20/9/22

Ionic Eq. (whole chap. in water)

Electrolyte: Conduct ϟ in molten or aq. state

Weak ϟlyte
- Ionise partially
- Eg:
  $CH_3COOH(aq.) \rightleftharpoons CH_3COO^- + H^+$
  $NH_4OH(aq.) \rightleftharpoons NH_4^+ + OH^-$

Strong ϟlyte
- Ionise completely
- Eg:
  $HCl(aq.) \rightarrow H^+ + Cl^-$
  $H_2SO_4(aq.) \rightarrow 2H^+ + SO_4^{2-}$

Factors affecting DoD —

1) Nature of ϟlyte: $\alpha \sim 1 \Rightarrow$ Strong.
$\alpha < 1 \Rightarrow$ Weak.

2) Temp.: $\boxed{\alpha \propto \text{Temp.}}$

as $\Delta H > 0$ for dissociation rxⁿs.

3) Dilution: $\boxed{\text{Dil.}\uparrow \Rightarrow \alpha\uparrow}$

as $K_{eq} = C\alpha^2$ and $C \propto \frac{1}{V}$ and dil. $\Rightarrow V\uparrow$

Common Ion Effect

Eg:

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

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

if added

rx^n affected goes bwrd

The suppression in DoD of a weak 4lyte in presence of strong 4lyte having common ion.

Acid Base Theories

1) Arrhenius Theory –

Acid	Base
Release H^+ in aq. sol^n	Release OH^- in aq. sol^n
Eg: HCl (aq.), CH_3COOH (aq.)	Eg: NaOH (aq.), NH_4OH (aq.)

- Limitations :

1) Free H^+ and OH^- do NOT exist in H_2O

$$H^+ \equiv H_3O^+ \equiv H_5O_2^+ \equiv \dots \equiv H^+(H_2O)_n$$

$$OH^- \equiv H_3O_2^- \equiv H_5O_3^- \equiv \dots \equiv OH^-(H_2O)_n$$

2) Doesn't explain acidic & basic nature of HCl, NH_3, $AlCl_3$, CaO, ...

2) Bronsted Lowry —

Acid	Base
Donate H^+	Accept H^+

- Conj. Acid - Base Pair :

$$\underset{\text{(Base)}}{NH_3} + \overset{\text{(Acid)}}{H_2O} \rightleftharpoons \underset{\text{(Conj. Acid)}}{NH_4^+} + \overset{\text{(Conj. Base)}}{OH^-}$$

☆

Slyte	Conj.
Strong	Weak
Weak	Strong

- Amphiprotic Species : Can donate as well as accept H^+.

Eg – HSO_4^-, HCO_3^-, ...

---

3) Lewis Theory —

Acid	Base
Accept l.p. of $\bar{e}$	Donate l.p. of $\bar{e}$
Electrophiles	Nucleophiles

- Acid :

1) (+ve) charged Species (H^+, Cl^+, CH_3^+, ...)

2) Neutral species, Incomplete Octet ($AlCl_3$, BF_3, $ZnCl_2$, ...)

3) Neutral species, Vacant d orbitals (PCl_5, $SiCl_4$, ...)

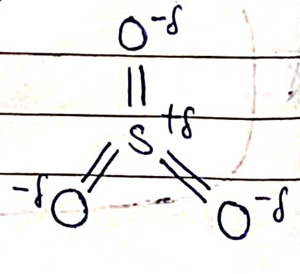
☆ 4) Comp. having multiple bonds b/w 2 E.N. atoms

CO_2

$$\overset{-\delta}{O}=\overset{+\delta}{C}=\overset{-\delta}{O}$$

Very much $+\delta$ on C

, SO_3



- Base :

1) (-ve) charged species (OH^-, F^-, Cl^-, CN^-, H^-, CH_3^-, ...)

2) Neutral species, ≥1 l.p. (H_2O, NH_3, NH_2-NH_2, ...)

Behavior of Monobasic Acid. —

Consider the weak monobasic acid.

R: $HA(aq.) \rightleftharpoons H^+(aq.) + A^-(aq.)$

Conc. I: C $\quad 0 \quad 0$

Conc. E: $C(1-\alpha)$ $\quad C\alpha \quad C\alpha$

$$K_a = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} \Rightarrow \boxed{K_a = \left(\frac{C\alpha^2}{1-\alpha}\right)}$$

(Diss. Const. of weak acid) (Ostwald's Dissociation Eqⁿ)

C – Conc. of weak acid. α – DoD of weak acid.

If $\boxed{\alpha < 0.02}$, we take $(1-\alpha) \sim 1$

$$\Rightarrow K_a \sim C\alpha^2 \Rightarrow \boxed{\alpha = \sqrt{\frac{K_a}{C}}}$$

(Ostwald's Dil. Law)

☆

$pH = -\log[H^+]$ $\quad pK_a = -\log(K_a)$

$pOH = -\log[OH^-]$ $\quad pK_b = -\log(K_b)$

Now, $pH = -\log([H^+]) = -\log(C\alpha)$

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

$$\Rightarrow \boxed{pH = \left(\frac{1}{2}\right)\left[pK_a - \log(C)\right]}$$

Behavior of Monoacidic Base –

Consider the weak monoacidic base.

R: $BOH\,(aq.) \rightleftharpoons OH^-\,(aq.) + B^+\,(aq.)$

Conc. I: C $\quad 0 \quad 0$

Conc. E: $C(1-\alpha)$ $\quad C\alpha \quad C\alpha$

$K_b = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} \Rightarrow \boxed{K_b = \left(\frac{C\alpha^2}{1-\alpha}\right)}$

(Diss. Const. of weak base) (Ostwald's Dissociation Eqⁿ)

C – Conc. of weak base $\quad$ α – DoD of weak base

If $\boxed{\alpha < 0.02}$, we take $(1-\alpha) \sim 1$

$$\Rightarrow K_b = C\alpha^2 \Rightarrow \boxed{\alpha = \sqrt{\frac{K_b}{C}}}$$

(Ostwald's Dil. Law)

Now, $pOH = -\log([OH^-]) = -\log(C\alpha)$

$$= -\log\left(C\sqrt{\frac{K_b}{C}}\right) = -\log\left(\sqrt{K_bC}\right)$$

$$\Rightarrow \boxed{pOH = \left(\frac{1}{2}\right)[pK_b - \log(C)]}$$

Q) $K_a(HCN) = 10^{-9}$; 0.1 M HCN

$\alpha = ?$, $[H^+] = ?$, $pH = ?$

A) ✓Assume $\alpha << 1 \Rightarrow \alpha = \sqrt{\frac{10^{-9}}{0.1}} \Rightarrow \boxed{\alpha = 10^{-4}}$

