$$

Type 2

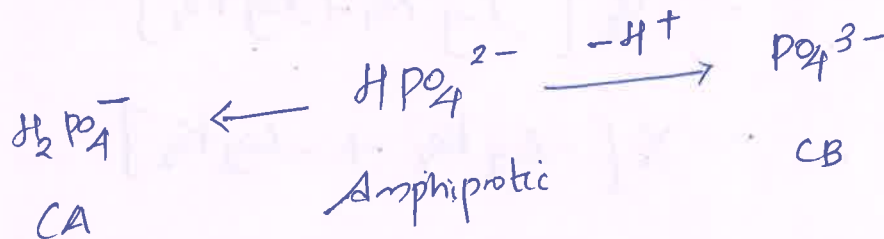
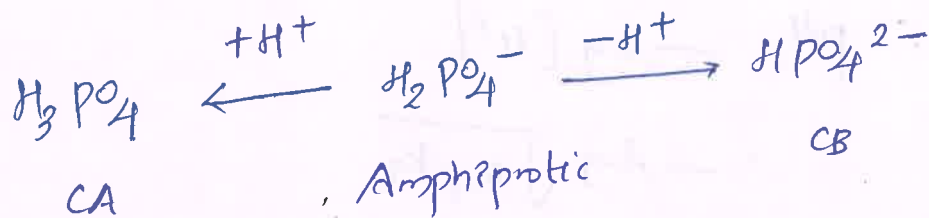
pH of aqueous solution of amphoteric species (can either donate or accept a proton)

Consider the reactions

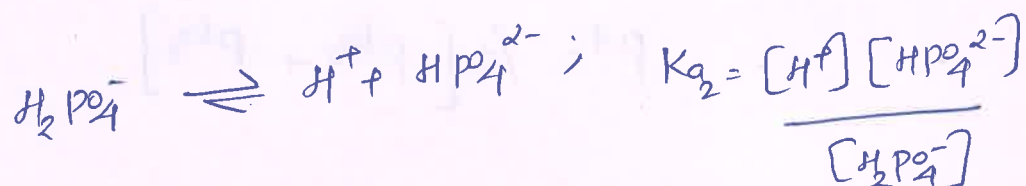
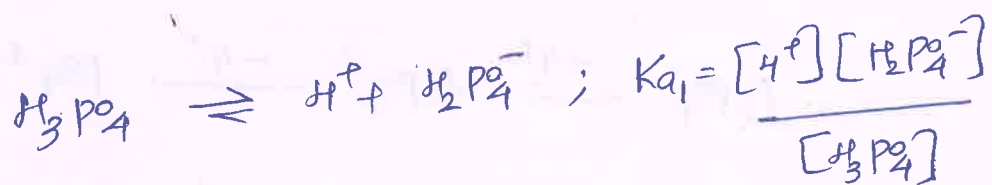
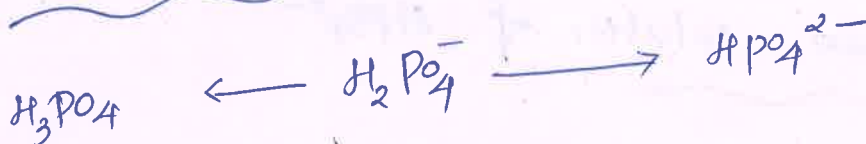


ie





pH of an aqueous solution of H_2PO_4^-



$$\text{Here, } K_{a1} \cdot K_{a2} = \frac{[\text{H}^+]^2 [\text{HPO}_4^{2-}]}{[\text{H}_3\text{PO}_4]}$$



$$\therefore [\text{HPO}_4^{2-}] = [\text{H}_3\text{PO}_4]$$

$$\therefore K_{a1} \cdot K_{a2} = [\text{H}^+]^2$$

$$[\text{H}^+] = \sqrt{K_{a1} \cdot K_{a2}}$$

$$\therefore pH = -\log [H^+]$$

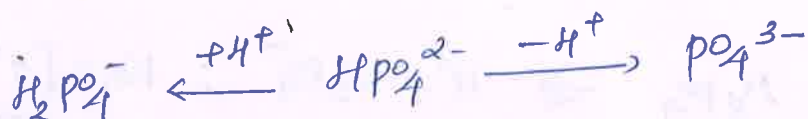
$$= -\log \sqrt{K_{a1} \cdot K_{a2}}$$

$$= -\frac{1}{2} [\log K_{a1} + \log K_{a2}]$$

$$= \frac{1}{2} [-\log K_{a1} + -\log K_{a2}]$$

$$\therefore pH = \frac{1}{2} [pK_{a1} + pK_{a2}]$$

pH of an aqueous solution of HPO_4^{2-}



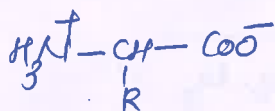
$$\therefore pH = \frac{1}{2} [pK_{a2} + pK_{a3}]$$

Type 10

pH of aqueous solution of amino acids ($\begin{smallmatrix} H_2N-CH-COOH \\ | \\ R \end{smallmatrix}$)

Amino acids are characterised by two pK values i.e. pK_1 for carboxylic acid and pK_2 for the amino group.

Isoelectric pH (pI) is the pH at which amino acid exists as a zwitter ion (dipolar ion)

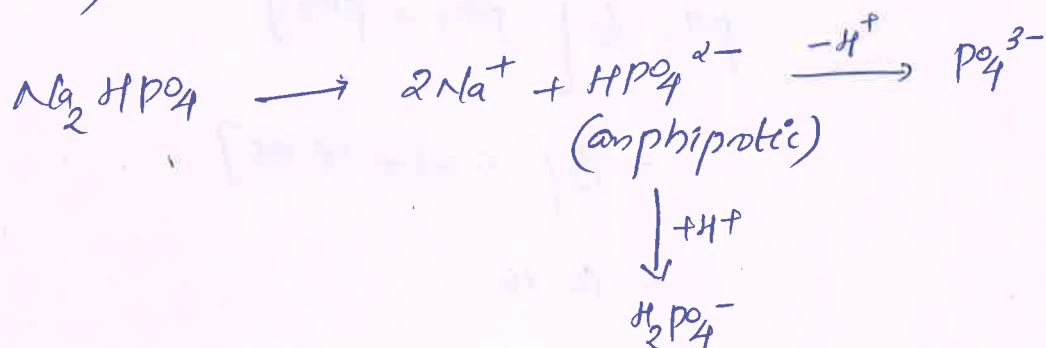


$$pI = \frac{1}{2} [pK_{a1} + pK_{a2}]$$

For amino acids with more than two ionizable groups, pI is the average of two pK_a values that are close to each other.

