Ionic Equilibrium

IONIC EQUILIBRIUM

In this chapter, we'll study about equilibrium of weak electrolytes.

There are 2 types of substances.

Non electrolyte – which does not ionise in their aqueous solution.

e.g:– urea, glocose, sucrose etc.

Electrolyte – which will dissociate into ions in their aqueous solution.

ELECTROLYTES

Strong Electrolytes

Completly dissociate into ions

$\alpha = 1$

e.g:– HCl, H_2SO_4, etc

Weak Electrolytes

Partially dissociate into ions

$\alpha < 1$

e.g:– CH_3COOH, NH_3, etc

We will frequently use an operator in this chapter $\equiv P$

$$P \equiv -\log$$

e.g.:- $-\log[H^+] = pH$ $\quad$ $-\log[OH] = pOH$

$-\log[Ka] = pKa$ $\quad$ $-\log[Kb] = pKb$

BASICS OF LOGARITHM

- $\log m^n = n \log m$
- $\log m/n = \log m - \log n$
- $\ln x = (\log_{o} x)\,2.303$
- $\log 10 = 1$
- $\log 1/x = -\log x$

- $\log m^n = \log m + \log n$
- $\log_a m = \dfrac{\log_b m}{\log_b a}$
- $\log 1 = 0$
- $\log 2 = 0.3$
- $\log 3 = 0.48$

- if $\log_a x = Y$
  antilog $x = a^Y$

QUESTION Calculate the following

① $\log 25$ $\quad$ ② $\log 1.8$ $\quad$ ③ $\log \frac{21}{7}$

④ $\log 5$ $\quad$ ⑤ $\log \frac{22}{3}$

Solution

① $\log 25 = \log(5)^2 = 2(\log 10/2)$

$2[\log 10 - \log 2]$

$2[1 - 0.3] = 2(0.7) = 1.4$

2. $\log 1{\cdot}8 = \log {}^{18}/_{10} = \log 18 - \log 10$

$= \log 3^2 \times 2 - 1$

$= 2(0{\cdot}48) + 0{\cdot}3 - 1$

$= 0{\cdot}96 + 0{\cdot}3 - 1 = 1{\cdot}26 - 1 \Rightarrow 0{\cdot}26$

3. $\log \frac{21}{7} = \log 3 \Rightarrow 0{\cdot}48$

4. $\log 5 = \log {}^{10}/_{2} = 1 - 0{\cdot}3 \Rightarrow 0{\cdot}7$

5. $\log \frac{22}{3} = \log 22 - \log 3$

$= \log 2 + \log 11 - 0{\cdot}48$

$= 0{\cdot}3 + \frac{\log 10 + \log 12}{2} - 0{\cdot}48$

$= -0{\cdot}18 +$

$\Rightarrow 0{\cdot}86$

Qus:-

1. $\log 1{\cdot}8 \times 10^{-5}$
2. $\log 14 \times 10^{-6}$
3. $\log 7 \times 10^{-5}$

Ans:-

1. $\log 1{\cdot}8 \times 10^{-5} = 0{\cdot}26 - 5 = -4{\cdot}74$
2. $\log 14 - 6 = \log 7 + 0{\cdot}3 - 6$

   $= 0{\cdot}84 + 0{\cdot}3 - 6$

   $= 1{\cdot}14 - 6 \Rightarrow -4{\cdot}86$
3. $\log 7 \times 10^{-5} = \log(7-5) = 0{\cdot}84 - 5$

   $\Rightarrow -4{\cdot}16$

REMEMBER

$\log 1{\cdot}8 = 0{\cdot}26$

$\log 7 = 0{\cdot}84$

$\log 5 = 0{\cdot}7$

$\log 2 = 0{\cdot}3$

$\log 3 = 0{\cdot}48$

ACID BASE CONCEPT

1. ARRHENIUS THEORY

According to Arrhenius, substances that provide H^+ ion in their aqueous solution are acids and substances which provide OH^- ion in their aqueous solution are base.

For eg:- $\underset{\text{acid}}{HCL} \rightleftharpoons H^+ + Cl^-$ $\underset{\text{base}}{NaOH} \rightleftharpoons Na^+ + OH^-$

2. BRONSTED AND LOWRY THEORY

Proton acceptors are bases and Proton donors are acid.

- $\underset{\text{base}}{B} + H^+ \longrightarrow BH^+$ ← Conjugate acid

  $\underset{\text{acid}}{HA} \rightarrow H^+ + A^-$ ← Conjugate base

for eg:- $\underset{\text{acid}}{H_2SO_4} \longrightarrow H^+ + HSO_4^{2-}$ ← Conjugate base

$\underset{\text{acid}}{HSO_4^-} \longrightarrow H^+ + SO_4^{2-}$ conjugate base

but $\underset{\text{acid}}{H_2SO_4} \longrightarrow 2H^+ + SO_4^{2-}$ ← Not Conjugate base

- $H_3PO_4 \longrightarrow H^+ + H_2PO_4^-$

  $H_2PO_4 \longrightarrow H^+ + HPO_4^{2-}$

  $HPO_4^{2-} \longrightarrow H^+ + PO_4^{3-}$

but acids Conjugate base

$\underset{\text{acid}}{H_3PO_4} \longrightarrow 3H^+ + PO_4^{3-}$ ← Not Conjugate base

3. LEWIS THEORY

Lone pair donors are base.
Lone pair acceptors are acids.

$$H_3N: \longrightarrow BF_3$$

▷ According to first two theories, water is a neutral solution but according to third theory H_2O is Lenius base.

PROPERTIES OF WATER

① It is a Neutral Solution.

② It is a pure liquid having concentration $= \frac{1000}{18} = \boxed{55.55 M} = 55.55$

③ At 25°C H_2O dissociates into H^+ and OH^- ion having concentration 10^{-7}M each.

$$\underset{(l)}{H_2O} \rightleftharpoons \underset{10^{-7}M}{H^+} + \underset{10^{-7}M}{OH^-} \qquad \Delta H > 0$$

④ K_w = ionic product of water

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

taking -log on both sides

$$-\log K_w = -\log [H^+][OH^-]$$

$$pK_w = -\log [H^+] - \log [OH^-]$$

$$\boxed{pK_w = p^H + pOH}$$

at 25°C $pK_w = \boxed{pH^+ + pOH = 14}$

We can predict the nature of solution by pH or pOH

ⓐ $[H^+] = [OH^-]$ Natural Solution

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

$$pH + pH = pOH + pH$$

$$2pH = 14$$

$$\boxed{pH = 7}$$

ⓑ. $[H^+] > [OH^-]$ Acidic solution

$$-\log[H^+] < -\log[OH^-]$$

$$pH + pH < pH + pOH$$

$$2pH < 14$$

$$\boxed{pH = 7}$$

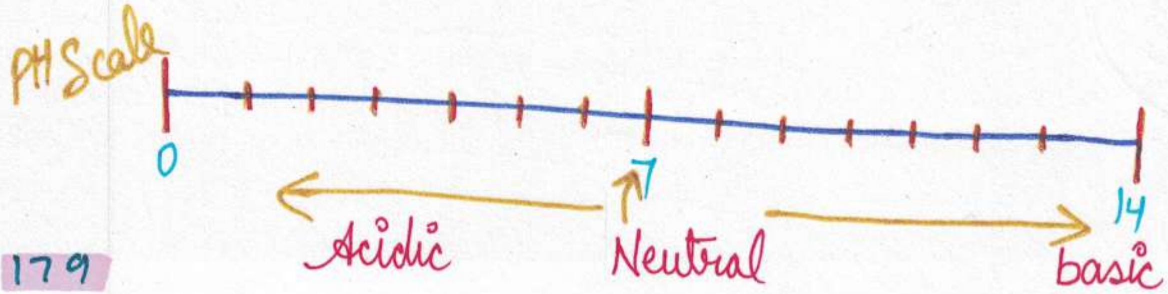
$[H^+] < [OH^-]$ Basic Solution

$$-\log[H^+] > -\log[OH^-]$$

$$pH + pH > pOH + pH$$

$$2pH > 14$$

$$\boxed{pH > 7}$$



Que. Predict the Nature of solu^n by looking at pH values if at 90°c $K_w = 10^{-13}$ for water.

ⓐ pH = 7 ⓑ pH = 6 ⓒ pH = 6.5 ⓓ pH = 8

Solu^n:- $pK_w = pH + pOH \Rightarrow 13$

Neutral Solu^n if $[H^+] = [OH^-]$

$$2pH = pH + pOH$$

$$pH = \frac{13}{2} = 6.5$$

acidic solu^n if $pH < 6.5$

basic solu^n if $pH > 6.5$

So now, ⓐ $pH > 6.5 \Rightarrow$ basic solu^n

$pH = 6$ ⓑ $pH < 6.5 \Rightarrow$ Neutral solu^n

ⓒ $pH = 6.5 \Rightarrow$ Neutral solu^n

$pH = 8$ ⓓ $pH > 6.5 \Rightarrow$ basic solu^n

Q. What will be effect on pH and pOH of solution if temparature will increase?

Solu^n:- On increasing temparature, K_w will increase hence, both $[H^+]$ and $[OH^-]$ if increase, so pH and pOH will both decrease.

⑤ Degree of Dissaciation of H_2O at 25°C

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$\begin{array}{llll} t=0 & c & & \\ t=t & c-x & x & x \end{array}$$

$$\boxed{\alpha = \frac{x}{c}}$$

$$\alpha = \frac{10^{-7}}{\frac{1000}{18}} = 1.8 \times 10^{-9}$$

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

ABSOLUTE DISSOCIATION CONSTANT
OR
IONISATION CONSTANT FOR WATER

$$H_2O \rightleftharpoons H^+ + OH^-$$

K_a = dissociation constant for weak acid

K_b = dissociation constant for weak base

at 25°C $K_a = K_b = \dfrac{[H^+][OH^-]}{[H_2O]}$

$$= \frac{10^{-7} \times 10^{-7}}{\frac{1000}{18}} = 1.8 \times 10^{-6}$$

$$\| -\log K_a = -\log K_b = -\log 1.8 \times 10^{-16} \|$$

$$pK_a = pK_b = -[0.26 - 16.00]$$

$$pK_a = pK_b = -[-15.74]$$

$$\boxed{pK_a = pK_b = 15.74}$$

On increasing temperature K_a K_b will increase pK_a, pK_b will decrease.

$$HA \rightleftharpoons H^+ + A^+$$

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

$$A^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HA_{(aq)} + OH^-_{(aq)}$$

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

$$K_aK_b = \frac{[H^+]\cancel{[A^-]}}{\cancel{[HA]}} \cdot \frac{\cancel{[HA]}[OH^-]}{\cancel{[A^-]}} \Rightarrow K_aK_b = [H^+][OH^-] \quad \boxed{K_aK_b = 10^{-14}}$$

$$\| -\log K_a - \log K_b = -\log 10^{-14} \|$$

$$\boxed{pK_a + pK_b = 14}$$

$K_a K_b = \text{Constant} = 10^{-14}$

$\because$ $K_a K_b$ is constant, if acid is strong, then it conjugate base should be weak.