✓ $[H^+] = (0.1)(10^{-4})$

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

✓ $pH = \left(\frac{1}{2}\right)[pK_a - \log(C)]$

$= \left(\frac{1}{2}\right)[9 + 1]$

$\Rightarrow \boxed{pH = 5}$

Q) $K_a(HCl) = 0.1$; 0.1 M HCl

$\alpha = ?$, $[H^+] = ?$, $pH = ?$

A) ✓Obviously $\alpha \sim 1$. $(0.1) = \frac{(0.1)\alpha^2}{1-\alpha}$

$\Rightarrow \alpha^2 + \alpha - 1 = 0$

$\Rightarrow \boxed{\alpha \sim 0.61}$

✓ $[H^+] = (0.1)(0.61)$

$\Rightarrow \boxed{[H^+] = 0.061}$ ✓ $pH = -\log(0.061)$

$\Rightarrow \boxed{pH = 1.2}$

Q) $K_a(HA) = 10^{-2}$; $[H^+] = 0.01$ M ; $C = ?$

A) $K_a = 10^{-2} = \frac{C\alpha^2}{1-\alpha}$ $[H^+] = C\alpha$

$\Rightarrow 10^{-2} = \frac{(0.01)\alpha}{(1-\alpha)} \Rightarrow \boxed{\alpha \simeq 0.5}$

$\Rightarrow \boxed{C = 0.02\ M}$

Assign Q23)

$$\begin{array}{llll} \text{R:} & HA & \rightleftharpoons & H^+ \quad + \quad A^- \\ \text{Conc. I:} & C & & 0 \qquad\quad 0 \\ \text{Conc. E:} & C(1-\alpha) & & C\alpha \qquad C\alpha \end{array}$$

$$K = \frac{(C\alpha)^2}{C(1-\alpha)} \Rightarrow K \sim C\alpha^2 \Rightarrow \boxed{\alpha \sim \sqrt{\frac{K}{C}}}$$

Now, $\alpha_{acetic} = \sqrt{\frac{K_{acetic}}{C}}$, $\alpha_{formic} = \sqrt{\frac{K_{formic}}{C}}$

$$\left(\frac{\alpha_{acetic}}{\alpha_{formic}}\right) = \sqrt{\frac{K_{acetic}}{K_{formic}}} = \sqrt{\frac{1.77\times10^{-4}}{1.75\times10^{-5}}} \Rightarrow \boxed{\left(\frac{\alpha_{acetic}}{\alpha_{formic}}\right) \sim 3.1}$$

Assign. Q26)

$$\begin{array}{llll} \text{R:} & HA & \rightleftharpoons & H^+ \quad + \quad A^- \\ \text{Conc. I:} & C & & 0 \qquad\quad 0 \\ \text{Conc. E:} & C(1-\alpha) & & C\alpha \qquad C\alpha \end{array}$$

$$C = \frac{(2\cdot 0.36/180)}{(250\times10^{-3})} \Rightarrow \boxed{C = 1.6\times10^{-2}}$$

$$K_a = \frac{(C\alpha)(C\alpha)}{C(1-\alpha)} \sim C\alpha^2 = \frac{[H^+]^2}{C}$$

$$\Rightarrow pK_a = 2pH + \log(C) \Rightarrow pH = \left(\frac{1}{2}\right)\left[pK_a - \log(C)\right]$$

$$\Rightarrow pH = \left(\frac{1}{2}\right)\left[9 - \log(4) + 4 - \log(16)\right] \Rightarrow \boxed{pH = 5.1}$$

Mixing of Weak Acids —

Let us take V_1 vol. of M_1 M HA_1 acid with diss. const. $= K_{a_1}$.

Similarly take V_2 vol. of M_2 M HA_2 acid with diss. const. $= K_{a_2}$.

Now final molarity $\neq \left(\frac{M_1V_1 + M_2V_2}{V_1+V_2}\right)$ as acids do <u>NOT</u> fully dissociate.

R:	HA_1 +	HA_2 $\rightleftharpoons$	H^+ +	A_1^- +	A_2^-
I:	M_1V_1	M_2V_2	0	0	0
E:	$M_1V_1(1-\alpha_1)$	$M_2V_2(1-\alpha_2)$	$\left(\begin{matrix}M_1V_1\alpha_1 \\ + M_2V_2\alpha_2\end{matrix}\right)$	$M_1V_1\alpha_1$	$M_2V_2\alpha_2$

Now, $K_{a_1} = (\alpha_1)\left(\frac{M_1V_1\alpha_1 + M_2V_2\alpha_2}{V_1+V_2}\right)$

and $K_{a_2} = (\alpha_2)\left(\frac{M_1V_1\alpha_1 + M_2V_2\alpha_2}{V_1+V_2}\right)$

Therefore, $[H^+] = \left(\frac{M_1V_1\alpha_1 + M_2V_2\alpha_2}{V_1+V_2}\right)$

$$= \sqrt{\left(\frac{1}{V_1+V_2}\right)\left[(M_1V_1)(\alpha_1)\left(\frac{M_1V_1\alpha_1 + M_2V_2\alpha_2}{V_1+V_2}\right) + (M_2V_2)(\alpha_2)\left(\frac{M_1V_1\alpha_1 + M_2V_2\alpha_2}{V_1+V_2}\right)\right]}.$$

$$\Rightarrow \boxed{\text{Molarity} = \sqrt{\frac{M_1V_1K_{a_1} + M_2V_2K_{a_2}}{V_1+V_2}}}$$

Self Dissociation of Water —

$$H_2O(l) \rightleftharpoons H^+(aq.) + OH^-(aq.)$$

Water is a very weak ⚡lyte, so it undergoes self diss. to a small extent.

- For pure water, $\boxed{[H_2O] = 55.5\ mol\,L^{-1}}$

Proof : $$M_{H_2O} = \frac{W\,(g)}{\underbrace{\begin{pmatrix}\text{Molar}\\ \text{Mass}\end{pmatrix}}_{\left(\frac{g}{mol}\right)} V\,(L)} = \frac{W\,(g)}{\underbrace{\begin{pmatrix}\text{Molar}\\ \text{Mass}\end{pmatrix}}_{\left(\frac{g}{mol}\right)} \cdot \frac{W\,(g)}{\rho\,(g/L)}} = \frac{\rho - (g/L)}{\begin{pmatrix}\text{Molar}\\ \text{Mass}\end{pmatrix} - (g/mol)}$$

$$\Rightarrow \quad M_{H_2O} = \frac{1000}{18}\ \frac{mol}{L} \quad \Rightarrow \quad \boxed{M_{H_2O} = 55.5\ \frac{mol}{L}}$$

- Now, $$\boxed{K_{eq.} = \frac{[H^+][OH^-]}{[H_2O]}} \rightarrow \boxed{K_{eq.} = \frac{K_w}{55.5}}$$

(Absolute Diss. Const. of water)
(Ionisation Const.)

$$\Rightarrow \quad \boxed{K_w = [H^+][OH^-]}$$

Ionic Product (Net eq. Const.)