Q-16

pH of $0.1M$ Na_2HPO_4 solution (pK_a for H_3PO_4 are 2.2, 7.2 and 12.0)



$$pH = \frac{1}{2} [pK_{a2} + pK_{a3}]$$

$$= \frac{1}{2} [7.2 + 12] = \frac{19.2}{2} = 9.6$$

Q-17

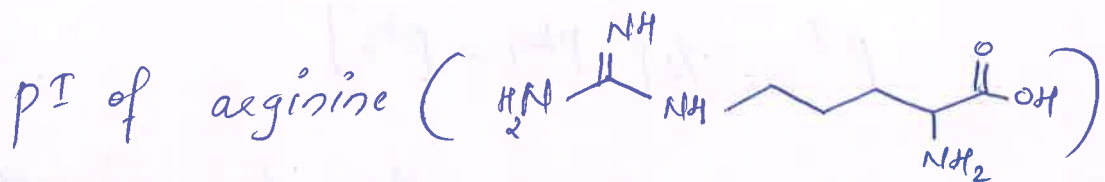
pI of glycine (H_2NCH_2COOH) where $pK_{a1} = 2.34$

and $pK_{a2} = 9.60$

$$pI = \frac{1}{2} [pK_{a1} + pK_{a2}] = \frac{1}{2} [2.34 + 9.60]$$

$$= 5.94$$

Q-18



where pK_{a1} (-COOH gp) = 2.17

pK_{a2} (alpha-ammonium group) = 9.04

pK_{a3} (guanidinium R group) = 12.48

$$\begin{aligned} pH &= \frac{1}{2} [pK_{a2} + pK_{a3}] \\ &= \frac{1}{2} [9.04 + 12.48] \\ &= 10.76 \end{aligned}$$

Buffer Solutions

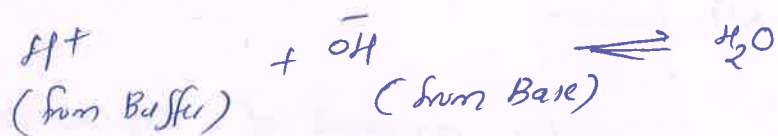
The solution which resists changes in the H^+ concentration on the addition of small amount of acid or base

Eg; H_2CO_3/HCO_3^- buffer system helps to maintain pH of blood between 7.26 to 7.42.

Buffer solutions are of three types;

- 1) Acidic Buffer \rightarrow WA + its salt with SB
- 2) Basic Buffer \rightarrow WB + its salt with SA
- 3) Neutral Buffer \rightarrow Salt of WA & WB

Similarly, if a few drops of NaOH are added to the buffer solution, it would provide OH^- ions. These would combine with H^+ ions due to partial dissociation of CH_3COOH molecules to form unionised H_2O molecules. This will make greater ionisation of CH_3COOH in order to restore H^+ ion concentration (Le Chatelier's principle).



Since the additional OH^- are neutralised by CH_3COOH molecules, pH of the solution does not change appreciably.

Henderson - Hasselbalch Equation

Consider a mixture of $\text{WA}(\text{HA})$ and its conjugate base A^- .



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

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

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

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

$$\text{or } pH = pK_a + \log \frac{[\text{conjugate base}]}{[\text{Acid}]} \quad \text{--- (1)}$$

Similarly for basic buffer,

$$pOH = pK_b + \log \frac{[\text{conjugate acid}]}{[\text{Base}]} \quad \text{--- (2)}$$

Equations (1) and (2) are Henderson-Hasselbalch equations

Buffer Capacity (β)

It is the resistance of a buffer to pH changes upon the addition of a SA or SB

$$\beta = \frac{dn}{dpH} ; \quad dn = \text{no of moles of acid/base added per litre of the buffer}$$

$dpH = \text{change in pH}$

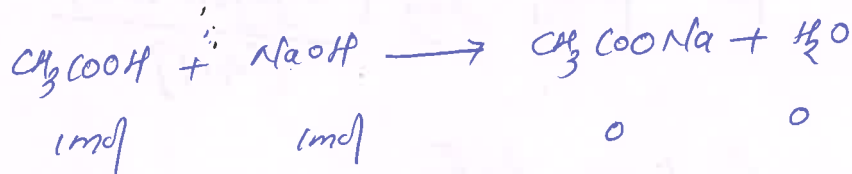
Buffer capacity is maximum when

i) $[A^-] = [HA]$ for acidic buffer

ii) $[B^+] = [BOH]$ for basic buffer

Q-19

pH of a solution obtained by mixing 200 mL 0.1 M CH_3COOH ($K_a = 2 \times 10^{-5}$) with 300 mL 0.02 M NaOH solution



Given:

200 mL 0.1 M

300 mL 0.02 M

20 mmol

6 mmol

0

0

(20 - 6) mmol

0

6 mmol

6 mmol

= 14 mmol

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

$$\begin{aligned} \text{p}K_a &= -\log(2 \times 10^{-5}) \\ &= 4.7 \end{aligned}$$

$$= 4.7 + \log \frac{\frac{6\text{ mmol}}{500\text{ mL}}}{\frac{14\text{ mmol}}{500\text{ mL}}}$$

$$= 4.7 + \log \frac{6}{14} = 4.33$$

Q-20

To 0.15 L of 0.05 M solution of HN_3 , 0.8 g of NaN_3 is added. pH if K_a of HN_3 is 3×10^{-5}

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

$$\text{p}K_a = -\log(3 \times 10^{-5}) = 4.52$$

$$\begin{aligned}
 [\text{NaN}_3] &= \frac{n_{\text{NaN}_3}}{V} \\
 &= \frac{w_{\text{NaN}_3}}{M_{\text{NaN}_3} \cdot V} \\
 &= \frac{0.8}{65 \times 0.15} = 0.082 \text{ M} = [\text{Na}^+] = [\text{N}_3^-]
 \end{aligned}$$

$$[\text{HN}_3] = 0.05 \text{ M}$$

$$\begin{aligned}
 \text{pH} &= \text{pK}_a + \log \frac{[\text{N}_3^-]}{[\text{HN}_3]} \\
 &= 4.52 + \log \left(\frac{0.082}{0.05} \right) \\
 &= 4.73
 \end{aligned}$$

Q-21

What weight of NaOH be added to 200 mL of a 0.16 M HOBr solution to produce a buffer solution of pH = 8.3, K_a of HOBr = 2×10^{-9} .

