Acid-Base Titrations!

→ involve reaction between acid and base to form salt and water.

→ involves neutralization reactions.

→ The pH of the solution changes during the course of titration.

→ The end-point detection in acid-base titration is based upon abrupt change in pH that occurs in the vicinity of the equivalence point.

→ The pH varies depending upon the titrand and titrant.

→ The selection of suitable indicator requires knowledge of pH changes that occur during the course of titration.

→ The plot of pH v/s volume of titrant is called as Neutralization - Titration Curve.

* Types of Acid-Base Titration (Based on strength of acid and Base):-

1. Strong Acid - Strong Base Titrations:- (both ions)

$$H^+ + {}^-OH \longrightarrow H_2O$$

2. Strong Acid - Weak Base Titrations:- (ion and molecule).

$$\underline{H^+} + \underline{NH_4OH} \rightleftharpoons H_2O + {}^+NH_4$$

3. Weak Acid - Strong Base Titrations:- (molecule and ion).

$$\underline{CH_3COOH} + \underline{{}^-OH} \rightleftharpoons CH_3COO^- + H_2O.$$

4. Weak Acid - Weak Base Titrations:- (both molecules)

$$\underline{CH_3COOH} + \underline{NH_4OH} \rightleftharpoons CH_3COO^- + \overset{+}{N}H_4 + H_2O$$

5. Polybasic acid - Strong Base Titrations:-

Basicity - no. of H^+

Polybasic - acids that can be hydrolyzed to give more than one proton.

$$H_2A + {}^-OH \rightleftharpoons HA^- + H_2O$$

$$HA^- + {}^-OH \rightleftharpoons A^{2-} + H_2O.$$

Ⓘ Strong Acid - Strong Base Titrations:-

50 cm^3 of strong acid v/s 0.1 M strong base

Titrant :- strong base   titrand :- strong acid.

a) Before equivalence point:-

Volume of 0.1 M NaOH added = V cm^3

Volume of 0.1 M NaOH added = V cm^3

Volume of acid neutralized = V cm^3

Volume of unneutralized acid = $(50 - V)$ cm^3

V $50 - V$

$M_1V_1 = M_2\underline{V_2}$

$$\underline{[HCl]} \times \underline{(50+V)} = \underline{0.1} \times \underline{(50-V)}$$

$$[HCl] = \frac{0.1 \times (50-V)}{(50+V)}$$

$$-\log[HCl] = -\log 0.1 - \log\frac{(50-V)}{(50+V)}$$

$$\boxed{pH = 1 + \log\frac{(50+V)}{(50-V)}}$$

b) At equivalence point:-

pH at equivalence point will be 7 as titrant and titrand are strong acid and strong base.

c) Beyond equivalence point:-

volume of base added = V cm^3.

Base remaining in excess = $(V-50)$ cm^3

① $V = \underline{52}$

$\underline{V-50}$. ②

② $V = 80$ 30

$80 - 50 = 30$

$$\underline{[^-OH]} \times \underline{(50+V)} = \underline{0.1} \times \underline{(V-50)}$$

$$[^-OH] = \frac{0.1 \times (V-50)}{(50+V)}$$

$$-\log[^-OH] = -\log 0.1 - \log\frac{(V-50)}{(V+50)}$$

$$\boxed{pOH = 1 + \log\frac{(V+50)}{(V-50)}}$$

$$\left\{\begin{aligned} &\log(ab) = \log a + \log b. \\ &\log\left(\frac{a}{b}\right) = \log a - \log b. \\ &\log\left(\frac{a}{b}\right) = -\log\left(\frac{b}{a}\right) \end{aligned}\right\}$$

$pH = 14 - pOH$

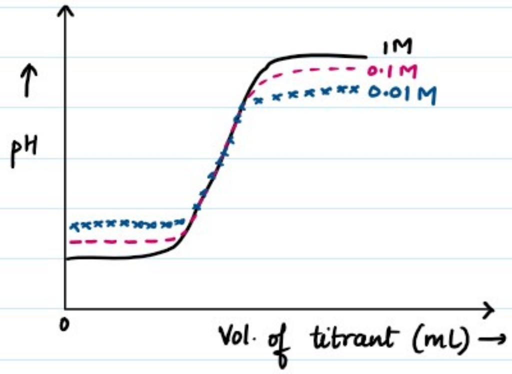
There is a abrupt change in pH from 4 to 10.