★ $\boxed{K_w = 10^{-14}\ mol^2 L^{-2} \text{ at } 25°C}$

- for pure H_2O at any temp,

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

- Since rx^n endothermic $\Rightarrow T\uparrow \Rightarrow K_w\uparrow$

  $\Rightarrow \boxed{K_w \text{ inc. with } T\uparrow}$

- At 25°C, $K_w = 10^{-14}$ & $[H^+] = [OH^-]$

  $\Rightarrow [H^+] = 10^{-7} \Rightarrow \boxed{pH = 7}$

- At 25°C, $K_w = 10^{-14}$ & $K_w = [H^+][OH^-]$

  $-\log(K_w) = -\log[H^+] - \log[OH^-] \Rightarrow \boxed{pH + pOH = 14}$

- Since, $T\uparrow \Rightarrow K_w\uparrow \Rightarrow [H^+]\uparrow \Rightarrow -\log[H^+]\downarrow$

  $\Rightarrow \boxed{pH \text{ dec. with } T\uparrow}$

398

Rel^n b/w Diss. Const. of Weak conj. Acid Base pair

(Acid) (Conj Base)

$$HA\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq.) + A^-\,(aq.)$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

(Conj Base) (Acid)

$$A^-\,(aq.) + H_2O \rightleftharpoons HA\,(aq.) + OH^-\,(aq.)$$

$$K_b = \frac{[HA][OH^-]}{[HA]}$$

Multiplying, $\boxed{K_a K_b = K_w}$

$$\Rightarrow \boxed{pK_a + pK_b = pK_w = \underbrace{14}_{\text{at } 25^\circ C}}$$

☆ Technically, $pH = -\log(\underbrace{a_H}_{\text{activity of H}})$

where $a_H = \underbrace{a_0}_{\text{activity coeff.}}[H^+]$

for dil. sol^n, $a_0 = 1 \Rightarrow a_H = [H^+]$

Q) Calc. pH of following sol^{n}s —

1) 0.0001 M HCl pH = 4

2) 0.0001 N H_2SO_4 pH = 4

☆ 3) 10^{-8} M HCl

A) Since conc. VERY low. We add $[H^+]$ due to water also.

$$[H^+] = [H^+]_{HCl} + [H^+]_{water} = 10^{-8} + \boxed{10^{-7}} \sim 10^{-8}\cdot 11$$

$$\Rightarrow pH = 8 - \log(11) \Rightarrow \boxed{pH \sim 6.9}$$

WRONG!

Now, the above method is SLIGHTLY wrong bcoz we neglected Common Ion Effect

Now, $$HCl \xrightarrow[\text{Complete Diss.}]{} H^+ + Cl^-$$

Let H_2O dissociate to give 'x' $\frac{mol}{L}$ H^+

$$K_w = [H^+][OH^-] \Rightarrow 10^{-14} = (10^{-8}+x)(x)$$

$$\Rightarrow x^2 + (10^{-8})x - (10^{-14}) = 0$$

The roots are $\sim 10^{-7}$, so we can safely use the wrong method.

4) 10^{-9} N $Ca(OH)_2$

A) $pOH = -\log(10^{-9} + 10^{-7}) \sim 6.9 \Rightarrow \boxed{pH = 7.1}$

Q) 500 mL of 10^{-5} M NaOH is mixed with 500 mL of 2.5×10^{-5} M $Ba(OH)_2$. To the resulting sol^n, 99 L of water is added. Calc. pH of final sol^n.

A) $$[OH^-]_{added} = \frac{(1/2)(10^{-5}) + (1/2)(2)(2.5 \times 10^{-5})}{100} = 3 \times 10^{-7} \text{ M}$$

$$[OH^-]_{water} \sim 10^{-7} \Rightarrow [OH^-] = 4 \times 10^{-7} \text{ M}$$

$$\Rightarrow pOH = 7 - 2\log(2) \sim 6.4$$

$$\Rightarrow \boxed{pH \sim 7.6}$$

Assign. Q 24) Let 'x' mol of each.

$$[H^+]_1 = [H^+]_2 \Rightarrow \sqrt{\frac{x(18 \times 10^{-6})}{V_1}} = \sqrt{\frac{x(36 \times 10^{-4})}{V_2}}$$

$$\Rightarrow \boxed{\left(\frac{V_1}{V_2}\right) = \left(\frac{1}{200}\right)}$$

Assign. Q29) $[H^+]_1 = [H^+]_2 \Rightarrow \sqrt{K_a\cdot(0.2)} = 4\times10^{-4}$

$\Rightarrow K_a = 8\times10^{-7}$

$pK_a + pK_b = 14 \Rightarrow pK_b = 14-7+3\log(2)$

$\Rightarrow pK_b = 7+\log(8) \Rightarrow \boxed{K_b = 1.25\times10^{-8}}$

Salt Hydrolysis

Neutralisation Rxn : Acid + Base $\rightleftharpoons$ Salt + Water

Salt Hydrolysis : Salt + Water $\rightleftharpoons$ Acid + Base

---

1) Strong Acid + Strong Base —

Eg : NaCl, KCl, K_2SO_4, ...

★ Salt always diss.

$NaCl + H_2O \rightleftharpoons NaOH + HCl$

$(Na^+ + Cl^-) + (H_2O) \rightleftharpoons (Na^+ + OH^-) + (H^+ + Cl^-)$

★ Strong Ions mein, Weak as it is

Net Rxn : $H_2O \rightleftharpoons H^+ + OH^-$

Net rx^n is unaffected by add^n of this salt.

⇒ This salt does NOT hydrolsis

⇒ Sol^n is neutral.

---

2) Strong Acid + Weak Base –

Eg : NH_4Cl, NH_4NO_3, $CuSO_4$, ...

☆ Strong Ions mein, Weak as it is

☆ Salt always diss.

$$NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl$$

$$(NH_4^+ + Cl^-) + (H_2O) \rightleftharpoons (NH_4OH) + (H^+ + Cl^-)$$

Net Rx^n : $NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$

Net rx^n IS affected ⇒ (Cationic hydrolysis ✓)

⇒ Sol^n is acidic

R :	NH_4^+	$+ H_2O$	$\rightleftharpoons$	NH_4OH	$+ H^+$
Conc. I :	C			0	0
Conc. E :	$C(1-h)$			Ch	Ch

h – Degree of hydrolysis

K_H – Hydrolysis Const.

$$\boxed{K_H} = \frac{[NH_4OH][H^+]}{[NH_4^+]} = \frac{Ch \cdot Ch}{C(1-h)} \sim \boxed{Ch^2}$$

Now, $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

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

Observe, $K_h K_b = [H^+][OH^-] \Rightarrow \boxed{K_h = \left(\frac{K_w}{K_b}\right)}$

Substituting, $\boxed{h = \sqrt{\frac{K_w}{K_b C}}}$

Now, $pH = -\log[H^+] = -\log(Ch)$

$$= -\log\left(\sqrt{\frac{K_w C}{K_b}}\right)$$

$$\Rightarrow \quad pH = \left(\frac{1}{2}\right)\left[pK_w - pK_b - \log(C)\right]$$

$$\Rightarrow \quad \boxed{pH = 7 - \left(\frac{1}{2}\right)\left[pK_b + \log\underbrace{(C)}_{\text{Conc. of Cation}}\right]}$$

3) Weak Acid + Strong Base —

Eg : CH_3COONa, KCN, Na_2CO_3, ...

☆ Salt always diss.

☆ Strong Ions mein Weak as it is

$$CH_3COONa + H_2O \rightleftharpoons CH_3COOH + NaOH$$

$$\hookrightarrow (CH_3COO^- + Na^+) + (H_2O) \rightleftharpoons (CH_3COOH) + (Na^+ + OH^-)$$

Net Rx^n : $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$

Net rx^n is affected $\Rightarrow$ (Anionic hydrolysis ✓)

$\Rightarrow$ Sol^n is Basic

R:	CH_3COO^- + H_2O $\rightleftharpoons$		CH_3COOH +	OH^-
Conc. I:	C		0	0
Conc. E:	$C(1-h)$		Ch	Ch

$$K_h = Ch^2 = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

Now, $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

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

Observe, $K_h K_a = [H^+][OH^-] \Rightarrow \boxed{K_h = \left(\frac{K_w}{K_a}\right)}$

Now, $pOH = -\log[OH^-] = -\log(Ch)$

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

$$\Rightarrow \boxed{pH = 7 + \left(\frac{1}{2}\right)\left[pK_a + \log(C)\right]}$$

Conc. of Anion

---

4) Weak Acid + Weak Base —

Eg: CH_3COONH_4, $(NH_4)_2CO_3$, ...