$$\text{pH} = \text{pK}_a + \log \frac{[\text{OBr}^-]}{[\text{HOBr}]}$$

$$\text{pK}_a = -\log(2 \times 10^{-9})$$

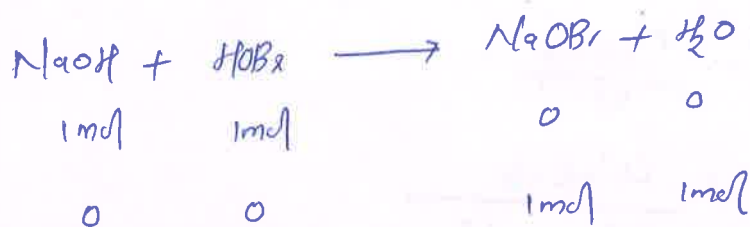
$$\begin{aligned}
 &= 9 - \log 2 \\
 &= 8.7
 \end{aligned}$$

$$8.3 = 8.7 + \log \frac{[\text{OBr}^-]}{[\text{HOBr}]}$$

$$\log \frac{[\text{OBr}^-]}{[\text{HOBr}]} = -0.4$$

$$\log \frac{[\text{HOBr}]}{[\text{OBr}^-]} = 0.4$$

$$\frac{[\text{HOBr}]}{[\text{OBr}^-]} = 2.5$$



Given

$$\begin{array}{ccccccc}
 x \text{ mmol} & & 200 \text{ mL} & & & & \\
 & & 0.16 \text{ M} & & 0 & & 0 \\
 & & = 32 \text{ mmol} & & & &
 \end{array}$$

$$\begin{array}{ccccccc}
 0 & & (32-x) \text{ mmol} & & x \text{ mmol} & &
 \end{array}$$

$$\frac{32-x}{x} = 2.5$$

$$32-x = 2.5x$$

$$3.5x = 32$$

$$x = \frac{32}{3.5} = 9.14 \text{ mmol}$$

$$n_{\text{NaOH}} = 9.14 \times 10^{-3} \text{ mol}$$

$$\begin{aligned}
 \therefore w_{\text{NaOH}} &= 9.14 \times 10^{-3} \times 40 \\
 &= 0.3656 \text{ g}
 \end{aligned}$$

Q-22

Addition of 150 mL 0.2 M HCl into 600 mL of Na_3PO_4 buffer with a pH of 7.39. changes pH into 7.03. Buffer capacity of Na_3PO_4 buffer is

$$n_{\text{HCl}} = MV = 0.2 \times 150 = 30 \text{ mmol} = 0.03 \text{ mol}$$

$$n_{\text{HCl}} \text{ per litre of buffer, } \Delta n \text{ or } dn = \frac{0.03}{0.6} = 0.05 \text{ M}$$

$$\Delta \text{pH} \text{ or } d\text{pH} = |7.03 - 7.39| = 0.36$$

$$\therefore \beta = \frac{0.05}{0.36} = 0.14$$

Salt Hydrolysis

Types of salts

- 1) Salt of SA + SB Eg: NaCl, KNO₃ etc
- 2) Salt of SA + WB Eg: NH₄Cl, NH₄NO₃ etc
- 3) Salt of WA + SB Eg: CH₃COONa, NaCN etc
- 4) Salt of WA + WB Eg: CH₃COONH₄, NH₄CN etc

Hydrolysis of salt → Common form of a chemical reaction where water is mostly used to break down the chemical bonds that exist between salts

A salt solution can be acidic, basic or neutral depending upon the nature of acids or bases from which the salt is derived.

"The weaker component (derived from WA or WB) only hydrolyse and stronger component (derived from SA or SB) undergo hydration and it will float around the solution as a spectator ion"

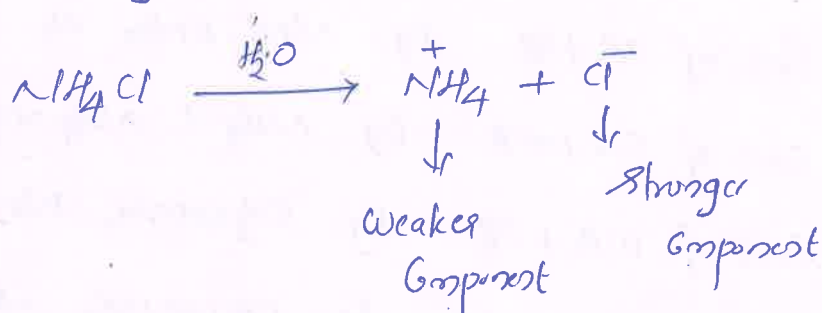
A) Hydrolysis of Salt of SA + SB

Eg: NaCl → Both Na⁺ and Cl⁻ ions are stronger components and just hydrated

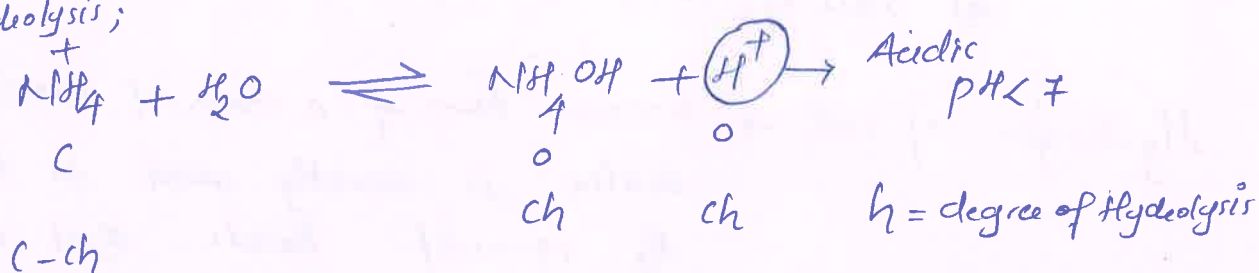
pH = 7 ⇒ Neutral

B) Salt of SA + WB

Eg: NH_4Cl



Cationic Hydrolysis;

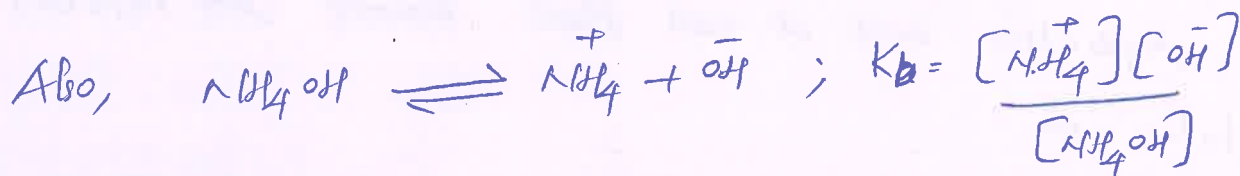


Hydrolysis Constant, $K_h = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]} = \frac{ch \cdot ch}{c(1-h)}$

If $h \ll 1$; $1-h \approx 1$, then

$$K_h = ch^2$$

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



Again, $K_b \cdot K_h = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} \times \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]} = [\text{H}^+][\text{OH}^-] = K_w$

or $K_b \cdot K_h = K_w$

or $K_h = \frac{K_w}{K_b}$

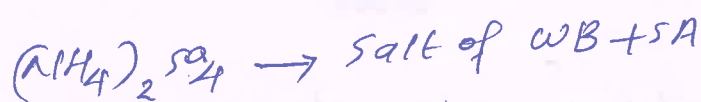
$$\begin{aligned}
 \text{pH} &= -\log [\text{H}^+] \\
 &= -\log c_h \\
 &= -\log \sqrt{K_h \cdot c} \\
 &= -\log \sqrt{\frac{K_w}{K_b} \cdot c}
 \end{aligned}$$

