IONIC EQUILIBRIUM

Electrolytes: Whose aqueous solution conduct electricity.

Electrolytes are classified into two groups.

- 1. **Strong Electroytes:** Are those whose ionization is almost 100%, in aqueous solution generally all ionic compounds are strong electrolytes e.g. NaCl, NaNO₃, HCl, KCl.
- 2. Weak Electrolytes: Whose degree of dissociation is < 10-15%. Generally covalent compounds are weak electrolytes. e.g. NH_4OH , CH_3COOH .

Strong and Weak electrolytes is a value term it only depends upon degree of ionization. Some times covalent compounds acts as a strong electrolytes in highly diluted solution.

$$K_a = C\alpha^2 \implies \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{K_a V} \qquad \alpha = \frac{\text{ionized molecules}}{\text{Total molecules}}$$

"The fraction of total no. of molecules of electrolytes dissolved, that ionizes at equilibrium is called degree of ionization or degree of dissociation."

For: unionized molecules $\square \square$ ionized molecules $\alpha \ll 1$

Generally strong and weak electrolyte property depends upon nature of solvent NaCl in H_2O acts strong electrolyte whereas CH_3COOH is weak electrolyte in water. But in liquid NH_3 , the dissociation of NaCl and CH_3COOH both are same.

1. Ostwald's Dilution Law

Ostwald pointed out that like chemical equilibrium, in ionic equilibrium we can apply law of mass action. An equilibrium between ionized and unionized molecules.

Consider a binary electrolyte having conc. C and degree of dissociation is α .

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

At. time = 0 C 0 0
At time = t $C(1 - \alpha) C \alpha C \alpha$

$$K_{eq} = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha \times C\alpha}{C(1 - \alpha)} = \frac{C\alpha^2}{1 - \alpha}, \text{ for a weak electrolyte } 1 - \alpha \cong 1$$

$$K_{eq} = C\alpha^2, \alpha = \sqrt{\frac{K_{eq}}{C}}$$

If 1 mole of AB is present in 'V' litre of solution.

$$C = \frac{1}{V} \implies \alpha = \sqrt{K_{eq} \times V}$$

Conc. of [A⁺] = Conc. [B⁻] = C\alpha = C \sqrt{\frac{K_{eq}}{C}} = \sqrt{K_{eq}C}

Limitation

- (i) This is only for weak electrolytes not for strong electrolytes.
- (ii) This law is not applicable for strong electrolytes because strong electrolytes are almost completely

ionized at all dilution and hence $\frac{\lambda^{C}}{\lambda^{\infty}}$ does not give accurate results.

2. Relative strength of Acids and Bases

For weak acids

Relative strength = $\frac{\text{Strength of I acid}}{\text{Strength of II acid}}$

For Acids HA_1 if concentration is C_1 and degree of dissociations α_1

 $HA_1 \square \bigoplus H^+ + A_1^- \implies [H^+] = C_1 \alpha_1$

For HA₂ if concentration is C_2 and degree of dissociation is α_2

 $\mathrm{HA}_{2} \boxminus \oplus \mathrm{H}^{+} + \mathrm{A}_{2}^{-} \implies [\mathrm{H}^{+}] = \mathrm{C}_{2} \alpha_{2}$

Then, Relative strength = $\frac{[H^+] \text{ furnished by I acid}}{[H^+] \text{ furnished by II acid}} = \frac{C_1 \alpha_1}{C_2 \alpha_2}$

R.S. =
$$\frac{C_1}{C_2} \times \sqrt{\left(\frac{K_{a_1}C_2}{K_{a_2}C_1}\right)} = \sqrt{\left(\frac{K_{a_1}C_1}{K_{a_2}C_2}\right)}$$

If C_1 and C_2 are same, then

$$R.S. = \sqrt{\left(\frac{K_{a_1}}{K_{a_2}}\right)}$$

Illustration 1:

Calculate the degree of ionization of 0.01 M solution of HCN, K_a of HCN is 4.8×10^{-10} . Also calculate hydronium ion concentration.

Solution:

The ionization of HCN may be represented as,

 $HCN(aq) + H_2O(\ell) \square \square CN^-(aq) + H_3O^+(aq)$

If degree of ionization of HCN is α then equilibrium concentration of various species are

$$[\text{HCN}] = C(1-\alpha), \qquad [\text{CN}^-] = C\alpha, \qquad [\text{H}_3\text{O}^+] = C\alpha$$

where C =concentration of HCN.

Applying law of chemical equilibrium

$$K_{a} = \frac{[CN^{-}][H_{3}O^{+}]}{[HCN]} = \frac{(C\alpha)(C\alpha)}{C(1-\alpha)} = \frac{C\alpha^{2}}{(1-\alpha)}$$

Since α is very small as compared with unity therefore, $1-\alpha$ in the denominator may be taken as 1.

$$\begin{split} \mathrm{K_a} &= \mathrm{C}\alpha^2 \implies \alpha = \sqrt{\frac{\mathrm{K_a}}{\mathrm{C}}} = \sqrt{\frac{4.8 \times 10^{-10}}{0.01}} = 2.2 \times 10^{-4} \,. \\ \mathrm{[H_3O^+]} &= \mathrm{C}\alpha = 0.01 \times 2.2 \times 10^{-4} = 2.2 \times 10^{-6} \,\,\mathrm{mol}\,\,\mathrm{L}^{-1} \,. \end{split}$$

Illustration 2:

Calculate the concentration of fluoroacetic acid which is required to get $[H^+] = 1.50 \times 10^{-3} M$. $[K_a, of acid = 2.6 \times 10^{-3}]$.

Solution:

$$FCH_{2}COOH \implies FCH_{2}COO^{-} + H^{+}$$

$$[FCH_{2}COO^{-}] = [H^{+}] = 1.5 \times 10^{-3}$$

$$\therefore 2.6 \times 10^{-3} = \frac{(1.5 \times 10^{-3})^{2}}{C - 1.5 \times 10^{-3}} \implies C - 1.5 \times 10^{-3} = 8.65 \times 10^{-4} \therefore C = 2.365 \times 10^{-3}$$

3. Common ion effect

The degree of dissociation of a weak electrolyte is suppressed by the addition of another electrolyte containing the common ion.

Quantitative Aspect

HA \square \square \square $H^+ + A^-$ its degree of dissociation be α .

$$\alpha = \sqrt{\frac{K_a}{C}}$$

BA (another electrolyte) added whose molarity is M, due to this the new degree of dissociation becomes α' .

As a result of common ion effect, the conc. of the ion, which is not common changes to make the K_a constant, because K only depends upon temperature not on concentration.

Note: The use of this phenomenon is made in quantities analysis to adjust the conc. of S^{--} ions in second group (reagent H_2S and HCl) and OH^- ion conc. in third group ($NH_4Cl + NH_4OH$).

Illustration 3:

Calculate the degree of ionization of 0.02 M acetic acid if its $K_a = 1.8 \times 10^{-5}$. What would be the degree of ionization if the solution also contains 0.01 M sodium acetate ? Solution:

 $CH_3COOH(aq)$ \square \square $CH_3COO^{-}(aq) + H^{+}(aq)$

The degree of ionization of this weak acid can be calculated by the approximate relation :

$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1.8 \times 10^{-5}}{0.02}} = 0.03 = 3 \times 10^{-2} .$$

Now let us calculate the degree of ionization when the solution also contains 0.01 M sodium acetate. Sodium acetate being a strong electrolyte would be completely ionized in solution. Let x mol L^{-1} of acetic acid be ionized.

$$CH_{3}COOH(aq) = CH_{3}COO^{-}(aq) + H^{+}(aq) \\ (0.02-x)M = CH_{3}COO^{-}(aq) + Na^{+}(aq) \\ 0.01M = CH_{3}COONa(aq) \longrightarrow CH_{3}COO^{-}(aq) + Na^{+}(aq) \\ (H^{+}] = x \mod L^{-1} \\ [CH_{3}COO^{-}] = (x + 0.01) \mod L^{-1} \approx 0.01 \mod L^{-1} \\ [CH_{3}COOH] = (x + 0.01) \mod L^{-1} \approx 0.02 \mod L^{-1} \\ [CH_{3}COOH] = (0.02 - x) \mod L^{-1} \approx 0.02 \mod L^{-1} \\ K_{a} = \frac{[H^{+}][CH_{3}COO^{-}]}{[CH_{3}COOH]} \implies 1.8 \times 10^{-5} = \frac{(x)(0.01)}{(0.02)} \\ x = \frac{1.8 \times 10^{-5} \times 0.02}{0.01} = 3.6 \times 10^{-5} M \\ Degree of ionization, \alpha = \frac{x}{0.02} = \frac{3.6 \times 10^{-5}}{0.02} = 1.8 \times 10^{-3}$$

Thus, it may noted that the degree of ionization of acetic acid has decreased from 3×10^{-2} to 1.8×10^{-3} due to the presence of sodium acetate.

Illustration 4:

Calculate the degree of ionization of pyridine $(C_{_5}H_{_5}N)$ in its 0.1 M solution $K_{_b}$ for pyridine is 1.5×10^{-9} . What would be the degree of ionization of pyridine if the solution also contain 0.1 M in NaOH?

Solution:

$$C_6H_5N + H_2O \rightleftharpoons C_6H_5 \overset{\oplus}{N}H + OH^{\Theta}$$
$$\alpha = \sqrt{\frac{K_b}{C}} = \sqrt{\frac{1.5 \times 10^{-9}}{0.1}} = 1.23 \times 10^{-4}$$

In presence of 0.1 M NaOH solution, common ion effect operates hence OH^- ions are poduced only by NaOH

$$\therefore \qquad 1.5 \times 10^{-9} = \frac{(0.1\alpha)(0.1)}{(0.1)}$$
$$\alpha = 1.5 \times 10^{-8}$$

4. Ionization of Water

Water is a weak electrolyte. It does not dissociate completely, the undissociated water and the dissociated H⁺, OH⁻ remain in the equilibrium. Let us take pure water whose density is 1 gram/c.c. and hence its concentration would be (1000/18 = 55.55 M). Let the degree of dissociation of water be α .

$$2H_2O(\ell) \blacksquare \blacksquare H_3O^+ + OH^-$$
$$C\alpha \quad C\alpha$$
$$K_{eq} = \frac{[H_3O^+][OH^-]}{H_2O}$$

 $K_{eq}[H_2O(\ell)] = [H_3O^+][OH^-]$

Since conc. of pure water remain constant

 $K_{eq}k = [H_3O^+][OH^-]$ $k_w = [H_3O^+][OH^-]$

 K_w = dissociation constant of water at 25°C, K_w comes out to be 1 × 10⁻¹⁴.

 K_w depends upon temperature dissociation of water gives equal no. of H_3O^+ and OH^- ions.

 $1 \times 10^{-14} = [H_3O^+]^2 = [OH^-]^2$

So $[H_{3}O^{+}] = [OH^{-}] = 10^{-7}$ mole/litre $pH = -log [H_{3}O^{+}] = -log [10^{-7}] = 7.$ $pOH = -log [OH^{-}] = -log 10^{-7} = 7.$ Note: In case of water $[H_{3}O^{+}]_{w} [OH^{-}]_{w} = 10^{-14}.$ But in case of acidic or basic solution. $[H_{3}O^{+}]_{T} [OH^{-}]_{T} = 10^{-14}$, where $[H_{3}O^{+}]_{T}$ and $[OH^{-}]_{T}$ are the conc. of $[H_{3}O^{+}]$ and $[OH^{-}]$ totally present in the solution.

5. pH Calculation

The pH of a solution is the negative logarithm (to the base 10) of the concentration (in moles per litre) of hydrogen ions which it contains.

 $pH = -log_{10} [H_{3}O^{+}]$ $pOH = -log_{10} [OH^{-}]$ $pk_{w} = -log_{10} [K_{w}]$ $k_{w} = [H^{+}] [OH^{-}]$ taking -ve log_{10} both side $-log K_{w} = -log [H_{3}O^{+}] + [-log (OH^{-})]$ $pK_{w} = pH + pOH$ at 25°C, $K_{w} = 1 \times 10^{-14}$, $pK_{w} = 14$ pH + pOH = 14

 K_{w} = is also called as auto protolysis constant, it increases with temperature.

Since with increase in temperature dissociation of water increases, therefore the value of K_w increases as the temperature is increased, however at all temperature $[H_3O^+]$ remain equal to $[OH^-]$ in pure water.

Illustration 5:

The K_w for $2H_2O \Longrightarrow H_3O^+ + OH^-$ changes from 10^{-14} at $25^{\circ}C$ to 9.62×10^{-14} at $60^{\circ}C$. What is pH of water at $60^{\circ}C$? What happens to its neutrality?

Solution:

 K_{w} for H₂O at 25°C = 10⁻¹⁴ $[H^+][OH^-] = 10^{-14}$ $(: K_w = [H^+] [OH^-])$ *.*.. $[H^+] = 10^{-7} M$ $\therefore \text{ pH} = 7$ K_{w} for H₂O at 60°C = 9.62 × 10⁻¹⁴ Now ... $[H^+] = [OH^-] = 9.62 \times 10^{-14}$ For pure water $[H^+] = [OH^-]$ $[H^+]^2 = 9.62 \times 10^{-14}$ *.*.. $[\mathrm{H^+}] = \sqrt{(9.62 \times 10^{-14})} = 3.10 \times 10^{-7} \mathrm{M}$ *.*.. $pH = -\log H^+ = -\log 3.10 \times 10^{-7}$ *.*.. pH = 6.51

Thus, pH of water becomes 6.51 at 60°C but the nature is neutral since calculation for pure water has been made, i.e., pH scale at 60°C becomes in between 0 to 13.02.

Illustration 6:

Calculate pH for (a) 0.0008M Mg(OH), (b) 0.01 N Ca(OH),

Solution:

(a)	$0.0008 M Mg(OH)_{2}$			
	$Mg(OH)_2 \longrightarrow M\tilde{g}^{+2} + 2C$)H−		
	$[OH^{-}] = 2 \times 8 \times 10^{-4} = 1$	$1.6 \times 10^{-3} \Rightarrow$	pOH = 2.8	∴ pH = 11.2
(b)	0.01N Ca(OH)_2			
	$Ca(OH)_2 \longrightarrow Ca^{+2} + 2OI$	H-		
	$[OH^{-}] = 0.01 N$	(:: equivalen	ts are always sar	ne)
	$[OH^{-}]=0.01 \text{ M} \Rightarrow pOH =$	$= 2 \implies pH = 12$		

6. pH determination for Weak Acids

Weak acids do not dissociate completely in the water their % degree of dissociation is very less. e.g. lets takes CH₃COOH (C mole/litre and having degree dissociation α).

CH₃COOH I CH₃COO⁻ + H⁺
C(1-
$$\alpha$$
) C α C α
K_{a(CH₃COOH)} = $\frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{C\alpha.C\alpha}{C(1-\alpha)}$
K_a = $\frac{C\alpha^2}{1-\alpha}$
if $\alpha \le 0.1$, then we can neglect $1-\alpha \cong 1$
K_a = $C\alpha^2 \implies \alpha = \sqrt{\frac{K_a}{C}}$
[H⁺] = $C\alpha = C \sqrt{\frac{K_a}{C}} = \sqrt{K_aC}$
pH = $-\log[H^+] = -\log_{10}[\sqrt{K_aC}]$

Note: For calculating the pH of a weak acid first of all we calculate α from the equation $K_a = \frac{C\alpha^2}{1-\alpha}$,

if α comes out to be ≤ 0.1 then $1 - \alpha$ will be taken as one and we use formula $K_a = C\alpha^2$ otherwise we would be use the formula

$$K_a = \frac{C\alpha^2}{1-\alpha}$$
 for all calculation.

Illustration 7:

pH of a solution is 10 in NaOH solution. What is concentration of NaOH? (a) What is molar concentration of Ca(OH), if its solution has pH of 12? **(b)** Solution: $[H^+] = 10^{-pH}$ (a) $[OH^{-}] = 10^{-pOH}$ NaOH is strong base, hence $[OH^{-}] = [NaOH]$ In pH = 10, pOH = 4 $[OH^{-}] = 10^{-4} = [NaOH]$ pOH = 2 : $[OH^{-}] = 10^{-2} M$ $pH of Ca(OH)_2 = 12$ (b) ... : $[Ca(OH)_2] = \frac{10^{-2}}{2}M = 0.5 \times 10^{-2} M$

[Every Ca(OH), gives two OH-ions]

Illustration 8:

A solution of HCl has a pH = 5. If one mL of its is diluted to 1 litre, what will be pH of resulting solution ? Solution:

 $\begin{array}{ccc} pH=5 & \Rightarrow & [H^+]=10^{-5} & \therefore & [HCl]=10^{-5} \ M \\ now using dilution formla, M_1V_1=M_2V_2 \\ 10^{-5}\times 1=M_2\times 1000 \Rightarrow M_2=10^{-8} \ M \\ At this low concentration, H^+ ions are also produced from water \\ \therefore & [H^+]=1.05\times 10^{-7} \Rightarrow pH=6.978 \end{array}$

7. Determination of pH of acids or bases

For strong acid

 $HC1 \longrightarrow H^+ + C1^-$

 $pH = -log[H^+]$

If conc. of HCl is less than 10^{-6} M than we take conc. of H⁺ from water into accounts i.e. 10^{-7} . Otherwise we would neglect the conc. of H⁺ from water.

e.g. find the pH of 10⁻⁸ M HCl

According to rule

 $pH = -log [H^+] = -log [10^{-8}] = 8$

But pH of an acid can't be 8 so we have to take contribution of H⁺ from water

Total H⁺ ion in solution = H⁺ (from HCl) + H⁺ (from H₂O) = $10^{-8} + 10^{-7} = 1.1 \times 10^{-7}$ mole/litre and hence

$$pH = -\log [H^+] = -\log [1.1 \times 10^{-7}] = 7 - \log 1.1 = 7 - 0.0414$$

$$rH = 6.05\% (A \text{ of } 4 \text{ of }$$

pH = 6.9586 (Acidic).

Same rule applies for pH of 10⁻⁸ M NaOH.

8. pH for the mixture of Weak Acid and Strong Acid

Let strong acid be HB whose conc. is C_1

$$\begin{array}{ccc} HB & \longrightarrow & H^+ + B^- \\ 0 & C_1 & C_1 \\ \text{and weak acid whose conc. is } C_2 \text{ and degree of dissociation is } \alpha \\ HA & \longrightarrow & H^+ & + A^- \\ C_2(1 - \alpha) & C_2 \alpha & C_2 \alpha \\ \text{Total } (H^+) \text{ conc. } = C_1 + C_2 \alpha \\ \text{pH} = -\log [C_1 + C_2 \alpha] \end{array}$$

$$K_{a(HA)} = \frac{[H^+][A^-]}{[HA]} = \frac{[C_1 + C_2\alpha][C_2\alpha]}{[C_2(1-\alpha)]}$$

Illustration 9:

What concentration of $HCOO^-$ is present in a solution of 0.015 M HCOOH and 0.02 M HCl ?

$$K_a$$
 for HCOOH = 1.8×10^{-4} .

Solution:

Given, $[\text{HCOOH}] = 0.015\text{M} \implies [\text{HCl}] = 0.02 \text{M}$ \therefore $[\text{H}^+]$ in solution = 0.02 M

The dissociation of HCOOH is suppressed due to common ion effect in presence of HCl. The $[H^+]$ is provided by HCl in solution.

HCOOH
$$=$$
 HCOO⁻ + H⁺
 $K_a = \frac{[H^+][HCOO^-]}{[HCOOH]}$
 $1.8 \times 10^{-4} = \frac{[0.02][HCOO^-]}{[0.015]}$ \therefore [HCOO⁻] = 1.35×10^{-4} M

Illustration 10:

Calculate [H⁺] in a 0.20 M solution of dichloroacetic acid ($K_a = 5 \times 10^{-2}$) that also contains 0.1 M sodium dichloroacetate. Neglect hydrolysis of sodium salt.

Solution:

$$\begin{array}{l} \text{CHCl}_2\text{COOH} \rightleftharpoons \text{CHCl}_2\text{COO}^- + \text{H}^+\\ \text{CHCl}_2\text{COONa} \longrightarrow \text{CHCl}_2\text{COO}^- + \text{Na}^+\\ \\ \therefore \qquad \text{K}_{a} = \frac{[\text{CHCl}_2\text{COO}^-][\text{H}^+]}{[\text{CHCl}_2\text{COOH}]} \implies 5 \times 10^{-2} = \frac{(0.1 + 0.2\alpha)(0.2\alpha)}{0.2(1 - \alpha)} \implies \frac{1}{2} = \frac{(1 + 2\alpha)\alpha}{1 - \alpha}\\ \\ \implies 1 - \alpha = 2\alpha + 4\alpha^2\\ \\ \therefore \qquad 4\alpha^2 + 3\alpha - 1 = 0 \implies \alpha = \frac{-3 \pm \sqrt{9 + 16}}{8} = \frac{-3 + 5}{8} = \frac{2}{8} = 0.25\\ \\ \therefore \qquad [\text{H}^+] = 0.2 \ \alpha = 0.2 \times 0.25 = 0.5\end{array}$$

9. pH calculation of solution of a mixture of two weak Acids in water

Let two weak acids be HA and HB and their conc. are C_1 and C_2 , α_1 is the degree of dissociation of HA in presence of HB (due to common ion effect) and α_2 be degree of dissociation of HB in presence of HA. In aqueous solution of HA and HB following equilibrium exists.

$$\begin{split} H_{A}^{+} & H_{2}O(1) \blacksquare \blacksquare H_{3}O^{+} & + A^{-} \\ \text{conc. at equi.} & C_{1}(1-\alpha_{1}) & C_{1}\alpha_{1} + C_{2}\alpha_{2} & C_{1}\alpha_{1} \\ H_{B}^{+} & H_{2}O(1) & \blacksquare \blacksquare H_{3}O^{+} & + B^{-} \\ C_{2}(1-\alpha_{2}) & (C_{1}\alpha_{1} + C_{2}\alpha_{2}) & C_{2}\alpha_{2} \\ K_{a[HA]}^{-} &= \frac{[H_{3}O^{+}][A^{-}]}{[HA]} = \frac{[C_{1}\alpha_{1} + C_{1}\alpha_{2}][C_{1}\alpha_{2}]}{C_{1}(1-\alpha_{1})} \\ K_{a[HB]}^{-} &= \frac{[H_{3}O^{+}][B^{-}]}{[HB]} = \frac{[C_{1}\alpha_{1} + C_{2}\alpha_{2}][C_{2}\alpha_{2}]}{[C_{2}(1-\alpha_{2})]} \\ pH &= -\log[H^{+}] = -\log[C_{1}\alpha_{1} + C_{2}\alpha_{2}] \end{split}$$

Illustration 11:

or

Calculate [H⁺] in a solution containing 0.1 M HCOOH and 0.1 M HOCN. K_a for HCOOH and HOCN are 1.8×10^{-4} and 3.3×10^{-4} .