methyl orange :- (acidic)

phenolphthalein :- (basic)

↑

phenolphthalein :- (basic)



STRONG ACID - STRONG BASE

2) Strong Acid - Weak Base Titrations :-

Titrant = Strong Acid

Titrand = Weak Base (ammonia, ammonium hydroxide, aniline)
NH_3 NH_4OH

$10\ cm^3$ 0.1 M WB v/s 0.1 M SA

$$HCl + NH_4OH \rightleftharpoons H_2O + \overset{+}{N}H_4 + Cl^-.$$

a) At the beginning :-

$$\begin{array}{ccccc} NH_4OH & \rightleftharpoons & \overset{+}{N}H_4 & + & \underline{^-OH} \\ C & & 0 & & 0 \\ (1-\alpha)c & & \alpha C & & \underline{\underline{\alpha C}} \end{array}$$

α = extent of dissociation.

$$K_b = \text{dissociation constant of base} = \frac{[NH_4^+][^-OH]}{[NH_4OH]}$$

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

But since α is small.

$$K_b = \alpha^2 C$$

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

$$\boxed{[^-OH] = \alpha C = \sqrt{\frac{K_b}{C}} \cdot C = \sqrt{K_b C}}$$

b) Some acid is added :- eg. $2\ cm^3$.

volume of acid added = $2\ cm^3$

b) Some acid is added :- eg. 2 cm^3.

volume of acid added = 2 cm^3
volume of salt formed = 2 cm^3
volume of unneutralized base = 8 cm^3
Total volume = 12 cm^3

$\rightarrow$ $[salt] \times 12\ cm^3 = 0.1 \times 2 cm^3$

$$[salt] = \frac{0.1 \times 2}{12}$$

$\rightarrow$ $[base] \times 12\ cm^3 = 0.1 \times 8\ cm^3$

$$[base] = \frac{0.1 \times 8}{12}$$

system :- NH_4OH + NH_4Cl. } **Basic Buffer System** .
WB   salt of WB

$$\boxed{pH = pK_w - pK_b - \log \frac{[salt]}{[base]}}$$

$pK_w = 14$.

c) At equivalence point :- (acidic)

volume of acid added = 10 cm^3
volume of salt added = 10 cm^3
total volume of sol^n = 20 cm^3

$[salt] \times 20 = 0.1 \times 10$

$$[salt] = \frac{0.1 \times 10}{20}$$

main Rxn :- $NH_4OH + HCl \rightleftharpoons \underline{\underline{NH_4^+}} + Cl^- + H_2O$

h = extent of hydrolysis

$\underline{NH_4^+} + H_2O \rightleftharpoons NH_4OH + H^+$

$\hookrightarrow$ K_h = hydrolysis constant = $\frac{[NH_4OH][H^+]}{[NH_4^+][H_2O]}$

$$\boxed{\begin{array}{lll} C & 0 & 0 \\ C-hC = C(1-h) & hC & hC \end{array}}$$

$NH_4OH \rightleftharpoons NH_4^+ + {}^-OH$.

$\hookrightarrow$ K_b = dissociation constant of base = $\frac{[NH_4^+][{}^-OH]}{[NH_4OH]}$

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

$$= \frac{\;\frac{[H^+][{}^-OH]}{[H_2O]}\;}{\frac{[NH_4^+][{}^-OH]}{[NH_4OH]}}.$$

$$= \frac{[H^+][\cancel{{}^-OH}]}{[H_2O]} \times \frac{[NH_4OH]}{\underline{[NH_4^+]}[\cancel{{}^-OH}]}$$

$H_2O \rightleftharpoons H^+ + {}^-OH$.

$[H_2O]$ $[NH_4^+][^-OH]$

$H_2O \rightleftharpoons H^+ + {}^-OH$.

Kw = dissociation constant of water = $\frac{[H^+][^-OH]}{[H_2O]}$

$K_h = \frac{[H^+][NH_4OH]}{[NH_4^+][H_2O]}$

$$K_h = \frac{[H^+][NH_4OH]}{[NH_4^+][H_2O]}$$

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

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

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

$$K_h = h^2c$$

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

$$[H^+] = hc$$

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

$$= \sqrt{K_h c}$$

$$= \sqrt{\frac{K_w}{K_b} \cdot c}$$ — (using 2)

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

$$\boxed{pH = \frac{1}{2}pK_w - \frac{1}{2}pK_b - \frac{1}{2}\log c}$$ **acidic**

d) Beyond equivalence point :-

no. of moles of acid in solⁿ = no. of moles of excess acid.