☆ Salt always diss.

☆ Strong Ions mein, Weak as it is.

$$CH_3COONH_4 + H_2O \rightleftharpoons CH_3COOH + NH_4OH$$

$$(CH_3COO^- + NH_4^+) + (H_2O) \rightleftharpoons (CH_3COOH) + (NH_4OH)$$

Net Rx^n: $CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + NH_4OH$

⇒ (Both cationic & anionic hydrolysis) ✓

R:	CH_3COO^-	$+ NH_4^+$	$+ H_2O \rightleftharpoons$	CH_3COOH	$+ NH_4OH$
				0	0
Conc. I:	C_1	C_2		C_1h	C_2h
Conc. E:	$C_1(1-h)$	$C_2(1-h)$			

$$K_h = \frac{(C_1h)(C_2h)}{C_1(1-h)\,C_2(1-h)} \Rightarrow K_h = h^2$$

$$\Rightarrow \boxed{h = \sqrt{K_h}}$$

① $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

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

② $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

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

Now, $K_h K_a K_b = K_w = [H^+][OH^-]$

$$\Rightarrow \boxed{K_h = \left(\frac{K_w}{K_a K_b}\right)} \quad \Rightarrow \boxed{h = \sqrt{\frac{K_w}{K_a K_b}}}$$

H^+ in rx^n present due to ①,

$$[H^+] = \frac{K_a[CH_3COOH]}{[CH_3COO^-]} = \frac{K_a \cdot C_1 h}{C_1(1-h)}$$

$$\Rightarrow [H^+] = K_a h$$

$$\Rightarrow \boxed{pH = 7 + \left(\frac{1}{2}\right)[pK_a - pK_b]}$$

5) Polyvalent cation/anion –

Eg: Na_2CO_3, $Na_2C_2O_4$, ...

Consider Na_2A, salt of H_2A weak diprotic acid.

Since Na comes from strong base, it remains in ion form $\Rightarrow$ NOT included in net rxn.

Weak acid H_2A has 2 K_{diss}, K_{a_1} & K_{a_2}

$$R_1: \; A^{2-} + H_2O \rightleftharpoons HA^- + OH^-$$

Conc. I: $\quad C \qquad\qquad 0 \qquad 0$

Conc. E: $\quad (C-x) \qquad (x) \qquad (x)$

Since A^{2-} & HA^- are conj. acid base pair,

$$\underbrace{K_{h_1}}_{\text{for } A^{2-}} \cdot \underbrace{K_{a_2}}_{\text{for } H_2A} = K_w \Rightarrow \boxed{K_{h_1} = \left(\frac{K_w}{K_{a_2}}\right)}$$

Now, $\quad R_2: \; HA^- + H_2O \rightleftharpoons H_2A + OH^-$

Conc. I: $\quad x \qquad\qquad 0 \qquad x$

Conc. E: $\quad (x-y) \qquad y \qquad (x+y)$

Since HA^- & H_2A are conj. acid base pair,

$$\underbrace{K_{h_2}}_{\text{for } A^{2-}} \cdot \underbrace{K_{a_1}}_{\text{for } H_2A} = K_w \Rightarrow \boxed{K_{h_2} = \left(\frac{K_w}{K_{a_1}}\right)}$$

At Eq : A^{2-} , HA^- , H_2A , OH^-

Conc : $(C-x)$, $(x-y)$, y , $(x+y)$

Now, $\boxed{K_{h_1} = \frac{(x-y)(x+y)}{(C-x)} = \left(\frac{K_w}{K_{a_2}}\right)}$

$$\boxed{K_{h_2} = \frac{(x+y)y}{(x-y)} = \left(\frac{K_w}{K_{a_1}}\right)}$$

Since $K_{a_1} >> K_{a_2}$, $x >> y$.

$\Rightarrow$ $\boxed{K_{h_1} = \left(\frac{x^2}{C-x}\right) = \left(\frac{K_w}{K_{a_2}}\right)}$, $\boxed{K_{h_2} = y = \left(\frac{K_w}{K_{a_1}}\right)}$

If $C >> x$,

$\boxed{K_{h_1} = \left(\frac{x^2}{C}\right) = \left(\frac{K_w}{K_{a_2}}\right)}$, $\boxed{K_{h_2} = y = \left(\frac{K_w}{K_{a_1}}\right)}$

$[OH^-] = x$, $[HA^-] = x$, $H_2A = y$

Q) $C = 0.01$, $K_{a_2} = 10^{-9}$, $K_{a_1} = 10^{-6}$, $K_{h_1} = ?$
$K_{h_2} = ?$
$[OH^-] = ?$

A) $K_{h_1} = \left(\frac{K_w}{K_{a_2}}\right) = \left(\frac{10^{-14}}{10^{-9}}\right) \Rightarrow \boxed{K_{h_1} = 10^{-5}}$

$K_{h_2} = \left(\frac{K_w}{K_{a_1}}\right) = \left(\frac{10^{-14}}{10^{-6}}\right) \Rightarrow \boxed{K_{h_2} = 10^{-8}}$

$K_{h_1} = \left(\frac{x^2}{c}\right) \Rightarrow x^2 = 10^{-5} \cdot 10^{-2} \Rightarrow \boxed{x \sim 3.3 \times 10^{-4}}$

---

6) Amphiprotic / Amphoteric Salts :—

Eg : $NaHCO_3$, NaH_2PO_4, $NaHSO_4$, ...

R_1 : $HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$

R_2 : $HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$

$$K_b(HCO_3^-) = \left(\frac{K_w}{K_{a_1}}\right) = \frac{[H_2CO_3][OH^-]}{[HCO_3^-]}$$

$$K_{a_2} = \frac{[CO_3^{2-}][H_3O^+]}{[HCO_3^-]}$$

On dividing, $\frac{(K_w/K_{a_1})}{(K_{a_2})} = \frac{[H_2CO_3][OH^-]}{[CO_3^{2-}][H_3O^+]}$

Assuming (very small value of K_{a_2} & $K_b(HCO_3^-)$
$[H_2CO_3] \sim [CO_3^{2-}]$ due to

Hence, $\left(\frac{K_w}{K_{a_1} K_{a_2}}\right) = \frac{[OH^-]}{[H_3O^+]} \Rightarrow [H_3O^+] = \sqrt{K_{a_1} \cdot K_{a_2}}$

$$\Rightarrow \boxed{pH = \left(\frac{1}{2}\right)\left(pK_{a_1} + pK_{a_2}\right)}$$

☆ for ~~salt~~ $M_k H_{(n-k)} A$, salt of $H_n A$ acid,

$$\boxed{pH = \left(\frac{1}{2}\right)\left(pK_{a_k} + pK_{a_{k+1}}\right)}$$

Q) Write exp^n of pH for —

● 1) Na_2H_2A A) $\left(\frac{1}{2}\right)\left(pK_{a_3} + pK_{a_2}\right)$

2) NaH_3A A) $\left(\frac{1}{2}\right)\left(pK_{a_2} + pK_{a_1}\right)$

3) Na_3HA A) $\left(\frac{1}{2}\right)\left(pK_{a_4} + pK_{a_3}\right)$

4) Na_4A A) (Use approach of polyprotic salt)

Q) find the pH of sol^n obtained by mixing 100 mL 0.2 M CH_3COOH & 100mL 0.2 M NaOH.