PH Calculation

Calculate pH of :-

1. 300 ml 0.1 M HCL

$[H^+] = \frac{0.1}{300} \times 1000$

$-\log(1/3) = \log 3$

$pH = 0.48$

300 ml = 0.1

$1000 ml = \frac{0.1}{300} \times 1000$

$= 1/3 N$

$HCL \longrightarrow H^+ + Cl^-$

$[H^+] = 0.1M$

$pH = -\log 0.1$ $\boxed{pH = 1}$

2. 500 ml 0.1M HCl

$\boxed{PH = 1}$

3. 300 ml 0.2 M HCl + 200 ml 0.4 M H_2SO_4

$[H^+]$ from HCL = 0.2 $[H^+]$ from H_2SO_4 = 0.8

total $[H^+] = 1$

$-\log[H^+] = -\log 1$

millimole of H^+ from HCl = 300 × 0.2 = 60

H^+ from H_2SO_4 = 0.8 × 200 = 160

$\log 11 = \frac{\log 12 + \log 10}{2}$

$= \frac{2(03) + 0.48 + 1}{2}$

$\log \frac{22}{5} = \frac{1.08 + 1}{2} \Rightarrow \frac{2.08}{2}$

$- \log 5$

$= 0.3 + 1.04 - [1 - 0.3]$

$= 1.34 - (0.7)$

$= 0.64$

Total = 160+60 = 220 millimole

$[H^+] = \frac{22\cancel{0}}{50\cancel{0}} = \frac{22}{50}$

$= -\log \frac{22}{50}$

$= -\left[\log \frac{22}{50} - \log 10\right]$

$= -\left[\log \frac{22}{5} - 1\right]$

$= -(0.64 - 1)$

PH = .36

$\boxed{pH = .36}$

▷ 300 ml 0.2 M H_2SO_4 + 300 ml 0.2 M HCl + 200 ml 0.2M HNO_3

mill. from $H_2SO_4 = 0.2 \times 300 \times 2$

$= 120$

from HCL $= 0.2 \times 300 = 60$

from $HNO_3 = 0.2 \times 200 = 40$

Total $= [H^+] = \frac{120 + 60 + 40}{800} = \frac{22\cancel{0}}{80\cancel{0}}$

$\log 11 + \log 2$

$= \log 11 \times 2$

$\log 22 = 1.34$

$-\log [H^+] = -\log \left(\frac{22}{80}\right)$

$= -[\log 2 + \log 11 - \log 8 - 1]$

$= -[1.34 - 0.9 - 1]$

$= -[0.44 - 1]$

$= 0.56$

4. 300 ml 0.1M NaOH

$[H^+] = 0$ $\quad p^{OH} = 1$

$p^H = 14 - 1$ $\quad \boxed{pH = 13}$

5. 300 ml 0.2M NaOH + 200 ml 0.2M $Ca(OH)_2$

$$[OH^-] = \frac{60+80}{500} = \frac{14\cancel{0}}{50\cancel{0}}$$

$$-\log[OH^-] = -\log\left[\frac{14}{50}\right]$$

$$= -\left[+\log 7 + \log 2 - 2\log 5 - \log 2\right]$$

$$-(.84 + 0.3 - 2(1-0.3) - 0.3)$$

$$-(.84 - 1.4)$$

$$= 0.56 \Rightarrow pH = 14 - 0.56 \Rightarrow 13.44$$

$$\boxed{pH = 13.44}$$

6. 300 ml 0.2M $Ca(OH)_2$ + 200 ml 0.2M NaOH + 300 ml 0.1M $Al(OH)_3$

$$[OH] = \frac{120+40+90}{800} = \frac{25\cancel{0}}{80\cancel{0}}$$

$$pOH = -\log\frac{25}{80}$$

$$= -\left[2\log 5 - 3\log\underset{-1}{2}\right]$$

$$= -\left[2(0.7) - 3\underset{-1}{(0.3)}\right]$$

$$= -\left[1.4 - \underset{-1}{0.9}\right] = 0.5$$

$$pH = 14 - 0.5 \Rightarrow 13.5$$

$$\boxed{pH = 13.5}$$

Acid + Base → Salt + Water

$$H^+ + OH^- \rightarrow H_2O$$

millimole of H^+ = millimole of OH^- → neutral

millimole of H^+ > millimole of OH^- → acidic

millimole of H^+ < millimole of OH^- → basic

Que:- 300 ml 0.2M NaOH + 200 ml 0.3M HCL

millimole $[OH^-] = 0.2 \times 300$ $= 60$ millimole $[H^+] = 0.3 \times 200$ $= 60$

millimole $[H^+]$ = millimole OH^-

$\boxed{pH = 7}$

Que:- 300 ml 0.3M HCL + 200 ml 0.2 M NaOH

millimole $H^+ = 90$ $OH^- = 40$

$Kw = [OH^-][H^+] = 0.06$ $H^+ > OH^-$ pH $H^+ = \frac{56}{500}$ millimole.

$pH = -\log \frac{6}{100} = -(0.78-2)$

acidic

1/10

$pH = 1$

Que:- 300 ml 0.2 M HCl + 200 ml 0.5M NaOH

milli $H^+ = 60$ milli $OH^- = 100$

$OH^- > H^+$

basic $pH > 7$

$pH = 1.1$

$\boxed{pH = 12.9}$

Que:- What is the pH of resulting solu^n if pH = 2 and pH = 4 are added in following volume ratio :-

ⓐ. 1:1 ⓑ 2:3 ⓒ. 3:2

Solu^n:- $2 = -\log H^+$

$10^{-2} = [H^+]$ $[OH^-] = 10^{-12}$

$10^{-2} = \frac{n_1}{V_1}$

$4 = -\log H^{-1}$

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

$10^{-10} = [OH^-]$

$10^{-4} = \frac{H_2}{V_2}$

$n_1 : H_2 = \frac{10^{-2}}{10^{-4}} = 10^2$ $V_2 = \frac{H_2}{10^{-4}}$

$[H^+] = \frac{n_1 + n_2}{\frac{2n2}{10^{-4}}} = \frac{10^2 n_2 + n_2}{\frac{2n2}{10^{-4}}} = \frac{10/n2}{2n^2/10^{-4}}$

$$[H^+] = \frac{101\times10^{-4}}{2}$$

$$-p^H = -(\log 101 - 4 - 0.3)$$

$$= -(2-4.3)$$

$$\boxed{p^H = 2.3}$$

2:3

$n_1 : n_2 = \frac{n_1+n_2}{2n_2}$ 2:3

$\frac{V_1}{V_2} = \frac{2}{3}$ $\frac{n_1 \times 10^{-4-2}}{10^{-2} \times n_2} = \frac{2}{3}.$

$\frac{n_1}{V_1} = 10^{-2}$

$\frac{n_1}{n_2} = \frac{2}{3}\times10^{2} = \frac{200}{3}$

$n_1 = \frac{200}{3} n_2$

$$[H^+] = \frac{10^{-2}V_1 + 10^{-4}V_2}{5V_1+V_2}$$

$$[H^+] = \frac{2V\times10^{-2} + 3V + 10^{-4}}{2V+3V}$$

$$= \frac{2\times10^{-2} + 3\times10^{-4}}{5}$$

$$[H^+] = \frac{0.02}{10} + \frac{0.0003}{5} = \frac{0.0203}{5}$$

$$= -\log\left(\frac{0.0205}{5}\right)$$

$$= -\left(\log\frac{2050}{10000} - 0.7\right)$$

$$= -(\log 200 - 4 - 0.7)$$

$$= -(\log 2 + 2 - 4.7)$$

$$= -(2.3 - 4.7)$$

$$\boxed{p^H = 2.4}$$

$3V \quad 10^{-2}H \qquad\qquad 2V \quad 10^{-4}$

$$[H^+] = \frac{0.03+0.0002}{5}$$

$$= \frac{0.0302}{5} \simeq \frac{0.0300}{5}$$

$$= -\log\left(\frac{0.03}{5}\right)$$

$$= -(\log 3 - 2 - 0.7)$$

$$= -(0.48 - 2.70)$$

$$= -(-2.22)$$

$$= 2.22$$

Que:- $pH = 12 \qquad pH = 10$

$[H^+] = 10^{-12} \qquad [H^+] = 10^{-10}$

(i) $V \quad 10^{-12}M \qquad V \quad 10^{-10}M$

$$[H^+] = \frac{10^{-12}+10^{-10}}{2} = \frac{0.01\times10^{-10}}{2} + 10^{-10}$$

$$[H^+] = \frac{1.01\times10^{-10}}{2}$$

$$pH^+ = (10 - 0.3)$$

$$= -(9.7)$$

$$\boxed{pH^+ = 9.7}$$

$pOH = 2 \qquad pOH = 4$

$[OH^-] = 10^{-2} \qquad [OH] = 10^{-4}$

(ii) $2V \quad 10^{-2}M \qquad 3V \quad 10^{-4}$

$$[OH^-] = \frac{0.02+0.0003}{5} = \frac{0.0200}{5}$$

$pOH = 2.4 \qquad pH = 14 - 2.4 = 11.6$

(iii) $pH = 2.2$

$pOH = 14 - 2.22 = 11.78$

Que:- $pH = 12$ $\quad$ $pH = 2$

$pOH = 2$ $\quad$ $pH = 2$

$[OH^-] = 10^{-2}$ $\quad$ $[H^+] = 10^{-2}$

$[H^+] = 10^{-12}$

▷ $2V\ 10^{-12}M$ $\quad$ $3V\ 10^{-2}M$

$$[H^+] = \frac{2\times10^{-12} + 3\times10^{-2}}{5}$$

$$= \frac{2\cdot\times0.00\,---+0.03}{5} \simeq \frac{0.03}{5}$$

$$pH = \left[-\log\frac{0.03}{5}\right] = -(0.48-2-0.7)$$

$$= -(-2-0.7)+0.48$$

$[OH^-] = 10^{-2}$ $\quad$ $[H^+] = 10^{-2}$

$10^{-2} = n/V_1$ $\quad$ $10^{-2} = n/V_2$

$10^{-2} = \frac{3n}{2V_2}$ $\quad$ $10^{-2} = n/V_2$

$n = \frac{2V_2}{3}\times10^{-2}$ $\quad$ $n = V_2\times10^{-2}$

millimole (OH^-) $\quad$ millimole $[H^+] \longrightarrow H_2O$

$3V\times10^{-2}$ $\quad$ $2V\times10^{-2}$

$[OH^-]$ $\quad$ $V\times10^{-2}$

$$[OH^-] = \frac{10^{-2}}{5} \Rightarrow -\log\left(\frac{10^{-2}}{5}\right)$$

$$\Rightarrow -(-2-0.7)$$

$$pH = 14-2.7 \Rightarrow 11.3$$

$3V\ 10^{-2} M\ H^+$ $\qquad$ $2V\ 10^{-2} M\ H^-$

$H^+ = V \times 10^{-2}$ $\qquad$ $[H^+] = \frac{10^{-2}}{5}$

$\boxed{p^H = 2.7}$

p^H Calculation for Weak Acid

$CH_3COOH\ (ka)$ $\qquad$ $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$t=0 \quad c$

$t=t \quad c(1-a) \quad c\alpha \quad c\alpha$

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

$1-\alpha \simeq 1$ $\qquad$ $\alpha = \sqrt{\frac{Ka}{c}}$

$[H^+] = ca = c\sqrt{\frac{ka}{c}} = \sqrt{cKa}$

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

$$\boxed{p^H = \frac{1}{2}(p^{Ka} - \log c)}$$

Que:- What is p^H of 0.1 M CH_3COOH $(Ka = 1.8 \times 10^{-5})$

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

$t=0 \quad 0.1$

$t=t \quad 0.1(1-\alpha) \quad 0.1\alpha \quad 0.1\alpha$

$Ka = \frac{c\alpha^2}{1-\alpha} \Rightarrow 1.8 \times 10^{-5} = \alpha^2 \times 0.1$

$\alpha = \sqrt{1.8 \times 10^{-5} \times 10}$

$\alpha = \sqrt{1.8 \times 10^{-4}}$

$\alpha = \sqrt{1.8} \times 10^{-2}$

$p^H = -\frac{1}{2}(0.26 - 6)$

$p^H = -\frac{1}{2}(-5.74) \Rightarrow 2.87$

$\% \alpha = \sqrt{1.8 \times 10^{-2}} \times 100$

$\sqrt{1.8}\% = 1.34\%$

if $K_a < 10^{-3}$, then it is weak acid.

pH Calculation for Weak Base

NH_3 or NH_4OH (K_b)

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

or

$$\begin{array}{llll} & NH_4OH \rightleftharpoons & NH_4 & + OH^- \\ t=0 & c & & \\ t=t & c(1-\alpha) & c\alpha & c\alpha \end{array}$$