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

$$\text{pH} = 7 - \frac{1}{2} [\text{p}K_b + \log c]$$

Q-23

pH of 0.05M aqueous solution of $(\text{NH}_4)_2\text{SO}_4$ if K_b for NH_3 is 2×10^{-5}



$$\begin{aligned}
 \text{pH} &= 7 - \frac{1}{2} [\text{p}K_b + \log c] & \text{p}K_b &= -\log K_b \\
 &= 7 - \frac{1}{2} [4.7 + \log(5 \times 10^{-2})] & &= -\log 2 \times 10^{-5} \\
 &= 7 - \frac{1}{2} [4.7 + 0.7 - 2] & &= 4.7 \\
 &= 7 - \frac{1}{2} \times 3.4 \\
 &= 5.3
 \end{aligned}$$

Q-24

A 0.01M aqueous solution of CH_3NH_2 is titrated against 0.005M HCl solution. If K_b for CH_3NH_2 is 4×10^{-4} , pH of solution at equivalence point is



1mol

1mol

0

$$\text{p}K_b = -\log K_b$$

$$= -\log(4 \times 10^{-4})$$

$$= 4 - 0.6$$

$$= 3.4$$

Given;

$V_1 \text{ mL}$
0.01M

$V_2 \text{ mL}$
0.005M

0

$$n_{\text{CH}_3\text{NH}_2} = M_1 V_1 = 0.01 V_1 \text{ mmol} = n_{\text{HCl}} \text{ at equivalence point}$$

$$= \frac{M_2 V_2}{2}$$

$$0.01 V_1 = 0.005 V_2$$

$$V_2 = \frac{0.01}{0.005} V_1 = 2 V_1$$

$$\therefore \text{Total volume at equivalence point} = V_1 + V_2$$

$$= V_1 + 2 V_1$$

$$= 3 V_1$$



0.01M
 $V \text{ mL}$

0.005M
 $2V \text{ mL}$

0

= 0.01V
mmol

= 0.01V
mmol

0.01V mmol

0

0

$$\therefore [\text{CH}_3\text{NH}_3^+ \text{Cl}^-] = \frac{n}{V} = \frac{0.01V}{3V} = \frac{0.01}{3} = 3.3 \times 10^{-3} \text{ M} = C$$

$$\text{pH} = 7 - \frac{1}{2} [\text{p}K_b + \log C] = 7 - \frac{1}{2} [3.4 + (-2.48)]$$

$$= 6.54$$

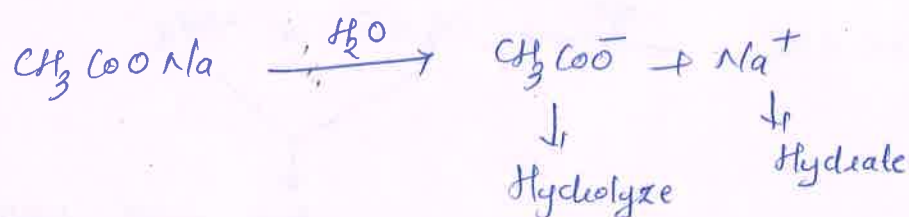
$$\log C = \log 3.3 \times 10^{-3}$$

$$= -3 + 0.52$$

$$= -2.48$$

c) Salt of WA + SB

Eg: CH_3COONa



Anionic Hydrolysis;



Also, $K_h = \frac{K_w}{K_a}$; $h = \sqrt{K_h/c}$

$$\text{pH} = 7 + \frac{1}{2} [\text{p}K_a + \log c]$$

Q-25

pH of 0.1M aqueous solution of NaNO_2 if K_a for HNO_2 is 7×10^{-4}

$\text{NaNO}_2 \rightarrow \text{Salt of SB + WA}$

$$\text{pH} = 7 + \frac{1}{2} [\text{p}K_a + \log c]$$

$$= 7 + \frac{1}{2} [3.16 + \log 0.1]$$

$$= 7 + \frac{1}{2} [3.16 - 1]$$

$$= 8.08$$

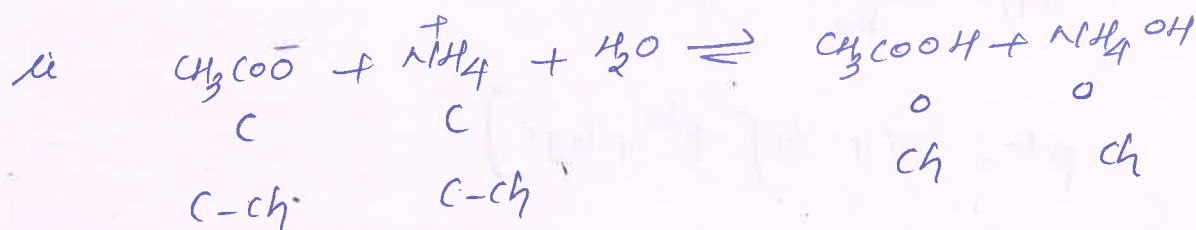
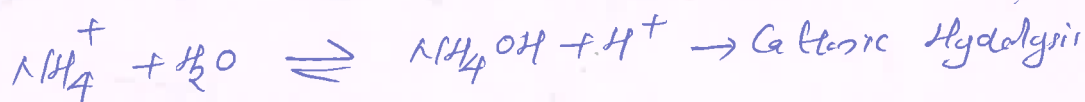
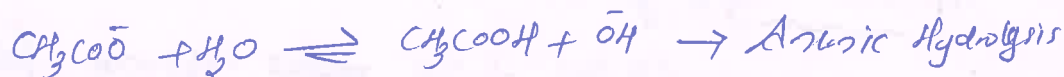
$$\begin{aligned} \text{p}K_a &= -\log 7 \times 10^{-4} \\ &= 4 - 0.84 \\ &= 3.16 \end{aligned}$$

D) Salt of WA + WB

Eg: NH_4CN , $\text{CH}_3\text{COONH}_4$ etc



Both will undergo hydrolysis



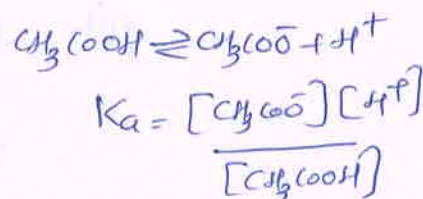
$$K_h = \frac{ch \cdot ch}{(c-ch)(c-ch)} = \frac{c^2 h^2}{c^2 (1-h)^2} \approx h^2$$

$$h = \sqrt{K_h}$$

Again,

$$K_h \cdot K_a \cdot K_b = K_w$$

$$K_h = \frac{K_w}{K_a \cdot K_b} \quad \text{AND}$$



$$K_a = \frac{(c-ch)[\text{H}^+]}{ch}$$

$$[\text{H}^+] = \frac{K_a \cdot ch}{c(1-h)} \approx K_a \cdot h$$

$$\text{pH} = -\log [\text{H}^+] = -\log K_a \cdot h$$

$$= -\log K_a \sqrt{K_h}$$

$$= -\log \sqrt{\frac{K_w}{K_a \cdot K_b} \cdot K_a^2}$$

$$= -\log \sqrt{\frac{K_w \cdot K_a}{K_b}}$$

$$pH = -\frac{1}{2} [\log K_w + \log K_a - \log K_b]$$

$$= \frac{1}{2} [pK_w + pK_a - pK_b]$$

$$pH = 7 + \frac{1}{2} [pK_a - pK_b] \rightarrow \text{Acidic or Basic depends upon } K_a \text{ and } K_b \text{ values}$$