$K_a (CH_3COOH) = 1.8 \times 10^{-5} \Rightarrow pK_a = 4.74$

A) ☆ Always write rx^n first.

$$R: CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

milli I:	20	20	0
milli E:	0	0	20

$$\boxed{[CH_3COOH] = \frac{20}{200 \cancel{\times 10^{-3}}} = \cancel{200}\ 0.1}$$

Now, CH_3COONa will hydrolyse.

$$pH = 7 + \left(\frac{1}{2}\right)(pK_a + \log C) = 7 + \left(\frac{1}{2}\right)(4.74 - 1)$$

$$\Rightarrow \boxed{pH = 8.87}$$

412

Q) What is pH of 0.5 M aq. NaCN sol^n?

$pK_b(CN^-) = 4.7$

A) $pK_a + pK_b = 14 \Rightarrow \boxed{pK_a = 9.3}$

$pH = 7 + \left(\frac{1}{2}\right)(pK_a + \log(C)) \Rightarrow \boxed{pH = 11.\cancel{0}5}$

Buffer Sol^n

Sol^n which resists change in pH upon add^n of small amt. of strong acid or base.

- Types of Mix. Buffer —

1) Acidic Buffer :— i) Weak Acid + Its basic salt

Eg : $CH_3COOH + CH_3COONa$, $HCN + NaCN$, ...

ii) Weak Acid + Its conj. base

Eg : $CH_3COOH + CH_3COO^-$, $HCO_3^- + CO_3^{2-}$, ...

(Strong base wrt. HCO_3^-

2) Basic Buffer :— i) Weak Base + Its acidic salt.

Eg: $NH_4OH + NH_4Cl$, $CH_3NH_2 + CH_3NH_3Cl$, ...

ii) Weak Base + Its conj. acid.

Eg: $NH_3 + NH_4^+$, $CH_3NH_2 + CH_3NH_3^+$, ...

- Simple Buffer —

Salt of weak acid & weak base.

Eg: CH_3COONH_4, NH_4CN, ...

pH of Acidic Buffer

Let $[CH_3COONa] = C_1$ & $[CH_3COOH] = C_2$

Now,

$$\begin{array}{lccc} R: & CH_3COONa \longrightarrow & CH_3COO^- & + \; Na^+ \\ I: & C_1 & 0 & 0 \\ E: & 0 & C_1 & C_1 \end{array}$$

Also,

$$\begin{array}{lccc} R: & CH_3COOH \rightleftharpoons & CH_3COO^- & + \; H^+ \\ I: & C_2 & C_1 & 0 \\ E: & C_2 - x & C_1 + x & x \end{array}$$

At Eq., $[CH_3COO^-] = C_1 + x$; $[H^+] = x$;
$[CH_3COOH] = C_2 - x$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \Rightarrow \boxed{K_a = \frac{(C_1 + x)\,x}{(C_2 - x)}}$$

$$\text{If } x \ll C_1, C_2 \Rightarrow \boxed{K_a = \left(\frac{C_1}{C_2}\right) x}$$

(Henderson & Hesselwich Eqn) :

$$\boxed{pH = pK_a + \log\left(\frac{\overset{(S)}{[\text{Conj Base}]}}{\underset{(a)}{[\text{Acid}]}}\right)}$$

2

Buffer Action –

i) Add^n of H^+ :

$$\begin{array}{lcccc} & & \text{L.R.} & & \\ R: & CH_3COO^- \;+ & H^+ & \longrightarrow & CH_3COOH \\ I: & S & x & & a \\ \approx E: & S-x & 0 & & a+x \end{array}$$

added with strong acid

$$\boxed{pH = pK_a + \log\left(\frac{S-x}{a+x}\right)}$$

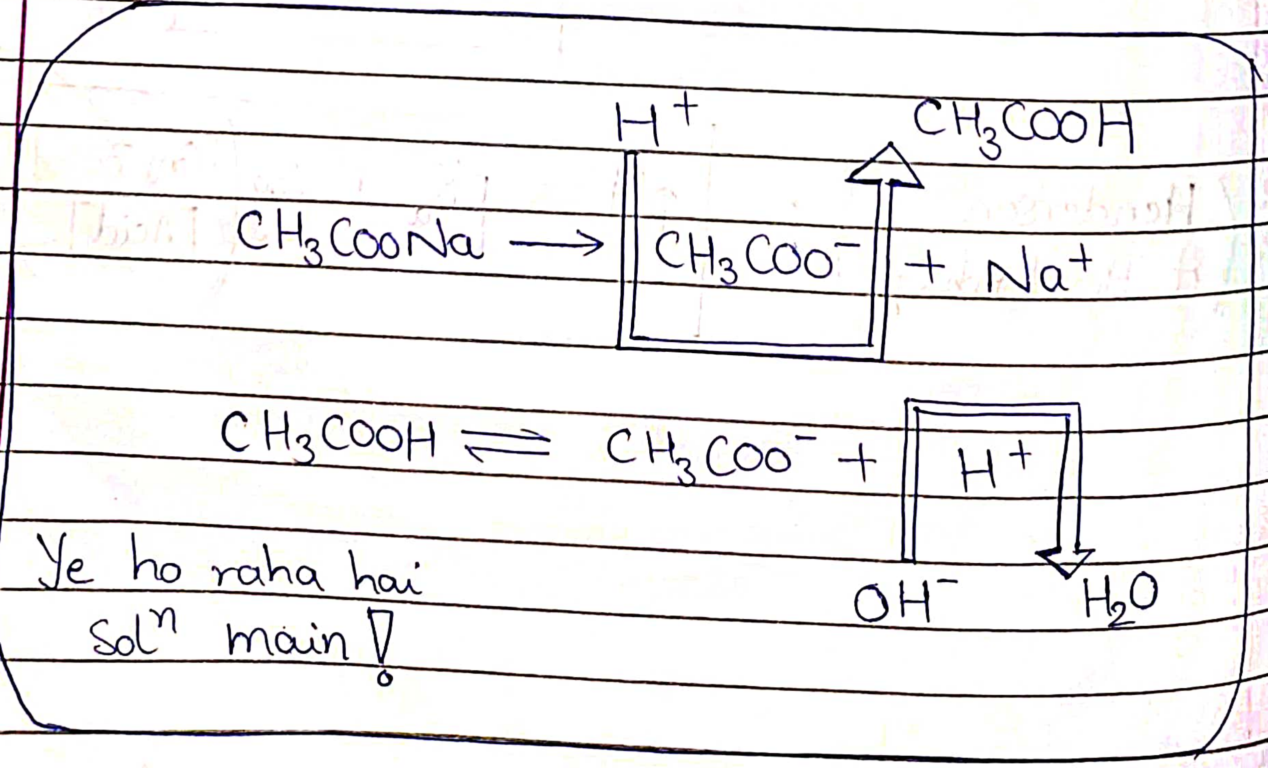
ii) Add^n of OH^- :

$$\begin{array}{lcccc} & & \text{L.R.} & & \\ R: & CH_3COOH \;+ & OH^- & \longrightarrow & CH_3COO^- + H_2O \\ I: & a & x & & S \\ \approx E: & a-x & 0 & & S+x \end{array}$$

added with strong base

$$\boxed{pH = pK_a + \log\left(\frac{S+x}{a-x}\right)}$$

☆



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

H^+ CH_3COOH

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

OH^- H_2O

Ye ho raha hai Sol^n main!

pH of Basic Buffer

Let $[NH_4Cl] = C_1$ & $[NH_4OH] = C_2$.