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

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

$1-\alpha \simeq 1$

$$K_b = c\alpha^2$$

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

$$[OH^-] = c\alpha = c\sqrt{\frac{K_b}{c}} \Rightarrow \sqrt{cK_b}$$

$$-\log[OH^-] = pK_b = -\tfrac{1}{2}(\log c + \log K_b)$$

$$= \tfrac{1}{2}(\log K_b - \log c)$$

Que:- What is pH of 0.1M NH_3 ($K_b = 1.8 \times 10-5$)

$$\begin{array}{llll} NH_3 + H_2O \rightleftharpoons & NH_4^+ & + OH^- \\ 0.1 & & \\ (0.1-x) & x & x \end{array}$$

$K_b = \frac{x^2}{0.1-x}$ $\quad x = \sqrt{K_b \times 0.1}$

$x = \sqrt{1.8 \times 10^{-6}}$ $\quad x = \sqrt{1.8 \times 10^{-3}}$

$$pK_b = \frac{1}{2}(\log 1.8\times10^{-5} - \log 0.1)$$

$$pH = -\frac{1}{2}\left[\frac{2.6}{2} - 3\right] = 3 - 0.13 = 2.87$$

$$pK_b = \frac{1}{2}[0.26 - 5 + 1]$$

$$= \frac{1}{2}[51.74] \Rightarrow 2.87$$

$$pH = 14 - 2.87 \Rightarrow 11.13$$

— Strong acid + Weak acid —

$$HCl + CH_3COOH \ (K_a)$$
$$c_1 \qquad\qquad c_2$$

$$HCl \longrightarrow H^+ + Cl^-$$
$$c_1 \qquad c_1$$

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$
$$c_2 - x \qquad\qquad x \qquad\qquad c_1 + x$$

$$K_a = \frac{x(c_1 + \cancel{x})}{c_2 - \cancel{x}}$$

$$[H^+] = c_1 + x$$
$$= c_1$$

$$x = \frac{c_2 K_a}{c_1}$$

Que:- $CH_3COOH + HCL$

$K_a = 1.8\times10^{-5}$ $\quad pH = ?$

$\alpha \ CH_3COOH$

$$1.8\times10^{-5} = \frac{c_1 x}{c_2}$$

$$x = 1.8\times10^{-5} \frac{\times \cancel{0.1}}{\cancel{0.1}}$$

$$\alpha = x/c_2 = \frac{1.8\times10^{-5}}{0.1} \Rightarrow 1.8\times10^{-4}$$

$$\%\,\alpha = 1.8\times10^{-2}\,\%$$

$$[H^+] = 0.1$$

$$-\log H^+ = -\log 0.1 \qquad \boxed{pH = 1}$$

dissociation of CH_3COOH is decreased further due to common ion effect.

In a sol^n of strong acid and weak acid p^H of sol^n will be generated by strong acid.

Strong base + Weak Base

$$\underset{c_1}{NaOH} + \underset{c_2}{NH_3}\,(k_b)$$

$$NaOH \longrightarrow Na^+ + OH^-$$

$$\underset{c_2-x}{NH_3} + H_2O \rightleftharpoons \underset{x}{NH_4} + \underset{c_1+x}{OH^-}$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$k_b = \frac{x(c_1+\cancel{x}^{0})}{c_2-\cancel{x}^{0}}$$

$$x = \frac{c_2 k_b}{c_1}$$

$$\alpha NH_3 = \frac{x}{c_2} \qquad [OH^-] = c_1+\cancel{x}^{0}$$

$$[OH^-] + c_1$$

Que.:- $\underset{0.1M}{NaOH} + \underset{0.1M}{NH_3}$ $\quad [k_b = 1.8\times10^{-5}]$

$[OH^-] = 0.1$

$p^{OH} = 1 \qquad p^H = 13$

$$x = \frac{C_2 K_b}{c_1} = 0.1\left(\frac{1.8\times10^{-5}}{0.1}\right)$$

$$\alpha = \frac{1.8\times10^{-5}}{0.1} = 1.8\times10^{-4}$$

$$\%\alpha = 1.8\times10^{-2}\,\%$$

p^H for strong base + weak base will be governed by strong base.

Weak Base + Weak Acid

$$\begin{array}{llll} & c_1 Ka & c' \, Ka & \\ & CH_3COOH & CH_3COO^- & H^+ \\ Ka_1 & c_1 - x & x & x+y \\ & CCl_3COOH & CCl_3COO^- & H^+ \\ Ka_2 & c_2 - y & y & x+y \end{array}$$

$$Ka_1 = \frac{x(x+y)}{c_1 - x} \Rightarrow C_{Ka} = x(x+y)$$

$$Ka_2 = \frac{y(x+y)}{c_2 - y} \Rightarrow c_2 Ka_2 = (x+y)y$$

$$c_1 Ka_1 + c_2 Ka_2 = (x+y)(x+y)$$

$$\boxed{(x+y) = \sqrt{c_1 Ka_1 + c_2 Ka_2}}$$

$$[CH_3COO^-] = x = \frac{c_1 Ka_1}{x+y} \qquad [CCl_3COO^-] = Y = \frac{c_2 Ka_2}{x+y}$$

$$x = \frac{c_1 Ka_1}{\sqrt{c_1 Ka_1 + c_2 Ka_2}} \qquad Y = \frac{c_2 Ka_2}{\sqrt{c_1 Ka_1 + c_2 Ka_2}}$$

$$\alpha_{CH_3COOH} = H/c_1 \qquad \alpha_{CCl_3COOH} = Y/c_2$$

Que $CCl_3COOH + CH_3COOH$

$0.1M \quad Ka = 7\times10^{-5} \qquad 0.1M \quad Ka = 2\times10^{-5}$

(i) $[H^+] = \sqrt{0.1\times7\times10^{-5} + 0.1\times2\times10^{-5}}$

$\sqrt{(7+2)\,10^{-6}} = 3\times10^{-3}$

$-\log[H^+] = pH = -\log(3\times10^{-3})$

$pH = -[0.48 \; -3]$ $\qquad \boxed{pH = 2.52}$

(ii) $[CH_3COO^-] = \frac{C_2Ka_2}{x+y} = \frac{0.1\times2\times10^{-5}}{3\times10^{-3}}$

$= 0.66\times10^{-3}$

$[CCl_3COO^-] = \frac{0.1\times7\times10^{-5}}{3\times10^{-3}} = 2.33\times10^{-3}$

(iii) $\alpha_{CH_3COOH} = \frac{x}{C_1} = \frac{0.66\times10^{-3}}{0.10}$

$= 6.6\times10^{-3}$

$\%\alpha = 0.66\%$

$\alpha_{CCl_3COOH} = 23.3\times10^{-3}$

$y/C_2 = 23.3\times10^{-3}$

$\%\alpha = 2.33\%$

Q. 200ml 0.1M HCl + 300ml 0.2M H_2SO_4 + 300ml 0.2M CH_3COOH $(Ka=2\times10^{-}$

$[H^+] = \frac{20+60\times2}{800} = \frac{14\cancel{0}}{80\cancel{0}}$

$-\log H^+ = pH = -\log 14/80$

$= -[\log 7 + 0.3 - \log 80]$

$= -[1.13 - (1.9)]$

$= [-0.77] = 0.77$

$\%\alpha_{CH_3COOH} = x/c = \frac{0.2\times2\times10^{-5}}{0.3} = \frac{0.4\times10^{-3}}{0.3}$

$= 1.33\times10^{-3}\times100$

$= 1.33\times10^{-1}$

$= 0.133\%$

$HCl \longrightarrow H^+ + Cl^-$

$H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-}$

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

0.2

$0.2-x \quad x \quad x$

$x = \sqrt{cKa}$

$x = \sqrt{0.2\times2\times10^{-5}} = 2\times10^{-5}$

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

$$\frac{60}{800} - x \qquad x \qquad \frac{140}{800} + x$$

$$Ka = \frac{\frac{140}{800}x}{60/800} \qquad x = \frac{\overset{1}{\cancel{2}}\times 10^{-5}\times 6}{\cancel{14}_{7}}$$

$$x = \frac{6}{7}\times 10^{-5}$$

$$\%\alpha_{CH_3COOH} = \frac{x}{60/\cancel{800}} \times 1\cancel{00}$$

$$= \frac{6}{7}\times\frac{10^{-5}}{60}\times 8 \Rightarrow \frac{8}{7}\times 10^{-5}$$

DILUTION

$$HCL \longrightarrow H^+ + Cl^-$$

$$0.1M \qquad 0.1$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$0.1+x \qquad x$$

$$(0.1+x)x = 10^{-14} \qquad [H^+] = 0.1 + 10^{-13}$$

$$x = 10^{-13} \qquad -\log[H^+] = \boxed{pH = 1}$$

$$\alpha_{H_2O} = x/c = \frac{10^{-13}}{1000/18} \simeq 1.8\times 10^{-15}$$

$$HCL \longrightarrow H^+ + Cl^-$$

$$10^{-2} \qquad 10^{-2}$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$10^{-2}+x \qquad x$$

$$(10^{-2}+x)x = 10^{-14} \qquad [H^+] = 10^{-2} + 10^{-2}$$

$$x = 10^{-12} \qquad \boxed{pH = 1}$$

$$\alpha_{H_2O} = \frac{10^{-12}}{\frac{1000}{18}} = 1.8\times 10^{-14}$$

$$HCl \longrightarrow H^+ + Cl^-$$
$$10^{-8}M \qquad 10^{-8}M$$

$$H_2O \rightleftharpoons \underset{10^{-8}+x}{H^+} + \underset{x}{OH^-}$$

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

$$x = \frac{-10^{-8} + \sqrt{10^{-16} + 4 \times 10^{-14}}}{2}$$

$$x = \frac{-10^{-8} + 10^{-8}\sqrt{401}}{2}$$

$$x = \frac{19}{2} \times 10^{-8}$$

$$[H^+] = 10^{-8} + \frac{19}{2} \times 10^{-8}$$
$$= \frac{21}{2} \times 10^{-8}$$

$$pH = -\log\left(\frac{21}{2} \times 10^{-8}\right)$$
$$pH = -[\log 21 - 0.3 - 8]$$
$$pH = -[0.7 + 0.6 - \underset{1.3}{8.3}]$$
$$pH = 7$$
$$\boxed{pH = 6.98}$$

Que

pH of $10^{-8}M$ NaOH

$$\underset{10^{-8}}{NaOH} \longrightarrow Na^+ + \underset{10^{-8}}{OH^-}$$

$$H_2O \rightleftharpoons \underset{x}{H^+} + \underset{10^{-8}+x}{OH^-}$$

$$(10^{-8}+x)\,x = 10^{-14}$$
$$x = 19/2 \times 10^{-8}$$

$$[OH^-] = 10^{-8} + \frac{19}{2} \times 10^{-8}$$

$$pOH = 6.98 \qquad pH = 14 - 6.98 = 7.02 \qquad \boxed{pH = 7.02}$$

$$-\log[H^+] = -\log\left[\frac{19}{2}\times10^{-8}\right]$$

$$= -\left[\log 19 \div 0.3 - 8\right]$$

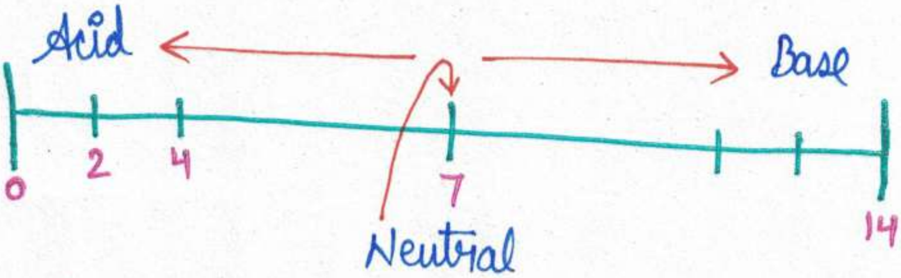
$$= \frac{0.48\times2+0.3+1.3}{2}$$

$$= \frac{0.96+1.6}{2}$$

$$= \frac{2.56}{2} \Rightarrow 1.28$$

$pH = 8.3 - 1.28$

$$\boxed{pH = 7.02}$$



If $[H^+] < 10^{-6}M$ Then consider water equilibrium catalyst are substances which can affect the rate of reaction. It can not disturb the equilibrium.