Solution:

In this problem both the acids contribute for $[H^+]$ due to appreciable dissociation. Thus,

HCOOH
$$\Box \Box \Box = H^+ + HCOO^ 0.1 - x$$
 $x + y$ $x - y$ $x = 0.1$ HOCN $\Box \Box \Box = H^+ + OCN^ 0.1 - y$ $x + y$ y $0.1 - y \cong 0.1$

Because [H⁺] will remain common in solution. Thus,

$$K_{\text{HCOOH}} = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]} = 1.8 \times 10^{-4} \qquad \dots (1)$$

$$K_{HOCN} = \frac{[H^+][OCN^-]}{[HOCN]} = 3.3 \times 10^{-4} \qquad \dots (2)$$

$$K_{\text{HCOOH}} = \frac{(x+y)x}{0.1} = 1.8 \times 10^{-4}$$
 ... (3)

$$K_{HOCN} = \frac{(x+y)y}{0.1} = 3.3 \times 10^{-4}$$
 ... (4)

Thus, by eqs. (3) and (4)

$$\frac{x}{y} = \frac{1.8}{3.3}$$
 or $y = 1.83$ x ... (5)

From Eq. (3) $(x+1.83x).x = 1.8 \times 10^{-5}$

$$\therefore$$
 x = 2.52×10⁻³

Therefore, $y = 4.61 \times 10^{-3}$ Thus, $[H^+] = x + y = 2.52 \times 10^{-3} + 4.61 \times 10^{-3} = 7.13 \times 10^{-3} M$

10. pH of a dibasic Acids and Polyprotic Acid

Let's take the eg. of a dibasic acid H₂A. Assuming both dissociation is weak. Let the initial conc. of H_2A is C and α_1 and α_2 be degree of dissociation for first and second dissocation.

$$H_{2}A \qquad \exists \blacksquare \qquad HA^{-} \qquad + \qquad H^{+}$$

$$C(1 - \alpha_{1}) \qquad C\alpha_{1} (1 - \alpha_{2}) \qquad C\alpha_{1} + C\alpha_{1}\alpha_{2}$$

$$HA^{-} \qquad \exists \blacksquare \qquad H^{+} \qquad + \qquad A^{--}$$

$$C\alpha_{1} (1 - \alpha_{2}) \qquad C\alpha_{1} + C\alpha_{1}\alpha_{2} \qquad C\alpha_{1}\alpha_{2}.$$

$$Ka_{1} = \frac{[HA^{-}][H^{+}]}{[H_{2}A]}$$

$$Ka_{1} = \frac{[C\alpha_{1}(1 - \alpha_{2})][C\alpha_{1} + C\alpha_{1}\alpha_{2}]}{C(1 - \alpha_{1})}$$

$$Ka_{2} = \frac{[H^{+}][A^{--}]}{[HA^{-}]} = \frac{[C\alpha_{1} + C\alpha_{1}\alpha_{2}][C\alpha_{1}\alpha_{2}]}{[C\alpha_{1}(1 - \alpha_{2})]}$$

After solving for α_1 and α_2 . We can calculate the H⁺ conc.

 $[\mathrm{H}^{+}] = \mathrm{C}\alpha_{1}^{+} + \mathrm{C}\alpha_{1}^{-}\alpha_{2}$ $pH = -\log [C\alpha_1 + C\alpha_1 \alpha_2]$

Illustration 12:

Find the concentrations of H^+ , HCO_3^- and CO_3^{-2} in a 0.01 M solution of carbonic acid if the pH of solution is 4.18. $K_1 = 4.45 \times 10^{-7}$, $K_2 = 4.69 \times 10^{-11}$.

Solution:

Given, pH = 4.18 =
$$-\log [H^+]$$
 \therefore $[H^+] = 6.61 \times 10^{-5} \text{ mol litre}^{-1}$
 $H_2CO_3 \square \square H^+ + HCO_3^- \Rightarrow K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$
or $4.45 \times 10^{-7} = \frac{[6.61 \times 10^{-5}][HCO_3^-]}{[0.01]}$ or $[HCO_3^-] = 6.73 \times 10^{-5} \text{ mol litre}^{-1}$

Again for dissociation of HCO_3^- , we have

HCO₃⁻ ☐

$$H^+ + CO_3^{-2}$$

 $K_2 = \frac{[H^+][CO_3^{-2}]}{[HCO_3^{-1}]} \text{ or } 4.69 \times 10^{-11} = \frac{[6.61 \times 10^{-5}][CO_3^{-2}]}{[6.73 \times 10^{-5}]}$
∴ $[CO_3^{-2}] = 4.78 \times 10^{-11} \text{ mol litre}^{-1}$

11. pH of mixture

Let one litre of an acidic solution of pH 2 be mixed with two litre of other acidic solution of pH 3. The resultant pH of the mixture can be evaluated in the following way.

Sample 2 Sample 1 pH = 2pH = 3 $[H^+] = 10^{-2} M$ $[H^+] = 10^{-3} M$ V = 1 litre V = 2 litre $M_1V_1 + M_2V_2 = M_R(V_1 + V_2)$ 10⁻² × 1 + 10⁻³ × 2 = M_R(1 + 2) $\frac{12 \times 10^{-3}}{3} = M_{R}$ $4 \times 10^{-3} = M_R$ (Here, $M_R =$ Resultant molarity) $pH_{R} = -\log[4 \times 10^{-3}] = 2.3980$ **Illustration 13:** Calculate the pH of the resultant mixture 10 mL of 0.2 M Ca(OH), +25 mL of 0.1 M HCl (a) $10 \text{ mL of } 0.01 \text{ MH}, SO_4 + 10 \text{ mL of } 0.01 \text{ MCa}(OH),$ (b) $10 \text{ mL of } 0.01 \text{ MH}_{,SO_{4}} + 10 \text{ mL of } 0.1 \text{ M KOH}.$ (c) Solution: (a) $Ca(OH)_2 + 2HCl \longrightarrow CaCl_2 + 2H_2O$ 2.5 2 0.75 $[Ca(OH)_2] = \frac{0.75}{35} \implies [OH^-] = 2 \times \frac{0.75}{35} = \frac{1.5}{35}$ *.*.. $pOH = 1.37 \implies$ pH = 12.63*.*.. $\begin{array}{c} \mathrm{H_2SO_4} + \mathrm{Ca(OH)_2} \longrightarrow \mathrm{CaSO_4} + 2\mathrm{H_2O} \\ 0.1 & 0.1 \end{array}$ (b) millimoles at t=0hence both will neutalise each other so solution will be neutrall, So pH=7 $H_2SO_4 + 2KOH \longrightarrow K_2SO_4 + 2H_2O$ (c) millimoles at t=00.1 1 0.8 $[\text{KOH}] = \frac{0.8}{20} = 0.04 \Rightarrow [\text{OH}^-] = 0.04 \Rightarrow \text{pOH} = 1.4$ pH = 12.6....

pK_{a} and pK_{b} for a conjugate acid-base pair

For an acid HX

$$HX = HX = H^{+} + X^{-}$$

$$K_{a} = \frac{[H^{+}][X^{-}]}{[HX]} \qquad \dots (A)$$

For conjugate base X^- of acid HX

 $X^- + H_2O \square \square HX + OH^-$

$$K_{b} = \frac{[HX][OH^{-}]}{[X^{-}]}$$
 ... (B)

By eqs. (A) and (B),

$$K_a \times K_b = [H^+][OH^-] = K_w$$

or $pK_{a} + pK_{b} = pK_{w} = 14$

Note : 1. *Stronger is acid, weaker is its conjugate base.*

2. Higher is the value of pK_a of an acid, lower is acid strength and higher is basic strength of its conjugate base.

12. Buffer Solution

A Buffer solution is that which resist the pH change by addition of small quantity of acid or alkali. There are three types of buffer (i) Acidic Buffer (ii) Basic Buffer (iii) Salt Buffer

Mechanism of Buffer Action:

Let us see why CH_3COONH_4 is a Buffer while NaCl is not. CH_3COONH_4 exists almost entirely in form of it's ion CH_3COO^- or NH_4^+ if an acid is added to that solution, the H⁺ ion furnished by the acid combine with CH_3COO^- ions to form feebly dissociated molecule of CH_3COOH .

 $CH_{3}COO^{-} + H^{+} \square \square CH_{3}COOH$

Since most of the H⁺ ions added are taken up by CH_3COO^- to form CH_3COOH which itself slightly dissociated, the pH of CH_3COONH_4 changes only slightly.

Now, suppose a base is added to CH_3COONH_4 solution the OH⁻ furnished by the base will be taken up by NH_4^+ ion to form feebly dissociated NH_4OH .

 $NH_{4}^{+} + OH^{-}$ $H_{4}OH$ $NH_{4}OH$

Since most of the OH⁻ ions are taken up by NH_4^+ ions to form feebly dissociated NH_4OH . Due to this very little change in the pH of CH_3COONH_4 solution occurs.

Now let us see why a solution of NaCl is not a Buffer. In aqueous solution it is almost entirely dissociated into Na⁺ and Cl⁻. If H⁺ ions are added to this solution the H⁺ combines with Cl⁻ to form HCl which completely dissociated due to strong electrolyte hence pH falls.

If OH^- ions are added to the solution, it will combine with Na^+ to form NaOH which will almost completely dissociated. Hence pH will rise.

13. Acid Buffer

A very common acidic buffer is prepared by mixing equimolar solutions of acetic acid and sodium acetate. Acetic acid is very slightly dissociated while sodium acetate, being a salt, is almost completely dissociated. The mixture thus contains CH_3COOH molecules as well as CH_3COO^- and Na^+ ions. Let us consider the buffer action of this mixture.

Suppose a strong acid is added to the above mixture. The H^+ ions added will be taken up immediately by CH₃COO⁻ ions to form very slightly dissociated CH₃COOH :

 $H^+ + CH_3COO^- \longrightarrow CH_3COOH_{Feebly dissociated}$

Thus, the H^+ ions added are neutralized by the acetate ions present in the mixture. There is very little change in the pH of the mixture.

If, on the other hand, a strong base is added, the OH^- ions added are neutralized by the acetic acid present in the mixture :

 $OH^- + CH_3COOH \longrightarrow CH_3COO^- + H_2O$

Thus, again, there is very little change in the pH of the mixture.

14. Calculation of pH of Acidic Buffer Solution

e.g. Mixture of
$$(CH_3COOH + CH_3COONa)$$

CH₃COOH \square \square CH₃COO⁻ + H⁺

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

Since most of CH_3COO^- comes from salt (CH_3COONa) and hence conc. of CH_3COO^- will be conc. of CH_3COONa .

$$K_a = \frac{[Salt][H^+]}{[Acid]} \implies [H^+] = \frac{K_a[Acid]}{[Salt]}$$

Taking (-ve) log both side

$$-\log [H^+] = -\log K_a - \log \frac{[Acid]}{[Salt]}$$

Handerson's equation $pH = pK_a + log \frac{[Salt]}{[Acid]}$

Illustration 14:

Calculate the ratio of pH of a solution containing 1 mole of $CH_3COONa + 1$ mole of HCl per litre and of other solution containing 1 mole $CH_3COONa + 1$ mole of acetic acid per litre.

Solution:

Case I: pH when 1 mole CH₃COONa and 1 mole HCl are present.

$$CH_{3}COONa + HC1 \longrightarrow CH_{3}COOH + NaCl$$
Before reaction 1 1 0 0
After reaction 0 0 1 1

$$\therefore \quad [CH_{3}COOH] = 1 M$$

$$\therefore \quad [H^{+}] = C.\alpha = C \sqrt{\left(\frac{K_{a}}{C}\right)} = \sqrt{(K_{a}.C)} = \sqrt{(K_{a})} \qquad \because C = 1$$

$$\therefore \quad pH_{1} = -\frac{1}{2} \log K_{a}$$

Case II : pH when 1 mole CH₃COONa and 1 mole of CH₃COOH; a acidic buffer solution forms \therefore [Salt] = 1 M, [Acid] = 1 M

$$\therefore [Sall] = 1 M, [Acid] = 1 M$$

$$\therefore \qquad pH_2 = -\log K_a + \log \frac{[\text{barl}]}{[\text{Acid}]}$$

$$pH_2 = -\log K_a$$

$$\therefore \qquad \frac{pH_1}{pH_2} = \frac{1}{2}$$

Illustration 15:

Calculate pH change when 0.01 mol CH_3COONa solution is added to one litre of 0.01 M CH_3COOH solution.

 K_a (CH₃COOH) = 1.8 × 10⁻⁵, pK_a = 4.74.

Solution:

On addition of CH_3COONa to CH_3COOH solution resulting solution will be a buffer solution hence on using Handerson eq. for acidic buffer.

$$pH = pK_{a} + \log \frac{[salt]}{[acid]}$$
$$= 4.74 \log \frac{0.01}{0.01} = 4.74$$

- :. For initial pH, $[H^+] = \sqrt{K_a \times C} = \sqrt{1.8 \times 10^{-5} \times 0.01} = 4.24 \times 10^{-4}$
- :. pH = 3.37 $\Delta pH = 4.75 - 3.37 = 1.37$

15. Basic Buffer

A mixture containing equimolar solutions of ammonium hydroxide and its almost completely dissociated salt, ammonium chloride, constitutes another good basic buffer. The mixture contains undissociated NH_4OH as well as NH_4^+ and Cl^- ions. The buffer action of this mixture may now be considered. If a strong acid is added, the H^+ ions added are neutralized by the base NH_4OH :

 $H^+ + NH_4OH \longrightarrow H_2O + NH_4^+$

If a strong base is added, the OH^- ions added are neutralized by NH_4^+ ions forming very slightly dissociated NH_4OH .

16. Calculation of pH of Basic Buffer Solution

e.g. Mixture of $(NH_4OH + NH_4Cl)$

$$NH_4OH \square \square NH_4^+ + OH^-$$

$$\mathbf{K}_{\mathrm{b}} = \frac{[\mathrm{NH}_{4}^{+}][\mathrm{OH}^{-}]}{[\mathrm{NH}_{4}\mathrm{OH}]}$$

Since most of NH_4^+ ions comes from salt (NH_4Cl) so we take NH_4^+ conc. as conc. of salt (NH_4Cl).

$$K_{b} = \frac{[Salt][OH^{-}]}{[Base]}$$
$$[OH^{-}] = \frac{K_{b} \times [Base]}{[Salt]}$$

Taking $(-\log_{10})$ both side

$$-\log [OH^{-}] = -\log 10 K_{b} - \log \frac{[Base]}{[Salt]}$$
$$pOH = pK_{b} + \log \frac{[Salt]}{[Base]}$$

Hence
$$pH = 14 - pOH at 14^{\circ}C$$
, $K_w = 1 \times 10^{-14} \text{ mol/litre}$

Illustration 16:

A buffer of pH 9.26 is made by dissolving x moles of ammonium sulphate and 0.1 mole of ammonia into 100 mL solution. If pK_b of ammonia is 4.74, calculate value of x.

Solution:

 $(NH_4)_2 SO_4 \implies 2 NH_4^+ + SO_4^{2-}$

Thus, every one mole of $(NH_4)_2 SO_4$ gives two moles of NH_4^+ .

 $\therefore \qquad \text{millimoles of NH}_3, (\text{NH}_4\text{OH}) = 100 \times 0.1 = 10 \text{ millimol} \\ \text{millimoles of (NH}_4)_2 \text{SO}_4 = 100 \times \text{x} = 100 \text{ x} \text{ millimol} \\ \text{millimoles of NH}_4^+ = 200 \times \text{x} = 200 \text{ x} \text{ millimol} \\ \end{array}$

 \therefore pH = 9.26 \therefore pOH = 14 - 9.26 = 4.74

$$pOH = pK_{b} + log \frac{[NH_{4}^{+}]}{[NH_{4}OH]}$$

$$4.74 = 4.74 + \log \frac{200x}{10}$$

$$\log 20x = 0 \implies 20x = 1 \implies x = \frac{1}{20} = 0.05.$$

Illustration 17:

50 mL of 0.1 M NaOH is added to 75 mL of 0.1 M NH₄Cl to make a basic buffer. If pK_a of NH₄⁺ is 9.26, Calculate pH.

5

Solution:

Using Handerson equation for basic buffer

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

: For
$$NH_4OH$$
, $\left(pK_a\right)_{NH_4^+} + \left(pK_b\right)_{NH_4OH} = 14$

$$\therefore \qquad \left(pK_{b}\right)_{NH_{4}OH} = 14 - 9.26 = 4.74$$

$$NH_{4}Cl + NaOH \longrightarrow NH_{4}OH + NaCl$$

$$t = 0 \qquad 7.5 \qquad 5$$

:.
$$pOH = 4.74 + \log \frac{2.5}{5} = 4.44$$
 :. $pH = 14 - 4.44 = 9.56$

17. Salt Buffer

A salt buffer is a solution of a salt which itself can act as a buffer. Such salt is the salt of a weak acid and weak base.

For example, $CH_3COONH_4 \square \square CH_3COO^- + NH_4^+$

When an acid is added, it reacts with CH₃COO⁻ to produce CH₃COOH and when a base is

added, it reacts with NH_4^+ to produce NH_4OH .

18. Buffer capacity or Buffer Index

Buffer capacity of a solution is defined in terms of buffer index which is the change in the concentration of Buffer acid (or base) required for change of it's pH value by one, keeping $(C_{salt} + C_{acid})$ or $(C_{base} + C_{salt})$ constant.

Let there be a buffer solution of volume 1 litre with 'x' mole of acid and 'S' moles of 'salt'.

$$pH = pK_a + \log_{10} \frac{S}{x - S}$$

$$pH = pK_a + \frac{1}{2.303} \log_e \frac{S}{x - S}$$

$$\frac{\partial(pH)}{\partial S} = \frac{1}{2.303} \left[\frac{1}{S} + \frac{1}{x - S} \right]$$

$$\frac{\partial(pH)}{\partial S} = \frac{1}{2.303} \left[\frac{x - S + S}{S(x - S)} \right]$$

$$\frac{\partial S}{\partial(pH)} = \frac{1}{2.303} \left[\frac{S(x - S)}{x} \right]$$

Maximum value of Buffer Index

$$B.I = \frac{1}{2.303} \frac{S(x-S)}{x}$$

$$\frac{d}{dS} (B.I) = \frac{1}{2.303} \left[\frac{1}{x} [x-2s] \right]$$
for maximum value of Buffer index
$$\frac{d}{dS} (B.I) = 0$$
After solving S = x/2
Thus $\frac{[Salt]}{[Acid]} = \frac{S}{x-S} = \frac{x/2}{x-x/2} = 1$

Hence max. value of Buffer index occurs when $\frac{[Salt]}{[Acid]} = 1$,

19. Buffer Range

It is difficult to give an exact limit upto which a buffer can be used it in generally accepted that a solution has useful buffer capacity provided that the value of [Salt]/[Acid] lie within the range of 10 to 0.1.Hence from Henderson equation

$$pK_a + log 0.1 < pH < pK_a + log_{10} 10$$

 $pK_a - 1 < pH < pK_a + 1$

Outside this range the Buffer capacity is too small to be of any practical application.

20. Hydrolysis of Salt

Salts are strong electrolytes when dissolved in water, they dissociated almost completely into cations or anions. If anion reacts with water it is called as anionic hydrolysis.

 $A^- + H_2O \longrightarrow HA + OH^-$ Alkaline solution (pH increases).

If cation reacts with water it is called as cationic hydrolysis.

 $B^+ + 2H_2O \longrightarrow B(OH) + H_3O^+$ Acidic solution (pH lowers down).

"The phenomenon of the interaction of anions and cations of the salt with H^+ and OH^- ions furnished by water yielding acidic or alkaline solution is known as salt hydrolysis.

For the study of hydrolysis salts are divided into 4 groups.

Hydrolysis of salt of strong Acid or weak base:

 NH_4Cl is a salt of weak base (NH_4OH) and strong acid (HCl). After hydrolysis resultant solution will be acidic due to presence of strong acid HCl.

$$NH_{4}Cl + H_{2}O \blacksquare \textcircled{P} NH_{4}OH + HCl$$

$$NH_{4}^{+} + Cl^{-} + H_{2}O \blacksquare \textcircled{P} NH_{4}OH + H^{+} + Cl^{-}$$

$$NH_{4}^{+} + H_{2}O \blacksquare \textcircled{P} NH_{4}OH + \underset{(acidic)}{H^{+}}$$

$$K_{h} = \frac{[NH_{4}OH][H^{+}]}{[NH_{4}^{+}]}$$

Relation B/w $K_{\rm h}, K_{\rm b}$ and $K_{\rm w}$:

 $NH_4OH = NH_4^+ + OH^-$

$$K_{b} = \frac{[NH_{4}^{+}][OH^{-}]}{[NH_{4}OH]} \qquad \dots (1)$$

 H_2O $H^+ + OH^-$

$$K_{w} = [H^{+}][OH^{-}] \qquad \dots (2)$$

Dividing (2) ÷ (1)
$$\frac{K_{w}}{K_{b}} = \frac{[H^{+}][OH^{-}]}{[NH_{4}^{+}][OH^{-}]} \times [NH_{4}OH]$$
$$\frac{K_{w}}{K_{b}} = K_{b}$$

Degree of hydrolysis

$$NH_{4}^{+} + H_{2}O = P NH_{4}^{+} + OH_{Ch}^{-}$$

$$K_{h} = \frac{Ch \cdot Ch}{C(1-h)} = Ch^{2} \qquad (1-h \cong 1)$$

$$h = \sqrt{\frac{K_{h}}{C}} \implies h = \sqrt{\frac{K_{w}}{K_{b}C}}$$

$$[H^{+}] = Ch = C\sqrt{\frac{K_{w}}{K_{b}C}} \implies [H^{+}] = \sqrt{\frac{K_{w} \times C}{K_{b}}}$$

$$Taking -log_{10} \text{ both side}$$

$$nH = \frac{1}{2} [nK - nK - log C] \implies nH = 7 - \frac{1}{2} nK - \frac{1}{2}$$

$$pH = \frac{1}{2} [pK_w - pK_b - \log C] \implies pH = 7 - \frac{1}{2} pK_b - \frac{1}{2} \log C$$

Illustration 18:

Calculate degree of hydrolysis and pH of 0.2 M solution of NH_4Cl . Given K_b for NH_4OH

is 1.8×10^{-5} .

Solution:

	NH ₄ Cl	+ H_2O	$\rm NH_4OH$ +	HC1		
Before hydrolysis	1		0	0		
After hydrolysis	1 —h		h	h		
Where h is degree of hydrolysis						

$$h = \sqrt{\left(\frac{K_{h}}{C}\right)} = \sqrt{\left[\frac{K_{w}}{K_{b}.C}\right]} = \sqrt{\frac{10^{-14}}{1.8 \times 10^{-5} \times 0.2}} = 5.27 \times 10^{-5}$$

From HCl, strong acid

$$\therefore \qquad [H^+] = C.h = C\sqrt{\left(\frac{K_h}{C}\right)} = \sqrt{(K_h.C)} = \sqrt{\left(\frac{K_w}{K_b}.C\right)} = \sqrt{\left(\frac{10^{-14} \times 0.2}{1.8 \times 10^{-5}}\right)} = 1.054 \times 10^{-5}$$

$$\therefore \qquad pH = -\log[H^+] = -\log 1.054 \times 10^{-5}$$

$$= 4.9771$$

Illustration 19:

Find out the amount of NH_4Cl dissolved in 500 mL to have pH = 4.5. K_b for NH_4OH is

Solution:

Using salt hydrolysis formula

$$pH = 7 - \frac{pK_b}{2} - \frac{\log c}{2} \implies 4.5 = 7 - \frac{4.74}{2} - \frac{\log c}{2} \implies \log c = 0.26$$

$$\therefore \quad c = 1.82 \text{ M}$$

$$\therefore \qquad W_{\text{NH}_4\text{Cl}} = \frac{1.82}{2} \times 53.5 = 48.7 \text{ gm}$$

Hydrolysis of salt of weak acid and strong base:

 CH_3COONa is a salt of weak acid (CH_3COOH) and strong base (NaOH). After hydrolysis resultant solution will be basic due to presence of strong base (NaOH).

$$CH_{3}COONa + H_{2}O(\ell) \blacksquare \textcircled{H} CH_{3}COOH + NaOH$$

$$CH_{3}COO^{-} + Na^{+} + H_{2}O(\ell) \blacksquare \textcircled{H} CH_{3}COOH + Na^{+} + OH^{-}$$

$$K_{h} = \frac{[CH_{3}COOH][OH^{-}]}{[CH_{3}COO^{-}]}$$

Relation between, K_h , K_w and K_a

$$CH_{3}COOH = CH_{3}COO^{-} + H^{+}$$

$$K_{a} = \frac{[CH_{3}COO^{-}][H^{+}]}{[CH_{3}COOH]} \dots (1)$$

$$H_{2}O = H^{+}OH^{-}$$

$$K_{w} = [H^{+}][OH^{-}] \qquad \dots (2)$$

Dividing equation (2) ÷ (1)

$$\frac{K_{w}}{K_{a}} = \frac{[H^{+}][OH^{-}] \times [CH_{3}COOH]}{[CH_{3}COO^{-}][H^{+}]} = \frac{[OH^{-}][CH_{3}COOH]}{[CH_{3}COO^{-}]} = K_{h}$$

Degree of Hydrolysis

$$\begin{split} & CH_3COO^- + H_2O(\ell) \exists \; \boxplus \; CH_3COOH + OH^- \\ \text{at time} &= 0 \qquad C \qquad 0 \qquad 0 \\ \text{at time} &= t \qquad C(1-h) \qquad Ch \qquad Ch \qquad Ch \\ & K_h &= \frac{Ch \cdot Ch}{C(1-h)} = Ch^2 \quad (1-h \cong 1) \text{ h should be smaller than } 0.1 \text{ than } 1-h=1. \\ & h &= \sqrt{\frac{K_h}{C}} \qquad \Rightarrow \qquad h = \sqrt{\frac{K_w}{K_aC}} \\ & OH^- = Ch \qquad \Rightarrow \qquad OH^- = C\sqrt{\frac{K_w}{K_aC}} = \sqrt{\frac{K_wC}{K_a}} \\ & H_3O^+ &= \frac{K_w}{[OH^-]} = K_w \sqrt{\frac{K_a}{K_wC}} = \sqrt{\frac{K_a \times K_w}{C}} \\ & Taking (-ve) \log both side \\ & -\log[H^+] = \frac{1}{2}\log K_w - \frac{1}{2}\log K_a + \frac{1}{2}\log C = \frac{1}{2}[pK_w + pK_a + \log C] \\ & pH = 7 + \frac{1}{2}pK_a + \frac{1}{2}\log C \end{split}$$

pH will be more than 7, hence resultant solution will be basic in nature.