Q-26

$$pK_a \text{ of } CH_3COOH = 4.76$$

$$pK_b \text{ of } NH_4OH = 4.74$$

pH of CH_3COONH_4 soln is

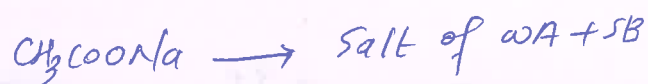
$$pH = 7 + \frac{1}{2} [pK_a - pK_b]$$

$$= 7 + \frac{1}{2} [4.76 - 4.74] = 7 + \frac{1}{2} \times 0.02$$

$$= 7.01$$

Q-27

Hydrolysis Constant of CH_3COONa in its 0.1M solution
If K_a of CH_3COOH is 1.8×10^{-5}



$$K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{1.8 \times 10^{-5}} = \frac{10^{-14}}{18 \times 10^{-6}} = \frac{10^{-8}}{18}$$

$$= 0.056 \times 10^{-8}$$

$$= 5.6 \times 10^{-10}$$

Solubility of Sparingly soluble salts - Solubility Equilibria

Solubility of ionic solids in water depends

upon

- 1) Lattice Enthalpy
- 2) Solvation Enthalpy

On the basis of solubility, salts are classified into 3 categories;

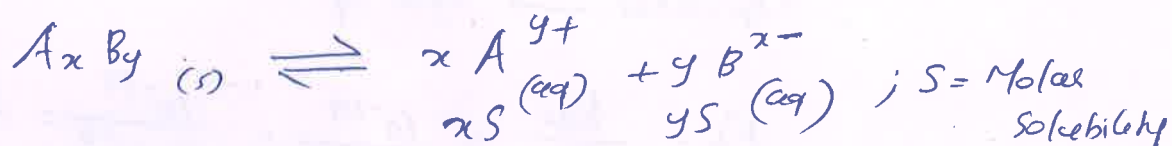
I) Soluble \rightarrow Solubility $> 0.1M$

II) Slightly soluble \rightarrow Solubility between $0.01M$ and $0.1M$

III) Sparingly soluble \rightarrow Solubility $< 0.01M$

Solubility Product Constant (K_{sp})

Consider a sparingly soluble salt, $A_x B_y (s)$



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

$$= [xS]^x [yS]^y$$

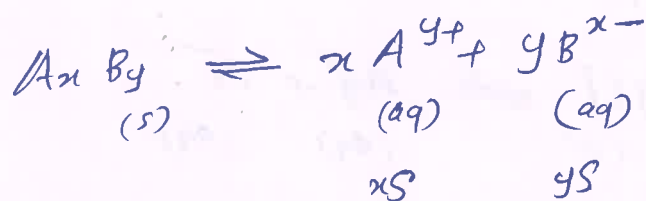
$$= x^x \cdot y^y \cdot S^{(x+y)}$$

$$\therefore K_{sp} = x^x \cdot y^y (S)^{x+y}$$

Type-1

Solubility of a salt of SA & SB in pure water

Generally,



$$K_{sp} = x^x \cdot y^y (S)^{x+y}$$

<u>Salt</u>	<u>Composition</u>	<u>K_{sp}</u>	<u>S</u>
1) AgCl, CaCO ₃ , AgBr etc	1:1	$K_{sp} = S^2$	$S = \sqrt{K_{sp}}$
2) Ag ₂ SO ₄ , Ag ₂ S, Al(OH) ₃ etc	$\begin{pmatrix} 2:1 \\ 1:2 \end{pmatrix}$	$K_{sp} = 4S^3$	$S = \left(\frac{K_{sp}}{4}\right)^{1/3}$
3) Al(OH) ₃	$\begin{pmatrix} 1:3 \\ 3:1 \end{pmatrix}$	$K_{sp} = 27S^4$	$S = \left(\frac{K_{sp}}{27}\right)^{1/4}$
4) La ₃ (PO ₄) ₄	$\begin{pmatrix} 3:4 \\ 4:3 \end{pmatrix}$	$K_{sp} = 6912 S^7$	$S = \left(\frac{K_{sp}}{6912}\right)^{1/7}$

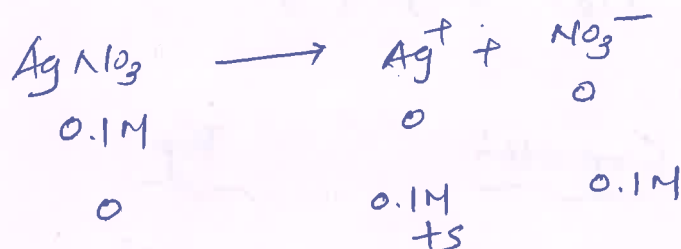
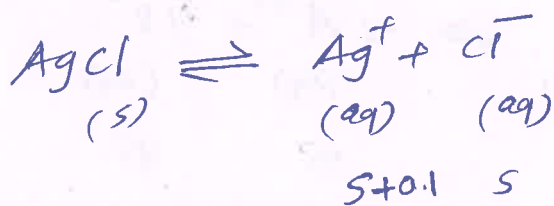
For a given type of salt,

$$K_{sp} \uparrow \quad S \uparrow$$

For different types of salt such as Mg(OH)₂ ($K_{sp} = 6.3 \times 10^{-11}$) and CaCO₃ ($K_{sp} = 1.4 \times 10^{-9}$), simple relations between K_{sp} and S do not operate. Here $K_{sp} \text{ CaCO}_3 > K_{sp} \text{ Mg(OH)}_2$ but $S_{\text{CaCO}_3} < S_{\text{Mg(OH)}_2}$