~~Now~~ At Eq, $[NH_4OH] = (C_2 - x)$; $[OH^-] = x$.
$[NH_4^+] = (C_1 + x)$

$$\Rightarrow \quad \boxed{pOH = pK_b + \log\left(\frac{\overset{(S)}{[\text{Conj. Acid}]}}{\underset{(b)}{[\text{Base}]}}\right)}$$

* For effective buffer solⁿ (industrial application),

Acidic	Basic
$0.1 \leq S/a \leq 10$	$0.1 \leq S/b \leq 10$
$\Rightarrow pH = pK_a \pm 1$	~~pH~~ $pOH = pK_b \pm 1$

* Buffer solⁿ at max. capacity when $S = a$
or $S = b$

* $(\text{Buffer Capacity}) = \left(\dfrac{\text{Change in mol of } H^+/OH^- \text{ per L}}{\Delta pH}\right)$

Q) Calc. pH of sol^n —

1) 100 mL of 0.1 M CH_3COOH + 100 mL of 0.1 M $NaOH$

2) 100 mL of 0.1 M CH_3COOH + 50 mL of 0.1 M $NaOH$

$\left(K_a(CH_3COOH) = 1.8 \times 10^{-5}\right)$

A) 1)

R:	CH_3COOH	+ $NaOH$	$\longrightarrow CH_3COONa$	+ H_2O
milli I:	10	10	0	
milli E:	0	0	10	

$C = \frac{10}{200} \Rightarrow C = 1/20$

Now, CH_3COONa will hydrolyse.

$pH = 7 + \left(\frac{1}{2}\right)\left(4.74 - \log(20)\right) \Rightarrow \boxed{pH = 8.7}$

2)

R:	CH_3COOH	+ $NaOH$	$\longrightarrow CH_3COONa$	+ H_2O
milli I:	10	5	0	
milli E:	5	0	5	

$S = 5/200$, $a = 5/200 \Rightarrow (S/a) = 1$

Buffer formed. $\Rightarrow \boxed{pH = 4.74}$

Q ★ 'Boric Acid + Borax' is a Buffer.

$$\underset{\text{(Borax)}}{Na_2B_4O_7} \xrightarrow[\text{of } H_2O]{\text{in presence}} B(OH)_4^- + \underset{\text{(Boric Acid)}}{B(OH)_3}$$

Its conj base in present
⇒ Buffer!

Q) ★ A solⁿ is made by mixing ~~0.1~~ 0.01 mol each of H_2CO_3, $NaHCO_3$, Na_2CO_3 and NaOH in 100 mL of H_2O. find pH of resulting solⁿ.

$(pK_{a_1}(H_2CO_3) = 6.37$ & $pK_{a_2} = 10.32)$

A) Acid react with strongest Base to neutralise it.

R:	H_2CO_3	+ $NaOH$	⟶ $NaHCO_3$
I:	0.01	0.01	0
E:	0	0	0.01

Now, buffer solⁿ ~~is~~ is present $\underset{(0.02\,mol)}{NaHCO_3} + \underset{(0.01\,mol)}{Na_2CO_3}$

$$\equiv \underset{(0.02\,mol)}{HCO_3^-} + \underset{(0.01\,mol)}{CO_3^{2-}}$$

weak acid
conj. base.

$$pH = pK_{a_2} + \log\left(\frac{S}{a}\right) = 10.32 + \log\left(\frac{0.01}{0.02}\right) \Rightarrow \boxed{pH = 10.02}$$

6

7/9/22

DATE
PAGE

Solubility & Solubility Product

Mainly soluble substance ⇒ Conc. $> 0.1\,M$

Partially soluble substance ⇒ $0.01\,M <$ Conc. $< 0.1\,M$

Sparingly soluble substance ⇒ Conc. $< 0.01\,M$

Eg - $AgCl$, $BaSO_4$, ...

Solubility - Max. no. of mol. of salt which can be dissolved in solⁿ at fix. temp.

C-1 : i) $AgBr(s)$ in pure water.

$$R:\ AgBr(s) \rightleftharpoons Ag^+(aq.) + Br^-(aq.)$$

Conc I: 0 0

Conc E: S S

$$\boxed{K_{sp} = S^2} = [Ag^+][Br^-] \Rightarrow \boxed{S = \sqrt{K_{sp}}}$$

K_{sp} - Solubility Product

S - Solubility

ii) R: $Ag_2CrO_4(s) \rightleftharpoons 2Ag^+ + CrO_4^{2-}$

Conc I: $0 \quad 0$
Conc E: $2S \quad S$

$K_{sp} = [Ag^+]^2[CrO_4^{2-}] = (2S)^2 S \Rightarrow \boxed{K_{sp} = 4S^3}$

$\Rightarrow \boxed{S = \left(\frac{K_{sp}}{4}\right)^{1/3}}$

C-2: If strong ↯lyte with common ion already present.

Eg - i) $AgBr(s) + HBr$

R: $AgBr \rightleftharpoons Ag^+ + Br^-$

Conc I: $0 \quad C$
Conc E: $S \quad C+S$

$K_{sp} = [Ag^+][Br^-] = S(S+C) \Rightarrow \boxed{K_{sp} \sim SC}$

$\Rightarrow \boxed{S \sim K_{sp}/C}$

ii) R: $PbCl_2$ ~~$+ HCl$~~ $\rightleftharpoons Pb + 2Cl^-$

($PbCl_2 + HCl$)

Conc I: $0 \quad C$
Conc E: $S \quad 2S+C$

$K_{sp} = S(2S+C)^2 \Rightarrow \boxed{K_{sp} \sim SC^2} \Rightarrow \boxed{S = \cancel{\sqrt{\frac{K_{sp}}{C}}}}$ (K_{sp}/C^2)

Q) Find K_{sp} of $Li_3Na_3(AlF_6)_2$.

A) R: $Li_3Na_3(AlF_6)_2 \rightleftharpoons 3Li^+ + 3Na^+ + 2AlF_6^{-3}$

Conc I: $0 \quad 0 \quad 0$

Conc E: $3S \quad 3S \quad 2S$

$$K_{sp} = (3S)^3(3S)^3(2S)^2 \Rightarrow \boxed{K_{sp} = 3^6 \cdot 2^2 S^8}$$

☆ Q) At 25°C, K_{sp} for $PbBr_2$ is 8×10^{-5}. If salt is 80% dissociated, what is solubility of $PbBr_2$?

A) S = Max. no. of mol. dissolved.

In this case $(0.8)S$ mol of salt dissolves.