The amount of catalyst before and after the reaction will be constant.

SALT HYDROLYSIS

Salts are of 4 kinds :-

1. Salt of strong acid, strong base

After complete neutralisation of strong acid with strong base, we'll get these type of salt.

e.g:- Nacl, K_2SO_4 etc.

2. Salt of strong acid and weak base

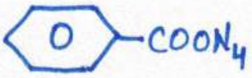
After complete neutralisation of strong acid and weak base, we'll get these type of salts.

e.g:- NH_4Cl, CH_3NH_3Cl etc.

3. Salt of strong base and weak acid

After complete neutralisation of weak acid and strong base, we'll get these type of salts.

e.g:- CH_3COONa ,



etc.

4. Salt of weak acid and weak base

After neutralisation of weak acid and weak base we'll get these type of salts.

e.g:- CH_3COONH_4 , $HCOONH_4$ etc.

when salt is dissolved in water, the anion or cation which comes from weak acid or base will react with H_2O, the process is called spectator ion.

1. Strong Acid + Strong Base

$$NaCl \longrightarrow Na^+ + Cl^-$$

$$[H^+] = [OH^-] = 10^{-7}$$

$$\boxed{p^H = 7}$$

2. Strong Acid + Weak Base

$$NH_4Cl \longrightarrow NH_4 + \boxed{Cl^-} \rightarrow \text{spectator}$$

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

t=0 c

t=t c(1-h) ch ch

$$K_h = \frac{[NH_3][H^+]}{[NH_4^+]} = \frac{ch^2}{1-h}$$ $1-h \simeq 1$

$H_3O^+ \equiv H^+$

h → degree of hydrolysis

K_h → hydrolysis constant

$$ch^2 = K_h$$

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

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} \frac{[H^+]}{[H^+]}$$

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

$$K_{b_{Ni_3}} \, K_{b_{NH_4^+}} = 10^{-14} = K_w$$

$$[H^+] = ch = c\sqrt{\frac{K_h}{c}} = \sqrt{cK_h}$$

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

$$-\log H^+ = p^H = -\frac{1}{2}(\log K_w + \log c - \log k_b)$$

$$= \frac{-1}{2}(\log 10^{-14} + \log c - \log k_b)$$

$$\boxed{p^H = 7 - \frac{1}{2}(\log c + p^{K_b})}$$

$p^H < 7$

QUE. What is the p^H of 0.1M NH_4Cl solution given K_b of $NH_3 = 1.8 \times 10^{-5}$
also K_b of $NH_3 = 1.8 \times 10^{-5}$
also calculate % hydrolysis of NH_4Cl

Sol^n:- $\underset{0.1}{NH_4Cl} \longrightarrow NH_4^+ + Cl^-$

$$NH_4^+ \longrightarrow NH_3 + H_3O^+$$

0.1(1-h)   0.1h   0.1h

$$h = \sqrt{\frac{K_h}{0.1}}$$

$$K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{1.8\times10^{-5}} = \frac{10^{-7}}{1.8}$$

$$h = \sqrt{\frac{10^{-9}}{1.8\times 0.1}}$$

$$h = \sqrt{\frac{10^{-9}}{1.8}} = \frac{\sqrt{1.8}}{1.8} = 10^{-5}$$

$$\% h = \frac{\sqrt{18}}{18}\times 10^{-3}$$

$$-\log x = \log\sqrt{\frac{10^{-15}}{1.8\times10^{-5}}} = \log x$$

$$= 5.13$$

* * *

$$p^H = \frac{7-1}{2}\left(p^{K_b}-1\right)$$

$$p^H = 7-\frac{1}{2}\left[5-0.26-1\right]$$

$$p^H = 7-\frac{1}{2}(3.74)$$

$$p^H = 7-1.87$$

$$\boxed{p^H = 5.13}$$

3. Weak Acid + Strong Base

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

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

c(1-h)   ch   ch

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

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

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

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

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

$$[OH^-] = ch = c\sqrt{\frac{K_h}{c}} = \sqrt{cK_h}$$

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

$$p^H = 14 + \frac{1}{2}(\log c - 14 + p^{ka})$$

$$\boxed{p^H = 7 + \frac{1}{2}(\log c + p^{ka})}$$

$$p^H > 7$$

basic solution

QUE. p^H of $0.1M$ CH_3COONa = ?

If K_a of $CH_3COOH = 1.8 \times 10^{-5}$

Also calculate % hydrolysis

Solu^n:- $CH_3COONa \rightarrow CH_3COO^- + Na^+$

$$\begin{array}{ccc} CH_3COONa & \rightarrow & CH_3COO^- + Na^+ \\ 0.1 & & 0.1 \end{array}$$

$$\begin{array}{lll} CH_3COO^- & CH_3COOH & + \; OH^- \\ 0.1(1-h) & 0.1h & 0.1h \end{array}$$

$$K_h = \frac{0.1(h^2)}{1-\cancel{h}^{\nearrow 0}}$$

$$h = \sqrt{\frac{K_h}{0.1}}$$

$$[OH^-] = 0.1h = 0.1\sqrt{\frac{K_h}{0.1}}$$

$$p^{oH} = -\frac{1}{2}(\log(0.1) + \log(10^{-14}) - \log K_a)$$

$$p^H = 7 + \frac{1}{2}\left(\underset{+14}{1-}\,0.26\right)$$

$$= 7 + \frac{15.26}{2}$$

$$= 7 + 1.87$$

$$\boxed{p^H = 8.87}$$

4. Salt of Weak Acid + Weak Base

$$CH_3COONH_4 \longrightarrow CH_3COO^- + NH_4^+$$

$$NH_4 + \overset{c}{CH_3COO^-} + H_2O \overset{c}{\rightleftharpoons} \overset{c}{CH_3COOH} + OH^- + H^+ + NH_3^-$$

t=0 $\quad c \quad c$

t=t $\quad c(1-h) \quad c(1-h)$

$$\downarrow\uparrow$$

$$CH_3COOH + NH_4OH$$

$$K_h = \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]} = \frac{\overset{ch}{ch}\,\overset{ch}{ch}}{c(1-h)\,c(1-h)}$$

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

$CH_3COO\,(k_a)$

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

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

$NH_4OH\,(k_b)$

$$NH_4OH \rightleftharpoons NH_3^+ + OH^-$$

$$K_b = \frac{[NH_3^+][OH^-]}{[NH_4OH]}$$

$$K_a \cdot K_b = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \cdot \frac{[NH_3^+][OH^-]}{[NH_4OH]}$$

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

$$\boxed{K_h = \frac{K_w}{K_a \cdot K_b}}$$

$$\frac{h}{1-h} = \sqrt{K_h}$$

$$h = \sqrt{K_h} - h\sqrt{K_h}$$

$$\boxed{h = \frac{\sqrt{K_h}}{1+\sqrt{K_h}}}$$

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

$$K_a = \frac{\cancel{c}(1-h)[H^+]}{\cancel{c}h}$$

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

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

$$pH = -\log[H^+] = -\frac{1}{2}(\log k_a + \log k_w - \log k_b)$$

$$\boxed{pH = 7 + \frac{1}{2}(pK_a - pK_b)}$$

1. if $K_a = K_b$ $pH = 7$ (Neutral Salt)
2. if $K_a > K_b$ $pK_a < pK_b$ $pH < 7$ (Acidic Salt)
3. if $K_a < K_b$ $pK_a > pK_b$ $pH > 7$ (Basic Salt)

In this case, K_h & pH are independent of the concentration.

BUFFER SOLUTION

Solution having constant pH is called buffer solution.

It is of 2 kind:-

1. ACIDIC BUFFER

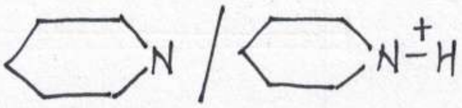
A Solution having weak acid with its conjugate base in significant amount.

2. BASIC BUFFER

A Solution having weak base with its conjugate acid in significant amount.

QUESTION Identify buffer :-

1	CH_3COOH / CH_3COO^-	☑	Acidic buffer
2		☑	Acidic buffer
3	NH_3 / NH_4Cl	☑	Basic buffer
4	CH_3NH_2 / CH_3NH_3Cl	☑	Basic buffer
5.	HCl / Cl^-	☒	Not buffer
6.	H_2SO_4 / HSO_4^-	☒	Not buffer
7.	H_2SO_4 / SO_4^{2-}	☒	Not buffer
8.	H_2S / HS^-	☑	Acidic buffer
9.	HS^- / S^{2-}	☑	Acidic buffer

10	H_2S/S^{2-}	✗	Not Buffer
11	H_3PO_4/HPO_4^{2-}	✗	Not Buffer
12	HPO_4^{2-}/PO_3^{2-}	✓	Acidic Buffer
13	NH_2NH_2/NH_2NH_3Cl	✓	Basic Buffer
14	$NH_2NH_2/(NH_3NH_3)Cl_2$	✗	Not Buffer
15		✓	Basic buffer

PH CALCULATION FOR ACIDIC BUFFER

CH_3COO^- / CH_3COOH

concentration :-	c_1	c_2	$c_1 = \frac{a}{V}$
moles :-	a	b	$c_2 = \frac{b}{V}$

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

$t=0$	c_2	c_1	
$t=t$	c_2-x	c_1+x	x

$$K_a = \frac{(c_1+\cancel{x})(x)}{c_2-\cancel{x}^{\,0}}$$

ignor x w t. c_1 & c_2

$$K_a = \left(\frac{c}{c_2}\right)x$$

$$\left\{ x=[H^+] \Rightarrow -\log x = -\log[H^+] \right\}$$
$$= pH$$

$$-\log K_a = -\log\left(\frac{c_1}{c_2}\right) - \log x$$

$$pK_a = -\log\left(\frac{c_1}{c_2}\right) + pH$$

$$pH = pKa + \log\left(\frac{c_1}{c_2}\right)$$

$$\boxed{pH = pKa + \log \frac{[salt]}{[Acid]}}$$ → Hinduson's equation

$$\boxed{pH = -pKa + \log\left[\frac{a}{b}\right]}$$ → Constant

I. If H_2O is added

$$pH = pKa + \log\left(\frac{a}{b}\right)$$

II. x mole HCl, $x \leq a, b$

$$CH_3COO^- + HCL \rightarrow CH_3COOH$$

a	x	b
$a-x$	[LR]	$b+x$

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

x is small

$$\boxed{pH = pKa + \log\left[\frac{b}{a}\right]}$$

III. Y mole NaOH, $Y \ll a, b$

$$CH_3COOH + NaOH \rightarrow CH_3COO^-$$

b	Y	a
$b-Y$	[LR]	$a+Y$

$$\boxed{pH = pKa + \log\left[\frac{a+Y}{b-Y}\right]}$$

Y is small

$$\boxed{pH = pKa + \log\left(\frac{a}{b}\right)}$$ → Constant

QUESTION 10 mole CH_3COOH is present with 10 mole CH_3COONa in 1 lt solution. what will be