$[H^+] \times$ Total Vol. $= 0.1 \times V_{exc}$.

$$[H^+] = \frac{0.1 \times V}{(20+V)}$$

$$-\log[H^+] = -\log 0.1 + \log\frac{(V+20)}{V}$$

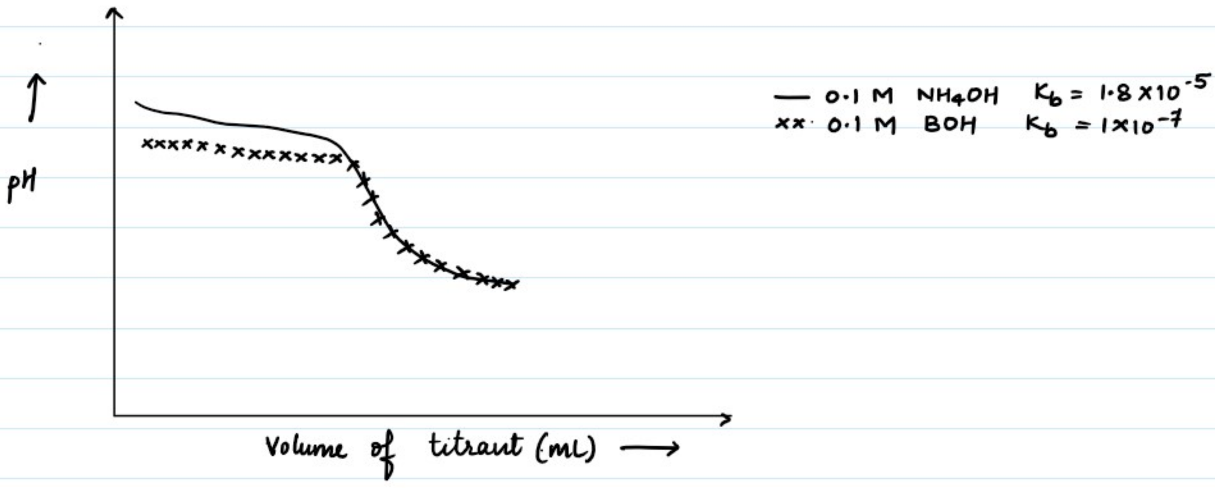
$$pH = 1 + \log \frac{(V+20)}{V}$$ Very Acidic !!!

pH at equivalence point is $\underline{\underline{5.3}}$.

methyl orange = 3.1 to 4.4

✓ bromocresol green = 3.8 to 5.4

✓ methyl red = 4.4 to 6.2



3. Weak acid v/s Strong Base Titrations :-

Titrant - Strong Base

Titrand - Weak acid.

10 cm^3 0.1 M CH_3COOH v/s 0.1 M NaOH.

$$CH_3COOH + NaOH \rightleftharpoons CH_3COO^- + Na^+ + H_2O$$

a) At the beginning :-

	$CH_3COOH \rightleftharpoons$	CH_3COO^-	$+ H^+$
$t=0$	C	0	0
$t=t_1$	$C-\alpha C$ $(1-\alpha)C$	$\underline{\underline{\alpha C}}$	$\underline{\underline{\alpha C}}$

α = extent of dissociation

$$K_a = \text{dissociation constant of acid} = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$K_a = \frac{\alpha C \cdot \alpha C}{(1-\alpha)C}$$

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

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

$$K_a = \alpha^2 C$$ (α is small, hence can be neglected)

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

$$[H^+] = \alpha C$$
$$= \sqrt{\frac{K_a}{C}} \cdot C$$
$$[H^+] = \sqrt{K_a C}$$

Taking negative logarithm,

$$-\log[H^+] = -\frac{1}{2}\log K_a - \frac{1}{2}\log C$$

$$\boxed{pH = pK_a - \frac{1}{2}\log C}$$

b) Some base is added :- eg. $2\,cm^3$.