Illustration 20:

Calcium lactate is a salt of weak organic acid and strong base, represented as $Ca(Lac)_{2}$. A saturated solution of $Ca(Lac)_{2}$ contains 0.13 mole of this salt in 0.50 L solution. The pOH of this solution is 5.60. Assuming a complete dissociation of the salt, calculate K_{a} of lactic acid.

Solution:

Formula of calcium lactate suggests that lactic acid is dibasic acid. Each mole of salt furnishes two moles of lactate ion

 $Ca(Lac)_2 \rightleftharpoons Ca^{2+} + 2 Lac^{-}$ 0.50 L solution contains = 0.13 mol of salt = 0.26 mol of lactate ion :. 1 L of solution contains = 0.52 mol of lactate ion

[lactate] = 0.52 M.

given pOH = 5.6

$$\therefore$$
 pH = 8.

using equation of pH for salt of weak acid and strong base

$$pH = 7 + \frac{pK_a}{2} + \frac{\log C}{2}$$

8.4 = 7 + $\frac{pK_a}{2} + \frac{\log 0.52}{2} = 7 + \frac{pK_a}{2} - 0.14$
 $pK_a = 3.08$
 $K_a = 10^{-3.08} = 8.3 \times 10^{-4}.$

Illustration 21:

What is the pH of a 0.5 M aqueous NaCN solution? pK_b of $CN^- = 4.70$.

Solution:

$$P^{H} = \frac{1}{2} \left[14 + pK_{a} + \log c \right] = \frac{1}{2} \left[14 + 9.3 + \log 0.5 \right] = 11.5$$

Hydrolysis of salt of Weak Acid and Weak Base:

Let's take the salt CH₃COONH₄ made of salt of weak acid (CH₃COOH) and Weak base (NH₄OH).

 $CH_{3}COONH_{4} + H_{2}O \blacksquare \textcircled{H} CH_{3}COOH + NH_{4}OH$ $CH_{3}COO^{-} + NH_{4}^{+} + H_{2}O \blacksquare \textcircled{H} CH_{3}COOH + NH_{4}OH$ $K_{h} = \frac{[CH_{3}COOH][NH_{4}OH]}{[CH_{3}COO^{-}][NH_{4}^{+}]}$

Relation between, $K_{h}, K_{w}, K_{a} \& K_{b}$

$$CH_{3}COOH \blacksquare \stackrel{\textcircled{}}{\bigoplus} CH_{3}COO^{-} + H^{+}$$

$$K_{a} = \frac{[CH_{3}COO^{-}][H^{+}]}{[CH_{3}COOH]} \dots (1)$$

$$NH_{4}OH \blacksquare \stackrel{\textcircled{}}{\bigoplus} NH_{4}^{+} + OH^{-}$$

$$K_{b} = \frac{[NH_{4}^{+}][OH^{-}]}{[NH_{4}OH]} \dots (2)$$

$$H_{2}O \blacksquare \stackrel{\textcircled{}}{\bigoplus} H^{+} + OH^{-}$$

$$K_{w} = [H^{+}][OH^{-}] \qquad \dots (3)$$

$$\frac{K_{w}}{K_{a} \times K_{b}} = \frac{[H^{+}][OH^{-}] \times [CH_{3}COOH][NH_{4}OH]}{[CH_{3}COO^{-}][H^{+}][NH_{4}^{+}][OH^{-}]}$$

$$\frac{K_{w}}{K_{a} \times K_{b}} = K_{h}$$

Degree of Hydrolysis

$$\begin{aligned} & CH_{3}COO^{-} + NH_{4}^{+} + H_{2}O \blacksquare \bigoplus CH_{3}COOH + NH_{4}OH \\ \text{at time} &= 0 \qquad C \qquad C \qquad 0 \qquad 0 \\ \text{at time} &= t \qquad C(1-h) \qquad C(1-h) \qquad Ch \qquad Ch \\ & K_{h} &= \frac{Ch \cdot Ch}{C(1-h)C(1-h)} = \frac{h^{2}}{(1-h)^{2}} \\ \text{if} \qquad h \leq 0.1, \quad 1-h \cong 1 \\ & \frac{h}{1-h} = \sqrt{\frac{K_{w}}{K_{a}K_{h}}} \end{aligned}$$

The acetic acid formed would partially decompose to give CH_3COO^- and H^+ . But because of common ion effect (that is, due to the unhyrolysed CH_3COO^-) it is possible to neglect the acetate ion coming from CH_3COOH .

Therefore $CH_3COOH \square \square CH_3COO^- + H^+$

$$C\alpha \qquad C(1-\alpha)$$

$$K_{a} = \frac{C(1-\alpha)[H^{+}]}{C\alpha}$$

$$K_{a} = \frac{[H^{+}]}{\alpha} \qquad (1-\alpha \cong 1)$$

$$[H^{+}] = K_{a}\alpha = K_{a}\sqrt{\frac{K_{w}}{K_{a}K_{b}}} = \sqrt{\frac{K_{w}K_{a}}{K_{b}}} \qquad \text{or} \qquad \mathbf{pH} = \frac{1}{2}\mathbf{pK}_{w} + \mathbf{pK}_{a} - \mathbf{pK}_{w}$$

This expression is independent of conc. of the salt.

- (i) if $K_a = K_b$, pH = 7 solution will be neutral
- (ii) if $K_a > K_b$, pH < 7, acidic solution
- (iii) if $K_a < K_b$ then pH > 7, alkaline solution

In the hydrolysis of salt of weak acid and a weak base such as NH_4CN , CH_3COONH_4 . Both the ions are hydrolysied, if we assume $K_a \cong K_b$, then the hydrolysis of the cation and anion of the salt occur approximately to equal extent for a salt which has $K_a < K_b$, it would be expected at the first glance that CN^- ions hydrolysed to a much greater extent than NH_4^+ ions. However, the hydrolysis of CN^- ions produced OH^- ions according to the equation.

 $CN^{-} + H_2O$ HCN + OH⁻

which can react with NH_4^+ ions as

 $OH^{-} + NH_{4}^{+} \square \square NH_{4}OH$

This latter reaction causes equilibrium in the from reaction to be displaced to the right. Because OH⁻ ions are removed from the solution. Also the production of OH⁻ by the former reaction displaces the latter reaction to the right. Therefore the hydrolysis of one ion drags the hydrolysis of the other ion along so that both the hydrolysis are fairly extensive not too far in extant from each other so it is fairly safe to assume that [HCN] = [NH₄OH], even in the case of the salt where $K_a \neq K_b$.

Illustration 22:

The dissociation constants for aniline, acetic acid and water at 25°C are 3.83×10^{-10} , 1.75×10^{-5} and 1.008×10^{-14} respectively. Calculate degree of hydrolysis of aniline acetate in a deci normal solution. Also report the pH. Solution:

 $\therefore \qquad \text{Aniline}^{+} + \text{Acetate}^{-} + \text{H}_2\text{O} \blacksquare \bigoplus \text{Aniline}^{+} + \text{Acetic acid}$ Before hydrolysis 1 1 0 0 0 After hydrolysis 1-h 1-h h h Let concentration of salt be C mol litre⁻¹ $\therefore \qquad K_h = \frac{[\text{Aniline}][\text{Acetic Acid}]}{[\text{Aniline}]^{+}[\text{Acetate}]^{-}} = \frac{\text{C.h.C.h}}{\text{C.(1-h).C.(1-h)}}$ $\therefore \qquad K_h = \frac{h^2}{(1-h)^2}$

$$\therefore \qquad \frac{h}{1-h} = \sqrt{(K_h)} \qquad \Rightarrow \qquad \frac{h}{1-h} = \sqrt{\left(\frac{K_w}{K_a.K_b}\right)} = \sqrt{\left(\frac{1.008 \times 10^{-14}}{1.75 \times 10^{-5} \times 3.83 \times 10^{-10}}\right)}$$
$$\therefore \qquad h = 54.95\%$$

Illustration 23:

Calculate the pH of an aqueous solution of 1.0 M ammonium formate assuming complete dissociation. (pK_a of formic acid = 3.8 and pK_b of ammonia = 4.8)

Solution

$$pH = \frac{1}{2} [pK_w + pK_a - pK_b] = \frac{1}{2} (14 + 3.8 - 4.8) = 6.5$$

21. Case IV : Salts of strong Acid + Strong Base

e.g., NaCl, KNO₃, ... etc.

This category of salts does not undergo salt hydrolysis

22. Solubility and solubility Product

A solution which remain in contact with excess of the solute is said to be saturated. The amount of a solute, dissolved in a given volume of a solvent (in 1 litre) to form a saturated solution at a given temperature, it termed as the solubility of the solute in the solvent at that temperature.

Molar Solubility:

No. of moles of solute dissolved in per litre of solution

Solubility Product:

In a saturated solution of a salt, there exists a dynamic equilibrium between the excess of the solute and ions furnished by that parts of the solute which has gone in solution. The solubility product of a sparingly soluble salt is given as product of the conc. of the ions raised to the power equal to the no. of times the ion occur in the equation after the dissociation of the electrolyte.

 $A_{x}B_{y} \boxminus \Box \Box xA^{y+} + yB^{x-}$ $K_{sp} = [A^{y+}]^{x}[B^{x-}]^{y}$ Let the solubility of AxBy is S then $K_{sp} = [xS]^{x}[yS]^{y}$ $K_{sp} = x^{x} \cdot y^{y}[S^{x+y}]$

The principle of solubility product is applicable for sparingly soluble salt.

23. Common-ion Effect on Solubility

The common ion present in the solution decrease the solubility of a given compound e.g. The solubility of $BaSO_4$ in Na_2SO_4 solution is smaller than that in an aqueous solution.

Consider saturated solution of AgCl. If a salt having either of the ion common to AgCl say KCl is added to it, then

 $AgCl_{(s)} + aq. \blacksquare \blacksquare Ag^{+} + Cl^{-}$ $KCl + aq. \longrightarrow K^{+} + Cl^{-}$

For AgCl $K_{SP} = [Ag^+][Cl^-]$

 $[Cl^-]$ Increases in solution due to presence of KCl and thus to have K_{sp} constant, $[Ag^+]$ will decrease or AgCl will precipitate out from solution, i.e., solubility of AgCl will decrease with increasing concentration of KCl in solution.

Let 0.1 M KCl_(aq.) solution with AgCl_(aq.). If solubility of AgCl is s mol litre⁻¹, then,

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

s being small in comparison to 0.1 and thus may be neglected therefore,

$$K_{sp} = s \times 0.1$$
 or $s_{AgCl} = \frac{K_{sp}}{0.1}$

where s is solubility of AgCl in presence of 0.1 M KCl_{aq}.

24. Ionic Product

For a solution of a salt at a specified concentration, the product of the concentration of the ions, each raised to the proper power, is called as the ionic product for a saturated solution in equilibrium with excess of solid, the ionic product is equal to solubility product.

At equilibrium, ionic product = solubility product

If ionic product is less than solubility product it means solution is unsaturated means more salt can be dissolve in it.

If ionic product greater than solubility it means solution is holding more salt than can dissolve in it, therefore ppt started till, until or unless ionic product becomes equal to K_{sn} .

25. Preferential Precipitation of Salts

Frequently, a solution contains more than one ion capable of forming a ppt. with another ion which is added to the solution. e.g., in a solution containing Cl⁻, Br⁻ and I⁻, if Ag⁺ ions are added then out of the three, the least soluble silver salt is ppt first. If the addition of Ag⁺ ions is continued, eventually a stage is reached when the next lesser soluble salt starts ppt along with the least soluble salt and so on if the stocihiometry of the ppted salts is the same, then the salt with the minimum K_{sp} or minimum solubility will ppted first followed by higher K_{sp} .

If the stoichiometry of the ppted salts is not the same, then with K_{sp} alone, we can't predict which ion will ppted first. e.g. a solution containing Cl⁻ and CrO₄⁻² both of these ions form ppt with Ag⁺ though the K_{sp} (AgCl) > K_{sp} (Ag₂CrO₄). Yet it is AgCl (less soluble) which ppted first when Ag⁺ ions added to the solution. In order to predict which ion (Cl⁻ or CrO₄⁻²) ppt first. We have to calculate the conc. of Ag⁺ ion needed to start ppt through the K_{sp} and given conc. of Cl⁻ and CrO₄⁻² if the conc. of Ag⁺ ions needed to start the ppt of CrO₄⁻² is larger than that of Cl⁻. Hence as AgNO₃ is added to the solution, the minimum of the two conc. of Ag⁺ to start the ppt will be reached first and thus the corresponding ion (Cl⁻ in this case) will be ppted in preference to the other. During the course of ppt conc. of Cl⁻ decreases and conc. of Ag⁺ increases when its's conc. become equals to the conc. required (of Ag⁺) for CrO₄⁻². At this stages the whole of Cl⁻ ions have been ppted the addition of more of AgNO₃ causes the ppt of both the ions together.

(i) Solubility of a salt of weak acid and strong base in Basic Buffer suppresses than pure water due to common ion effect. But in acidic buffer solution soubility increase than pure water.

(ii) Solubility of salt of weak acid and weak base in pure water: Let the solubility of salt be S, and y mol/litre is the amount of salt getting hydrolysed.

Due to hydrolysis of salt from equation (2)

$$K_{h} = \frac{[CH_{3}COOH][NH_{4}OH]}{[CH_{3}COO^{-}][NH_{4}^{+}]} = \frac{y.y}{(S-y)(S-y)}$$
$$K_{h} = \left(\frac{y}{S-y}\right)^{2}$$

and we also know that

$$K_{h} = \frac{K_{w}}{K_{a}K_{b}}$$

26. Solubility of a salt of weak acid and weak base in acidic buffer

Let the solubility of salt be S and y be the amount of weak acid being formed.

$$CH_{3}COONH_{4} \boxminus CH_{3}COO^{-} + NH_{4}^{+}$$

$$S - y \qquad y$$

$$CH_{3}COO^{-} + H^{+} \longrightarrow CH_{3}COOH \qquad \dots (2)$$

$$S - y \qquad (from Acidic Buffer) \qquad y$$

$$K_{sp} = [CH_{3}COO^{-}][NH_{4}^{+}] = [S - y] [y] = y [S - y]$$
for equation (2)
$$\frac{1}{K_{a(CH_{3}COOH)}} = K'_{a} = \frac{[CH_{3}COOH]}{[CH_{3}COO^{-}][H^{+}]} = \frac{y}{(S - y)(H^{+})}$$

Solubility of CH₃COONH₄ in acidic buffer would be higher than in pure water

27. Solubility of a salt of weak acid and weak base in basic buffer

Similarly CH₃COONH₄
$$\square \square$$
 CH₃COO⁻ + NH₄⁺
y S - y
NH₄⁺ + OH⁻ $\square \square$ NH₄OH
S - y (from buffer) y
K_{sp(CH₃COONH₄)} = [CH₃COO⁻][NH₄⁺] \Rightarrow K_{sp} = y(S - y)
 $\frac{1}{K_b} = K'_b = \frac{[NH_4OH]}{[NH_4^+][OH^-]} = \frac{y}{(S - y)(OH^-)}$

The solubility of $CH_3COONH_4^+$ in basic buffer would be higher than pure water.

Illustration 24:

A 100.0 mL sample is removed from a water solution saturated with $CaSO_4$ at 25°C. The water is completely evaporated from the sample and a deposit of 0.24 g $CaSO_4$ is obtained. What is K_{sp} for $CaSO_4$ at 25°C?

Solution:

 $CaSO_4(s) \rightleftharpoons Ca^{2+} (aq) + SO_4^{2-} (aq), K_{sp} = ?$

Data shows that the solubility of $CaSO_4$ is 0.24 g per 100 mL.

:.
$$[CaSO_4] = \frac{0.24}{100} \times \frac{1000}{136} \text{ mol } L^{-1} = 0.01765 \text{ M}$$

$$\therefore$$
 [Ca²⁺] = [SO₄²⁻] = 0.01765 M.

:.
$$K_{sp} = [Ca^{2+}] [SO_4^{2-}] = (0.01765)^2 = 3.115 \times 10^{-4}.$$

Illustration 25:

Zn salt is mixed with $(NH_{*})_{2}S$ of molarity 0.021 M. What amount of Zn^{2+} will remain unprecipitated in 12 mL of the solution? K_{SP} of $ZnS = 4.51 \times 10^{-24}$.

Solution:

(i) $K_{sp} = [Zn^{+2}] [S^{-2}]$

$$4.51 \times 10^{-24} = [Zn^{+2}] \times 0.021 \implies [Zn^{+2}] = 2.15 \times 10^{-22} \text{ M}$$

amount = 2.15 × 10⁻²² × 65.4 × $\frac{12}{1000}$ = 1.68 × 10⁻²² g

Illustration 26:

...

Calculate the solubility of AgCN in a buffer solution of pH = 3. Given K_{sp} of AgCN = 1.2 × 10⁻¹⁶ and K_a for HCN = 4.8 × 10⁻¹⁰.

Solution:

28. Solubility of AgCl in an aqueous solution containing NH₃

Let the amount of NH₃ initially be 'a' M. if the solubility of salt be 'b' mole/ litre.

AgCl(s) Ag^+ + Cl- $\begin{array}{c} 0\\ \mathbf{b}-\mathbf{y} \end{array}$ At time = 0b 0 at time = t y Ag^+ + $2NH_3 \square \square Ag(NH_3)_2^+$ (aq.) b-y a-2yy where y is the amount of Ag⁺ which reacted with NH₃. $K_{sp} = [Ag^+][Cl^-] = (b - y)y$ $\left[Ag(NH_{2})^{+}\right]$ V

$$K_{f} = \frac{[Mg(MH_{3})_{2}]}{[Ag^{+}][NH_{3}]^{2}} = \frac{g}{(b-y)(a-2y)}$$

After knowing the value of K_{sp} and K_{f} the value of solubility can be calculated.

29. Acid-base Indicators

An acid & base indicator are substance which changes it's colour within limits with variation in pH of the solution to which it is added. Indicators, in general are either organic weak acid or weak bases with a characteristics of having different colours in the ionized and unionized form e.g. phenophthalein is a weak acid (ionized form is pink and unionized form is colourless).

Acidic Indicator Action (e.g. HPh)

HPh (Phenolpthalein) is a colourless weak acid

$$\begin{array}{c} HPh\\ Colourless \end{array} \stackrel{\frown}{=} H^{+} + Ph^{-}\\ (Pink) \end{array}$$
$$K_{IN} = \frac{[H^{+}][Ph^{-}]}{[HPh]} \end{array}$$

If the solution is acidic, the H⁺ by the acid increases and since K_{in} is constant and it does not depend upon the concentration so HPb also increases mean equilibrium will shift towards left means solution remain colourless. By addition of alkali, OH⁻ will be furnished and that OH⁻ will combines with H⁺ of HPh to form water and equilibrium will moves towards right and therefore solution becomes pink. Thus HPh appears colourless in acidic and pink in alkaline solution pH range of HPh is (8.3–10).

$$pH = pK_{In} + \log \frac{[In^{-}]}{[HIn]}$$

The colour of the indicator changes from colour A to colour B at a particular point known as end point of indicator. At this point $[HIn] = [In^{-}]$ means $pH = pK_{ln}$ (at this point half of indicator is in the acid form and half in the form of its conjugate form.

30. Indication (Basic) action of MeOH (Methyl Orange)

When MeOH is dissolved in water and undergoes dissociation to a small extent. The undissociated molecules are yellow while dissociated Me⁺ are red in colour.

$$\underset{\text{yellow}}{\text{MeOH}} \blacksquare \textcircled{\text{Me}}^{+} + \underset{\text{red}}{\text{OH}}^{-}$$

If the solution is acidic, the H⁺ furnished by the acid combines with OH⁻ ions furnished by the indicators to form undissociated water. This shifts the equilibrium towards right giving red coloured solution. Therefore in acid solution, this indicator gives red colour. In the presence of alkali, OH⁻ increases and due to common ion effect the dissociation of MeOH surpress means equilibrium will shifts towards left. Hence the solution in alkaline medium remains yellow in colour.

Colour of solution depends upon relative amount of ionized form to unionized form (ratio of Me⁺/ MeOH).

In general pH range of indicator lies B/w $pK_{ln} - 1$ to $pK_{ln} + 1$

Case 1:
$$pH = pK_{ln} - 1$$

Means
$$\frac{In^-}{[HIn]} = 0.1 = 10\%$$

Percentage ionization of indicator would be

$$\frac{\text{In}^{-}}{[\text{In}^{-}] + [\text{HIn}]} \times 100\% = \frac{0.10 \text{ HIn}}{0.10 \text{ HIn} + (\text{HIn})} \times 100\%$$
$$= \frac{1}{11} \times 100 = 9.1\%$$

In fact, $pH = pK_{In} - 1$ is the maximum pH upto which the solution has a distinct colour characteristic of HIn. At pH smaller than this value, more of the indicator is present in the unionized form.

Thus at $pH \leq pK_{in}$ -1, the solution has a colour characteristic of HIn.

Case 2 : at $pH = pK_{In} + 1$

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

Percentage of ionization of indicator is

$$\frac{[\text{In}^-]}{[\text{In}^-] + [\text{HIn}]} \times 100\% = \frac{10 [\text{HIn}]}{10 [\text{HIn}] + [\text{HIn}]} \times 100\% = \frac{1000}{11} = 91\%$$

Thus most of the indicator is present in the ionized form In^- and solution gets the colour characteristic. Infact $pH = pK_{In} + 1$ is the minimum pH upto which the solution has a distinct characteristic of In^- . At pH greater than this value, still more of the indicator is present in the ionized form. Thus at $pH \ge pK_{In} + 1$, the solution has a colour characteristics of In^- .

Illustration 27:

An indicator is a weak acid and pH range of its colour is 3.1 to 4.5. If the neutral point of the indicator lies in the centre of the hydrogen ion concentrations corresponding to the given pH range, calculate the ionization constant of the indicator.