(i) the pH of this solution

(ii) if 2 lt water is added

(iii) 2 mole NaOH added

(iv) 2 mole KCL added

(i)

$$\underset{10}{CH_3COOH} \rightleftharpoons \underset{10}{CH_3COO^-} + H^+$$

$$pH = pKa + \log\left(\frac{a}{b}\right)$$

$$pH = -\log(1.8 \times 10^{-5}) + \log\left(\frac{10}{10}\right)$$

$$pH = -(0.26-5) + \log 1$$

$$pH = 5 - 0.26 = 4.74$$

(ii) If 2 lt water is added

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

$$[acid] = 10/2 = 5$$

$$[Salt] = 5$$

$$pH = pKa + \log\left[\frac{5}{5}\right]$$

$$pH = 4.74$$

(iii) If 2 Mole HCL is added

$$CH_3COOH + HCL \rightarrow CH_3COOH$$

10   2

10-2=8   0   10+2=12

$$pH = 4.74 + \log\left[\frac{\cancel{12}^{3}}{\cancel{8}_{2}}\right]$$

$$pH = 4.74 + 0.48 - 0.3$$

$$pH = 4.92$$

iv $CH_3COO^- + HCl \longrightarrow CH_3COOH$

10	2	10
8	LR	12

$$pH = 4.74 + \log\left(\frac{8}{12}\right)$$

$$pH = 4.74 + 0.3 - 0.48$$

$$pH = 4.56$$

PH CALCULATION FOR BASIC BUFFER

NH_4^+/NH_3 (K_b)

a	b	$c_1 = \frac{a}{V}$
c_1	c_2	$c_2 = \frac{b}{V}$

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

c_2	c_1	
$c_2 - x$	$c_1 + x$	x

$$[-\log x = pOH]$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \left(\frac{c_1+x}{c_2-x}\right)x$$

$$-\log k_b = -\log\frac{c_1}{c_2} - \log x$$

$$pK_b = -\log\frac{c_1}{c_2} + pOH$$

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

$$pOH = pK_b + \log\left[\frac{a}{b}\right]$$

1. Dilution $pH = 14 - pOH$

2. x mole HCL is added.

$$NH_3 + HCL \longrightarrow NH_4^+$$

$$\begin{array}{ccc} b & x & a \\ b-x & [LR] & a+x \end{array}$$

$$p^{OH} = p^{K_b} + \log\left(\frac{a+x}{b-x}\right)$$

3. Y mole NaOH is added

$$NH_4 + NaOH \longrightarrow NH_3$$

$$\begin{array}{ccc} a & Y & b \\ a-Y & [LR] & b+Y \end{array}$$

$$p^{OH} = p^{K_b} + \log\left(\frac{a-Y}{b+Y}\right)$$

QUE. 10 mole NH_3 is taken with 10 mole NH_4^+ in 1 lt solu^n. what will b the p^H of solu^n

i. $K_b = 1.8 \times 10^{-5} \rightarrow$ of NH_3

ii. if 2 lt H_2O is added

iii. if 2 mole HCL added

iv. 2 mole NaOH added

Solu^n:- i.

$$\underset{10}{NH_3} + H_2O \rightleftharpoons \underset{10}{NH_4} + OH^-$$

$$p^{OH} = p^{K_b} + \log\left(\frac{10}{10}\right)$$

$$p^{OH} = -\log(1.8 \times 10^{-5})$$

$$p^{OH} = 4.74$$

$$p^{OH} = 14 - 4.74 = 9.26$$

ii. No effect on delution

$$p^H = 9.26$$

iii $NH_3 + HCL \longrightarrow NH_4^+$

$t\neq0$ 10 2 10

$t=t$ $10-2$ $10+2$

8 12

$p^{OH} = 4.74 + \log \frac{\cancel{12}}{\cancel{8}} \frac{3}{2}$

$p^{OH} = 4.74 + 0.48 - 0.3$

$p^{OH} = 4.92$

$p^{OH} = 14 - 4.92 = 9.08$

iv $p^{OH} = 4.74 + 0.3 - 0.48$

$= 5.04 - 0.48$

$= 4.56$

$p^{OH} = 14.00 - 4.56$

$= 9.44$

QUE What is PH?

i 500 ml 0.1 M CH_3COOH $(Ka = 10^{-5})$

$CH_3COOH \longrightarrow CH_3COO^- + [H^+]$

$[H^+] = \sqrt{cKa}$

$[H^+] = \sqrt{0.1 \times 10^{-5}}$

$[H^+] = \sqrt{10^{-6}}$

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

$p^H = -\log(10^{-3}) = 3$

ii 500 ml 0.1 M COOH + 100 ml 0.1 M NaOH

$CH_3COOH + NaOH \longrightarrow CH_3COO^-$

millimole 50 10

40 [LR] 10

This is a buffer solution

$pH = pKa + \log\left(\frac{1\cancel{0}}{4\cancel{0}}\right)$

$pH = -\log(10^{-5}) + \log(1/4)$

$pH = 5 + 0 - 2(0.3)$

$pH = 5 - 0.6$

$pH = 4.4$

iii 500 ml 0.1M CH_3COOH + 300 ml 0.1M NaOH

$CH_3COOH + NaOH \rightarrow CH_3COO^-$

50	30	
50-30	[LR]	30

This is a buffer solution

$pH = 5 + \log\left(\frac{3\cancel{0}}{2\cancel{0}}\right)$

$pH = 5 + \log 3 - \log 2$

$pH = 5 + 0.48 - 0.3$

$pH = 5.18$

IV 500 ml 0.1M CH_3COOH + 500 ml 0.1M NaOH

$CH_3COOH + NaOH \rightarrow CH_3COONa$

50	50	50

$[CH_3COONa] = \frac{50}{1000} = \frac{5}{100}$

Salt hydrolysis

$pH = 7 + \frac{1}{2}[\log.c + pKa]$

$pH = 7 + \frac{1}{2}\left[\log\left(\frac{5}{100}\right) + 5\right]$

$pH = 7 + \frac{1}{2}[0.7 - 2 + 5]$

$pH = 7 + \frac{1}{2}(3.7)$

$pH = 7 + 1.85$

$pH = 8.85$

Y. 500 ml 0·1M CH_3COOH + 700 ml 0·1M NaOH

$$CH_3COOH + NaOH \longrightarrow CH_3COO^-$$

50	70	
[LR]	70 − 50 = 20	50

Weak base + strong base

$[OH^-]$ governed from strongbase

$$[OH^-] = \frac{20}{1200} = \frac{1}{60}$$

$$pOH = -\log(1/60) = \log 60 = \log 2 + \log 3 + 1$$

$$= 0·3 + 0·48 + 1$$

$$= 1·78$$

$$pH = 14 - 1·78$$

$$pH = 12·26$$

WEAK POLYPROTIC ACID

H_2S (Ka_1, Ka_2) $Ka_1 >> Ka_2$

$Ka_1 \rightarrow$ $H_2S \rightleftharpoons H^+ + HS^-$

c − x   x + y   x

$HS^- \rightleftharpoons H^+ + S^{2-}$

$Ka_2 \rightarrow$ x − y   x + y   y

We can ignore
x wrt c
y wrt x

$$Ka_1 = \frac{[H^+][HS]}{[H_2S]} = \frac{(x+y)(x)}{c-x}$$

$Ka_1 >> Ka_2$

$$Ka_1 = \frac{x^2}{c} \qquad x = \frac{c}{\sqrt{cKa_1}}$$

$[H^+]$ will be governed from I^{st} step

$$Ka_2 = \frac{[H^+][S^{2-}]}{[HS^-]} = \frac{(x+\cancel{y})(y)}{(x-\cancel{y})} = Y$$

$$Y = Ka_2 = [S^{2-}]$$

$$\alpha_{H_2S} = \frac{x}{c} \quad \% \alpha_{H_2S} = 0.1\%$$

$$\underset{c-x}{H_3PO_4} \rightleftharpoons \underset{x+y+z}{H^+} + \underset{x}{H_2PO_4^-}$$

$$Ka_1 = \frac{(x+y+z)x}{c-x} = \frac{x^2}{c}$$

$$\underset{x-y}{H_2PO_4^-} \rightleftharpoons \underset{x+y+z}{H^+} + \underset{y}{HPO_4^{2-}}$$

$$Ka_2 = \frac{(x+y+z)y}{x-y} \simeq Y = Ka_2$$

$$\underset{x-Y}{HPO_4^{2-}} \rightleftharpoons \underset{x+Y+z}{H^+} + \underset{Y}{PO_4^{3-}}$$

$$Ka_3 = \frac{(x+Y+z)z}{Y-z} \simeq \frac{xz}{Y} = Ka_3$$

where H^+ is governed from strong acid (outside).

$$\underset{c_1}{HCL} + \underset{c_2}{H_2S}$$

$$\underset{c_2-x}{H_2S} \rightleftharpoons \underset{c_1+2x}{2H^+} + \underset{x}{S^{2-}}$$

$$Ka = ka_1 \cdot ka_2 = \frac{[H^+]^2[S^{2-}]}{[H_2S]}$$

$Ka_1, Ka_2, \underset{\underset{c_1}{\downarrow}}{[H^+]} \underset{\underset{c_2}{\downarrow}}{[H_2S]}$ will be given $[S^{-2}]$ can be calculated.

SOLUBILITY AND SOLUBILITY PRODUCT

In this section, we'll study about sparingly soluble salts.

$$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$$

$$S\ \frac{\text{mole}}{\text{lt}} \qquad S \qquad S$$

$$k_{sp} = [Ag^+][Cl^-] = S.S = S^2$$

$$S = \sqrt{K_sP}$$

K_{sp} = solubility product

K_{sp} only depend on temperature.

on addition of solid at a particular temparature will have no effect on solubility.

solvent → H_2O

e.g:- $PbCl_{2\,(s)} \rightleftharpoons Pb^{+2}_{(aq)} + 2Cl^-_{(aq)}$

$$K_{sp} = [Pb^{+2}][Cl^-]^2 = S.(2S)^2 = 4S^3$$

$$S^3 = \frac{K_sP}{4}$$

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

S is solubility of $PbCl_2$

Generalise

$$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$$

$$x^3 \qquad y^s$$

$$k_{sp} = (xs)^x(ys)^y = x^y\, y^y\, s^{x+y}$$

e.g:- $Na_3AlF_6 \rightleftharpoons 3Na^+ + AlF_6^{3-}$

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

$K_{sp} = 27s^4$

$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$

Ionic product $I.P = [Ag^+][Cl^-]$

if $I.P = K_{sP}$ saturated solution
$I.P < K_{sP}$ unsaturated solution
$I.P > K_{sP}$ supersaturated solution
(ppt occur)

{ Remember Q_c, K_c!! }

SOLUBILITY IN COMMON ION

QUE. AgCl ($K_{sp} = 10^{-10}$)

(i) What will be solubility in water
(ii) what will be solubility in 0.1M KCl solun
(iii) what will be solubility in 0.1M $AgNO_3$ solun

Solun:- (i) $AgCl_{(s)} \rightleftharpoons \underset{s}{Ag^+_{(aq)}} + \underset{s}{Cl^-_{(aq)}}$

$K_{sp} = s^2$

$s = \sqrt{K_sP}$

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

$= 10^{-5}$

(ii) $KCl \rightarrow K^+ + Cl^-$

$0{\cdot}1 \quad 0{\cdot}1 \quad 0{\cdot}1$

$0{\cdot}1 + s'$

$AgCl \rightleftharpoons Ag^+ + Cl^-$

$s' \quad 0{\cdot}1 + s'$

$K_{sp} = s'(0{\cdot}1 + s)$

$10^{-10} = 10^{-1} s'$

$s' = 10^{-9}$ mol/lt

(iii) $AgCl \rightleftharpoons Ag^+ + Cl^-$

$s'' \quad 0{\cdot}01 + s''$

$10^{-10} = 10^{-2} s''$

$s'' = 10^{-8}$ mol/lt

$PbCl_2$ ($K_{sp} = 4 \times 10^{-12}$)

What will be solubility

(i) in H_2O

(ii) in 0.01M HCl

(iii) in 0.01M $Pb(NO_3)_2$

(i) $PbCl_2 \rightleftharpoons Pb^+ + 2Cl^-$

$s \quad s \quad 2s$

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

$\frac{4 \times 10^{-12}}{4} = s^3$ $\quad s = 10^{-4}$ mol/lt

(ii) $PbCl_2 \rightleftharpoons Pb^{+2} + 2Cl^-$

$s' \quad 10^{-2} + 2s'$

$K_{sp} = (10^{-2} + 2s)^2 s'$

$\frac{4 \times 10^{-\cancel{12}\ 10}}{\cancel{10^{-2}}\ 10^{-2}} = s'$ $\quad s' = 4 \times 10^{-8}$

iii $PbCl_2 \rightleftharpoons \underset{s''}{Pb^{+2}} + \underset{10^{-2}+2s''}{2Cl^-}$

$$4\times10^{-12} = s''(10^{-2}+2s'')^2$$

$$PbCl_2 \rightleftharpoons \underset{S+10^{-2}}{Pb^{+2}} + \underset{2S}{2Cl^-}$$

$$Pb(NO_3)_2 \longrightarrow Pb^{+2} + 2NO_3^{2-}$$

$$4\times10^{-12} = (s+10^{-2})(2s)^2$$

$$4\times10^{-12} = 10^{-2}\times 4s^2$$

$$10^{-10} = s^2$$

$$\boxed{S = 10^{-5}}$$

Here, solubility is decreasing due to common ion.