volume of base added $= 2\,cm^3$

volume of acid neutralized $= 2\,cm^3$

volume of salt formed $= 2\,cm^3$

volume of unneutralized acid $= 8\,cm^3$

Total volume of solution $= 12\,cm^3$

→ $[salt] \times \underline{12}\,cm^3 = 0.1\,M \times \underline{2}\,cm^3$

$$[salt] = \frac{0.1 \times 2}{12}$$

→ $[acid] \times 12\,cm^3 = 0.1\,M \times 8\,cm^3$.

$$[acid] = \frac{0.1 \times 8}{12}$$

CH_3COOH ⟶ weak acid

$CH_3COO^- Na^+$ ⟶ salt of weak acid

} Acidic Buffer System.

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

c) At equivalence point :- (~10 mL of base is added)   ~ **BASIC**

all acid is neutralized, salt is formed.

volume of base added = 10 cm^3

volume of acid neutralized = 10 cm^3

volume of salt formed = 10 cm^3

Total volume of sol^n = 20 cm^3

$$[salt] \times 20\,cm^3 = 0.1\,M \times 10\,cm^3$$

$$[salt] = \frac{0.1\,M \times 10\,cm^3}{20\,cm^3}$$

ain Rxn. → $CH_3COOH + NaOH \rightleftharpoons \underline{\underline{CH_3COO^-}} + Na^+ + H_2O$.

① $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + \underline{OH^-}$

	CH_3COO^-	H_2O	CH_3COOH	OH^-
t=0	C	–	0	0
t=t,	(1-h)C		hC	$\underline{hC}$

K_h = hydrolysis constant of acid.

h = extent of hydrolysis.

✓ K_h = hydrolysis constant $= \frac{[CH_3COOH][^-OH]}{[CH_3COO^-][H_2O]}$ ✓

$$K_h = \frac{hC \cdot hC}{(1-h)C} = \frac{h^2C^2}{(1-h)C} = \frac{h^2C}{(1-h)}$$

$$K_h = h^2C$$

$$h = \sqrt{\frac{K_h}{C}} \quad — ①$$

$$K_h = \frac{K_w}{K_a}. \quad — ②$$

② $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

K_a = dissociation of weak acid $= \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$ ✓

$$= \frac{\frac{[H^+][^-OH]}{H_2O}}{\frac{[CH_3COO^-][H^+]}{[CH_3COOH]}}$$

$$= \frac{\cancel{[H^+]}[^-OH][CH_3COOH]}{(H_2O][CH_3COO^-]\cancel{[H^+]}}$$

③ $H_2O \rightleftharpoons H^+ + {}^-OH$

K_w = dissociation constant of water $= \frac{[H^+][^-OH]}{[H_2O]}$

$$K_h = \frac{[CH_3COOH][^-OH]}{[H_2O][CH_3COO^-]}$$

$$K_h = \frac{K_w}{K_a}$$

m

$[OH] = hC$

$pK_w = 14$.

$[OH] = hC$

$= \sqrt{\frac{K_h}{C}} \cdot C$ (using 1).

$\underline{\underline{pK_w = 14}}$.

$= \sqrt{K_h C}$

$= \sqrt{\frac{K_w C}{K_a}}$ (using 2) — ③

aking -ve log,

$-\log[OH] = -\frac{1}{2}\log K_w + \frac{1}{2}\log K_a - \frac{1}{2}\log C$

$$\boxed{pOH = \frac{1}{2}pK_w - \frac{1}{2}pK_a - \frac{1}{2}\log C}$$ ✓

$[H^+][OH] = K_w$.

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

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

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

$$\boxed{pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a + \frac{1}{2}\log C}$$ ✓

ⓓ Beyond equivalence point :- (extra base is added).

volume of base = V

Total volume = (20+V)