R: $PbBr_2 \rightleftharpoons Pb^{2+} + 2Br^-$

Conc I: $0 \quad 0$

Conc E: $(0.8)S \quad (1.6)S$

$$K_{sp} = [0.8S][1.6S]^2 = 8 \times 10^{-5} \Rightarrow \boxed{S = \left(\frac{10^{-4}}{2.56}\right)^{1/3}}$$

i) Precipitate formation —

Eg : $AgBr(s) \rightleftharpoons Ag^+(aq.) + Br^-(aq.)$

$\boxed{Q = [Ag^+][Br^-]}$ at ANY pt. of time

Ionic product

$Q < K_{sp}$: Ppt. NOT form
$Q = K_{sp}$: Eq. Condt.
$Q > K_{sp}$: Ppt. will form

Q) ~~The ppt. of CaF_2 ($K_{sp} = 1.7 \times 10^{-10}$) obtained when equal vol. of following ions mixed~~

ii) Simultaneous Solubility —

($Salt_1 + Salt_2$) where both have a common ion.

Eg: ($BaSO_4 + SrSO_4$)

R: $BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$
Conc E: $x \quad x$

R: $SrSO_4 \rightleftharpoons Sr^{2+} + SO_4^{2-}$
Conc E: $y \quad y$

At. Eq, $[Ba^{2+}] = x$
$[Sr^{2+}] = y$
$[SO_4^{2-}] = (x+y)$

$K_{sp} = x(x+y)$ $\qquad$ $K'_{sp} = y(x+y)$

$$\Rightarrow \boxed{[SO_4^{2-}] = \sqrt{K_{sp} + K'_{sp}}} \quad \text{\&} \quad \boxed{\left(\frac{K_{sp}}{K'_{sp}}\right) = \left(\frac{x}{y}\right)}$$

---

iii) <u>Solubility of AgCN in pure water</u> —

CN^- being conj. base of HCN (weak acid), it hydrolyses.

$$\begin{array}{llcc} R: & AgCN \rightleftharpoons & Ag^+ & + \; CN^- \\ \text{Conc } E: & & x & x \end{array}$$

$$\begin{array}{llcc} R: & CN^- + H_2O \rightleftharpoons & HCN & + \; OH^- \\ \text{Conc } E: & (x-y) & y & y \end{array}$$

At. Eq, $[CN^-] = (x-y)$
$[HCN] = y$

$K_{sp} = \cancel{x^2}\; x(x-y)$, $\qquad K_h = \left(\frac{y^2}{x-y}\right)$

$$\Rightarrow \boxed{K_{sp} \cdot K_h = xy^2}$$

- If Basic medium intro. ⇒ Solubily of AgCN dec.

- If Acidic medium intro. ⇒ Solubility of AgCN inc.

---

iv) Solubility of AgCl in aq. NH_3 —

Assume init. conc. of $NH_3 = Z$.

$$\text{R}: AgCl \rightleftharpoons Ag^+ + Cl^-$$
$$\text{Conc E}: \qquad\qquad x \qquad x$$

Ag^+ reacts with NH_3 to form $\underbrace{\text{Tollen's Reagent}}$

$$\text{R}: Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)]^+$$
$$\text{Conc E}: (x-y) \quad (z-2y) \qquad y$$

Since product very stable $(z-2y) \sim (z-2x)$

At Eq; $[Ag^+] = (x-y)$, $[NH_3] = (z-2x)$, $[(Ag(NH_3))^+] = y \sim x$
$[Cl^-] = x$

$$K_{sp} = x(x-y) \quad ; \quad K_f = \frac{x}{(x-y)(z-2\underset{x}{\cancel{y}})^2}$$

$$\Rightarrow \boxed{K_{sp} \cdot K_f = \frac{x^2}{(z-2x)^2}}$$

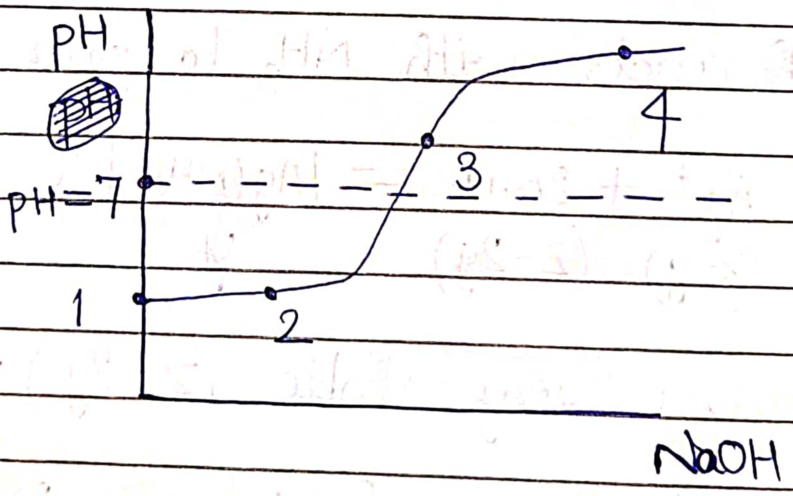
Acid Base Titration

1) Weak Acid + Strong Base :

Beaker	Burette
CH_3COOH	NaOH

We have to check 4 pts —

1) Initial (Acidic Sol^n)
2) Before Eq. pt. (Acidic Buffer)
3) At Eq. pt. (Salt Hydrolysis)
4) After Eq. pt. (Basic Sol^n)



Suitable Indicator : Phenolpthalein

2) Strong Acid + Weak Base :

Beaker	Burette
NH_4OH	HCl

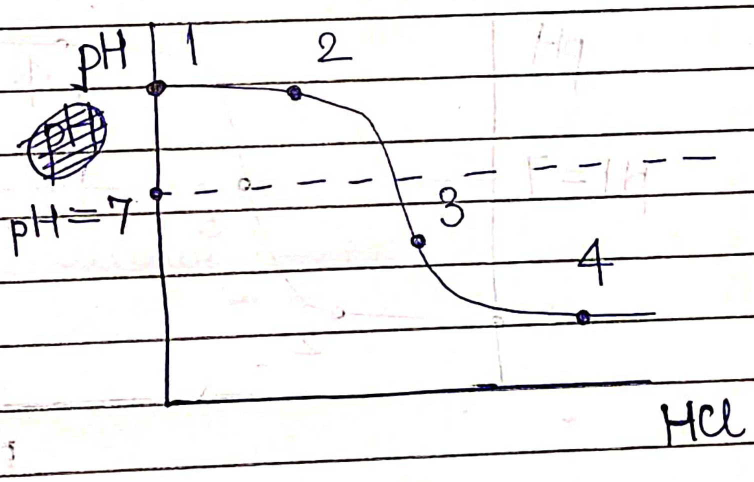
We have to check 4 pts —

1) Initial (Basic Solⁿ)

2) Before Eq. pt. (Basic Buffer)

3) At Eq. pt. (Salt Hydrolysis)

4) After Eq. pt. (Acidic Solⁿ)