Type-2

Solubility of a salt of SA & SB in presence of a common ion (incapable of forming complex)



$$K_{sp}(\text{AgCl}) = [\text{Ag}^+][\text{Cl}^-] = (s+0.1)(s)$$

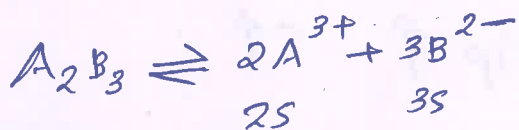
$$s+0.1 \approx 0.1 \quad \text{because } s \ll 0.1$$

$$K_{sp} = 0.1 \times s$$

$$s = \frac{K_{sp}}{0.1}$$

Q-28

Solubility of A_2B_3 in pure water if its K_{sp} is 1.08×10^{-23}



$$K_{sp} = (2s)^2(3s)^3 = 108s^5$$

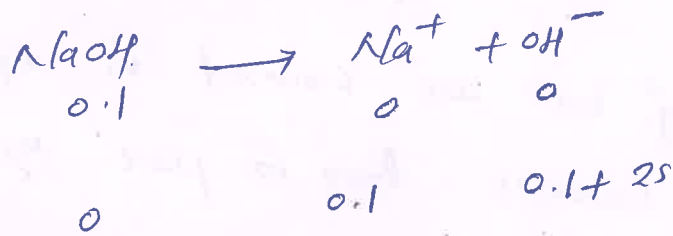
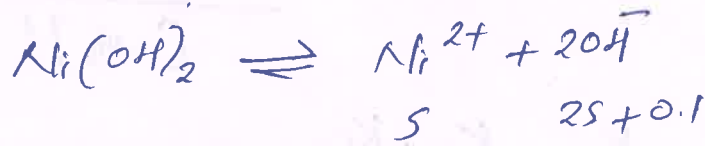
$$1.08 \times 10^{-23} = 108s^5$$

$$s^5 = 10^{-25}$$

$$s = (10^{-25})^{1/5} = 10^{-5}M$$

Q-29

Molar solubility of $\text{Ni}(\text{OH})_2$ in 0.1M NaOH if the K_{sp} of $\text{Ni}(\text{OH})_2 = 2 \times 10^{-15}$



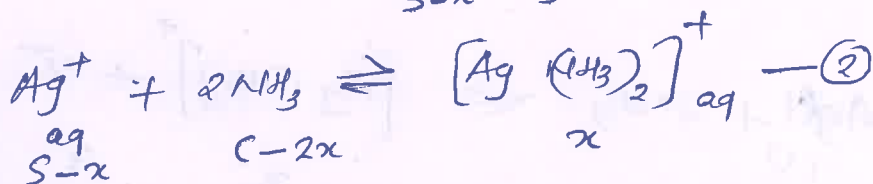
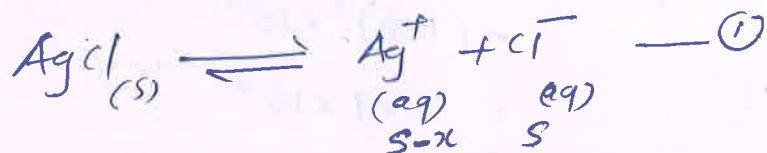
$$K_{sp} = [\text{Ni}^{2+}] [\text{OH}^-]^2 = s(2s + 0.1)^2$$

$$2 \times 10^{-15} = s(0.1)^2$$

$$s = 2 \times 10^{-13} \text{ M}$$

Type-3

Solubility of salt of SA and SB in a solvent capable of forming complex



From (1)

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] \quad \text{--- (a)}$$

From (2)

$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2]^+}{[\text{Ag}^+][\text{NH}_3]^2} \quad \text{--- (b)}$$

① + ② \Rightarrow



$$K_c = \frac{[\text{Ag}(\text{NH}_3)_2]^+ [\text{Cl}^-]}{[\text{NH}_3]^2}$$

Also, $K_c = K_{sp} \cdot K_f$

Here, Ag^+ ions are consumed in eqn ② \therefore solubility of AgCl increases than in pure H_2O

Generally,

$$K_{sp} = (s-x)s$$

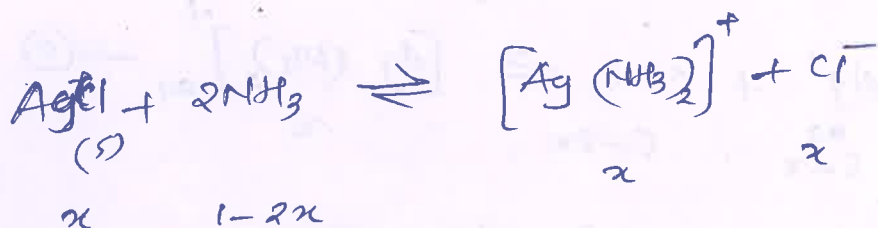
$$K_f = \frac{x}{(s-x)(c-2x)^2}$$

Q-30

Molar solubility of AgCl in 1M NH_3 if $K_{sp} = 1.7 \times 10^{-10}$

and K_f of $[\text{Ag}(\text{NH}_3)_2]^+$ is 1.7×10^7

$$\begin{aligned} K_c &= K_{sp} \cdot K_f = 1.7 \times 10^{-10} \times 1.7 \times 10^7 \\ &= (1.7)^2 \times 10^{-3} \\ &= 2.89 \times 10^{-3} \end{aligned}$$



$$2.89 \times 10^{-3} = \frac{x^2}{x(1-2x)^2} = \left(\frac{x}{1-2x} \right)^2$$

(AgCl is pure solid)

$$\begin{aligned}\frac{x}{1-2x} &= \sqrt{2.89 \times 10^3} \\ &= \sqrt{28.9 \times 10^4} \\ &= 5.4 \times 10^{-2}\end{aligned}$$

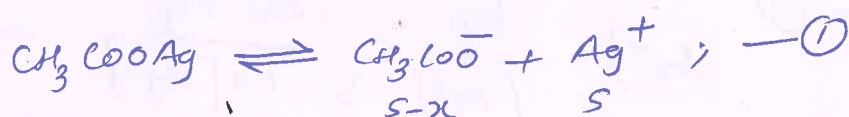
$$x = 5.4 \times 10^{-2} - 10.8 \times 10^{-2} x$$

$$1.108 x = 5.4 \times 10^{-2}$$

$$x = 0.049 \text{ M}$$

Type-4

Solubility of a salt of weak acid and strong base in pure water:



From (1)

$$K_{sp} = (s-x)s$$

$$K_h = \frac{K_w}{K_a} = \frac{x^2}{(s-x)}$$

} solubility \uparrow due to hydrolysis of anion

From (1) and (2), Applying the material balance

$$[\text{Ag}^+] = [\text{CH}_3\text{COO}^-] + [\text{CH}_3\text{COOH}] \text{---(3)}$$

$$\text{From (1)} \quad K_{sp} = [\text{CH}_3\text{COO}^-][\text{Ag}^+]$$

$$\therefore [\text{CH}_3\text{COO}^-] = K_{sp} / [\text{Ag}^+] = \frac{K_{sp}}{s}$$

From (2)

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

$$[CH_3COOH] = \frac{K_h [CH_3COO^-]}{[OH^-]}$$

$$x = K_h \frac{s-x}{x}$$

$$x^2 = K_h (s-x) = \frac{K_w}{K_a} \cdot \frac{K_{sp}}{s}$$

$$\therefore x = \sqrt{\frac{K_w \cdot K_{sp}}{K_a \cdot s}}$$

From eqn (3) $[Ag^+] = \frac{K_{sp}}{[Ag^+]} + \sqrt{\frac{K_w \cdot K_{sp}}{K_a [Ag^+]}} \quad \text{--- (4)}$

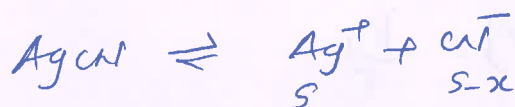
Multiplying both sides of the eqn (4) with $[Ag^+]$

$$[Ag^+]^2 = K_{sp} + \sqrt{\frac{K_w \cdot K_{sp}}{K_a}} [Ag^+]$$

Solve for $[Ag^+] = s$, molar solubility of Ag_2CO_3 in water.