Solution:

$$pH = -\log [H_3O^+], \text{ or } \log [H_3O^+] = -pH$$

 \therefore [H₃O⁺] = antilog of (-pH)

for pH = 3.1 $[H_3O^+]_1$ = antilog of (-3.1) = antilog of ($\overline{4.9}$) = 7.94×10⁻⁴

for pH = 4.5 $[H_3O^+]_2$ = antilog of (-4.5) = antilog of ($\overline{5.5}$) = 3.16×10⁻⁵

Since neutral point lies at the centre of the hydrogen ion concentration in the given pH range, hence $[H_3O^+]$ at the neutral point

$$[H_{3}O^{+}] = \frac{[H_{3}O^{+}]_{1} + [H_{3}O^{+}]_{2}}{2}$$
$$= \frac{7.94 \times 10^{-4} + 3.16 \times 10^{-5}}{2} = 4.13 \times 10^{-4} \text{ M}$$

Let indicator be HIn behaving as weak acid, then

HIn + H₂O
$$\implies$$
 H₃O⁺ + In⁻
 $K_{In} = \frac{[H_3O^+][In^-]}{[HIn]}$ [ionization constant of indicator is K_{In}]
= [H₃O⁺] {since at neutral point [In⁻] = [HIn]} = 4.13 \times 10^{-4}.

Illustration 28:

Calculate the pH at which an acid indicator with $K_a = 1 \times 10^{-5}$ changes colour when the indicator concentration is 1×10^{-3} M. Also report the pH at which coloured ion is 80% present.

Solution:

$$pH = pK_{In} + \log \frac{[In^{-}]}{[HIn]}$$

For colour change, $\frac{[In^{-}]}{[HIn]} = 1$
 \therefore $pH = pK_{In} = -\log(1 \times 10^{-5}) = 5$

now
$$[In^{-}] = 80, [HIn] = 20$$

 $\therefore \qquad pH = 5 + \log \frac{80}{20} = 5.6$

31. Ostwald's Theory

According to this theory:

- (a) The colour change is due to ionization of the acid-base indicator. The unionized form has different colour than the ionized form.
- (b) The ionization of the indicator is largely affected in acids and bases as it is either a weak acid or a weak base. In case, the indicator is a weak acid, its ionization is very much low in acids due to common H⁺ ions while it is fairly ionized in alkalies. Similarly if the indicator is a weak base, its ionization is large in acids and low in alkalies due to common OH⁻ ions.

Considering two important indicators phenophthalein (a weak acid) and methyl orange (a weak base), Ostwald theory can be illustrated as follows:

Phenolphthalein: It can be represented as HPh. It ionizes in solution to a small extent as:

$$\begin{array}{c} \text{HPh} \\ \text{Colourless} \end{array} \stackrel{\square}{=} \begin{array}{c} \begin{array}{c} \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} H^+ + Ph^- \\ Pink \end{array}$$

Applying law of mass action,

$$K = \frac{[H^+][Ph^-]}{[HPh]}$$

The undissociated molecules of phenolphthalein are colourless while Ph^- ions are pink in colour. In presence of an acid, the ionization of HPh is practically negligible as the equilibrium shifts to left hand side due to high concentration of H^+ ions. Thus, the solution would remain colourless. On addition of alkali, hydrogen ions are removed by OH^- ions in the form of water molecules and the equilibrium shifts to right hand side. Thus, the concentration of Ph^- ions increases in solution and they impart pink colour to the solution.

$$HIn_{Acid form} + H_{2}O = H_{3}^{+}O + H_{3}^{-}O + H_$$

At equivalence point;

 $[\mathrm{In}^-]\!=\![\mathrm{HIn}]$ and $p\mathrm{H}\!=\!p\mathrm{K}_{\mathrm{In}}$

Methyl orange: It is a weak base and can be represented as MeOH. It is ionized in solution to give Me⁺ and OH⁻ ions.

$$\operatorname{MeOH}_{\operatorname{Yellow}} \square \square = \operatorname{Me}_{\operatorname{Red}}^{+} + \operatorname{OH}^{-}$$

Applying law of mass action

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

In presence of an acid, OH⁻ ions are removed in the form of water molecules and the above equilibrium shifts to right hand side. Thus, sufficient Me⁺ ions are produced which impart red colour to the solution. On addition of alkali, the concentration of OH⁻ ions increases in the solution and the equilibrium shifts to left hand side (due to common ion effect), i.e., the ionization of MeOH is practically negligible. Thus, the solution acquires the colour of unionized methyl orange molecules, i.e., yellow.

This theory also explains the reason why phenolphthalein is not a suitable indicator for titrating a weak base against strong acid. The OH⁻ ions furnished by a weak base are not sufficient to shift the equilibrium towards right hand side considerably, i.e., pH is not reached to 8.3. Thus, the solution does not attain pink colour. Similarly, it can be explained why methyl orange is not a suitable indicator for the titration of weak acid with strong base.

Quinonoid Theory: According to this theory:

(a) The acid-base indicators exist in two tautomeric forms having different structures. Two forms are in equilibrium. One form is termed benzenoid form and the other quinonoid form.



(b) The two forms have different colours. The colour change is due to the interconversion of one tautomeric form into other.

(c) One form mainly exists in acidic medium and the other in alkaline medium. Thus, during titration the medium changes from acidic to alkaline or vice-versa. The change in pH converts one tautomeric form into other and thus, the colour change occurs. Phenolphthalein has benzenoid form in acidic medium and thus, it is colourless while it has quinonoid form in alkaline medium which has pink colour.



Methyl orange has quinonoid form in acidic solution and benzenoid form in alkaline solution. The colour of benzenoid form is yellow while that of quinonoid form is red.



Dissociation of acids and base

For a weak acid HA HA \implies H⁺+A⁻ $K_a = 10$ When the concentration of acid is 10 M, then

- Q.1 What is the degree of dissociation of acid?
- **Q.2** With respect to Q. 1 what will be the concentration of H^+ ion ?
- Q.3 When the concentration of acid is reduced to 1 M, then what is the degree of dissociation ?
- **Q.4** With Respect to Q. 3 what is the concentration of H^+ ion ?
- Q.5 Now the concentration of acid is further reduced to 0.1 M, what is the degree of dissociation?
- **Q.6** With respect to Q. 5 now what is the concentration of H^+ ion ?
- II. Degree of dissociation of a weak acid having concentration 10⁻³ M is 0.1, then
- **Q.7** Calculate the K_a of the acid?

I.

- **Q.8** Calculate the concentration of H^+ ion ?
- III. A weak acid having $K_a = 2.5 \times 10^{-5}$ gives $[H^+] = 1.3 \times 10^{-4}$ M.
- Q.9 On the basis of above information, what will be the degree of dissociation of acid?
- Q.10 What will be the concentration of acid
- IV. In a 10^{-2} M solution of acid HA having $K_a = 10^{-4}$,
- **Q.11** What will be the $[H^+]$?
- V. For an acid HA having $K_a = 2.1 \times 10^{-4}$ & molecular weight = 90.
- **Q.12** Calculate the amount of acid which should be dissolved in 10 ℓ of solution having $\alpha = 8\%$?
- VI In a 10% dissociated solution of a weak acid HA, concentration of H^+ ion is 3.5×10^{-3} M, then
- **Q.13** Calculate the K_a for the acid

Daily Practice Problems - 02

(Q-1 to Q-9)

Generally all organic acids are weak acids. Acetic acid (CH₃COOH) & formic acid (HCOOH) both are organic acids, hence both are weak acids & most commonly used in ionic equilibrium CH₃COOH is weaker than HCOOH due to +I effect of $-CH_3$ group. Stronger acid has higher value of Ka & weaker acid has smaller value of Ka. Thus for

$CH_3COOH \longrightarrow CH_3COO^- + H^+$	$K_a = 1.8 \times 10^{-5}$
$HCOOH \longrightarrow HCOO^- + H^+$	$K_a = 1.8 \times 10^{-4}$

- **Q.1** What will be the degree of dissociation and H⁺ion concentration , when concentration of acetic acid is 1 M ?
- Q.2 What will be the degree of dissociation and H^+ ion concentration, if 1M formic acid is taken?

- **Q.3** What will be the degree of dissociation and H^+ ion concentration, when concentration of acetic acid is reduced to 0.1 M?
- **Q.4** What will be the degree of dissociation and H^+ ion concentration, when 0.1 M HCOOH is considered?
- $\label{eq:Q.5} What will be the degree of dissociation and H^{+} ion concentration , when the concentration of acetic acid is further reduced to 10^{-2} M}$
- **Q.6** What will be the degree of dissociation and H^+ ion concentration, now 10^{-2} M HCOOH is taken, then
- Q.7~ What will be the degree of dissociation and $\rm H^{\scriptscriptstyle +}$ ion concentration , when concentration of acetic acid is $10^{-4}\,M$
- **Q.8** What will be the degree of dissociation and H⁺ ion concentration, similarly, now 10⁻⁴ M HCOOH is considered
- Q.9 What will be the degree of dissociation and $\rm H^{+}$ ion concentration, finally concentration of acetic acid is reduced to 10^{-5} M
- **Q.10** In a 5 ℓ solution of acetic acid, having $\alpha = 1\%$ and $K_a = 1.8 \times 10^{-5}$. Calculate the amount of acetic acid present in the solution ?
- **Q.11** What is the α of 0.1 M acetic acid?
- **Q.12** How much water must be added in 900 ml of 0.1 M CH₃COOH solution to triple its degree of dissociation (Assume $\alpha < 5\%$ is negligible)?
- **Q.13** When 35 gm of NH_4OH is dissolved in 10 ℓ of water, then what will be the degree of dissociation
- Q.14 Calculate the concentration of OH- ion in the above question?
- **Q.15** How much amount of CH_3NH_2 dissolve in 2ℓ of water so that it produces concentration OH^- is equal to 5×10^{-4} M, is [Given K_b of $CH_3NH_2 = 2 \times 10^{-6}$]

Common ion effect

Whenever any electrolyte (strong/acid) producing common ion is dissolved in the solution of weak acid & weak base, concentration of common ion increases but degree of dissociation of weak acid or weak base decreases hence concentration of other ion also decreases. In terms of concentration, more is the concentration of common ion, more will be the increase in the degree of dissociation. In terms of nature of electrolyte, more strong electrolyte changes degree of dissociation more. **Case I : Mixture of strong electrolyte + weak electrolyte**

- Q.1 Calculate the degree of dissociation of 0.1 M CH₃COOH in presence of 2M HCl solution ?
- Q.2 Calculate the concentration of H^+ ion in the above question -
- **Q.3** Calculate the pH of the solution containing 0.1 M HNO₃ & 0.1 M HCOOH ? [K_a of HCOOH is 1.8×10^{-4}]
- **Q.4** Calculate the degree of dissociation of 1 M CH₃COOH in presence of 1 M (CH₃COO)₂Pb having degree of dissociation 80% and 3 M (CH₃COO)₂ Ca?
- **Q.5** What is the $[H^+]$ & $[CH_3COO^-]$ in the above question ?

- **Q.6** Calculate the degree of dissociation of 1 M CH₃COOH in presence of 2 M HClO₄ + 0.1 M HCl having $\alpha = 95\%$, ?
- **Q.7** What is $[H^+]$ & $[CH_3COO^-]$ in the above Q.?
- **Q.8** Calculate the degree of dissociation and $[OH^-]$ in 0.1 M NH₄OH, in presence of 1.2 M (NH₄)₃PO₄ having $\alpha = 50\%$?
- **Q.9** Calculate the degree of dissociation and $[OH^-]$ in 0.1 M NH₄OH, In presence of 2 M Ca(OH)₂ having $\alpha = 90\%$?
- **Q.10** Calculate the degree of dissociation and $[OH^{-}]$ in 0.1 M NH₄OH, In presence of 0.1 M (NH₄)₂SO₄.
- **Q.11** Calculate the degree of dissociation and $[OH^-]$ in 0.1 M NH₄OH, In presence of 1.8 M Al(OH)₃ having $\alpha = 10\%$.
- **Q.12** Calculate the amount of $(NH_4)_2SO_4$ having degree of dissociation 75% which should be dissolved in 1500 ml of 1 M NH₄OH to decrease its degree of dissociation by 200 times ?
- **Q.13** 500 ml of 0.2 M H₂SO₄ is mixed with 1500 ml of 0.1 M HCOOH solution. If K_a for formic acid is 1.8×10^{-4} , Calculate the pH of the final solution?
- Q.14 0.1 M CH₃COONa is mixed with 0.05 M HCl, Calculate the final pH of the solution?

Common ion effect

Case-II : Mixture of two weak electrolytes

- **Q.1** A solution contains 0.09 M HCl, 0.09 M CCl₂HCOOH, and 0.1 M CH₃COOH. If total $[H^+] = 0.1$ and K_a for CH₃COOH = 10⁻⁵, Calculate the K_a for CCl₂HCOOH?
- **Q.2** If 0.1 M CH₃COOH is mixed with 0.1 M CH₂ClCOOH, then calculate the total [H⁺] [Given : $K_a CH_3 COOH = 1.8 \times 10^{-5}$, $K_a CH_2 ClCOOH = 1.8 \times 10^{-4}$]
- **Q.3** In a solution containing 0.1 M HCOOH and 0.1 M HOCN, Calculate [H⁺]? Given : K_a for HCOOH and HOCN are 1.8×10^{-4} and 3.3×10^{-4}
- **Q.4** What will be happen on addition of ammonium chloride to a solution of NH_4OH ?

(Q.5-Q.6)

Considering a 0.1 M H₃PO₄ solution, answer the questions given below : [Given : $K_1 = 7.5 \times 10^{-3}$, $K_2 = 6.2 \times 10^{-8}$, $K_3 = 3.6 \times 10^{-13}$]

- **Q.5** Calculate the $[H^+] \& [H_2PO_4^-]$ in given solution?
- **Q.6** Calculate the concentration of $[H_3PO_4]$ at equilibrium ?
- Q.7 When will be happen the degree of dissociation of a weak electrolyte increases?
- **Q.8** Calculate the amount of H_2SO_4 solution, which should be mixed with 500 ml of 0.1 M H_2S solution to obtain concentration of sulphide ion equal to 10^{-20} moles/litre. [Given : K_a for H_2S is 1.3×10^{-21}]

(Q.9–Q.11)

A solution is prepared by mixing one mole of HA with one mole of HB, diluting to a total volume of 1 dm³ with water. Both HA and HB are weak acids which dissociate according to the following reversible reactions.

 $HA + H_2O \Longrightarrow H_3O^+ + A^-; \qquad K_1 = 1.0 \times 10^{-6} M$ $HA + H_2O \Longrightarrow H_3O^+ + B^-; \qquad K_2 = 1.0 \times 10^{-6} M$

Q.9 Write the equilibrium concentrations of H_3O^+ ?

Q.10 What will be the equilibrium concentrations of A^- and B^- ?

Q.11 How does the presence of HB affect the dissociation of HA?

(Q.12–Q.13)

The dissociation constant of HF and HNO_2 are 6.71×10^{-4} M and 4.5×10^{-4} M, respectively. Concentration is 0.5 M in HF and 0.5 M in HNO₂, then -

Q.12 What will be pH of the solution?

Q.13 Calculate the ratio of $[F^-]$ to $[NO_2^-]$ in a solution ?

Daily Practice Problems - 05

Dissociation of water

Q.1	What is the ionization constant and degree of dissociation of water at 25°C?
(Q.2-	-Q.3) The degree of ionization of water was found to be 1.28×10^{-8} .
Q.2	What is the ionization constant of water at 90°C?
Q.3	What is the ionic product of water at this temperature?
Q.4	The ionic product of water is $1 \times 10^{-14} (\text{mol/l})^2$. Calculate the number of H ⁺ ions that present in one millionth part of 1 ml of pure water?

- **Q.5** The pH of pure water at 25° and 35°C are 7 and 6 respectively. Calculate the heat of formation of water from H⁺ and OH⁻?
- **Q.6** K_w for $2H_2O \longrightarrow H_3O^+ + OH^-$ changes from 10^{-14} at 25°C to 9.62×10^{-14} at 60°C. Calculate the pH of water at this temperature (60°C) ?
- **Q.7** If K_w of water at 50°C is 5×10^{-14} , then what will be the nature of solutions having pH = 7, pH = 6 & pH = 8.2 respectively?

Q.8 The value of ionic product of water at various temperature are given below $\theta_c / {}^{\circ}C$ 0 25 40 $K_w \times 10^{-14}/M^2$ 0.114 1.008 2.919 Write the pH value of the pure water at 0°C, 25°C & 40°C respectively?

Q.9 The ionic product of water at 100°C is 55 times than that at 25°C. Calculate the value of pH of water at 100°C ?

Q.10 Calculate the pH of a solution at 25°C which is twice as alkaline as pure water?

Concentration of H^+ and OH^- in aq. solution of acid and base

- $\textbf{Q.1} \quad \text{Calculate the [H^+] and [OH^-] in a solution obtained by dissolving 0.365 g of HCl in 5\ell \ of water ?}$
- **Q.2** On dissolving w gm of H_2SO_4 in 10 ℓ of pure water, concentration of H^+ ion changed by 10,000 times as compared to H^+ ion in pure water at 25°C. Calculate the value of w?
- **Q.3** Calculate the concentration of H⁺ ion in 10^{-5} M H₂SO₄ & 3.1×10^{-3} M HClO₄ respectively?
- (Q.4–Q.6)

When 36.5 μ gm of HCl is dissolved in 1 litre of water, the solution will be acidic in nature due to increase in concentration of H⁺ ion, then find out-

- **Q.4** Calculate the concentration of H^+ ion in the above solution if we neglect H^+ due to water ?
- **Q.5** Calculate the concentration of H^+ ion in the above solution if we consider H^+ due to water.
- Q.6 What will be the % error in the above two questions ?

(Q.7–Q.9)

A small amount of acid brings large difference in $\rm H^+$ ion concentration. If 10^{-7} moles of HCl are dissolved in 1 litre of water then find out -

- **Q.7** Calculate the Concentration of H^+ ion in the above solution if we neglect H^+ due to water ?
- $\textbf{Q.8} \quad Calculate the concentration of H^{+} ion in the above solution if we consider H^{+} due to water $?$}$
- Q.9 Calculate the % error in the above two questions?
- **Q.10** Calculate the $[H^+]$ & $[OH^-]$ ion in 10^{-6} M H₂SO₄ solution ?
- **Q.11** Calculate the concentration of H⁺ ion and OH⁻ ion in a solution obtained by mixing 600 ml of 10^{-2} M H₂SO₄, 800 ml of 10^{-3} M HNO₃ and 1100 ml of 10^{-7} M HCl?
- **Q.12** Calculate the concentration of H⁺ ion in 0.1 M HA solution having $K_a = 10^{-14}$?
- **Q.13** Calculate $[H^+]$ and $[OH^-]$ ion in a 8 litre solution containing 9.25 gm/l of Ca(OH)₂ at 25°C?
- **Q.14** Calculate the concentration of H^+ and OH^- ion in 10^{-8} M NaOH?

Daily Practice Problems - 07

pH and pOH

- **Q.1** Calculate the pH of 0.1 M CH_3 COOH?
- **Q.2** Calculate the pH of $0.1 \text{ M NH}_4\text{OH}$?
- **Q.3** Calculate the pH of 0.1 M HCOOH?
- **Q.4** Calculate the pH of 1 M CH₃COOH?
- **Q.5** Calculate the pH of 0.1 M HA $(K_a = 10^{-2})$?
- **Q.6** Calculate the pH of 10^{-6} M HCl, 10^{-7} M HCl & 10^{-8} M HCl respectively?
- **Q.7** Calculate the pH of 0.1 M CH₃COOH in presence of 0.1 M CH₃COONa?

- **Q.8** Calculate the pH of a solution obtained by mixing 200 ml of HCl solution having pH = 1 with 300 ml of NaOH having pH = 13?
- **Q.9** If $1 \text{ ml of } 10^{-6} \text{ M HCl is diluted to } 100 \text{ ml. Calculate the change in pH ?$
- Q.10 When 200 ml of solution of pH=2 is mixed with 300 ml of solution of pH=3, Calculate the pH of the resulting solution?
- Q.11 What volume of NaOH solution having pH = 11 should be added in 1 litre of 0.1 M HCl solution to increase its pH by 2 units?
- **Q.12** The pH of a solution is 5.0. To this solution sufficient acid is added to decrease the pH to 2.0. What will be the increase in hydrogen ion concentration ?
- **Q.13** The pH of a solution is 2. Its pH is to be changed to 4. Calculate the H⁺ ion concentration of original solution?
- Q.14 An acid solution of pH 6 is diluted hundred times. Calculate the pH of the solution?
- **Q.15** The pH value of 0.1 mol/litre HCl is approximately 1. Calculate the approximate pH value of 0.05 mol/litre H₂SO₄?
- **Q.16** How much water must be evaporated from 5 litre of 10^{-3} M HCl to change its pH by 2 units?
- **Q.17** How much water must be added in 1 litre of 10^{-2} M H₂SO₄ to change its pH by 3 units?
- **Q.18** Calculate the pH of the solution obtained by mixing 300 ml of 0.1 M NH₄OH with 700 ml of 0.1 M NaOH solution ?
- Q.19 How much Ca(OH), must be added in 5 litre of water to change its pH by 3 units?
- **Q.20** What is the correct order of the following equimolar (0.1 M) solution in increasing order of pH? CH_3COOH , NH_4OH , $Ca(OH)_2$, $H_2S \& H_2O$
- **Q.21** When 100 ml of 0.1 M NH_4OH is mixed with 100 ml of 0.1 M NaOH, calculate the final pH of the solution?
- **Q.22** In the above question if instead of NH_4OH , CH_3COOH of same volume & concentration is taken & volume of NaOH is reduced to one half of the initial, then calculate the final pH of the solution.
- **Q.23** Consider the following equimolar (0.1 M) solution HCl, H_2SO_4 , NaOH, $Mg(OH)_2$ HClO₄, $\alpha = 30\%$ $\alpha = 40\%$ $\alpha = 80\%$ $\alpha = 90\%$ $\alpha = 10\%$ Write the increasing order of pH in above species?

Acidic Buffer

Note: Always write acid-Base reaction first and identify the solution. (Buffer, salt, Strong Acid or Strong Base)

Handerson equation for acidic buffer $pH = pK_a + log \frac{[Salt]}{[Acid]}$.

- **Q.1** Calculate pH of solution which contains 0.1 M CH₃COOH and 0.1 M CH₃COONa pK_a of CH₃COOH = 4.74?
- **Q.2** Calculate pH of solution which contains 0.1 M HCOOH and 0.2 M $(\text{HCOO})_2\text{Ca.pK}_a$ of HCOOH = 3.74 ?