Suitable Indicator : Methyl Orange

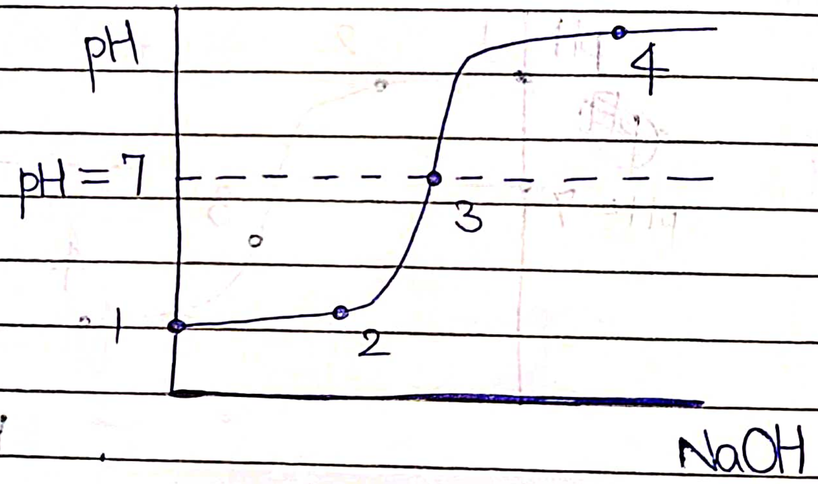
3) Strong Acid + Strong Base :

Beaker	Burette
HCl	NaOH

We have to check 4 pts —

1) Initial (Acidic Solⁿ) 2) Before Eq. Pt. (Acidic Solⁿ)

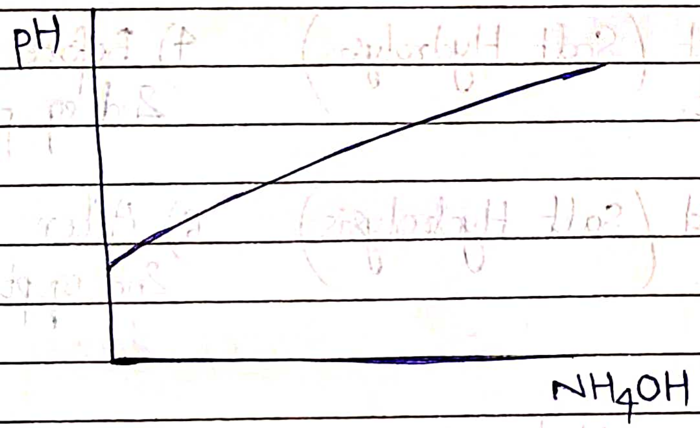
3) At Eq. Pt. (Neutral) 4) After Eq. Pt. (Basic Solⁿ)



Suitable Indicator : Phenolpthalein & Methyl Orange

4) Weak Acid + Weak Base :

Beaker	Burette
CH_3COOH	NH_4OH



Suitable Indicator : No indicator suitable

☆ For determining suitable indicator, eq. pt. of titration should lie in the working range of indicator.

☆ For indicator to work, pH vs Titrant should have steep portion so that indicator changes color quickly.

16

DATE
PAGE

★ Q) Plot pH vs NaOH graph of $H_2CO_3 + NaOH$ (NaOH added dropwise)

A) 1) Initial (Acidic Solⁿ)

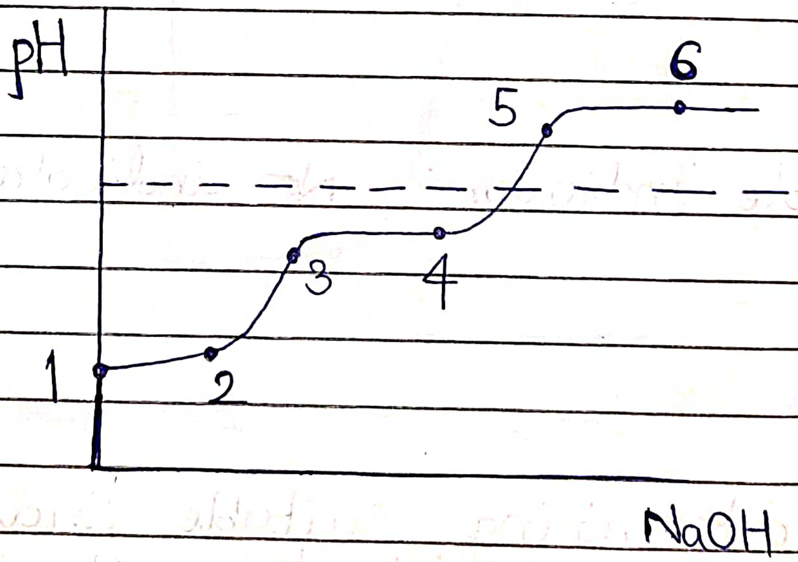
2) Before 1st eq. pt. (Acidic Buffer)

3) At 1st eq. pt. (Salt Hydrolysis)

4) Before 2nd eq. pt. (Acidic Buffer)

5) At 2nd eq. pt. (Salt Hydrolysis)

6) After 2nd eq. pt. (Basic Solⁿ)



Indicators

They are either weak organic acids or weak organic bases.

They give idea about completion of rx^n in titration by changing color.

1) Phenolphthalein (HPh) –

It is weak ~~organic~~ acid.

$$HPh \rightleftharpoons H^+ + Ph^-$$

HPh	Ph^-
Acidic	Basic
Unionised form (UIF)	Ionised form (IF)
Colorless	Pink

Working Range : 8.2 to 10

2) Methyl Orange (MeOH) –

It is weak organic base.

$$MeOH \rightleftharpoons Me^+ + OH^-$$

MeOH	Me^+
Basic	Acidic
UIF	IF
Yellow	Red

Working Range : 3.2 to 4.8

3) General Acidic Indicator (HIn) –

$$HIn \rightleftharpoons H^+ + In^-$$

$$K_{In} = \frac{[H^+][In^-]}{[HIn]} \Rightarrow \boxed{pH = pK_{In} + \log\left(\frac{[In^-]}{[HIn]}\right)}$$

4) General Basic Indicator (InOH) –

$$\boxed{pOH = pK_{In} + \log\left(\frac{[In^+]}{[InOH]}\right)}$$

Color — Working Range

(due to If)	(Transition)	(due to UIf)
	0.1 10	
$\left(\frac{UIf}{If}\right) \leq 0.1$	$0.1 \leq \left(\frac{UIf}{If}\right) < 10$	$\left(\frac{UIf}{If}\right) \geq 10$

Working range for Acidic In. : $pK_{In} - 1 \leq pH \leq pK_{In} + 1$

Working range for Basic In. : $pK_{In} - 1 \leq pOH \leq pK_{In} + 1$

Q) Find range of most suitable indicator to be used for titration of NaX (0.1 M, 10mL) with 0.1 M HCl.

$(K_b(X^-) = 10^{-6})$.

A)

R:	NaX	+ HCl	$\rightleftharpoons$ NaCl	+ HX
milli I:	1	1	0	0
milli E:	0	0	1	1

$\{V = 10 + 10\}$ $\qquad pH = (pK_a - \log(C))/2$

$$\Rightarrow pH = \frac{(14-6) - \log(10^{-1}/2)}{2} \Rightarrow pH = 4.65$$

$$\Rightarrow \boxed{pK_{In} \in [3.65, 5.65]}$$

DATE
PAGE

Imp. Pts. —

1) Salt of Strong Acid & Strong Base containing acidic H is Acidic.

Eg: $KHSO_4$, $NaHSO_4$, ...