Q-31

Calculate the molar solubility of $AgCN$, considering hydrolysis of CN^- ion. Given $K_{sp} AgCN = 2 \times 10^{-16}$ and $K_a HCN = 6 \times 10^{-10}$



Applying material balance,

$$[Ag^+] = [CN^-] + [HCN]$$

$$= \frac{K_{sp}}{[Ag^+]} + \sqrt{\frac{K_w \cdot K_{sp}}{K_a [Ag^+]}}$$

$$[Ag^+]^2 = K_{sp} + \sqrt{\frac{K_w \cdot K_{sp}}{K_a}} [Ag^+]$$

$$= 2 \times 10^{-16} + \sqrt{\frac{10^{-14} \times 2 \times 10^{-16}}{6 \times 10^{-10}}} [Ag^+]$$

$$= 2 \times 10^{-16} + \sqrt{\frac{10^{-20}}{3}} [Ag^+]$$

$$\approx \sqrt{\frac{10^{-20}}{3}} [Ag^+] \left[2 \times 10^{-16} \ll \sqrt{\frac{10^{-20}}{3}} [Ag^+] \right]$$

$$[Ag^+]^2 = \sqrt{\frac{10^{-20}}{3}} [Ag^+]$$

$$[Ag^+]^3 = \frac{10^{-20}}{3} [Ag^+]$$

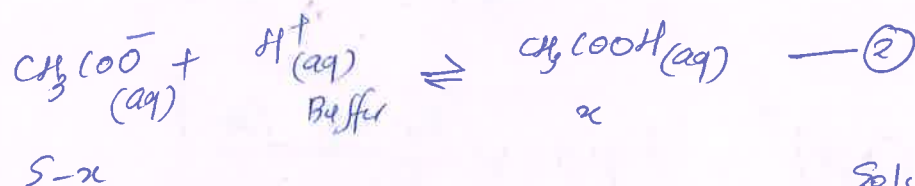
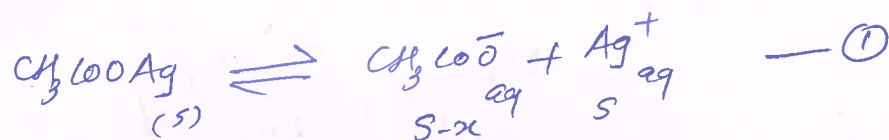
$$[Ag^+]^3 = \frac{10^{-20}}{3} = 0.333 \times 10^{-20} = 3.33 \times 10^{-21}$$

$$[Ag^+] = (3.33 \times 10^{-21})^{1/3} = 1.5 \times 10^{-7}$$

$$\text{Molar solubility of AgCN} = 1.5 \times 10^{-7} \text{ M}$$

Type-5

Solubility of a salt of WOA and SB in acidic Buffer



Solubility ↑

From (1)

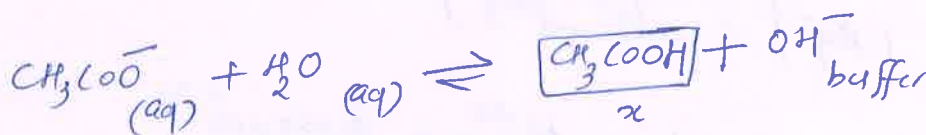
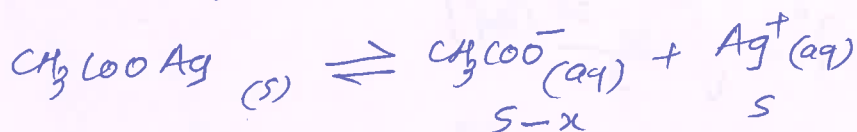
$$K_{sp} = (S-x)S$$

From (2)

$$\frac{1}{K_a} = \frac{x}{(S-x)[\text{H}^+]_{\text{buffer}}}$$

Type-6

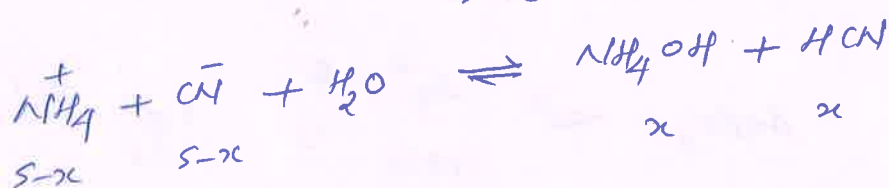
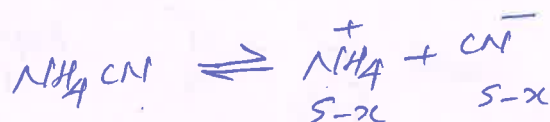
Solubility of a salt of WOA and SB in basic buffer



$[\text{OH}^-] \uparrow \therefore [\text{CH}_3\text{COO}^-] \uparrow \therefore \text{solubility} \downarrow$

$$K_{sp} = (S-x)S$$

$$K_h = \frac{x[\text{OH}^-]_{\text{buffer}}}{(S-x)} = \frac{K_w}{K_a}$$

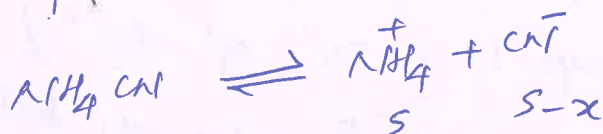
Type-7Solubility of a salt of WA and WB in pure H_2O 

$$K_{sp} = (s-x)^2$$

$$K_h = \frac{x^2}{(s-x)^2} = \frac{K_w}{K_a \cdot K_b}$$

Type-8

Solubility of a salt of WA and WB in acidic buffer

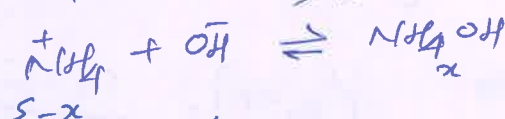


$$K_{sp} = s(s-x)$$

$$\frac{1}{K_a} = \frac{x}{(s-x)[H^+]_{buffer}}$$

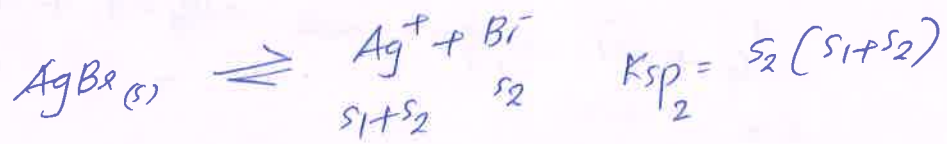
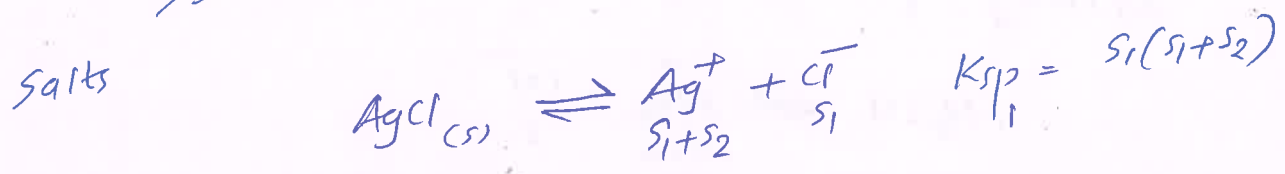
Type-9