SIMULTANEOUS SOLUBILITY

$$AgCl_{(s)} \rightleftharpoons \underset{s_1+s_2}{Ag^+_{(aq)}} + \underset{s_1}{Cl^-_{(aq)}}$$

$$Ksp_1 = (s_1+s_2)s_1$$

$$Ag\,CN_{(s)} \rightleftharpoons \underset{s_1+s_2}{Ag^+_{(aq)}} + \underset{s_2}{CN^-_{(aq)}}$$

$$Ksp_2 = (s_1+s_2)s_2$$

$$Ksp_1 + Ksp_2 = (s_1+s_2)(s_1+s_2)$$
$$= (s_1+s_2)^2$$
$$s_1+s_2 = \sqrt{Ksp_1 + Ksp_2}$$

SELECTIVE - PRECIPITATION

QUE In a solution $[I^-] = [Br^-] = [Cl^-] = 0.01M$
$AgNO_3$ is added slowly.

(i) Which ion will precipitate first?

(ii) What will be % precipation of first ion, when 2nd will start precipitating?

(iii) What will be % precipitation of other ions when last ion will start precipitating.

(Given :- Ksp of AgCl = 10^{-10}, Ksp of AgBr = 10^{-13})
Ksp of AgI → 10^{-16}

Solⁿ :- for AgCl $[Ag^+][Cl^-] = K_{sp}$

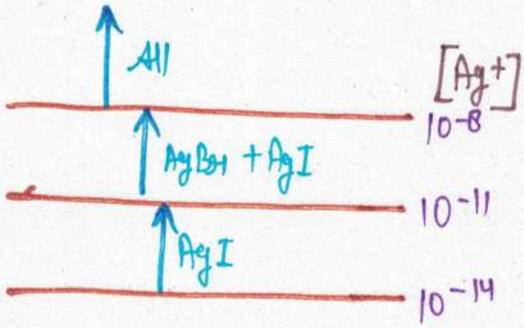
$$[Ag^+] = \frac{10^{-10}}{10^{-2}} = 10^{-8}$$

for AgBr $[Ag^+][Br^-] = 10^{-13}$

$$[Ag^+] = \frac{10^{-13}}{10^{-2}} = 10^{-11}$$

for AgI $[Ag^+][I^-] = 10^{-16}$

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



(i) AgI will precipitate first.

(ii) When AgBr will start precipitating.
$[Ag^+] = 10^{-11}$

for AgI = $[Ag^+][I^-] = 10^{-16}$

$$[I^-] = \frac{10^{-16}}{10^{-11}} = 10^{-5}$$

$$\% \text{remain} = \frac{10^{-5}}{10^{-2}} \times 100 = 0.1\%$$

$$\% \text{ppt} = 100 - 0.1$$

$$= 99.9\%$$

III $[Ag^+] = 10^{-8}$

for AgI $[Ag^+][I^-] = 10^{-16}$

$$[I^-] = \frac{10^{-16}}{10^{-8}} = 10^{-8}$$

$$\% \text{remain} = \frac{10^{-8}}{10^{-2}} \times 100 = 10^{-4}\%$$

$$\% \text{ ppt} = 100 - 0.0001$$

$$= 99.9999\%$$

for AgBr $[Ag^+][Br^-] = 10^{-13}$

$$[Br^-] = \frac{10^{-13}}{10^{-8}} = 10^{-5}$$

$$\% \text{remain} = \frac{10^{-5}}{10^{-2}} \times 100 = 10^{-1}$$

$$\% \text{ ppt} = 100 - 0.1 = 99.9\%$$

THEORY OF INDICATORS

Indicators are organic substances which have different colours in ionised and unionised form.

phenolpthalein :- slightly basic medium

$$\underset{\text{colourless}}{HPh} \rightleftharpoons H^+ + \underset{\text{pink}}{Ph^-}$$

$$K_a = \frac{[H^+][Ph^-]}{[HPh]} \Rightarrow -\log K_a = -\log [H^+] - \log \frac{[Ph^-]}{[HPh]}$$

$$CH_3COOH + NaOH \longrightarrow PH = 7 + \frac{1}{2}(\log c + Pk_a)$$

range = 8.3 to 10

$$\frac{[Ph^-]}{[HPh]} \geqslant 10$$ pink

$$\frac{[Ph^-]}{[HPh]} \leqslant 10$$ colourless

Methyle orange :- Acidic medium

$$\underset{\text{Yellow}}{MeOH} \rightleftharpoons \underset{\text{red}}{Me^+} + OH^-$$

eg:- NH_4Cl

$$P^H = 7 - \frac{1}{2}(\log c + P^{K_b})$$

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

$$p^{OH} = p^{Kb} + \log \frac{[Me^+]}{[MeOH]}$$

$p^{OH} = p^{Kb} + 1$

p^H range :- 3 to 5

if $\frac{[Me^+]}{[MeOH]} \geq 10$ red

$\frac{[Me^+]}{[MeOH]} \leq 10$ Yellow

BEFFER ACTION

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ (weakly ionise)

$CH_3COONa \rightleftharpoons CH_3COO^- + Na +$ (highly ionise)

- If small amount of acid is added in above buffer the following reac^n will occur :-

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

$Ka' = \frac{1}{Ka} = 10^5$

Hence the added HCl will be almost completely furnished and p^H change would not occur.

as $(Ka \geq 10^3)$

- If small amount of base is added in above buffer then

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

$\frac{1}{K_H} = \frac{ka}{kw}$

$= \frac{10^{-5}}{10^{-14}} = 10^{+9}$

Hence the added base will be alive finished & p^H change would not occure.

PH of ACIDIC BUFFER

(as $K_a > 10^3$)

$$p^H = p^{Ka} + \log\left[\frac{salt}{acid}\right]$$

$$p^H = p^{Ka} + \log\left[\frac{conjugate\ base}{acid}\right]$$

Que. $p^H = ?$

a. 0·1M CH_3COOH + 0·1M CH_3COONa ($p^{Ka} = 4·74$)

$$p^H = p^{Ka} + \cancel{\log\left(\frac{0·1}{0·1}\right)}$$

b. equal volume of 0·1M CH_3COOH + 0·05 M $NaOH$

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

t=t	0·1V	·005V		
t=0	0·10V − 0·05x 0·05V	0	0·05 x 0·05 Y	

$$p^H = p^{ka} + \log\left(\frac{0·05V}{0·05V}\right) = 4·74$$

Range of Buffer:– $\frac{1}{10} \leq \left[\frac{CH_3COONa}{CH_3COOH}\right] \leq 10$

i·e:– $p^{ka}-1$ to $p^{ka}+1$

By using an acidic Buffer, solu^n of p^H from $p^{ka}-1$ to $p^{ka}+1$ can be formed.

★ In any type of 2 solutions mixtures.

★ 1. p^H difference b/w them is 1, then p^H of resulting mixture will be = lower solutions p^H + 0·26

★ 2. p^H difference is 2, then p^H of resulting solu^n = Lower p^H + 0·29

★ 3. p^H difference > 2, then p^H of resulting solu^n = Lower p^H + 0·3

BUFFER CAPACITY ϕ

Power of buffer to resist change in its pH on addition of a small amount of an acid or a base.

$$\phi = \frac{\text{no. of moles of acid/base added in 1 lt sol}^n}{\text{change in pH}}$$

$$\phi = \frac{d(n)}{d(pH)}$$

for max^n buffer capacity (∞), pH change should be zero

Acidic buffer :- $CH_3COOH + CH_3COONa$

moles a s

$$\phi = \frac{2.303(as)}{a+s}$$

Basic buffer :- $\phi = \frac{2.303(bs)}{b+s}$

For max^n buffer capacity

[Acid] = [salt]

or

[Base] = [salt]

QUESTION Among the following, which sol^n has max^n buffer capacity

(i) 6 gm CH_3COOH + 82 gm CH_3COONa

(ii) 6.00 gm CH_3COOH + 82 gm CH_3COONa

(iii) 60 gm CH_3COOH + 8.2 gm CH_3COONa

(iv) 6 gm CH_3COOH + 8.2 gm CH_3COONa ↘ Moles are equal

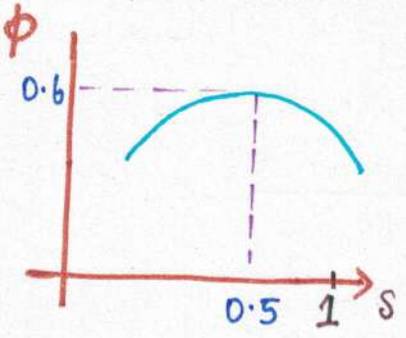
$6/10 < \frac{82}{82}$

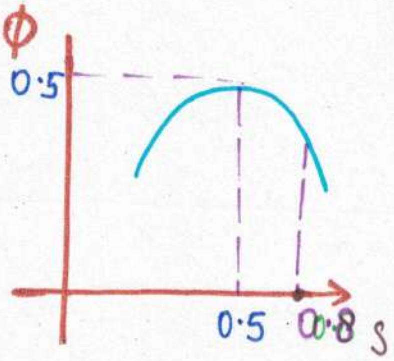
$\frac{6.00}{60} > \frac{82}{82}$

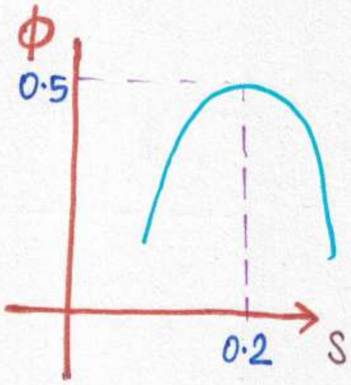
$\frac{60}{60} > \frac{82}{82}$

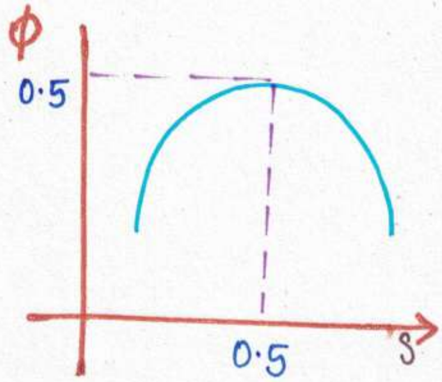
$6/60 = \frac{8.2}{82}$

QUESTION In an acidic buffer, acid (a) and salt (s) has a+s =1. If a graph of buffer capacity will be salt amount is plotted then currect occure.









SOLUTION :- $\left[\phi = 2.303 \frac{as}{a+s} = \frac{2.303 \times 0.25}{1} = 0.57575\right]$

INDICATORS AND TITRATIONS

Solutions which are used to detect the end point (equivalence pt) in acid base tibration.