$[base] \times (20+V) = 0.1 \times V$

$[base] = \frac{0.1 \times V}{(20+V)}$

T

$-\log[OH] = -\log 0.1 + \log\frac{(20+V)}{(V)}$

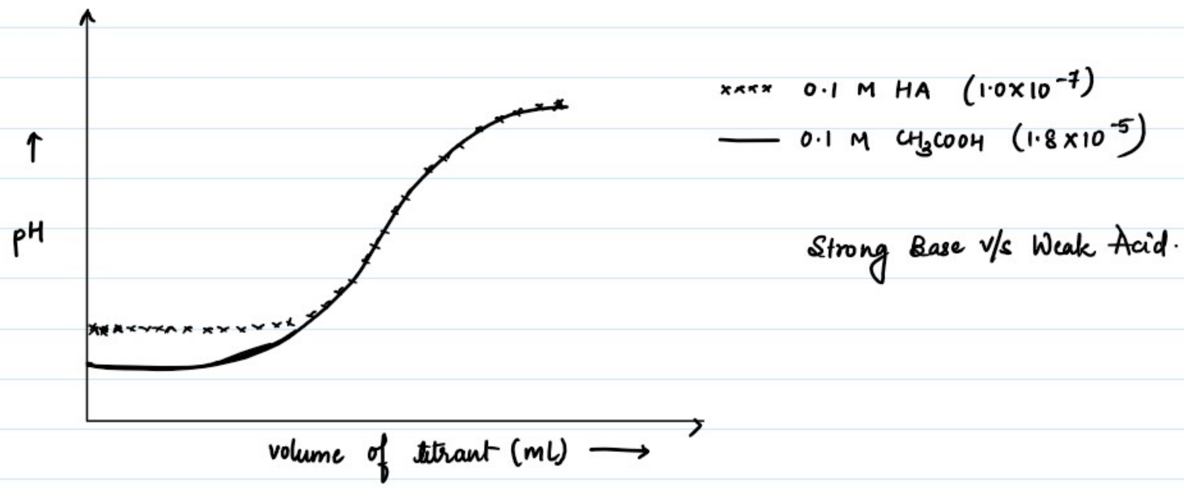
$$\boxed{pOH = 1 + \log\frac{(20+V)}{V}}$$

· pH at equivalence point is $\underline{8.7}$.

↳ phenolphthalein = 8.3 to 10 ✓

↳ thymolphthalein = 9.3 to 10.5

- phenolphthalein = 8.3 to 10 ✓
- thymolphthalein = 9.3 to 10.5
- thymol blue = 8.0 to 9.6 ✓



Strong Base v/s Weak Acid.

④ Weak Acid - Weak Base Titrations :-

10 cm^3 0.1 M CH_3COOH v/s 0.1 M NH_4OH

$$NH_4OH + CH_3COOH \rightleftharpoons CH_3COO^- + NH_4^+ + H_2O.$$

Titrant – Base } Usually.
Titrand – Acid }

ⓐ At the begining :-

only AcOH is present.

$$\boxed{pH = pKa - \frac{1}{2}\log C}$$

ⓑ Some base is added.

cal flask { weak acid } Acidic Buffer System.
{ salt of weak acid }

$$\boxed{pH = pKa + \log\frac{[salt]}{[acid]}}$$

ⓒ At equivalence point :-

all acid is neutralized and salt is formed.

all acid is neutralized and salt is formed.

volume of base added = 10 cm^3

volume of salt formed = 10 cm^3.

Total volume of sol^n = 20 cm^3.

$$[salt] \times 20 = 0.1 \times 10$$

$$[salt] = \frac{0.1 \times 10}{20}$$

main Rxn:- $CH_3COOH + NH_4OH \rightleftharpoons CH_3COO^- + NH_4^+ + H_2O$.

①

$$\begin{array}{ccccccc} CH_3COO^- & + & NH_4^+ & + & H_2O & \rightleftharpoons & CH_3COOH & + & NH_4OH \\ c & & c & & - & & 0 & & 0 \\ \underline{\underline{(1-h)c}} & & (1-h)c & & & & hc & & hc \end{array}$$

Conc

K_h = hydrolysis constant of salt = $\frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]}$

$$= \frac{hc \cdot hc}{(1-h)c\,(1-h)c}$$

$$= \frac{h^2 \cancel{c^2}}{(1-h)^2 \cancel{c^2}}$$

$$K_h = \frac{h^2}{(1-h)^2}$$

$K_h = h^2$ (since 'h' i small)

$h = \sqrt{K_h}$ ——①

②

$$\begin{array}{ccccc} CH_3COOH & \rightleftharpoons & CH_3COO^- & + & H^+ \\ c & & 0 & & 0 \\ (1-\alpha)c & & \alpha c & & \alpha c \end{array}$$

K_a = dissociation constant for acid = $\frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$.