Q.3	100 ml of 0.1 M NaOH is mixed in a container containing 200 ml of 0.2 M HA (a weak acid). Find pH of solution (Ka of HA is 10 ⁻⁶)?
Q.4	When 100 ml of 0.2 M CH ₃ COOH with 50 ml of 0.1 M Mg(OH) ₂ , calculate the pH of the final solution
Q.5	Calculate the amount of calcium formate which should be added in 500 ml of 0.1 M HCOOH to obtained a solution with $pH=4$? [Given : K_a of HCOOH = 1.8×10^{-4}]
(Q.6-	Q.10)
	$50 \text{ ml of } 0.1 \text{ M CH}_3\text{COOH}$ is titrated with 0.1 M NaOH solution.
Q.6	Calculate pH of the solution after the addition of 0 ml of NaOH solution ?
Q.7	Calculate pH of the solution after the addition of 10 ml of NaOH solution ?
Q.8	Calculate pH of the solution after the addition of 25 ml of NaOH solution ?
Q.9	Calculate pH of the solution after the addition of 40 ml of NaOH solution?
Q.10	Calculate pH of the solution after the addition of 60 ml of NaOH solution ?
(Q.11	–Q.12) A weak acid (HA) is titrated with a strong base (NaOH) pH of the solution at 1/4th neutralisation of the acid is 4.52. Enough strong acid (HCl) 25 meq is now added in the above solution to completely convert the salt and total volume of the solution is 1 ℓ .
Q.11	What is the K_a of the acid?
Q.12	What will be the Final pH of the solution?
Q.13	A buffer solution with pH = 4 is to be prepared from sodium acetate and acetic acid. If solution contains 1 litre of N/10 acetic acid, how many mole of CH ₃ COONa be added ? [$K_a = 1.85 \times 10^{-5}$]
(Q.14	-Q15)

In a one litre of an aqueous solution containing 0.020 mole of propionic acid having $K_a = 1.34 \times 10^{-5}$ at 25°C

- Q.14 How many moles of sodium propionate should be added in the above solution to obtain a buffer solution of pH = 4.75?
- Q.15 When 0.010 mole of HCl dissolved in above buffer solution, Calculate pH of the solution?

Daily Practice Problems - 09

Basic Buffer

Handerson equation for basic buffer $pOH = pK_b + log \frac{[Salt]}{[Base]}$

- **Q.1** Write the pH of a solution which contains equal concentration NH_4Cl and NH_4OH ?
- **Q.2** Write the pH of the solution obtained by mixing 20 ml of 0.1 M HCl with 50 ml of 0.1 M NH_4OH ?
- **Q.3** Find the volume of 0.5 M H_2SO_4 solution which should be added in 100 ml of 0.4 M NH_4OH solution to obtain a solution with pH = 9?

(Q.4-	-Q.5)
Q.4	20 ml of 0.2 M HNO ₃ is added to 50 ml of 0.2 M NH_4OH to give 70 ml of solution. What will be the pH of the solution?
Q.5	What additional volume of 0.2 M HNO_3 required to make pOH of the solution 4.74?
(Q.6-	-Q.7) 200 ml of 0.2 M NH ₄ OH is mixed with 100 ml of 0.1 M H ₂ SO ₄ solution, then
Q.6	Calculate the final pH of the solution?
Q.7	What change in pH when 20 ml of 0.1 M NaOH is added in the above buffer solution?
Q.8	How many mole of NH ₄ Cl must be added to one litre of 1.0 M NH ₄ OH to have a buffer of pH = 9. $K_{_{NH_4OH}} = 1.8 \times 10^{-5}$?
Q.9	Calculat the amount of $(NH_4)_2SO_4$ in g which must be added to 500 ml of 0.2 M NH ₃ to yield a solution of pH = 9.35. K _b for NH ₃ = 1.78×10^{-5} ?
(Q.10	D-Q.14) 100 ml of 0.5 M NH_4OH is titrated with 0.2 M HCl solution, then Calculate the pH of the solution after the addition of:
Q.10	0 ml of above HCl solution?
Q.11	50 ml of above HCl solution?
Q.12	100 ml of above HCl solution?
Q.13	200 ml of above HCl solution?

Q.14 300 ml of above HCl solution?

Daily Practice Problems - 10

Salt hydrolysis

- Q.1Find pH of (Given K_a of acidic acid = 10^{-5} , formic acid = 10^{-4} , K_b of $NH_4OH = 10^{-5}$)(i) 0.01 M NH_4Cl (ii) $10^{-3} \text{ M CH}_3COONa$ (iii) $2M \text{ CH}_3COONH_4$ (iv) 10^{-2} M HCOONa (v) 0.5 M HCOONH_4 (vi) $2M \text{ MgCl}_2$
- **Q.2** Find amount of (Given K_a of acidic acid = 10^{-5} , formic acid = 10^{-4} , K_b of NH₄OH = 10^{-5}) (i) CH₃COONa dissolved in 200 ml to have pH = 9 (ii) HCOONa dissolved in 21 to have pH = 10 (iii) NH₄Cl dissolved in 100 ml to have pH = 5
- **Q.3** 20 g of a salt NaA having molecular mass 100 g/mole whn dissolved in 200 ml of water results a solution having pH=11. Calculate K_a of acid HA
- **Q.4** 50 ml of 0.1 M CH₃COOH is mixed with 50 ml of 0.1 M NaOH. Find pH of solution. [K_a of CH₃COOH = 10^{-5}]
- **Q.5** Calculate the final pH of the solution obtained by mixing 200 ml of 0.1 M NH_4OH with 50 ml of 0.2 M H_2SO_4
- **Q.6** When equal volume of equimolar (0.1 M) solution of $NH_4OH \& NH_4Cl$ is mixed then calculate the hydrolysis constant & the degree of hydrolysis of salt formed ?
- **Q.7** Calculate pH of the following solutions (i) 100 ml of 0.1 M CH₃COOH + 0 ml of 0.1 M NaOH. (ii) 100 ml of 0.1 M NH₄OH + 0 ml of 0.1 M HCl

(iii) 100 ml of 0.1 M CH₃COOH + 20 ml of 0.2 M Ca(OH)₂ (iv) 100 ml of 0.3 M NH₄OH + 150 ml of 0.2 M HCl (v) 200 ml of 0.1 M HCOOH + 300 ml of 0.1 M H₂SO₄ (vi) 100 ml of 0.5 M CH₃COOH + 500 ml of 0.1 M NH₄OH (vii) 300 ml of 0.2 M CH₂COOH + 500 ml of 0.12 M NaOH

- **Q.8** If we prepared an aqueous solution by mixing 100 ml of 0.2 M HCOOH with 100 ml of 0.2 M NaOH, then what will be the degree of hydrolysis & hydrolysis constant of salt formed? [Given : K_{a} (HCOOH) = 1.8×10^{-4}] -
- **Q.9** An aqueous solution is prepared by mixing 100 ml of 0.1 M CH₃COOH & 100 ml of 0.1 M NaOH. Calculate the Degree of hydrolysis? [K_a (CH₃COOH) = 1.8×10^{-5}]-
- **Q.10** 100 ml of 0.1 M CH₃COOH is mixed with 50 ml of 0.1 M NaOH solution and pH of the resulting solution is 5. Calculate the change in pH if 100 ml of 0.05 M NaOH is added in the above solution?

Daily Practice Problems - 11

Salt hydrolysis

- **Q.1** How much must a 0.2 M solution of sodium acetate be diluted at 25°C in order to double the degree of hydrolysis?
- **Q.2** when 100 ml of 0.1 M solution of CH_3COOH is mixed with 100 ml of 0.1 M NaOH solution. What will be the pH of resulting solution?
- **Q.3** The dissociation constant of acetic acid is 1.8×10^{-5} what will be the value of hydrolysis constant for 0.1 M sodium acetate?
- **Q.4** What is the percentage hydrolysis of NaCN in N/80 solution ? When the dissociation constant for HCN is 1.3×10^{-9} and $K_w = 1 \times 10^{-14}$.
- **Q.5** The dissociation constant for NH_4OH is 1.8×10^{-5} . Calculate the degree of hydrolysis of 0.2 M NH_4Cl solution?
- **Q.6** In the hydrolytic equation $A^- + H_2O \longrightarrow HA + OH^-K_a = 1 \times 10^{-5}$. Calculate the degree of hydrolysis of 0.001 M solution of the salt?
- **Q.7** If pK_{b} for CN⁻ at 25°C is 4.7, Calculate the pH of 0.5 M aqueous NaCN solution ?
- **Q.8** The degree of hydrolysis of a salt of weak acid and weak base in its 0.1 M solution is found to be 50%. If the molarity of the solution is 0.2 M, Calculate the percentage hydrolysis of the salt ?
- **Q.9** 100 mL of 1 N NH₄OH ($K_b = 5 \times 10^{-5}$) is neutralised to equivalence point by 1 N HCl. What will be pH of solution at equivalence point?
- **Q.10** If equilibrium constant for the reaction between BOH and HCl is 10¹², Calculate the pH of 10⁻² M BCl solution?
- **Q.11** It is found that 0.1 M solution of three sodium salts NaX, NaY and NaZ gave pH 7.0, 9.0 and 11.0 respectively.

Write the correct order of increasing strength of acid HX, HY, HX ?

- Q.12 In the above question, find the ionisation constants of the acids, if possible?
- Q.13 In the following reaction,

 $CN^- + HN_3 \longrightarrow HCN + N_3^ K_a(HCN) = 1.4 \times 10^{-10}$, $K_a(HN_3) = 1.5 \times 10^{-5}$, find the equilibrium constant for the reaction at 25°C ?

	Solubility product						
Q.1	Write the equation for d (i) PbBr ₂ (v) Ag ₂ CO ₃ (ix) Li ₃ Na ₃ (AlF ₆) ₂ (xiii) A ₃ B ₄	lissociation of following (ii) Hg_2CrO_4 (vi) Sb_2S_3 (x) Hg_2I_2 (xiv) CaF_2	salts and determine their (iii) BaC_2O_4 (vii) $AgCNS$ (xi) $Ba_3(PO_4)_2$ (xv) Ag_2CrO_4	solubility in terms of K_{sp} . (iv) Fe(OH) ₃ (viii) Ag ₃ PO ₄ (xii) Ca ₅ (PO ₄) ₃ F			
Q.2	(i) K_{sp} of AgCl is 1.8×10^{-10} . Find the solubility of AgCl in pure water in moles per litre? (ii) In the above question calculate the solubility in gram per litre?						
Q.3	Calculate solubility of	AB_2 in pure water. K_{sp} o	$fAB_2 = 25.6 \times 10^{-8}$				
Q.4	Solubility of a A_2B salt	in pure water is 2×10^{-5}	moles in 100 ml. Calcu	late K _{sp} of salt			
Q.5	K_{sn} of AgBr is 4×10^{-13}	and [Ag ⁺] is a solution	is 1×10^{-6} m/l what is [E	Br ⁻] in that solution.			
Q.6	If K_{sp} of AgI is 8.5 × 10 ⁻¹⁷ . Calculate the maximum amount of AgI which can be dissolved in 2500 ml of water?						
Q.7	Calculate the volume of water needed to dissolve 1 g of $BaSO_4(K_{sn} = 1.1 \times 10^{-10})$ at 25°C?						
Q.8	How many grams of CaC ₂ O ₄ will dissolve in distilled water to make one litre of saturated solution of it ? (K_{sn} of CaC ₂ O ₄ = 2.5 × 10 ⁻⁹ mol ² lit ⁻²)						
Q.9	At 20°C, the Ag^+ ion co calculate the solubility	ncentration in a saturated product of Ag ₂ CrO ₄ ?	d solution Ag_2CrO_4 is 1.5	5×10^{-4} mole/lit. Ag 20°C,			
Q.10	0 In the system $CaF_2(s) Ca^{2+}(ag) + 2F^-$ if the concentration of Ca^{2+} ions made 4 times calculate the change in concentration of F^- ions ?						
Q.11	Concentration of Ag ⁺ ion in a saturated solution of Ag ₂ CrO ₄ is 5.4×10^{-6} g/litre when the salt is 50% dissociated. Calculate the solubility product of Ag ₂ CrO ₄ ?						
Q.12	2 For an experiment $Pb(OH)_2$ is taken, if salt is 80% dissociated & K_{sp} of $Pb(OH)_2$ is 8 × 10 ⁻⁶ . Find the solubility of salt in moles/litre? (ii) what will be the solubility in gms/litre?						
Q.13	pH of a saturated solut	ion of A(OH) ₃ is 10. Ca	lculate K_{sp} of A(OH) ₃ at	25°C.			
Q.14	Solubility of As_2S_3 is 7	.38 mg in 10ml of water	. Calculate K_{sn} of As_2S_3 .				

Q.15 K_{sp} of A₃B₄ is 6.912×10^{-18} . Calculate solubility of A₃B₄.

Daily Practice Problems - 13

Solubility in presence of common ion

- Q.1Solubility product of AgCl is 1.8×10^{-10} , then find out solubility of AgCl in(i)0.1 M NaCl(ii) 0.2 M AgNO_3 (iii) 2 M CaCl_2 (iv)pure water.
- P–II K_{sp} of PbCl₂ is 4 ×10⁻¹⁵ calculate its solubility in–
- Q.2 pure water
- Q.3 0.2 MAICl, solution
- **Q.4** $5 \times 10^{-3} \text{ M Pb}_3(\text{PO}_4)_2$ solution
- Q.5 0.02 M NaCl solution

Q.6 $0.4 \text{ M Pb}(\text{NO}_3)_2$ solution

- **Q.7** Find the solubility of AgCl in : (i) pure water (ii) 0.01 M NaCl [Given $K_{sp} AgCl = 1 \times 10^{-10} \text{ g/L}$]
- **Q.8** The solubility product of AgCl is 4×10^{-10} at 298 K. Find the solubility of AgCl in 0.04 M CaCl₂?
- **Q.9** Find the molar solubility of PbI₂ in 0.2 M Pb(NO₃)₂ solution in terms of solubility product, K_{sn} .
- **Q.10** K_{sn} of Zn(OH)₂ is 4.5×10^{-17} find its solubility in a solution having pH = 10.
- **Q.11** Find the Solubility of Mg(OH)₂ having K_{sp} equal to 8.9×10^{-13} , in a solution containing 500 ml of 0.2 M NH₄OH and 500 ml of 0.4 M Ca(OH)₂?
- **Q.12** Find the molar solubility of As_2S_3 in 0.3 MAl_2S_3 solution in terms of solubility product K_{sp} or As_2S_3 ?

Daily Practice Problems - 14

Precipitate formation

- **Q.1** A solution 10^{-5} M Ag⁺ ions and 10^{-5} M Cl⁻ ion. If K_{sp} of AgCl is 1.8×10^{-10} then ppt of AgCl will form or not?
- **Q.2** K_{sp} of PbI₂ is 8 × 10⁻¹². A solution contains 2 × 10⁻³ M Pb⁺² ions and 2 × 10⁻⁴ M I⁻ ions. Predict ppt of PbI₂ will form or not
- **Q.3** K_{sp} of AgBr is 5×10^{-13} . If equal volumes of 8×10^{-8} M AgNO₃ solution is mixed with 2×10^{-5} M NaBr solution then ppt of AgBr will form or not.
- **Q.4** K_{sp} of A_2B_3 is 3.5×10^{-20} if 200 ml of 10^{-3} M A⁺³ ion is mixed with 200 ml of 10^{-4} M B⁻² ion then ppt of A_2B_3 will form or not.
- **Q.5** In which of the following cases the ppt of $PbCl_2(K_{sp}) = 1.6 \times 10^{-5}$) is obtained when equal volumes of the following solution are mixed. Justify your answers. (i) $10^{-2} \text{ M Pb}^{+2} + 10^{-2} \text{ M Cl}^{-1}$ (ii) $10^{-2} \text{ M Pb}^{+2} + 10^{-1} \text{ M Cl}^{-1}$
- **Q.6** In which of the following cases the precipitate of $CaF_2 (K_{sp} = 1.7 \times 10^{-10})$ is obtained when equal volumes of the following are mixed. (i) $10^{-4} Ca^{2+} + 10^{-4} M F^{-}$ (ii) $10^{-2} M Ca^{2+} + 10^{-3} M F^{-}$ (iii) $10^{-5} M Ca^{2+} + 10^{-3} M F^{-}$ (iv) $10^{-3} M Ca^{2+}$ and $10^{-3} M F^{-}$
- **Q.7** K_{sp} of Mn(OH)₂ is 2 × 10⁻¹³. A solution is prepared by mixing 10⁻⁵ M Mn⁺² salt and 10⁻⁴ M NaOH solution. Will precipitate of Mn(OH)₂ form or not ?
- **Q.8** K_{sp} of PbI₂ is 2 × 10⁻¹⁰. 50 ml of 10⁻² M Pb(NO₃)₂ is mixed with 150 ml of 3 × 10⁻⁴ M CaI₂ solution. Predict whether ppt of PbI₂ will form or not.
- **Q.9** Equal volumes of 0.02 M CaCl₂ and 0.04 M Na₂SO₄ are mixed, will a precipitate form ? (K_{sp} of CaSO₄ = 4 × 10⁻⁴)
- **Q.10** To Ag_2CrO_4 solution over its own precipitate, CrO_4^{-2} ions are added. This result in decrease in Ag^+ concentration. Explain.
- **Q.11** What is the minimum concentration of SO₄^{2–} required to precipitate BaSO₄ in a solution containing 1×10^{-4} mole of Ba²⁺? K_{sn} for BaSO₄ = 4 × 10⁻¹⁰
- $\label{eq:Q.12} \begin{array}{ll} At \ 18^{\circ}C, \ the \ solubility \ product \ of \ AgCl \ is \ 1.8 \times 10^{-10}. \ In \ a \ solution, \ the \ value \ of \ [Ag^+] \ is \ 4 \times 10^{-3} \\ mol/lit. \ Calculate \ value \ of \ [Cl^-] \ to \ precipitate \ AgCl \ from \ this \ solution \end{array}$

- **Q.13** What would be the pH at which $Fe(OH)_2$ begins to precipitate from a solution containing 0.009 M Fe^{+2} ions. K_{sn} of $Fe(OH)_2$ is 1.8×10^{-15} .
- **Q.14** How many grams of CaBr₂ (MM = 200) can be added to 250 ml of 0.01 M solution of silver nitrate to just start the precipitation of silver bromide. K_{sp} of AgBr is 5.0×10^{-13} .
- **Q.15** K_{sp} of PbI₂ is 4 × 10⁻⁹ calculate concentration of I⁻ erquired to precipitate PbI₂ from a solution containing 0.02 M Pb(NO₃)₂.
- **Q.16** Will a precipitate of Mg(OH)₂ be formed in a 10^{-3} M solution of Mg(NO₃)₂. If the pH of solution is adjusted to 9. Ksp of Mg(OH)₂ = 8.9×10^{-12} .
- **Q.17** A solution contains 0.1 M Zn⁺² ions and is saturated with H₂S. Calculate amount of HCl which should be added in 500 ml of solution to prercipitate ZnS. K_{sp} of ZnS = 13.5 × 10⁻²³. K_1 of H₂S = 10⁻⁷ and K₂ of H₂S = 1.5 × 10⁻¹⁴. concentration of H₂S in saturated solutin is 0.1M.
- **Q.18** A solution has 0.02 M A⁺² and 0.1M NH₄OH calculate the concentration of NH₄Cl required to prevent the formation of A(OH)₂ in solution. K_{sp} of A(OH)₂ is 2 × 10⁻¹² and K_b of NH₄OH is 10⁻⁵.
- **Q.19** A solution contains a mixture of $Ag^+(0.1M)$ and $Hg_2^{+2}(0.1M)$ which are to be separate by selective percipitation.
 - (i) Cal [I⁻] req. to ppt AgI
 - (ii) Cal [I⁻] req. to ppt Hg,I,
 - (iii) which one will ppt first AgI or Hg,I,
 - K_{sp} of AgI = 8.5 ×10⁻¹⁷ and $\tilde{K_{sp}}$ of Hg₂I₂ = 2.5×10⁻²⁶.
- **Q.20** Calculate simultaneous solubility of AgCNS and AgBr in a solution of water K_{sp} of AgB = 5 × 10⁻¹³ and K_{sp} of AgCNS = 10⁻¹²

ANSWER SHEET

Daily Practice Problems - 01

1.	0.618	2.	6.18 M	3.	0.916	4.	0.916
5.	0.99	6.	0.099	7.	1.1×10^{-5}	8.	$10^{-4}M$
9.	0.161	10.	$8.06 imes 10^{-4}$ M	M 11.	$9.5 \times 10^{-4} \mathrm{M}$	12.	27.17 gm
13.	3.9×10^{-4}						

Daily Practice Problems - 02

1.	$4.24 \times 10^{-3}, 4.24 \times 10^{-3}$	2.	$1.34 \times 10^{-2}, 1.34 \times 10^{-2}$	0-2	
3.	$1.34 \times 10^{-2}, 1.34 \times 10^{-3}$	4.	$4.24 \times 10^{-2}, 4.24 \times 10^{-2}$	0-3	
5.	$4.24 \times 10^{-2}, 4.24 \times 10^{-4}$	6.	$0.125, 1.25 \times 10^{-3}$		
7.	$0.34, 3.4 \times 10^{-5}$	8.	$0.715, 7.15 \times 10^{-5}$	9.	$0.71, 7.1 \times 10^{-6}$
10.	54 gm	11.	1.34 ×10 ⁻²	12.	$7.2~\ell$
13.	1.34×10^{-2}	14.	1.34×10^{-3}	15.	7.75 gm

Daily Practice Problems - 03

1.	9×10^{-6}	2.	2 M	3.	1		
4.	2.36×10 ⁻⁶	5.	$[CH_{3}COO^{-}] = 7.6$	$5; [H^+] = 2$.36 ×1	0-6	
6.	8.6 ×10 ⁻⁶	7.	$[CH_{3}COO^{-}] = 8.6$	5×10 ⁻⁶ ;[H	$[^{+}] = 2.$	095	
8.	$10^{-5}, 10^{-6}$	9.	$5 \times 10^{-6}, 3.6$	10.	9 × 3	$10^{-5}, 9 \times$	10-6
11.	$3.34 \times 10^{-5}, 0.54$	12.	112. 1 gm	13.	1	14.	4.74

Daily Practice Problems - 04

1	1.25×10^{-2}	2.	4.44×10^{-3}	3.	$7.13 \times 10^{-3} \text{ M}$
4.	concentration of OH ⁻ decreas	es			
5.	$[\mathrm{H}^+] = [\mathrm{H}_2\mathrm{PO}_4^-] = 0.076 \mathrm{M}$	6.	0.024 M	7.	on increasing concentration
8.	2.79 gm	9.	1.414 ×10 ⁻³]	М	
10.	$[A^-] = [B^-] = 0.707 \times 10^{-3} M$	Λ			
11.	increases the concentration of	°H ₃ O⁺,s	suppresses the di	issociat	tion of HA

12. 1.63 **13.** 1.49

Daily Practice Problems - 05

1.	$1.8 \times 10^{-16}, 1.8 \times 10^{-16}$	⁹ 2.	$9.07 \times 10^{-15} \text{ M}$	3.	$5.04 \times 10^{-13} \text{ M}^2$		
4.	60.3 million	5.	-84.55 kcal/mole	6.	6.51		
7.	basic, acidic, basic	8.	7.47, 7.00, 6.76	9.	6.13	10.	7.3

1.	$[H^+] = 2 \times 10^{-3}, [OH^-] = 5 \times$	< 10 ⁻¹²		2.	0.49 g
3.	2×10^{-5} M, 3.1×10^{-3} M	4.	10^{-6}	5.	1.0099×10^{-6}
6.	0.99 %	7.	10^{-7}	8.	1.615×10^{-7}
9.	61.5 %	10.	$[H^+] = 2 >$	× 10 ⁻⁶ [OH	$[-] = 5 \times 10^{-9}$
11.	$5.12 \times 10^{-3}, 0.19 \times 10^{-11}$	12.	1.045 ×10	0-7	
13.	$[OH^{-}] = 0.25, [H^{+}] = 4 \times 10^{-1}$	¹⁴ 14.	0.95×10^{-10}	$^{-7}$, 1.05 ×	10-7

Daily Practice Problems - 07

1.	2.87	2.	11.13	3.	2.37	4.	2.37
5.	1.57	6.	6, 6.79, 6.98	7.	4.74	8.	12.3
9.	0.98	10.	2.33	11.	49.5 litre	12.	1000 times
13.	decreased 100	times		14.	6.98	15.	1
16.	4.95 litre			17.	999 litre	18.	12.85
19. 21	0.0185 gm	20. 22	CH ₃ COOH < 4 74 23	$H_2 S < I$ H S	$H_2O < NH_4OH$ O < HCl < HC	< Ca(O 10 < N	$H)_2$ 2OH < Mg(OH)
41.	12.1	44.	т./т 23	• $\Pi_2 S$	O_4 and and	10 ₄ < 1	$aom (mg(om)_2)$