Solubility of a salt of WA and WB in basic buffer



$$K_{sp} = s(s-x) \quad \text{and} \quad 1/K_b = \frac{x}{(s-x)[OH^-]_{buffer}}$$

Type-10 Simultaneous solubility of two or more sparingly soluble salts



$$\text{Here } \frac{K_{sp1}}{K_{sp2}} = \frac{s_1}{s_2} \quad \left(\begin{array}{l} \text{if both} \\ K_{sp}'s \text{ are} \\ \text{comparable} \end{array} \right)$$

Applications

Precipitation of group radicals in Gatin Analysis

eg. Group-I $[\text{Pb}^{2+}, \text{Ag}^+, \text{Hg}_2^{2+}]$
Group Reagent = dil. HCl

Here $[\text{Ag}^+][\text{Cl}^-] > K_{sp}$ for AgCl \Rightarrow precipitation starts

Q-32

Determine the simultaneous solubility of CaSO_4 and BaSO_4

$$K_{sp} \text{ of } \text{CaSO}_4 = 2 \times 10^{-4}; \quad K_{sp} \text{ of } \text{BaSO}_4 = 1.5 \times 10^{-9}$$

$$K_{sp} \text{ CaSO}_4 \gg K_{sp} \text{ BaSO}_4$$

$$\therefore [\text{SO}_4^{2-}] = \sqrt{K_{sp} \text{ CaSO}_4} = \sqrt{2 \times 10^{-4}} = 1.414 \times 10^{-2}$$

$$\text{For } \text{BaSO}_4, \quad [\text{Ba}^{2+}] = \frac{1.5 \times 10^{-9}}{1.414 \times 10^{-2}} = 1.06 \times 10^{-7}$$

Q-33

Determine simultaneous solubility of MgF_2 ($K_{sp} = 7.3 \times 10^{-9}$) and CaF_2 ($K_{sp} = 1.7 \times 10^{-10}$)

Here both K_{sp} values are comparable

$$K_{sp} \text{MgF}_2 = 7.3 \times 10^{-9} = [\text{Mg}^{2+}][\text{F}^-]^2 = S_1(2S_1 + 2S_2)^2$$

$$K_{sp} \text{CaF}_2 = 1.7 \times 10^{-10} = [\text{Ca}^{2+}][\text{F}^-]^2 = S_2(2S_1 + 2S_2)^2$$

$$\frac{[\text{Mg}^{2+}]}{[\text{Ca}^{2+}]} = 43 = \frac{S_1}{S_2}$$

$$K_{sp} \text{MgF}_2 = S_1 \times 4(S_1 + S_2)^2 = 4S_1\left(S_1 + \frac{S_1}{43}\right)^2$$

$$7.3 \times 10^{-9} = 4S_1\left(\frac{44}{43}S_1\right)^2$$

$$= 4.1S_1^3$$

$$\therefore S_1 = \left(\frac{7.3 \times 10^{-9}}{4.1}\right)^{\frac{1}{3}} = (1.78 \times 10^{-9})^{\frac{1}{3}}$$

$$= 1.2 \times 10^{-3} \text{ M}$$

$$S_2 = \frac{S_1}{43} = \frac{0.028 \times 10^{-3}}{43}$$

$$= 2.8 \times 10^{-5}$$

Type - (11)

Selective precipitation

Due to difference in solubility of sparingly soluble salts, it is possible to separate certain ions from each other when they are present together in a solution.

Q-34

A solution contains $0.1M Mg^{2+}$ and $0.1M Sr^{2+}$. The concentration of H_2CO_3 is adjusted to a value of $0.05M$. What range of pH values would permit the separation of these metal ions as their carbonates? $K_{sp} MgCO_3 = 3.5 \times 10^{-8}$
 $K_{sp} SrCO_3 = 9.3 \times 10^{-11}$
 For H_2CO_3 , $K_{a1} = 4.3 \times 10^{-7}$, $K_{a2} = 5.6 \times 10^{-11}$

$$[CO_3^{2-}] \text{ required for ppt}^n \text{ of } SrCO_3 = \frac{K_{sp}}{[Sr^{2+}]}$$

$$= \frac{9.3 \times 10^{-11}}{0.1}$$

$$= 9.3 \times 10^{-9} M$$

$$[CO_3^{2-}] \text{ required for ppt}^n \text{ of } MgCO_3 = \frac{K_{sp}}{[Mg^{2+}]}$$

$$= \frac{3.5 \times 10^{-8}}{0.1}$$

$$= 3.5 \times 10^{-7} M$$

$$\text{At } [CO_3^{2-}] = 9.3 \times 10^{-9} M, [H^+]^2 = \frac{K_a [H_2CO_3]}{[CO_3^{2-}]}$$

$$\left[H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-} \right]$$

$$K_a = K_{a1} \cdot K_{a2} = \frac{[H^+]^2 [CO_3^{2-}]}{[H_2CO_3]}$$

$$[H^+] = \sqrt{\frac{4.3 \times 10^{-7} \times 5.6 \times 10^{-11} \times 0.05}{9.3 \times 10^{-9}}}$$

$$= 1.13 \times 10^{-5}$$

$$pH = 4.94$$

At $pH < 4.94$; $[CO_3^{2-}] < 9.3 \times 10^{-9} M$, neither Sr^{2+} nor Mg^{2+} will precipitate.

$$\text{At } [\text{CO}_3^{2-}] = 3.5 \times 10^{-7} \text{ M}$$

$$[\text{H}^+] = 1.85 \times 10^{-6}$$

$$\text{pH} = 5.73$$

If pH is between 4.94 and 5.73, $[\text{CO}_3^{2-}]$ will be between $9.3 \times 10^{-9} \text{ M}$ and $3.5 \times 10^{-7} \text{ M}$ and only SrCO_3 will precipitate.

At $\text{pH} > 5.73$, $[\text{CO}_3^{2-}] > 3.5 \times 10^{-7}$, MgCO_3 will be precipitated

out.