Indicator		pH range		colour change
Methyle orange	→	5.2 - 4.5	→	Yellow to orange
Methyle red	→	4.4 - 6.5	→	Yellow to red
Litmus	→	5.5 - 7.5	→	red to blue

Phenol red → 6·8 - 8·4 → red to Yellow

Phenolphthalein → 8·3 - 10·5 → colourless to pink

1. OSTIVALD THEORY

Indicators are solu^n of weak acid or weak base which will ionise less in one medium than in other. Both ionise and unionised forms have different colours.

- Phenolphthalein is a weak acid which ionise as

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

unionised form → colourless

ionised form → pink

In acidic medium HPh is colourless

In Basic medium HPh is pink

- Methyl orange is a weak base which ionise as

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

unionised form → Yellow

ionised form → Orange

In acidic medium Me(OH) is Orange

In Basic medium Me(OH) is yellow

- usually one form which is present in Large percentage (>50%) will show its colour. But according to human eye sensitivity, one form is 10 times higher than the other, then the solution will show its colour.

$$\underset{\substack{1 \\ 1-\alpha}}{HIn} \rightleftharpoons \underset{\substack{0 \\ \alpha}}{H^+} + \underset{\substack{0 \\ \alpha}}{In^-}$$

$$\left[\frac{In^-}{HIn}\right] > 10$$ (colour of In^- will be there)

$$\frac{\alpha}{1-\alpha} \geqslant 10$$

$$11\alpha \geqslant 10$$

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

$$\alpha \geqslant 0.91$$

% ionisation $\geqslant$ 91 %

$$\left[\frac{In^-}{HIn}\right] \leq \frac{1}{10}$$ (colour of HIn will be there)

$$\frac{\alpha}{1-\alpha} \leq \frac{1}{10}$$

$$\alpha \leq \frac{1}{11}$$

$$\alpha \leqslant 0.091$$

% ionisation $\leqslant$ 9.1 %

PH OF INDICATOR SOLUTION

Solution of indicator will act as buffer.

Hence

pH of acid indicator $pH = pKa + \log\left[\frac{IN^-}{HIN}\right]$

or. $pH = pKa + \log\left[\frac{\alpha}{1-\alpha}\right]$

pH of basic indicator $pH = pKa + \log\left[\frac{\text{conj. acid}}{\text{base}}\right]$

QUE. Calculate the p^H of acid indicator solⁿ which ionise to 30% in solution ($pK_{In} = 4.7$)

Solⁿ:- $p^H = pka + \log\left(\frac{\alpha}{1-\alpha}\right)$

$p^H = 4.7 + \log\left(\frac{6.3}{0.7}\right)$

$\alpha = 0.3$

$pka = 4.7$

$4.7 + 0.4.8 - 1$

$-.84 + 1$

$= 5.18 - 0.84 = 4.34$

$pka = 4.34$

QUE. An Acid indicator show (blue) colour in acidic form and red in basic form. Blue colour will appear only when acidic form is 10 times higher than basic form and red colour will appear only when basic form is 5 times greater than acidic form what will be pH range of indicator? ($pK_{In} = 5$)

Solⁿ:- $\underset{\text{acidic}}{HIn} \rightleftharpoons \underset{\text{basic}}{In^-} + H^+$

Blue colour $p^H = pka + \log\left[\frac{In^-}{HIn}\right]$

$p^H = 5 + \log(1/10)$

$p^H = 5 - 1 = 4$

$\boxed{p^H = 4}$

$\left[\frac{HIn}{In^-}\right] > 10$

Red colour $p^H = 5 + \log 5$

$p^H = 5 + 0.699$

$p^H = 5.699$

$\boxed{p^H = 5.699}$

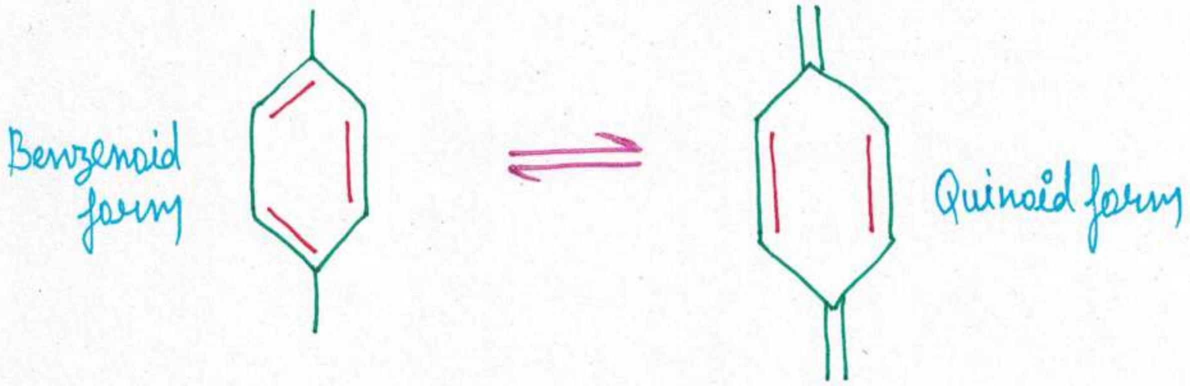
$\left[\frac{In^-}{HIn}\right] > 5$

p^H of indicator is of range 4 to 5.422 in the Question.

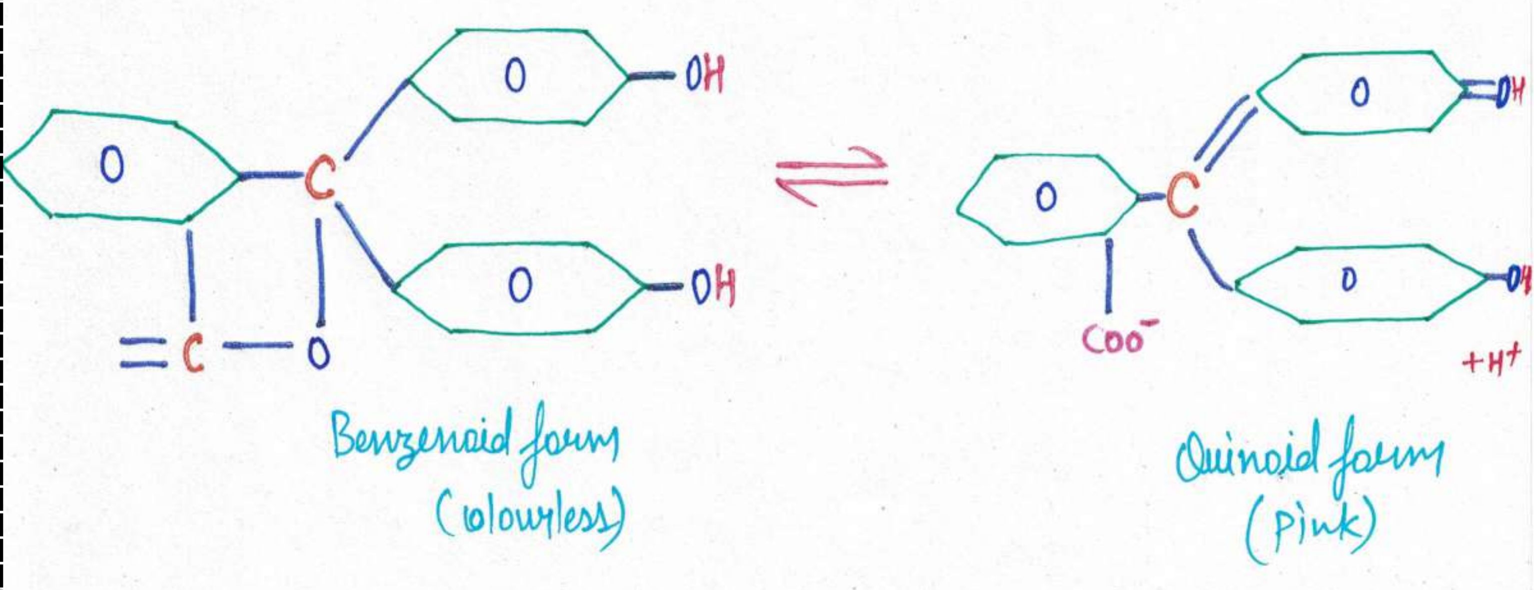
2. QUINOID THEORY

Indicators are solu^n of weak organic acid or weak organic base.

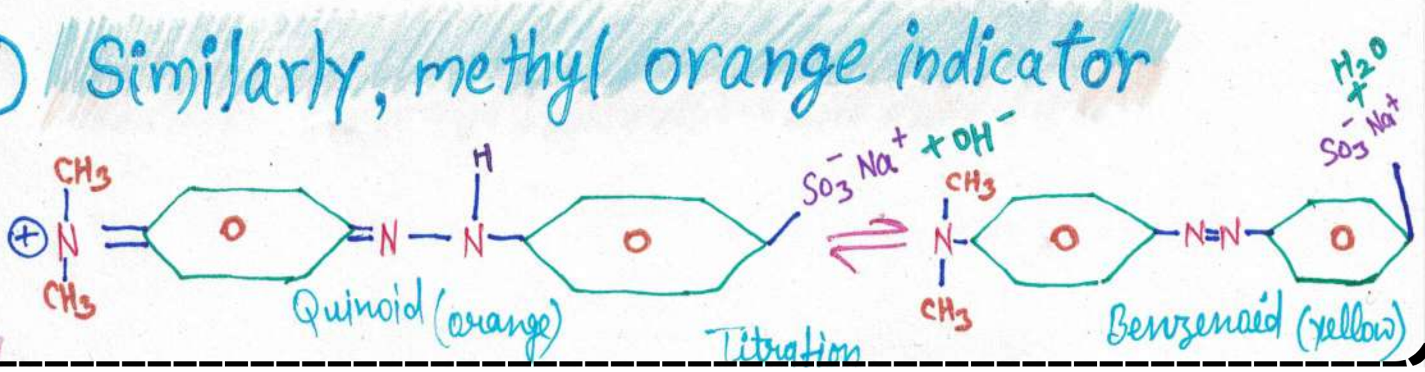
Indicators exist in the solu^n either in quinoid form or in benzenoid form in which quinoid form is dark in colour.



○ Phenolphthalein indicator

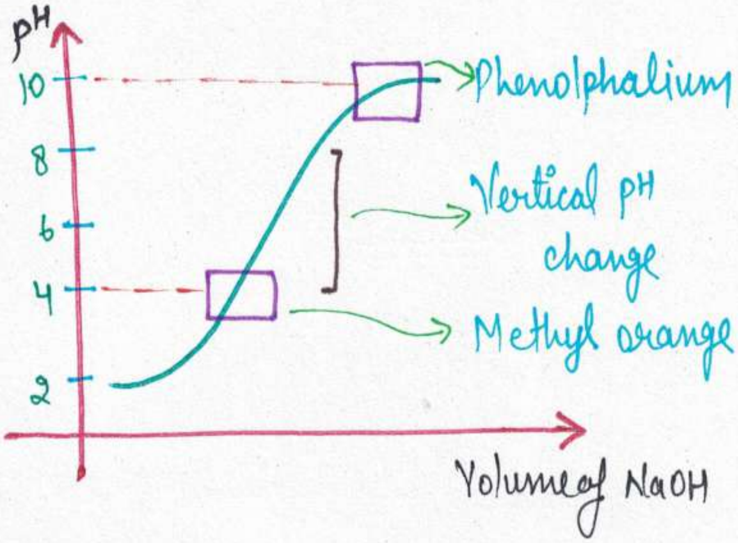


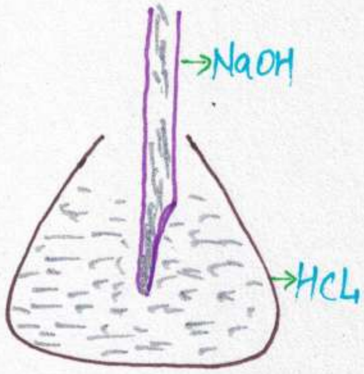
○ Similarly, methyl orange indicator



- The process in which end point is deducted by using an indicator.
- Selection of indicator is based on a vertical pH change in a titration.