Daily Practice	Problems - 08
-----------------------	---------------

1	4.74	2.	4.34	3.	5.52	4.	4.74
5.	5.85 g	6.	2.87	7.	4.14	8.	4.74
9.	5.34	10.	11.96	11.	10 ⁻⁵	12.	3
13.	0.018	14.	0.015 mole	15.	4.09		

Daily Practice Problems - 09

1.	4.74	2.	9.44	3.	25.8 ml	4.	9.44
5.	5 ml	6.	9.25	7.	0.027	8.	1.80
9.	5.248 g	10.	11.48	11.	9.86	12.	9.44
13.	8.66	14.	1.6				

Daily Practice Problems - 10

1.	(i) 5.5	(ii) 8	(iii) 7	(iv) 8	(v) 6.5	(vi) 7
2.	(i) 1.64 gm	(ii) 13.6 kg	(iii) 0.53	5 gm 3	6. 10 ⁻⁸	
4.	8.85 5.	5.67	6. k	$K_{\rm h} = 5.55 \times 10^{-1}$	h^{10} , $h = 1.05 \times 10^{10}$	0-4
7.	(i) 2.87 (ii)	11.13 (iii) 5	.34 (iv)	5.13 (v) 3.4	(vi) 7 (vii) 8	.8
8.	$K_{h} = 5.55 \times 10^{-10}$	$10^{-11}, h = 1.67$	× 10 ⁻⁵ 9	1.05×1	0 ⁻⁴ 10. 3	.8

1.	four times	2.	8.72	3.	5.56×10^{-10}
4.	2.48	5.	5.27×10^{-5}	6.	10^{-3}
7.	11.5	8.	50%	9.	5.0
10.	11.8	11.	HZ < HY < HX		
12.	$K_{a}(HY) = 10^{-5} M, K_{a}$	$_{a}(HZ) =$	= 10 ⁻⁹ M	13.	1.07×10^{5}

Daily Practice Problems - 12

2.	(i) 1.34×10^{-5}	(ii) 1.	93 mg		
3.	$4 \times 10^{-3} \text{ m/l}$	4.	3.2 ×10 ⁻¹¹		
5.	$Br^{-}=4 \times 10^{-7} \text{ m/l}$	6	$5.42 \times 10^{-5} \text{ gm}$		
7	410 litre	8	0.0064 gm	9	1.68×10^{-12}
10	1/2	11	6.25×10^{-23}	12	(i) 1.57×10^{-2} (ii) 3.79
13	3.34×10^{-17}	14.	26.24×10^{-12}	15.	10 ⁻³ m/l

Daily Practice Problems - 13

1	(i) 1.8 × 10 ⁻⁹	(ii) 9 ×	10-10	(iii)	4.5 × 1	0-11	(iv) 1.34×10^{-5}
2.	10 ⁻⁵ M	3.	$1.11 \times 10^{-14} \text{ M}$		4.	2.58 ×1	0 ⁻⁷ M
5.	$10^{-11} M$	6.	$5 \times 10^{-8} \text{ M}$		7.	(i) 10 ⁻⁵	m/l (ii) 10 ⁻⁸ m/l
8.	$5 \times 10^{-9} \mathrm{M}$	9.	$\left(\frac{\mathrm{K_{sp}}}{\mathrm{0.8}}\right)^{\!\!1/2}$		10.	4.5 × 1	0-10
11.	55.63×10^{-13}	12.	$\sqrt{\frac{K_{sp}}{2.918}}$				

Daily Practice Problems - 14

1.	No	2.	Yes	3.	No	4.	No
5.	(i) no ppt obta	ained	(ii) ppt will obtained				
6.	(i) no ppt obta	ained	(ii) ppt will obtained	(iii) n	o ppt obtained	(iv)no	ppt obtained
7.	No	8.	Yes	9.	No		
11.	$4 \times 10^{-6} \mathrm{M}$	12.	4.5×10^{-8}	13.	7.65		
14.	1.25×10^{-9} g	m 15.	$4.47 \times 10^{-4} \mathrm{M}$	16.	No	17.	6.01 gm
18.	0.1 M	19.	(i) 8.5 × 10 ⁻¹⁶ (ii) 5 ×	10 ⁻¹³ (ii	ii)AgI		
20.	$4.08 \times 10-7$, 8.16 ×	10-7				

Solved Example Subjective

Problem 1:

The self ionization constant for pure formic acid, $K = [HCOO H_2^+][HCOO^-]$ has been estimated as 10^{-6} at room temperature. What percentage of formic acid molecules in pure formic acid are converted to formate ion? The density of formic acid is 1.22 g/cm^3 .

Solution:

Given density of formic acid = 1.22 g/cm^3

 \therefore Weight of formic acid in 1 litre solution = 1.22×10^3

Thus, [HCOOH] = $\frac{1.22 \times 10^3}{46}$ = 26.5 M

Since in case of auto ionization $[HCOO H_2^+][HCOO^-] = 10^{-6}$

:. $[HCOO^{-}] = [HCOO H_{2}^{+}] = 10^{-3}.$

Now % dissociation of HCOOH = $\frac{[\text{HCOO}^-] \times 100}{[\text{HCOOH}]} = \frac{10^{-3}}{26.5} \times 100 = 0.004\%$

Problem 2:

Calculate the concentration of all species of significant concentrations present in 0.1 M H_3PO_4 solution. $K_1 = 7.5 \times 10^{-3}$, $K_2 = 6.2 \times 10^{-8}$, $K_3 = 3.6 \times 10^{-3}$.

I step
$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$$
;
 $K_1 = 7.5 \times 10^{-3}$

 II step $H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$;
 $K_2 = 6.2 \times 10^{-8}$

 III step $HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$;
 $K_3 = 3.6 \times 10^{-13}$

Solution:

for I step :
$$H_3PO_4 \implies H^+ + H_2PO_4^-$$

0.1 0 0
0.1 - C C C
 $K_1 = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = \frac{C.C}{(0.1-C)}$
7.5 × 10⁻³ = $\frac{C^2}{(0.1-C)}$
 $\therefore C = 0.024 \therefore [H^+] = 0.024 M$
 $[H_2PO_4^-] = 0.024 M$
 $[H_3PO_4] = 0.1 - 0.024 = 0.076 M$

The value of K_1 is much large than K_2 and K_3 . Also dissociation of II and III steps occurs in presence of H⁺ furnished in I step and thus, dissociation of II and III steps is further suppressed due to common ion effect.

For II step	$H_2 P O_4^-$	→ H ⁺ +	$HPO_{4}^{2-};$
	0.024	0.024	0
	(0.024 - y)	(0.024 + y)	У

The dissociation of $H_2PO_4^-$ occurs in presence of $[H^+]$ furnished in step I.

Thus,
$$K_2 = \frac{[H^+][HPO_4^{2^-}]}{[H_2PO_4^{-}]}$$

or $6.2 \times 10^{-8} = \frac{(0.024 + y)y}{(0.024 - y)}$
 \therefore y is small $\therefore 0.024 - y \approx 0.024$ and neglecting y².
 $\therefore 6.2 \times 10^{-8} = \frac{0.024y}{0.024}$ \therefore y = 6.2 × 10⁻⁸
or $[HPO_4^{2^-}] = K_2 = 6.2 \times 10^{-8}$.
For III step : $HPO_4^{2^-} \rightleftharpoons H^+ + PO_4^{3^-}$
 $(6.2 \times 10^{-8} - x) \quad (0.024 + x) \times x$
 $\therefore K_3 = \frac{[H^+][PO_4^{3^-}]}{[HPO_4^{2^-}]} = \frac{(0.024 + x).x}{(6.2 \times 10^{-8} - x)}$
Again neglecting x² and assuming, $6.2 \times 10^{-8} - x = 6.2 \times 10^{-8}$
 $\therefore 3.6 \times 10^{-13} = \frac{0.024x}{6.2 \times 10^{-8}}$
 $\therefore x = \frac{3.6 \times 10^{-13} \times 6.2 \times 10^{-8}}{0.024} = 9.3 \times 10^{-19}$.

Problem 3:

If CH_3COOH (Ka = 10⁻⁵) reacts with NaOH at 298 K, then find out the value of the maximum rate constant of the reverse reaction at 298 K at the end point of the reaction. Given that the rate constant of the forward reaction is 10⁻¹¹ mol⁻¹ L sec⁻¹ at 298 K. Also calculate

Arrhenius parameter for backward reaction if $\Delta H_{298} = 44$ kcal and $E_{a(f)} = 94$ kcal.

Solution:

$$CH_{3}COOH + NaOH \rightleftharpoons CH_{3}COONa + H_{2}O;$$

$$K_{c} = 10^{-11} \text{ mol}^{-1} \text{ L sec}^{-1}$$

The backward reaction is of hydrolysis of sodium acetate

$$K_{\rm C} = \frac{K_{\rm for}}{K_{\rm bac}} = (K_{\rm h})^{-1} = \left[\frac{K_{\rm W}}{K_{\rm a}}\right]^{-1} = \frac{K_{\rm a}}{K_{\rm W}}$$

$$K_{\rm bac} = \frac{K_{\rm for}}{K_{\rm a}} \times K_{\rm W} = \frac{10^{-11} \times 10^{-14}}{10^{-5}} = 10^{-20}$$
Given, $\Delta H_{298} = 44$ kcal and $E_{\rm a_{\rm f}} = 94$ kcal
 $\Delta H = E_{\rm a_{\rm f}} - E_{\rm a_{\rm b}}$
 $44 = 94 - E_{\rm a_{\rm b}}$

$$E_{\rm a_{\rm b}} = A_{\rm b} \times e^{-E_{\rm abac}/RT}$$
 $10^{-20} = A_{\rm b} \times e \left(\frac{-50 \times 10^{3}}{2 \times 298}\right) \therefore A_{\rm b} = 2.71 \times 10^{+16}.$

Problem 4:

The pH of pure water at 25°C and 35°C are 7 and 6 respectively. Calculate the heat of formation of water from H^+ and OH^- .

Solution:

At 25°C;
$$[H^+] = 10^{-7}$$

 $K_w = 10^{-14}$
At 35°C; $[H^+] = 10^{-6}$
 $K_w = 10^{-12}$
Now using
2.303 log₁₀ $\frac{K_{w_2}}{K_{w_1}} = \frac{\Delta H}{R} \left[\frac{T_2 - T_1}{T_1 \times T_2} \right]$
2.303 log10 $\frac{10^{-12}}{10^{-14}} = \frac{\Delta H}{2} \left[\frac{308 - 298}{298 \times 308} \right]$
 $\therefore \quad \Delta H = 84551.4 \text{ cal/mol}$
 $= 84.551 \text{ kcal/mol}$
Thus H₂O $\rightleftharpoons H^+ + \text{OH}^-$; $\Delta H = 84.551 \text{ kcal/mol}$
 $H^+ + \text{OH}^- \rightleftharpoons H_2\text{O}$; $\Delta H = -84.551 \text{ kcal/mol}$

Problem 5:

Calculate the pH of solution obtained by mixing 10 mL of 0.1 M HCl and 40 ml of 0.2 M H_2SO_4 .

Solution:

Milli-equivalent of H⁺ from HCl = $10 \times 0.1 = 1$ Milli-equvalent of H⁺ from H₂SO₄ = $40 \times 0.2 \times 2 = 16$

$$\therefore$$
 Total meq. of H⁺ in solution = 1 + 16 = 17

$$\therefore \qquad [H^+] = \frac{17}{50} = 3.4 \times 10^{-1} \qquad \qquad \left(\because [H^+] = \frac{\text{Meq.}}{\text{V}_{\text{in mL}}} \right)$$

:. $pH = -\log [H^+] = -\log 0.34$ pH = 0.4685

Problem 6:

Calculate the pH of a solution which contains 100 mL of 0.1 M HCl and 9.9 mL of 1.0 M NaOH.

Solution:

$$\begin{array}{rcl} HCl &+& NaOH \longrightarrow & NaCl &+& H_2O\\ t = 0 & 100 \times 0.1 & 9.9 \times 1\\ t = t & 10-9.9 & 9.9-9.9 = 0 & 9.9 \\ [H^+] \, left \, from \, HCl = \frac{0.1}{109.9} = 9.099 \times 10^{-4} \, M\\ pH = -\log \, H^+ = -\log 9.099 \times 10^{-4}\\ pH = 3.0409 \end{array}$$

Problem 7:

...

...

Calculate [H⁺] in a solution containing 0.1 M HCOOH and 0.1 M HOCN. K_a for HCOOH and HOCN are 1.8 $\times 10^{-4}$ and 3.3 $\times 10^{-4}$.

Solution:

In this problem both the acids contribute for [H⁺] due to appreciable dissociation. Thus,

Because [H⁺] will remain common in solution. Thus,

$$K_{\text{HCOOH}} = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]} = 1.8 \times 10^{-4} \qquad \dots (1)$$

$$K_{HOCN} = \frac{[H^+][OCN^-]}{[HOCN]} = 3.3 \times 10^{-4} \qquad \dots (2)$$

or

$$K_{\text{HCOOH}} = \frac{(x+y)x}{0.1} = 1.8 \times 10^{-4} \qquad \dots (3)$$

$$K_{HOCN} = \frac{(x+y)y}{0.1} = 3.3 \times 10^{-4} \qquad \dots (4)$$

Thus, by (3) and (4)

 $\frac{x}{y} = \frac{1.8}{3.3}$ or y = 1.83 x ... (5) From (3) $(x + 1.83x) \cdot x = 1.8 \times 10^{-5}$ \therefore $x = 2.52 \times 10^{-3}$ Therefore $y = 4.61 \times 10^{-3}$ Thus, $[H^+] = x + y = 2.52 \times 10^{-3} + 4.61 \times 10^{-3} = 7.13 \times 10^{-3} \text{ M}$

Problem 8:

A 0.1 M solution of weak acid HA is 1% dissociated at 25°C. What is its K_a? If this solution is with respect to NaA 0.2 M, what will be the new degree of dissociation of HA and pH? Solution:

For weak acid HA : $\alpha_{\text{HA}} = \frac{1}{100} = 0.01$, [HA] = 0.1 M

: $K_a = C\alpha^2 = 0.1 \times (0.01)^2 = 10^{-5}$

Now 0.2 M NaA, a salt of HA, is added to it resulting a buffer solution of [HA] = 0.1 M and [NaA] = 0.2 M.

- $\therefore \quad pH = -\log 10^{-5} + \log \frac{0.2}{0.1}$ pH = 5.3010Also $HA \rightleftharpoons H^{+} + A^{-}$ $1 \qquad 0 \qquad 0$ $(1 \alpha) \qquad \alpha \ \alpha$
- \therefore [A⁻] is provided by NaA since dissociation of HA in presence of NaA is suppressed due to a common ion effect.

$$\therefore \qquad K_{a} = \frac{[H^{+}][A^{-}]}{[HA]} = \frac{(C\alpha) \times 0.2}{C(1-\alpha)} = 10^{-5}$$
$$\therefore \qquad \alpha = 5 \times 10^{-5}$$

Problem 9:

Calculate the amount of $(NH_{4})_{2}SO_{4}$ in g which must be added to 500 mL of 0.2 M NH₃ to yield a solution of pH = 9.35. K_{b} for $NH_{3} = 1.78 \times 10^{-5}$.

Solution:

pOH = - log K_b + log
$$\frac{[Salt]}{[Base]}$$

or pOH = - log K_b + log $\frac{[NH_4^+]}{[NH_4OH]}$
∴ [NH_4^+] is obtained from salt (NH_4)₂SO₄.
∴ pH = 9.35
∴ pOH = 14 - 9.35 = 4.65
∴ Millimole of NH₄OH in solution = 0.2 × 500 = 100
Let millimole of NH₄⁺ added in solution = a
∴ [NH_4^+] = $\frac{a}{500}$; [NH₄OH] = $\frac{100}{500}$
4.65 = log 1.78 × 10⁻⁵ + log $\frac{a/500}{100/500}$
4.65 = 4.7496 + log $\frac{a}{100}$ ∴ a = 79.51
∴ Millimole of (NH₄)₂SO₄ added = $\frac{a}{2} = \frac{79.51}{2} = 39.755$
∴ $\frac{W}{132} \times 1000 = 39.755$
∴ W_{(NH₄)₂SO₄ = 5.248 g}

Solved Example Objective

Problem 1:

A solution of HCl is diluted so that its pH changes by 0.3. How does concentration of H^+ ion change?

(a) 0.5 times of initial value(b) 0.3 times of initial value(b) 10^{-3} times increases(d) None

Solution: (a)

Let H⁺ ion concentration changes by x factor. \therefore pH = $-\log [H_3O^+]$ \therefore pH + Δ pH = $-\log \{x(H_3O^+)\} = -\log x - \log [H_3O^+]$ or Δ pH = $-\log x = 0.3$ $\therefore x = 0.5$

Problem 2:

The pH of 0.1M CH₃COOH is 2.873. What is pH of 0.1M NH₄OH. $K_a(CH_3COOH) = 1.8 \times 10^{-5}$ and $K_b(NH_4OH) = 1.8 \times 10^{-5}$ (a) 11.127 (b) 2.873 (b) 7 (d) 9.53.

Solution: (a)

Since $K_a(CH_3COOH) = K_b(NH_4OH)$ and concentration are equal so pH (CH_3COOH) = pOH (NH_4OH) pH = 2.873 \therefore pH = 14 - pOH = 14 - 2.873 = 11.127

Problem 3:

Liquid ammonia ionises to a slight extent. At - 50°C, its ion product is $K_{NH_3} = \left[NH_4^+ \right] \left[NH_2^- \right] = 10^{-30}$. How many amide ions, NH_2^- are present per mm³ of pure liquid ammonia. (a) 6.023×10^{23} (b) 6.023×10^{15} (b) 6.023×10^{14} (d) 6.023×10^{-15} . Solution: .:(b) $\left[NH_2^- \right] = \sqrt{K_{NH_3}} = \sqrt{10^{-30}} = 10^{-15}$

$$n_{NH_2^-} = MV = 10^{-15} \frac{MOI}{L} \times \frac{1L}{10^6 \text{ mm}^3} = 10^{-9} \text{ mol}$$

Number of NH_2^- ions = $6.023 \times 10^{23} \times 10^{-9}$ ions = 6.023×10^{14} ion

Problem 4:

To a 50 ml of 0.1 M HCl solution, 10 ml of 0.1 M NaOH is added and the resulting solution is diluted to 100 ml. What is change in pH of the HCl solution? (a) 4.398 (b) .398 (b) 0.1M (d) None. Solution: (b) Before adding HCl solution $pH = 1 [\because [HCl] = [H_3O]^+ = 10^{-1} M]$ $n_{HCl} (initially) = MV = 0.1 M \times 0.05 L = 5 \times 10^{-3} mol$ $n_{NaOH} added = MV = 0.1 M \times 0.01 L = 1 \times 10^{-3} mol$ $\begin{array}{cccc} HCl &+ & NaOH \longrightarrow & NaCl + H_2O \\ t = 0 & 5 \times 10^{-3} \, mol & 1 \times 10^{-3} \, mol & 0 \\ & 4 \times 10^{-3} \, mol & 0 \\ V_{final} = 100 \, ml = 0.1 \, L \\ [HCl] = \frac{n}{V} = \frac{4 \times 10^{-3} \, mol}{0.1L} = 4 \times 10^{-2} \, M \\ pH = -\log \left[H_3O^+\right] = 2 - \log 4 = 2 - 2 \, \log 2 = 2 - 2 \times 0.301 = 2 - 0.602 = 1.398 \\ Increase in pH = (1.398 - 1) = 0.398 \end{array}$

Problem 5:

What amount of solid sodium acetate be added into 1 litre of the 0.1 M CH3COOH solutionso that the resulting solution has pH almost equal to pK_a (CH3COOH) = 4.74(a) 12gm(b) 5 gm(b) 10 gm(d) 14.924 gm.Solution:

Since the resulting solution be acidic buffer, one may use Henderson equation.

$$pH = pK_{a} + log \frac{[CH_{3}COO^{-}]}{[CH_{3}COOH]}$$

Let n mol of CH₃COONa be added to do so

or,
$$pH = 4.74 + log \frac{\frac{n \text{ mol}}{vL}}{\frac{0.1 \text{ mol}}{vL}}$$

or,
$$5 = 4.74 + \log \frac{\pi}{0.1}$$

or,
$$\log \frac{n}{0.1} = 0.26$$

or,
$$\frac{n}{0.1} = antilog \ 0.26 = 1.8197$$

 $\therefore \qquad n = 0.18197 \text{ mol} \cong 0.182 \text{ mol}$

Amount of sodium acetate = 0.182×82 gm = 14.924 gm

Problem 6:

To a 100 ml solution of 0.1 M CH, COONa and 0.1 M CH, COOH, 0.4 gm of solid NaOH was added. Assuming volume remains constant, calculate the change in pH value? Given that pK_{a} (CH₃COOH) = 4.74. (a) .125 (b).225 (b).01 (d).872. Solution: (d) Before NaOH addition, $pH = pK_a = 4.74$ [Since [CH₃COO⁻] = [CH₃COOH]] The following reaction occurs due to NaOH addition. $H_2CCOOH + NaOH \longrightarrow H_2CCOONa + H_2O$ 0.001 mol t = 00.01 mol 0 -0.001 mol-0.001 mol0.001 mol (0.01 - 0.001) mol 0.001 mol

 $n_{H_3CCOONa} = 0.01 \text{ mole}$

After reaction, $n_{CH_3COOH} = 0.009 \text{ mol}$

$$n_{CH_{3}CCOO^{-}} = (0.01 + 0.001) \text{ mol} = 0.011 \text{ mol}$$

$$pH = pK_{a} + \log \frac{[CH_{3}COO^{-}]}{[CH_{3}COOH]}$$

$$= 4.74 + \log \frac{0.011/V}{0.009/V} = 4.74 + \log \frac{11}{9} = 4.74 + 0.0872$$
change in pH = log $\frac{11}{9} = 0.872$

Problem 7:

A weak base (BOH) with $K_b = 10^{-5}$ is titrated with a strong acid, HCl. At $3/4^{th}$ of the equivalent point, pH of the solution is: (a) 14 = 5 + 1002 (d) 0 = 522

(a) $5 + log 3$	(b) $3 - log 3$	(c) $14 - 5^{-1}$	+ <i>logs</i>	(<i>a</i>) 8	8.523.
Solution: (d)					
Let the initial equ	uvalent of BOH be x				
-	BOH +	HCl —	P BCl	+	H,O
Initial equivalent	Х	3/4x	0		0 2
At 3/4 th eqv. pt.	$x - \frac{3x}{4} = \frac{x}{4}$	0	$\frac{3}{4}x$		$\frac{3}{4}x$
$pOH = pK_b + loc$	$g\frac{[salt]}{[Base]} = 5 + \log \frac{3x \times 4}{4 \times x}$				
pH = 14 - 5 - 10	3 = 8.523				

Problem 8:

When equal volumes of the following solutions are mixed, precipitation of $AgCl(K_{sn} = 1.8)$ \times 10⁻¹⁰) will occur only with

- (a) $10^{-4} M [Ag^+]$ and $10^{-4} M [HCl]$ (b) $10^{-5} M [Ag^+]$ and $10^{-5} M [Cl^-]$

(a)

(c) $10^{-6}M [Ag^+]$ and $10^{-6}M [Cl^-]$ (d) $10^{-10}M [Ag^+]$ and $10^{-10}M [Cl^-]$.