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

$$= K_a \cdot \frac{hc}{(1-h)c}$$

$$= K_a \cdot \frac{h}{(1-h)}$$

$[H^+] = K_a\sqrt{K_h}$. — ② (using 1)

③ $NH_4OH \rightleftharpoons NH_4^+ + {}^-OH$.

K_b = dissociation constant of base = $\frac{[NH_4^+][{}^-OH]}{[NH_4OH]}$. — ③

④ $H_2O \rightleftharpoons H^+ + {}^-OH$.

K_w = dissociation constant for water = $\frac{[H^+][{}^-OH]}{[H_2O]}$ — ④

$$K_h = \frac{K_w}{K_a K_b} = K_w \times \frac{1}{K_a} \times \frac{1}{K_b}. \quad — ⑤$$

$$K_h = \frac{\cancel{[H^+]}\cancel{[{}^-OH]}}{[H_2O]} \times \frac{[CH_3COOH]}{[CH_3COO^-]\cancel{[H^+]}} \times \frac{[NH_4OH]}{[NH_4^+]\cancel{[{}^-OH]}}$$

$$K_h = \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]}$$

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

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

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

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

$$\boxed{pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a - \frac{1}{2}pK_b.}$$

d) Beyond equivalence point :-

Total volume of sol^n = (20+V) V = Vol. of extra base.

d) Beyond equivalence point :-

Total volume of $sol^n = (20+V)$ V = Vol. of extra base.

$$[Base] \times (20+V) = 0.1 \times V$$

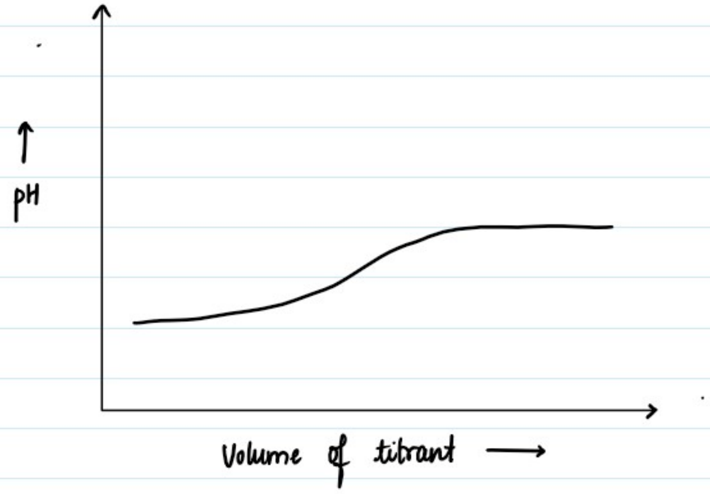
$$[Base] = \frac{0.1 \times V}{(20+V)}$$

$$-\log[Base] = -\log 0.1 + \log\frac{(20+V)}{V}$$

$$\boxed{pOH = 1 + \log\left(\frac{20+V}{V}\right)}$$

pH at equivalence point varies.

$pH = 7$ $K_a = K_b$
$pH < 7$ $K_a > K_b$
$pH > 7$ $K_a < K_b$



- pH change is gradual. No sudden change in pH. hence no sharp point.
- Hence mixed indicator is used.
- However, visual indicator should be avoided.

* **Polybasic Acid v/s Strong Base :-**

- polybasic acid reacts with water in dissociation reaction yielding H^+/H_3O^+.

$$H_2A + H_2O \rightleftharpoons HA^- + H_3O^+$$

$HA^- + H_2O \longrightarrow A^{2-} + H_3O^+$ ⟶ Rxn will be suppressed.

$$H_2A + H_2O \rightleftharpoons HA^- + H_3O^+$$

$$HA^- + H_2O \rightleftharpoons A^{2-} + \underline{\underline{H_3O^+}} \quad \rightarrow \text{Rxn will be suppressed.}$$

→ such substances are not strong electrolytes and extent of dissociation is less than 100%

→ each step ⟶ considered as primary stage is suppressed by H_3O^+ from the previous stage.

∴ Polybasic Acids ⟹ Represents dissociation of weak acid.

→ no. of steps of acid depends upon nature of polybasic acid.