Solution:

We look for that case where the ionic product exceeds the K_{sn}

$$[Ag^+][C1^-] = \left(\frac{1}{2} \times 10^{-4}\right)^2 = 2.5 \times 10^{-5}$$

Problem 9:

The solubility products of $Al(OH)_3$ and $Zn(OH)_2$ are 8.5 × 10⁻²³ and 1.8 × 10⁻¹⁴ respectively. If $NH_{A}OH$ is added to a solution containing Al^{3+} and Zn^{2+} ions, then substance precipitated first is:

(b) Zn(OH), (c) Both together $(a) Al(OH)_{3}$ (d) None at all. Solution: (a)

Solubility of $Al(OH)_3$ is lesser than $Zn(OH)_2$.

Problem 10:

How many gram of CaC_2O_4 will dissolve in one litre of saturated solution? K_{sp} of CaC_2O_4 is 2.5×10^{-9} mol⁻² and its molecular weight is 128. (a) 0.0064g (b) 0.0128g (c) 0.0032g (d) 0.0640g.

Problem 11:

In the hydrolytic equilibrium $A^{-} + H_{2}O = HA + OH^{-}$ $K_a = 1.0 \times 10^{-5}$. the degree of hydrolysis of 0.001M solution of the salt is (c) 10^{-5} (d) 10^{-6} . (b) 10⁻⁴ (a) 10⁻³ (a)

Solution:

$$h = \sqrt{\left[\frac{K_{h}}{C}\right]} = \sqrt{\left[\frac{K_{w}}{K_{a} \cdot C}\right]} = \sqrt{\left[\frac{10^{-14}}{10^{-5} \times 0.001}\right]} = 10^{-3}$$

Problem 12:

For preparing a buffer solution of pH 6 by mixing sodium acetate and acetic acid, the ratio of concentration of salt and acid ($K_a = 10^{-5}$) should be

(b) 10:1 (c) 100:1 (a) 1:10 (d) 1:100. *(b)*

Solution:

$$pH = pK_a + \log \frac{[salt]}{[acid]}$$
$$= 5 + \log \frac{10}{1} \text{ if } [salt]/[acid] = 10:1, \text{ then } pH = 6$$

Problem 13:

Let the solubilite is of AgCl in H₂O, 0.01 M CaCl₂; 0.01 M NaCl and 0.05M AgNO₃ be S₁, S₂, S_{*}, S_{*} respectively. What is the correct relationship between these quantities.

(a)
$$S_1 > S_2 > S_3 > S_4$$

(b) $S_1 > S_2 = S_3 > S_4$
(c) $S_1 > S_3 > S_2 > S_4$
(d) $S_4 > S_2 > S_3 > S_1$.
ion: (c)

Solution:

Solubility of AgCl in water = $\sqrt{K_{sp}} = s_1$ In 0.01 M CaCl₂ it is given by $K_{sp} = s \times (0.01 \times 2 + s) \therefore s_2 = \frac{K_{sp}}{0.02}$

In 0.01 M NaCl it is given by

$$K_{sp} = s \times (0.01 + s) \therefore s_3 = \frac{K_{sp}}{0.01}$$

In 0.05 M AgNO₃ it is given by

$$K_{sp} = s \times (0.6 + s) \therefore s_4 = \frac{K_{sp}}{0.05}$$

The solubilities are derived by neglecting s in comparison to 0.02, 0.01 and 0.05.

Problem 14:

The pH at which Mg(OH), begins to precipitate from a solution containing 0.10M Mg^{2+} ions $[K_{p} \text{ of } Mg(OH)_{2} = 1 \times 10^{-11}]$ is (a) 5 *(b)* 9 (c) 4 (d) 10. Solution: *(b)* When Mg(OH), starts precipitation, then $[Mg^{2+}] [OH^{-}]^2 = K_{sp} \text{ of } Mg(OH)_2$ $[0.1] [OH^{-}]^{2} = 1 \times 10^{-11}$ $\therefore [OH^{-}] = 10^{-5}M$ \therefore pOH = 5 $\therefore pH = 14 - pOH$ pH = 14 - 5 = 9**Problem 15:** The concentration of hydroxyl ion in solution left after mixing 100 mL of 0.1 M MgCl, and 100 mL of 0.2 M NaOH $(K_{sp} \text{ of } Mg(OH)_2 = 1.2 \times 10^{-11} \text{ J is}$ (b) 2.8×10^{-2} (c) 2.8×10^{-4} (a) 2.8×10^{-3} (d) 2.8×10^{-5} . Solution: (c) MgCl₂ + 2NaOH ---? Mg(OH)₂ + 2NaCl mM before 10 20 0 0 0 0 10 20 mM after reaction thus, 10 m mole of Mg(OH), are formed. The product of $[Mg^{2+}]$ $[OH^{-}]^2$ is therefore $\left[\frac{10}{200}\right] \times \left[\frac{20}{200}\right]^2 = 5 \times 10^{-4}$ Which is more than

 K_{sp} of Mg(OH)₂. Now solubility (S) of Mg(OH)₂ can be derived by $K_{sp}^{-r} = 4S^3$

∴ S =
$$\sqrt[3]{\frac{K_{sp}}{4}} = 1.4 \times 10^{-4}$$

∴ [OH⁻] = 2S = 2.8 × 10⁻⁴

PRACTICE PROBLEMS

PP-1

- 1. Calculate
 - K_{a} for $H_{2}O(K_{w} = 10^{-14})$ K_{h} for B(OH), K_{a} (B(OH)) = 6 × 10⁻¹⁰ (i) (ii) K_{a} for HCN, K_{b} (CN⁻) = 2.5 × 10⁻⁵ (iii)
- Calculate the ratio of degree of dissociation (α_2/α_1) when 1 M acetic acid solution is diluted to 1/100 2. times.[given $K_{a} = 1.8 \times 10^{-5}$]
- 3. Calcualte the ratio of degree of dissociation of acetic acid and hydrocyanic acid (HCN) in 1 M their respective solution of acids. [Given $K_{a(CH_{3}COOH)} = 1.8 \times 10^{-5}$; $K_{a(HCN)} = 6.2 \times 10^{-10}$]
- 4. Calculate

(a) K_a for a monobasic acid whose 0.10 M solution has pH of 4.50

- (b) $K_{\rm b}$ for a monoacidic base whose 0.10 M solution has a pH of 10.50
- 5. Calculate pH of following solutions:
 - (a) 0.1 M HCl (b)
 - $0.1 \text{ M CH}_{3}\text{COOH} (\text{K}_{2} = 1.8 \times 10^{-5})$ (c) (d) (f)
 - (e) 10⁻⁸ M HCl
 - 10⁻⁶ M CH,COOH (g)
- $0.1 \text{ M H}_{2}\text{SO}_{4} (50 \text{ ml}) + 0.4 \text{ M HCl} 50 (\text{ml})$ 0.1 M NH₄OH ($K_{\rm b} = 1.8 \times 10^{-5}$)
- 10-10 M NaOH
- 10⁻⁸ M CH,COOH (h)
- 0.1 M HA + 0.1 M HB [K (HA) = 2×10^{-5} ; K (HB) = 4×10^{-5}] (i)
- Decimolar solution of Baryta (Ba(OH),), diluted 100 times. (i)
- (k) 10^{-3} mole of KOH dissolved in 100 L of water.
- 0.5 M HCl (25 ml) + 0.5 M NaOH(10 ml) + 40 ml H₂O **(1)**
- equal volume of HCl solution (PH = 4) + 0.0019 N HCl solution. (m)
- The value of K_w at the physiological temperature (37°C) is 2.56×10^{-14} . What is the pH at the neutral 6. point of water at this temperature, where there are equal number of H⁺ and OH⁻?
- 7. Calculate the number of H⁺ present in one ml of solution whose pH is 13.
- Calcualte change in concentration of H⁺ ion in one litre of water, when temperature changes from 298 8. K to 310 K. Given $K_w(298) = 10^{-14}K_w(310) = 2.56 \times 10^{-14}$.
- K_w for H₂O is 9.62×10^{-14} at 60°C. What is pH of water at 60°C. 9. (i)
 - (ii) What is the nature of soliton at 60°C whose. (a) pH = 6.7(b) pH = 6.35
- pH of a dilute solutoin of HCl is 6.95. Calculate molarity of HCl solution. 10.
- 11. The pH of aqueous solution of ammonia is 11.5. Find molarity of solution. $K_{\rm h}$ (NH₄OH) = 1.8×10^{-5} .
- The solution of weak monoprotic acid which is 0.01 M has pH = 3. Calculate K_a of weak acid. 12.
- 13. Boric acid is a weak monobasic acid. It ionizes in water as B(OH)₃ + H₂O \square B(OH)₄⁻ + H⁺ : K_a = 5.9 × 10⁻¹⁰. Calculate pH of 0.3 M boric acid.
- Calculate [H⁺] and [CHCl₂COO⁻] in a solution that is 0.01 M in HCl and 0.01 M in CHCl₂COOH. 14. Take (K = 2.55×10^{-2}]
- Calcualte the percent error in the $[H_3O^+]$ concentration made by neglecting the ionisation of water in 15. a 10⁻⁶ M NaOH solution.
- Calculate $[H^+]$, $[CH_3COO^-]$ and $[C_7H_5O_2^-]$ in a solution that is 0.02 M in acetic acid and 0.01 M in 16. benzoic acid. K_a (acetic) = 1.8×10^{-5} , K_a (benzoic) = 6.4×10^{-5} .
- 17. At 25°C, the dissociation constant of HCN and HF are 4×10^{-10} and 6.7×10^{-4} . Calculate the pH of a mixture of 0.1 M HF and 0.1 M HCN.

PP-2

1. K_a for HA is 4.9×10^{-8} . After making the necessary approximation, calculate for its decimolar solution.

(a) % dissociation (B) OH^- concentration. (c) pH

- 2. Calculate the concentration of fluoroacetic acid which is required to get $[H^+] = 1.6 \times 10^{-3} \text{ M. K}_a$ of acid = 2.6×10^{-3} .
- 3. Liquid ammonia ionises to a slight extent. At -50 °C, its selfionisation constant, $K_{NH_3} = [NH_4^+]$ [NH_2^-] = 10⁻³⁰. How many amide ions, are present per cm³ of pure liquid ammonia? Assume N = 6.0×10^{23} .
- 4. The self ionisation constant for pure formic acid, $K = [HOOCH_2^+] [HCOO^-]$ has been estimated as 10^{-6} at room temperature. What a percentage of formic acid molecules in pure formic acid are converted to formate ion? The density of formic acid is 1.22 g/cm^3 .
- 5. Prove that degree of dissociation of a weak acid is given by:

$$\alpha = \frac{1}{1+10^{(pK_a-pH)}}$$

where K_a is its dissociation constant.

- 6. Determine degree of dissociation of 0.05 M NH_3 at 25°C i a solution of pH = 11.
- 7. K_1 and K_2 for dissociation of H_2S are 4×10^{-3} and 1×10^{-5} . Calculate sulphide ion concentration in 0.1 M H₂S solution. Also report [H⁺] and pH.
- 8. Calculate pH of (1) 10^{-3} N HNO₃, (2) 10^{-3} M H₂SO₄, (3) 10^{-3} N H₂SO₄, (4) 0.01 N HCl, (5) 10^{-8} N HCl,
- 9. Calculate pH for acid solution having $[H^+]$ as (a) $[H^+] = 0.05 \text{ M}$ (b) $[H^+] = 10^{-8} \text{ M}$.
- 10. Calculate pH for:

(a) 0.001 N NaOH, (b) 0.01 N Ca(OH)₂ (c) 0.01 M Ca(OH)₂ (d) 10^{-8} M NaOH (f) 0.0008 M Mg(OH)₂.

Assume complete ionisation of each.

- 1. Determine the [S^{2–}] in a saturated (0.1 M) H₂S solution to which enough HCl has been added to produce a [H⁺] of 2×10^{-4} , K₁ = 10⁻⁷, K₂ = 10⁻¹⁴.
- 2. Calculate [H⁺], [H₂PO₄⁻], [HPO₄²⁻] and [PO₄³⁻] in a 0.01 M solution of H₃PO₄. Take $K_1 = 7.225 \times 10^{-3}$, $K_2 = 6.8 \times 10^{-8}$, $K_3 = 4.5 \times 10^{-13}$.
- 3. Calculate the pH of a 0.1 M solution of $H_2NCH_2CH_2NH_2$; ethylenediamine (en). Determine the en H_2^{2+} . Concentration in the solution. K_{b_1} and K_{b_2} values of ethylenediamine are 8.5×10^{-5} and 7.1×10^{-8} respectively.
- 4. What are the concentrations of H⁺, HSO₄⁻, SO₄²⁻ and H₂SO₄ in a 0.20 M solution of sulphuric acid? Given H₂SO₄ \longrightarrow H⁺ + HSO₄⁻; stronge HSO₄⁻ \square H⁺ + SO₄²⁻; K₂ = 1.3 × 10⁻² M
- 5. What are the concentration of H⁺, H₂C₂O₄, HC₂O₄⁻ and C₂O₄²⁻ in a 0.1 M solution of oxalic acid? [K₁ = 5.9×10^{-2} M and K₂ = 6.4×10^{-5} M]

6. Nicotine, $C_{10}H_{14}N_2$, has two basic nitrogen atoms and both can react with water to give a basic solution. Nic (aq) + H₂O (l) \Box NicH⁺ (aq) + OH⁻ (aq)

NicH⁺ (aq) + H₂O (l) \Box NicH₂²⁺ (aq) + OH⁻ (aq)

 $K_{_{b1}}$ is 7×10^{-7} and $K_{_{b2}}$ is $1.1\times10^{-10}.$ Calculate the approximate pH of a 0.020 M solution.

7. Ethylenediamin, $H_2N-C_2H_4-NH_2$, can interact with water intwo steps, giving OH⁻ in each step. Calcualte the concentraiton of OH⁻ and $[H_3N-C_2H_4-NH_3]^{2+}$ in a 0.15 M aqueous solution of the amine. $K_1 = 8.5 \times 10^{-5}$, $K_2 = 2.7 \times 10^{-8}$ for the base.



- 1. Calculate pH of basic solution having $[OH^-]$ as (a) $[OH^-] = 0.05 \text{ M}$ (b) $[OH^-] = 10^{-8} \text{ M}$.
- 2. Calculate pH of: (a) 0.002 N acetic acid having 2.3% dissociation. (b) 0.02 N NH₄OH having 2.3% dissociation.
- 3. What is $[H^+]$ for a solution in which (i) pH = 3 (ii) pH = 4.75?
- 4. The K_w for $2H_2O \implies H_3O^+ + OH^-$ changes from 10^{-14} at 25°C to 9.62×10^{-14} at 60°C. What is pH of water at 60°? What happens to its neutrality?
- 5. 2g of NaOH are dissolved in water to make 1 litre solution. What is pH of solution?
- 6. $100 \text{ mL of HCl gas at 25^{\circ}C}$ and 740 mm pressure were dissolved in one litre of water. Calculate the pH of solution. Given V.P. of H₂O at 25^{\circ}C is 23.7 mmm.
- 7. Find the concentrations of H⁺, HCO₃⁻ and CO₃²⁻ in a 0.01 M solution of carbonic acid if the pH of solution is $4.18 \text{ K}_1 = 4.45 \times 10^{-7}$, $\text{K}_2 = 4.69 \times 10^{-11}$.
- 8. Calculate the [Cl⁻], [Na⁺], [H⁺], [OH⁻] and pH of resulting solution obtained by mixing 50 mL of 0.6 N HCl and 50 mL of 0.3 N NaOH.
- 9. Calculate the pH of solution obtained by mixing 10 mL of 0.1 M HCl and $40 \text{ mL of } 0.2 \text{ M H}_2\text{SO}_4$.
- 10. Calculate the pH of a solution which contains 100 mL of 0.1 M HCl and 9.9 mL of 1.0 M NaOH.

PP-5

- 1. What is the OH⁻ concentration of a 0.08 M solution of CH₃COONa. [K_a(CH₃COOH) = 1.8×10^{-5}]
- 2. Calcualt the pH of a 2.0 M solution of $NH_4Cl. [K_b(NH_3) = 1.8 \times 10^{-5}]$
- 3. 0.25 M solution of pyridinium chlroide $C_5H_6N^+Cl^-$ was found to have a pH of 2.669. What is K_b for pyridine, C_5H_5N ?
- 4. Calculate the extent of hydrolysis & the pH of $0.02 \text{ M CH}_3\text{COONH}_4$. [K_b (NH₃) = 1.8×10^{-5} , K_a (CH₃COOH) = 1.8×10^{-5}]
- 5. Calculate the hydrolysis in a 0.06 M solution of KCN. $[K_{a}(HCN) = 6 \times 10^{-10}]$
- 6. Calcualte the extent of hydrolysis of 0.005 M K₂CrO₄. [K₂ = 3.1×10^{-7} for H₂CrO₄] (It is essentially strong for first ionization)
- 7. Calcualte the percent hydrolysis in a 0.0100 M solution of KCN $K_a = 6.2 \times 10^{-10}$])
- 8. A 0.010 M solution of $PuO_2(NO_3)_2$ was found to have pH of 4.0. What is the hydrolysis constant, K_{h^2} for PuO_2^{2+} , and what is K_{h} for PuO_2OH^+ ?
- 9. Calcualte the pH of 1.0×10^{-3} M sodium phenolate, NaOC₆H₅, K_a for HOC₆H₅ is 1.05×10^{-10} .

What is the pH 0.01 M NaHCO₃? $K_1 = 4.5 \times 10^{-7}$, $K_2 = 4.5 \times 10^{-11}$ for carbonic acids. 10.

11. Calculate pH of 0.05 potassium hydrogen phthalate, $KHC_8H_4O_4$.

- 12. Calculate OH⁻ concentration at the equivalent point when a solution of 0.1 M acetic acid is titrated with a solution of 0.1 M NaOH. K_a for the acid= 1.9×10^{-5} .
- 13. The acid ionization (hydrolysis) constant of Zn^{2+} is 1.0×10^{-9} .
 - Calculate the pH of a 0.001 M solution of ZnCl, (a)
 - (b) What is the basic dissociation constant of $Zn(OH)^+$?

- What are [H⁺], [A⁻] and [B⁻] in a solution that is 0.03 M HA and 0.1 M HB? K_a for HA and HB are 1. 1.38×10^{-4} and 1.05×10^{-10} respectively.
- 2. What concentration of HCOO⁻ is present in a solution of 0.015 M HCOOH and 0.02 M HCl? K_a for HCOOH = 1.8×10^{-4}
- 3. Calculate the pH of a solution of given mixtures: (a) $(2g CH_3COOH + 3g CH_3 COONa)$ in 100 mL of mixture; $K = 1.8 \times 10^{-5}$

(b) 5 mL of 0.1 M NH₄OH + 250 mL of 0.1 M NH₄Cl;

$$K = 1.8 \times 10^{-5}$$

$$K_{h} = 1.8 \times 10$$

- (c) (0.25 mole of acid + 0.35 mole of salt) in 500 mL mixture: $K_a = 3.6 \times 10^{-4}$
- Calculate the pH of a buffer solution prepared by dissolving 30 g of Na₂CO₃ in 500 mL of an 4. aqueous solution containing 150 mL of 1 M HCl. Ka for $H_2CO_3 = 5.63 \times 10^{-11}$.
- 5. A weak acid HA after treatment with 12 mL of 0.1 M strong base BOH has a pH of 5 at the end point, the volume of same base required is 26.6 mL. Calculate K₂ of acid.
- 6. A solution of weak acid was titrated with base NaOH. The equivalence point was reached when 36.12 mL of 0.1 M NaOH have been added. Now 18.06 mL 0.1 M HCl were added to titrated solution, the pH was found to be 4.92. What is K_a of acid?
- 7. Calculate [H⁺] in a 0.20 M solution of dichloroacetic acid ($K_a = 5 \times 10^{-2}$) that also contains 0.1 M sodium dichloroacetate. Neglect hydrolysis of sodium salt.
- 8. 20 mL of 0.2 M NaOH are added to 50 mL of 0.2 M acetic acid ($K_a = 1.8 \times 10^{-5}$). (1) What is pH of solution? (2) Calculate volume of 0.2 M NaOH required to make the pH of solution 4.74.
- 9. Calculate the ratio of pH of a solution containing 1 mole of CH₃COONa + 1 mole of HCl per litre and of other solution containing 1 mole CH₂ COONa+1 mole of acetic acid per litre.
- 10. A 0.1 M solution of weak acid HA is 1% dissociated at 25°. What is its K_a? If this solution is w.r.t NaA 0.2 M, what will be the new degree of dissociation of HA and pH?

PP_7

- 1. Calculate the hydronium ion concentration and pH at the equivalence point in the reaction of 22.0 mL of 0.10M acetic acid, CH₃COOH, with 22.0 mL of 0.10 M NaOH.
- 2. Calculate the hydronium ion concentraiton and the pH at the equivalence point in a titration of 50.0 mL of 0.40 M NH₃ with 0.40 M HCl.
- 3. In the titration of a solution of a weak acid HX with NaOH, the pH is 5.8 after 10.0 mL of NaOH solution has been added and 6.402 after 20.0 mL of NaOH has been added. What is the ionization constant of HX?
- 4. The equivalent point in a titration of 40.0 mL of a solution of a weak monoprotic acid occurs when 35.0 mL of a 0.10 M NaOH solution has been added. The pH of the solution is 5.75 after the additoin of 20.0 mL of NaOH solution. What is the dissociation constant of the acid.
- 5. Phenol, C_6H_5OH , is weak organic acid that has many uses, and more than 3 million ton are produced annually around the world. Assume you dissolve 0.515 g of the compound in exactly 100 mL of water and then titrate the resulting solution with 0.123 M NaOH.

 $C_6H_5OH(aq) + OH^-(aq) \rightarrow C_6H_5O^-(aq) + H_2O(l)$ What are the concentrations of all of the following ions at the equivalence point: Na⁺, H₃O⁺, OH⁻ and C₆H₅O⁻? What is the pH of the solution ? [K₃(phenol) = 1.3×10^{-10}]

- 6. A weak base (50.0 mL) was titrated with 0.1 M HCl. The pH of the solution after the addition of 10.0 mL and 25.0 mL were found to be 9.84 and 9.24, respectively. Calculate K_b of the base and pH at the equivalence point.
- 7. A weak acid (50.0 mL) was titrated with 0.1 M NaOH. The pH values when 10.0 mL and 25.0 mL of base have been added are found to be 4.16 and 4.76, respectively. Calcualte Ka of the acid and pH at the equivalence point.
- 8. $CH_3COOH (50 \text{ mol}, 0.1 \text{ M})$ is titrated against 0.1 M NaOH solution. Calculate the pH at the addition of 0 ml, 10 ml, 20 ml, 25 ml, 40 ml, 50 ml of NaOH. K_a of CH₃COOH is 2×10^{-5} .

- 1. Calculate the composition of an acidic buffer solution made up of HA and NaA of total molarity 0.29 having pH = 4.4 and $K_a = 1.8 \times 10^{-5}$.
- 2. $0.1 \text{ M CH}_3\text{COOH}$ solution is titrated against 0.05 M NaOH solution. Calculate pH at 1/4 th and 3/ 4 stages of neutralization of acid. The pH for 0.1 M CH₃COOH is 3.
- 3. 24 mL of a sample of clear saturated solution of PbI₂ requires 10 mL of a certain AgNO₃(aq.) for its titration. What is the molarity of this AgNO₃ (aq.)? K_{sp} for PbI₂ = 4 × 10⁻⁹.
- 4. K_{sp} of PbCl₂ is 10⁻¹³. What will be [Pb²⁺] in a solution prepared by mixing 100 mL of 0.1 M Pb(NO₃)₂ and 1 mL of 1 M HCl?
- 5. Ksp of PbBr₂ is 8×10^{-5} . If the salt is 80 % dissociated in solution, calculate the solubility of salt in g per litre.
- 6. A solution contains a mixture of $Ag^+(0.10 \text{ M})$ and $Hg_2^{2+}(0.10 \text{ M})$ which are to be separated by selective precipitation, Calculate the maximum concentration of iodide ion at which one of them gets precipitated almost completely. What % of that metal ion is precipitated?
- 7. 1.75 g of solid NaOH are added to 0.25 dm³ of 0.1 M NiCl₂ solution. Calculate: (a) mass of Ni(OH)₂ forms (b) pH of final solution Given K_{sp} of Ni(OH)₂ = 1.6 × 10⁻¹⁴

- 8. Calculate the [OH⁻] of a solution after 100 mL of 0.1 M MgCl₂ is added to 100 mL of 0.2 M NaOH. K_{sn} of Mg(OH)₂ is 1.2×10^{-11} .
- 9. A mixture of water and AgCl is shaken until a saturated solution is obtained. Now the solution is filtered and 100 mL of clear solution of filtrate is mixed with 100 mL of 0.03 M NaBr. Should a precipitate form? K_{sp} of AgCl and AgBr are 1×10^{-10} and 5×10^{-13} .
- 10. Calculate pH of a saturated solution of Mg(OH)₂ K_{sp} for Mg(OH)₂ is 8.9×10^{-12} .