ⓐ Dibasic Acid :-

$$H_2A \rightleftharpoons H_3O^+ + HA^- \qquad Ka_1$$

$$HA^- \rightleftharpoons H_3O^+ + A^{2-} \qquad \underline{Ka_2}$$

$\frac{Ka_1}{Ka_2} \geqslant 10^4$; mixture behaves as weak acid.

① It will be considered as monobasic / monoprotic system with certain Ka.
② We will get buffer system of H_2A & HA^-
③ first equivalence, hydrolysis of SB v/s WA.

$$pH = \frac{1}{2}(pKa_1 + pKa_2)$$

④ we will have buffer system HA^- & A^{2-}
⑤ second equivalence, hydrolysis of SB v/s WA

$$pH = \frac{1}{2}(pKw + pKa_2 + \log C)$$

⑥ excess of NaOH/ Base.

ⓑ Triprotic acids :-

t Eq. pt :- $pH = \frac{1}{2}(pKa_1 + pKa_2)$

d Eq. pt :- $pH = \frac{1}{2}(pKa_2 + pKa_3)$

rd Eq. pt :- $pH = \frac{1}{2}(pKw + pKa_3 + \log C)$

* ratio of $\frac{Ka_1}{Ka_2}$ weakens, then equivalence point is not detected.

maleic acid v/s NaOH :- 2nd equivalence pt. detected more accurately than 1st.

carbonic acid v/s NaOH :- 2nd equivalence point not detected.

- Boric acid v/s NaOH :- no sharp change in pH at equivalence pt.

Phosphoric acid v/s NaOH :- 3rd stage not detected.

Acids with dissociation constant less than 10^{-7} cant be titrated.

Boric Acid ≡ Weak acid.
sodium salt get hydrolyzed to NaOH. Thus pH increases. No sharp change in pH values.

* Amino acid v/s SB.

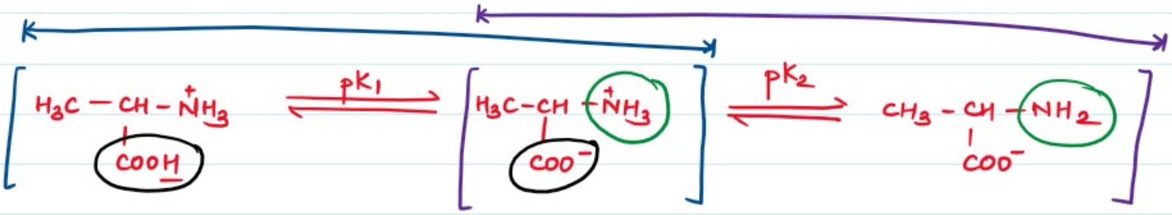
→ dipolar species. (positive and negative charge both present)
→ Zwitter ions.
→ Amphoteric nature (reacts with both acid and base)

1s → $\underset{pK_1}{\underline{\alpha\text{- COOH}}}$ and $\underset{pK_2}{\underline{\alpha\text{- NH}_3^+}}$ are responsible for two characteristic pK values.

2n

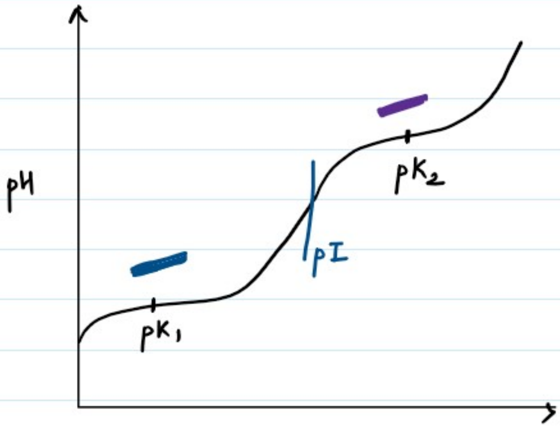
$pK_1 = K_1$ = acidic part
3 $pK_2 = K_2$ = basic part

pI = Isoelectric point = pH at which it exists as Zwitter ion (both charges present) $= \frac{1}{2}(pK_1 + pK_2)$



$$\left[H_3C-\underset{COOH}{CH}-\overset{+}{N}H_3 \xrightleftharpoons{pK_1} H_3C-\underset{COO^-}{CH}-\overset{+}{N}H_3\right] \xrightleftharpoons{pK_2} CH_3-\underset{COO^-}{CH}-NH_2$$

(Zwitter Ion)



Thank - You