PP-9

- 1. The value of K_{sp} for the slightly soluble salts MX and QX_2 are each equal to 4.0×10^{-18} . Which salt is more soluble? Explain your answer fully.
- 2. The solubility of PbSO₄ water is 0.038 g/L. Calculate the solubility product constant of PbSO₄.
- 3. Calculate the solubility of Mg(OH)₂ in water. $K_{sp} = 1.2 \times 10^{-11}$.
- 4. How many mol CuI ($K_{sp} = 5 \times 10^{-12}$) will dissolve in 1.0 L of 0.10 M NaI solution?
- 5. A solution of saturated CaF_2 is found to contain 4.1×10^{-4} M fluoride ion. Calcualte the K_{sp} of CaF_2 . Neglect hydrolysis.
- 6. The solubility of ML_2 (formula weight, 60 g/mol) in water is 2.4×10^{-5} g/100 mL solution. Calculate the solutbility product constant for ML_2 .
- 7. What is the solubility (in mol/L) of Fe(OH)₃ in a solution of pH = 8.0? [K_{sp} for Fe(OH)₃ = 1.0×10^{-36}]
- 8. The solubility of Ag, CrO_4 in water is 0.044 g/L. Determine the solubility product constant.
- 9. Calculate ethe solubility of A_2X_3 in pour water, assuming that neither kind of ion reacts with water. For A_2X_3 , $[K_{sp} = 1.1 \times 10^{-23}]$
- 10. Determine the solubility of AgCl in 0.1 M BaCl₂. [K_{sp} for AgCl = 1×10^{-10}]
- 11. What mass of Pb²⁺ ion is left in solution when 50.0 mL of 0.20 M Pb(NO₃)₂ is added to 50.0 mL of 1.5 M NaCl? [Given K_{sp} for PbCl₂ = 1.7 × 10⁻⁴]
- 12. A solution has a Mg²⁺ concentration of 0.0010 mol/L. Will Mg(OH)₂ precipitate if the OH⁻ concentration of the solution is $[K_{sp} = 1.2 \times 10^{-11}]$ (a) 10⁻⁵ mol/L (b) 10⁻³ mol/L
- 13. Calculate solubility of PbI₂ ($K_{sp} = 1.4 \times 10^{-8}$) in water at 25°C, which is 90% dissociated.
- 14. Calcualte solubility of AgCN ($K_{sp} = 4 \times 10^{-16}$) in a buffer solution of PH = 3]

- 1. 0.1 millimole of CdSO₄ are present in 10 mL acid solution of 0.08 N HCl. Now H_2S is passed to precipitate all the Cd²⁺ ions. What would be the pH of solution after filtering off precipitate, boiling of H_2S and making the solution 100 mL by adding H_2O ?
- 2. Zn salt is mixed with $(NH_4)_2$ S of molarity 0.021 M. What amount of Zn²⁺ will remain unprecipitated in 12 mL of the solution? K_{sp} of ZnS = 4.51 × 10⁻²⁴.
- 3. 10 ml of 0.3 M Na₂SO₄ are mixed with 20 mL solution having initially 0.1 M Ca²⁺ and 0.1 M Sr²⁺ in it. What are the final concentrations of Ca²⁺, Sr²⁺ and SO₄²⁻ in solution? Given K_{sp} of SrSO₄ = 7.6 × 10⁻⁷ and K_{sp} of CaSO₄ = 2.4×10^{-5} .

- 4. The solubility of $CaCO_3$ is 7 mg/litre. Calculate the solubility product of $BaCO_3$ from this information and from the fact that when Na_2CO_3 is added slowly to a solution containing equimolar concentration of Ca^{2+} and Ba^{2+} , no precipitate is formed until 90% of Ba^{2+} has been precipitated as $BaCO_3$.
- 5. The solubility of Mg(OH)₂ is increased by the addition of NH₄⁺ ion. Calculate: (a) K_C for Mg(OH)₂ + 2NH₄⁺ \implies 2NH₃ + 2H₂O + Mg²⁺ K_{sp} of Mg(OH)₂ = 6 × 10⁻¹², K_b of NH₃ = 1.8 × 10⁻⁵ (b) Find the solubility of Mg(OH)₂ in a solution containing 0.5 M NH₄Cl before addition of Mg(OH)₂?
- 6. 100.0 mL of a clear saturated solution of Ag₂SO₄ is added to 250.0 mL of a clear saturated solution of Ag₂SO₄ is added to 250.0 mL of a clear saturated solution of PbCrO₄. Will any precipitate form and if so what? Given, Ksp values for Ag₂SO₄, Ag₂CrO₄, PbCrO₄ and PbSO₄ are 1.4×10^{-5} , 2.4×10^{-12} , 2.8×10^{-13} and 1.6×10^{-8} respectively.
- 7. 2M solution of Na_2CO_3 is boiled in a closed container with excess of CaF_2 . Very little amount of $CaCO_3$ and NaF are formed. If the solubility product of $CaCO_3$ is x and molar solubility of CaF_2 is y, find the molar concentration of F- in the resulting solution after equilibrium is attained.
- 8. 250.0 mL of saturated clear solution of CaC_2O_4 (aq.) requires 6.3 mL of 0.00102 M KMnO₄ (aq.) in acid medium for complete oxidation of $C_2O_4^{2-}$ ions. Calculate the K_{sp} of CaC_2O_4 .
- 9. K_{sp} for SrF₂ = 2.8 × 10⁻⁹ at 25°C. How much NaF should be added to 100 mL of solution having 0.016 M in Sr²⁺ ions to reduce its concentration to 2.5 × 10⁻³ M?
- 10. Bromophenol blue is an indicator with a value of $K_a = 6.84 \times 10^{-5}$. At what pH is will work as in indicator? Also report the % of this indicator in its basic form at a pH of 4.84.



- 1. A certain solution has a hydrogen ion concentration 4×10^{-3} M. For the indicator thymol blue, pH is 2.0 when half the indicator is in unionised form. Find the % of indicator in unionised form in the solution with $[H^+] = 4 \times 10^{-3}$ M.
- 2. At what pH does an indicator change colour if the indicator is a weak acid with $K_{ind} = 4 \times 10^{-4}$. For which one(s) of the following neutralizations would the indicator be useful? Explain (A) NaOH + CH₂COOH (B) HCl + NH₂ (C) HCl + NaOH
- 3. What indicator should be used for the titration of 0.10 M KH₂BO₃ with 0.10 M HCl? $K_a (H_3BO_3) = 7.2 \times 10^{-10}$
- 4. Bromophenol blue is an indicator with a K_a value of 6×10^{-5} . What % of this indicator is in its basic form at a pH of 5?
- 5. An acid base indicator has K_a of 3×10^{-5} . The acid form of the indicator is red & the basic form is blue. By how much must the pH change in order to change the indicator form 75% red to 75% blue?
- 6. Calculate the Simultaneous solubility of AgSCN and AgBr. K_{sp} (AgSCN) = 1.1 × 10⁻¹², K_{sp} (AgBr) = 5 × 10⁻¹³.
- 7. Calculate F⁻ in a solution saturated with respect of both MgF₂ and SrF₂. Ksp {MgF₂} = 9.5 × 10^{-9} , K_{sp}(SrF₂) = 4 × 10⁻⁹.
- 8. Equal volumes of 0.02 M AgNO₃ and 0.02 M HCN were mixed. Calculate [Ag⁺] at equilibrium. Take Ka(HCN) = 9×10^{-10} , K_{sp} (AgCN) = 4×10^{-16} .
- 9. Assuming no change in volume, calculate the minimum mass of NaCl necessary to dissolve 0.010 mole AgCl in 100 L solution. $[K_f(AgCl_2^-) = 3 \times 10^5, K_{sp} = (AgCl) = 1 \times 10^{-10}]$

10. A recent investigation of the complexation of SCN⁻ with Fe³⁺ led of 130, 16, and 1.0 for K_1, K_2 and K_3 respectively. What is the overall formation constant of Fe(SCN)₃ from its components ions, and whta is the dissocation constant of Fe(SCN)₃ into its simplest ions on the basis of these data?

11. How much AgBr could dissolve in 1.0 L of 0.40 M NH₃? Assume that $Ag(NH_3)_2^+$ is the only complex formed. $[K_f(Ag(NH_3)_2^+) = 1 \times 10^8; K_{sp}(AgBr) = 5 \times 10^{-13}]$

PP-12

- 1. Determine [OH⁻] of a 0.050 M solution of ammonia to which has been added sufficient NH₄Cl to make the total [NH₄⁺] equal to 0.100 M [K_{b(NH₃)} = 1.8×10^{-5}]
- 2. Calculate the pH of a solution prepared by mixing 50.0 mL of 0.200 M HC₂H₃O₂ and 50.0 mL of 0.100 M NaOH. [$K_{a(CH_{3}COOH)} = 1.8 \times 10^{-5}$]
- 3. A buffer of pH 9.26 is made by dissolving x moles of ammonim sulphate and 0.1 mole of ammonia into 100 mL solution. If pK_{b} of ammonia is 4.74, calculate value of x.
- 4. 50 mL of 0.1 M NaOH is added to 75 mL of 0.1 M NH_4Cl to make a basic buffer. If pK_a of NH_4^+ is 9.26, calcualte pH.
- 5. (a) Determine the pH of a 0.2 M solution of pyridine C_5H_5N . $K_b = 1.5 \times 10^{-9}$.
 - (b) Predict the effect of addition of pyridinium ion $C_5H_5NH^+$ on the position of the quilibrium. Will the pH be raised or lowered?

(c) Calculate the pH of 1.0 L of 0.10 M pyridine solution to which $0.3 \text{ mol of pyridinium chloride } C_5H_5NH^+Cl$, has been added, assuming no change in volume.

- 6. Calculate the pH of a solution which results from the mixing of 50.0 ml of 0.3 M HCl with 50.0 ml of 0.4 M NH₃. [K_b (NH₃) = 1.8×10^{-5}]
- 7. Calculate the pH of a solution made by mixing 50.0 ml of 0.2 M NH₄Cl & 75.0 ml of 0.1 M NaOH. $[K_b (NH_3)=1.8 \times 10^{-5}]$
- A buffer solution was prepared by dissolving 0.02 mol propionic acid & 0.015 mol sodium propionate in enough water to make 1.00 of solution. (K_a for propionic acid is 1.34 × 10⁻⁵]
 (a) What is the pH of the buffer?
 - (b) What would be the pH if 1.0×10^{-5} mol HCl were added to 10 ml of the buffer?
 - (c) What would be the pH if 1.0×10^{-5} mol NaOH were added to 10 ml of the buffer?

(d) Also report the percent change in pH of original buffer in cases (b) and (c).

9. A solution was made up to be 0.01 M in chloroacicitc acid (ClCH₂COOH) and also 0.002 M in sodium chloroacetate ClCH₂COONa. What is [H⁺] in the solution? $K_a = 1.5 \times 10^{-3}$.

- 1. Calculate the percentage hydrolysis in 0.003 M aqueous solution of NaOCN. K_a for HOCN = 3.33×10^{-4} .
- 2. Calculate the pH of 0.1 M K₃PO₄ solution. The third dissociation constant of orthophosphoric acid is 1.3×10^{-12} . Assume that the hydrolysis proceeds only in the first step.
- 3. Equilibrium constant for the acid ionisation of F^{3+} to $Fe(OH)^{2+}$ and H^+ is 6.5×10^{-3} . What is the maximum pH which could be used so that at least 95% of the total Fe^{3+} in a dilute solution exists as Fe^{3+} ?

The acid inoisation constant for

$$Zn^{2+} + H_2O \Longrightarrow Zn(OH)^+ + H^+$$

is 1.0×10^{-9} . Calculate the pH of 0.0010 M solution of ZnCl₂. Also calculate basic dissociation of $Zn(OH)^+$.

- The dissociation constants for aniline, acetic acid and water at 25°C are 3.83×10^{-10} , 1.75×10^{-5} 5. and 1.008×10^{-14} respectively. Calculate degree of hydrolysis of aniline acetate in a deci normal solution. Also report the pH.
- Calculate pH of the following mixtures. Given that $K_a = 1.8 \times 10^{-5}$ and $K_b = 1.8 \times 10^{-5}$ 6. (a) $50 \text{ mL of } 0.10 \text{ M NaOH} + 50 \text{ mL of } 0.05 \text{ M CH}_3\text{COOH}$ (b) 50 mL of 0.05 M NaOH + 50 mL of 0.10 M CH₂COOH (c) 50 mL of 0.10 M NaOH + 50 mL of 0.10 M CH₂COOH (d) 50 mL of 0.10 M NH₄OH + 50 mL of 0.05 M HCl (e) 50 mL of 0.05 M $NH_4OH + 50$ mL of 0.10 M HCl (f) $50 \text{ mL of } 0.10 \text{ M NH}_4\text{OH} + 50 \text{ mL of } 0.10 \text{ M HCl}$ (g) $50 \text{ mL of } 0.06 \text{ M NH}_4\text{OH} + 50 \text{ mL of } 0.05 \text{ M CH}_3\text{COOH}$.
- 7. The vapour pressure of 0.01 molal solution of weak base BOH in water at 20°C is 17.536 mm. Calculate Kb| for base. Aqueous tension at 20°C is 17.540 mm. Assume molality and molarity same.
- 8. A 0.01 M aqueous solution of weak acid HA has an osmotic pressure 0.293 atm at 25°C. Another 0.01 M aqueous solution of the weak acid HB has an osmotic pressure of 0.345 atm under the same conditions. Calculate equilibrium constants of two acids for their dissociation.
- 9. The salt $Zn(OH_2)$ is involved in the following two equilibria.

 $Zn(OH)_2(s) \Longrightarrow Zn^{2+}(aq.) + 2OH^-(aq.)$ $K_{sp} = 1.2 \times 10^{-17}$ $Zn(OH)_2(s) + 2OH^- \implies Zn(OH)_4^{2-}(aq.)$ $K_{c} = 0.12$ Calculate the [OH-] at which solution of Zn(OH), be a minimum. Also Find the solubility of Zn(OH), at this pH.

4.

ANSWERS PRACTIC PROBLEMS

PP-1

1. 4. 5.	(i) 1.8×10^{-16} , (a) $K_a = 10^{-8}$, (a) + 1, (b) 0.5 (b) 0.(b) 1, (c)	(ii) $1.66 \times$ (b) $K_{b} = 10$ 22, (c) 2.87	10 ⁻⁵ (iii) 4 ×) ⁻⁶ 7, (d) 11.13 (10 ⁻¹⁰ (e) 6.97	2. , (f) 7, (g	10 g) 6.01 (h) 6.97	3. (i) 2.61,	170.4 , (j) 11.30
6. 9. 12 14. 15. 16.	(k) 9 (l) 1, (m) 6.81 (i) 6.51 , (ii) Bat 1.11×10^{-4} [H ⁺] = $1.612 \times$ error = 1% [H ⁺] = 10^{-3} M, 2.08	7. 6.0 sic, (b) Acid 13 4.8 $\times 10^{-2}$ M, [C , [CH ₃ COC	022×10^{7} dic 87 CHCl ₂ COO ⁻ $0^{-}] = 3.6 \times 1^{7}$	10.] = 6.12 $0^{-4} M, $	8. 2.31 × 26×10^{-5} $[C_7H_5O_2]$	0.6×1 $10^{-8} M$ $^{3} M$ $^{-}] = 6.4$	0 ⁻⁷ × 10 ⁻⁴]	11. 0.5: M	56 M
17.	2.00		PP-	2					
1. 2. 6. 8. 10.	(a) 0.7% (b) 7 2.37 × 10 ⁻³ M 2% (1) 3 (2) 2.6 (a) 11 (b) 12 (c)	7 × 10 ⁻⁴ mo 3. 7. 989 (3) c) 12.3010	$\begin{array}{c} & 11 \\ \text{ol litre}^{-1} (c) \\ & 6 \times 10^{5} \\ & 0.018 \\ \hline \\ 0 & 3 \\ (4) \\ 2 \\ (d) \\ 7.02 \\ (f) \end{array}$	H = 4.1 5 ions M (5) 6.9 0 11.204	5, 1.43 > 788 41	× 10 ⁻¹⁰ r 9.	nol litre 4. (a) 1.30	0.004%	5.98
			PP-	3					
1. 2. 3. 5. 7.	$[S^{2-}] = 2.5 \times 10^{-1}$ $[H^+] = [H_2PO_4]$ pH = 11.46, [e] 0.0528 M, 0.00 $[OH^-] = 3.57 \times 10^{-1}$	10^{-15} $nH_2^{2+} = 5.623$ $nH_2^{2+} = 7.$ $472 \text{ M}, 0.0$ $\times 10^{-3} \text{ M}, [2]$	× 10 ⁻³ , [HP 1 × 10 ⁻⁸ M 528 M, 0.00 $H_2 en$] ²⁺ = 2.	$O_4^{2-}] = 0$ 00064 N 7 × 10 ⁻⁸	6.8 × 10 4. A 6. M	^{–8} , [PO ₄ 0.2116 10.07	$[3^{-}] = 5.4$ M, 0.11	441 × 10 .84 M, 0) ^{–18}).0116 M,0
			PP-	4					
1. 3. 6. 8. 9.	(a) 12.6989 (b (i) 10 ⁻³ M (ii) 1 2.4142 0.3 M, 0.015 M 0.4685) 6.96 1.7782 × 1(7. M, 0.15 M,	$^{-5}$ M 6.61 × 6.6 × 10 ⁻¹⁴	2. 4. 10 ⁻⁴ m/ M, pH = 10.	a) 4.33 6.51, no (l, 6.73 × = 0.8239 3.0409	72 (b) 9 eutral : 10 ⁻⁴ m.	9.6628 /l, 4.78	5. × 10 ⁻¹¹ 1	12.6989 n/ <i>l</i>
			PP-	5					
1. 4. 7. 10.	[OH ⁻] = 6.664 0.56%, pH = 7 4.0% 8.34	× 10 ^{−6} 11. 4.1	2. 5. 8. 19 12.	pH = 4 1.667 10 ⁻⁶ , 1 5.12 ×	1.477 % 0 ⁻⁸ 10 ⁻⁶ M		3. 6. 9. 13.	$K_{b} = 6.$ 0.26% pH = 10 (a) 6	25×10^{-10} 0.43 (b) 10^{-5}
			PP-	6					
1. 3. 5.	2.04×10^{-3} M (a) 4.7851, (b) 8.219×10^{-6}	, 5.15 × 10 7.5563 (c)	⁻⁹ M 3.5898 6.	2. 4. 1.2 × 1	1.35×10.197 10^{-5}	10 ⁻⁴ M	7.	0.05	
8.	(1) 4.5686, (2)	25 mL	9.	<u>1</u> 2			10.	5.3010	$, 5 \times 10^{-5}$

65

CHEMISTRY

1. 4. 6. 8.	8.71 2.37 × 10 ⁻⁶ $K_{b} = 1.8 \times 10^{-6}$ (i) 2.85, (ii) 4)−⁵, 5.27 .0969, (i	ii) 4.522	2. 5. 7. 29, (iv) 4	4.98 pH = 8.73 4.699, (1	8.73, [N v) 5.301,	$[a^+] = 0.$	3. .0379 , [599	7.94 × [C ₆ H ₅ O	$(10^{-7})^{-7} = 0.0373$	
PP-8											
1. 4. 7. 10.	0.09 M, 0.20 9.4 × 10^{-2} mo (a) 2.082 g (b 10.4168	M 1 litre ⁻¹ 0) 8.06	2. 5. 8.	4.5228 12.48 2.8 ×	8, 5.47 g litre ⁻¹ 10 ⁻⁴	71	3. 6. 9.	5×10 5×10 7.5×10) ⁻³) ⁻¹³ M, 9 10 ⁻⁸	99.83 %	
	PP-9										
1. 4. 7 10. 12. 14.	QX ₂ is more s [Cu ⁺] = 5×1 1.0×10^{-18} M 5×10^{-10} M (a) no precipit 2.1×10^{-5}	oluble 0 ⁻¹¹ M I	ll occur, (2. 5. 8. 11. (b) a pre	$1.6 \times$ $3.4 \times$ $8.8 \times$ 12 mg	10 ⁻⁸ 10 ⁻¹¹ 10 ⁻¹² will form	n	3. 6. 9. 13.	1.4 × 2.6 × 1.0 × 1 1.6 ×	10 ⁻⁴ 10 ⁻¹⁶ 10 ⁻⁵ mol/lit 10 ⁻³	
PP-10											
1. 3. 4.	$2 \\ 3.3 \times 10^{-2} \text{ M} \\ 4.9 \times 10^{-10} \\ \boxed{2}$, 3.3 × 1	2. 0 ⁻² M, 1 5.	1.677 .05 × 1 1.85 ×	$\times 10^{-22}$ 0^{-3} M, $\times 10^{-2}$,	g/12 mI 7.17 × 1 0.081M	2. 0 ⁻⁴ M 6.	Ag ₂ Cr	O ₄ will J	ppt	
7.	$\sqrt{\frac{8y^3}{x}}$	8.	4.09 ×	10-9		9.	0.1178	8g	10.	80%	
				PP-	-11						
1. 3. 4. 6. 8. 11.	$[HI_n] = 28.57$ (methyl red), 85.71% $4 \times 10^{-7} \text{ mol/l}$ $[Ag^+] = 6.667$ $2.8 \times 10^{-3} \text{ M}$	% one with L AgBr, 7 × 10 ⁻⁵	pH=5.3 9×10 ⁻⁷ M	2. 22 as m 5. mol/L/ 9.	(b) (c) idpoint ΔpH = AgSCN 19.3 k) of colou: = 0.954	r range 7. 10.	3×10 $K_d = 1$	$^{-3} M$ /K _f = 4	.8 × 10 ⁻⁴	
				PP-	-12						
1. 4. 6. 8. 9.	$[OH^{-}] = 9.0 \times$ 9.56 8.7782 (a) 4.7525 (b) $[H^{+}] = 2.5 \times$	× 10 ⁻⁶) 4.697, (10 ⁻³	(c) 4.798	2. 5. 7. 3 (d) 1.1	4.74 (a) pH 9.372 34% or	I = 9.239 4 n acid ad	3. 9 (b) lov Idition (0.05 m wered (c).96% or	pH = 4 $pH = 4$ $pH = 4$	4.699 dditoin.	
PP-13											
1. 5. 6. 7.	10 ⁻² 54.95% (a) 12.3979, (9.74 × 10 ⁻⁴	2. (b) 4.744 8.	12.436 47 (c) 8. 4.83 ×	56 7218 (0 10 ⁻⁴ ,2	3. d) 9.255 85 × 1	0.9083 53 (e) 1.0 0 ⁻³	3 6021 (f)	4.) 5.2782	pH = 0	5	