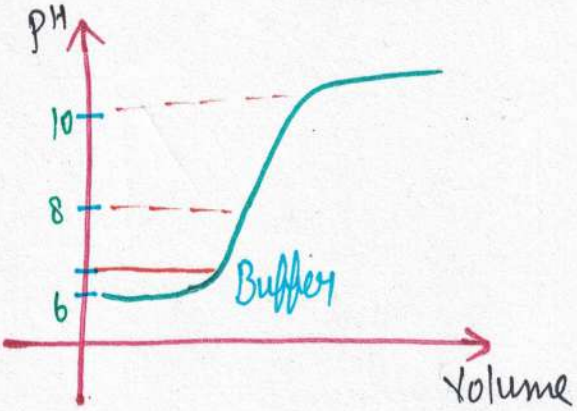
1. Titration of a Strong Acid and strong Base

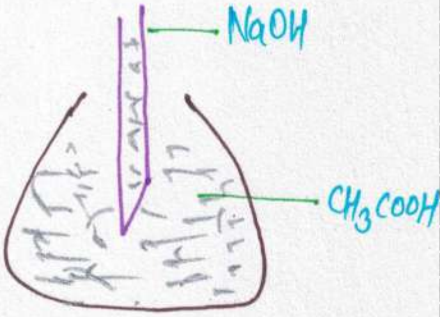




Vertical pH change is from 4 to 10

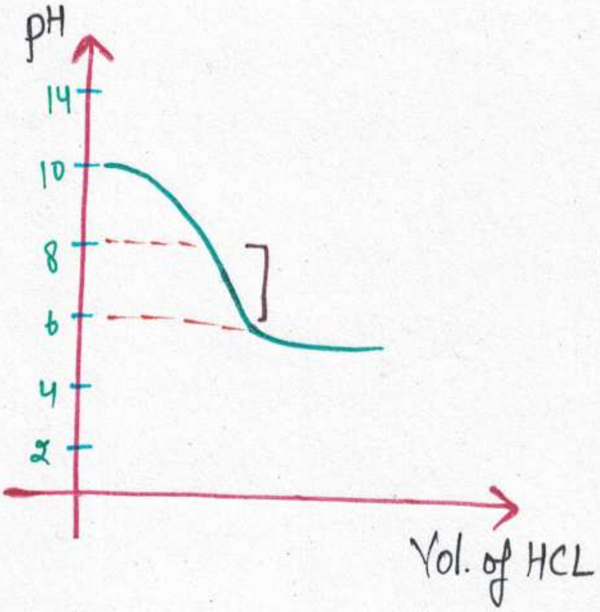
2. Titration of Weak Acid with Strong Base

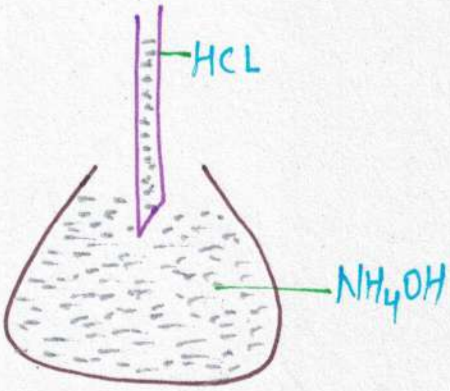




Vertical pH change is from 7 to 10

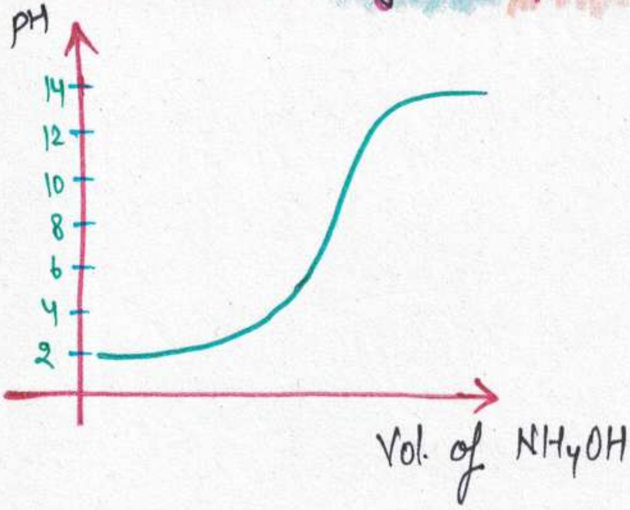
3. Titration of Weak base and strong acid

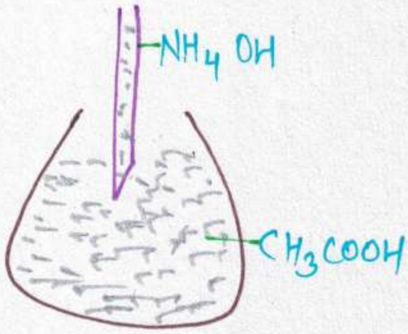




Vertical pH change is from 10 to 7

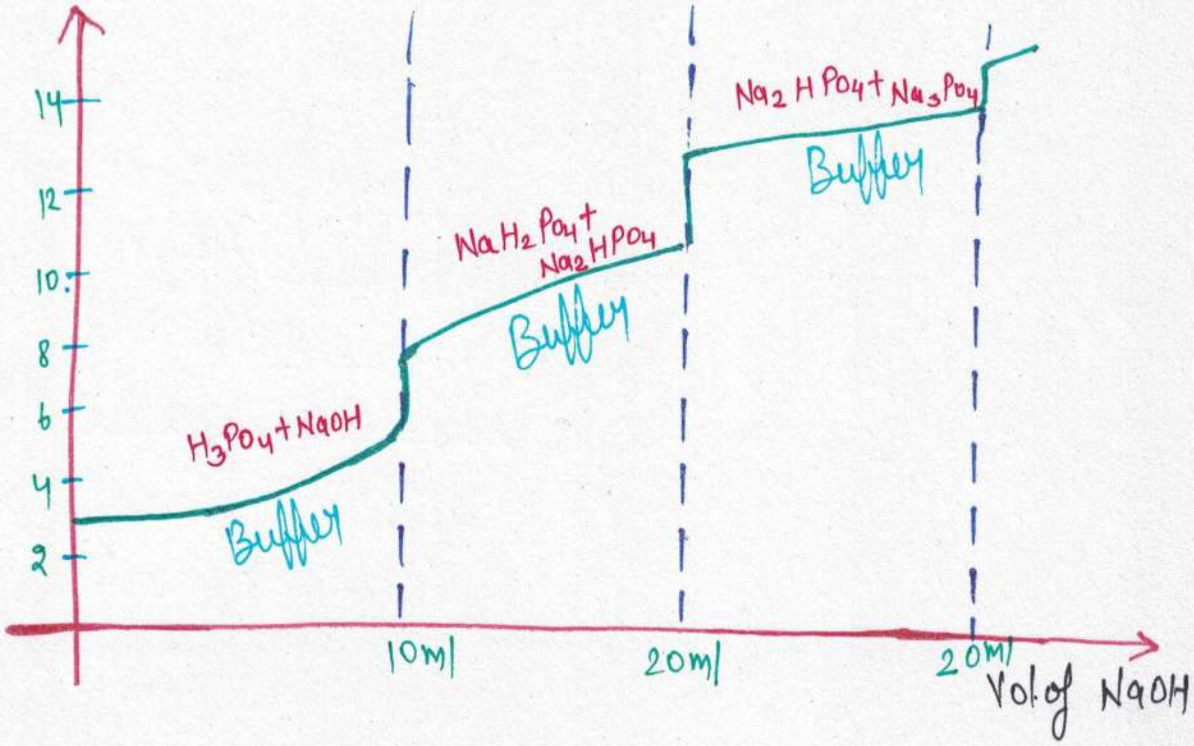
4. Titration of Weak acid and Weak base





No Vertical pH change here

5. Titration of Weak Polyprotic acid and strong base



No. of Buffer formed will depend on polyprotic index of weak acid.

IONIC EQUILIBRIUM

SHORT NOTES

"P" operator take (-log) of the variables.

eg:- $p^{H} = -\log(H^+)$ $p^{ka} = -\log(ka)$

At 25°C, the $kw = 10^{-14}$

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$kw = [H^+][OH^-] = 10^{-14} \text{———} ①$$

Taking -log on bothside of ①

$$\boxed{p^{H} + p^{OH} = 14}$$

$p^{H} = 7$ → Neutral

$p^{H} < 7$ → Acidic

$p^{H} > 7$ → Basic

p^H Calculation:- $p^H = -\log[H^+] = -\log\left(\frac{\text{moles of } H^+}{\text{volume}}\right)$

e.g.:- 300ml of 0.1M HCL

millimoles of $(H^+) = 0.1 \times 300 = 30$, volume $= 300$

$$p^H = -\log\left(\frac{30}{300}\right) = -\log(10^{-1}) = 1$$

For strong acids:- Calculate p^H of 300ml 0.3M H_2SO_4

millimoles of $H^+ = 300 \times 0.3 \times \underset{\substack{\downarrow \\ 2H^+ \text{ present}}}{2} = 180$

volume $=$ 300 ml

$\therefore [H^+] = \frac{180}{300}$, $p^H = -\log\left(\frac{180}{300}\right)$

p^H calculation for Weak Acid:-

$$\begin{array}{lccc} & CH_3COOH & \rightleftharpoons CH_3COO^- & + H^+ \\ t=0 & C & & \\ t=t & 1-\alpha & C\alpha & C\alpha \end{array}$$

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

$$p^H = -\log\left(\sqrt{K_a C}\right)$$

$$\boxed{p^H = \frac{1}{2}\left(-\log C + pK_a\right)}$$

p^H Calculation for (strong + weak) Acid

- Here, p^H will be governed by the strong acid only.
- Thus, only take $[H^+]$ of strong acid as the $[H^+]$ of the weak acid will be ignored.

pH calculation for (strong + Weak) Base

- Here, pH will be governed by the strong base only as the [OH] coming from weak base can be ignored.

Weak acid + Weak acid

$(C_1\ Ka_1)$ (C_2, Ka_2)

e.g:- CH_3COOH eg:- CCl_3COOH

$$\begin{array}{lccc} & CH_3COOH \rightleftharpoons & CH_3COO^- & + H^+ \\ t=t & C_1-x & x & x+y \end{array}$$

$$\begin{array}{lccc} & CCl_3COOH \rightleftharpoons & CCl_3COO^- & + H^+ \\ t=t & C_2-y & y & y+x \end{array}$$

$$x+y = [H^+] = \sqrt{C_1Ka_1 + C_2Ka_2}$$

$$p^H = -\log(x+y)$$

Salt hydrolysis

SA = Strong acid
WA = Weak acid

a. Salt of SA + SB

NaCl
NaOH + HCl
(SB) (SA)

K_2SO_4 etc
KOH + H_2SO_4

b. Salt of SA + WB

NH_4Cl CH_3NH_3Cl

NH_3 + HCL
(WB) (SA)

c. Salts of SB + WA

$CH_3COO^- \, Na^+$,

$$\underset{(SB)}{NaOH} + \underset{(WA)}{CH_3COOH}$$

d. Salts of WA + WB

CH_3COONH_4 , $HCOONH_4$

$$\underset{(WA)}{CH_3COOH} \qquad \underset{(WB)}{NH_3}$$

Here, instead of kw, ka, kb ; we need to use K_H (hydrolysis) as to get the correct answer.

e.g:- $NH_4Cl \longrightarrow NH_4^+ + Cl^- \rightarrow$ (No role)

↓ Now hydrolyse etc.

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

t=0	c			
t=t	c(1-h)		ch	ch

$$K_h = \frac{(ch)^2}{c(1-\cancel{h})^0} = (ch^2) \Rightarrow \boxed{h = \sqrt{\frac{K_h}{c}}}$$

$\boxed{K_h = \frac{K_w}{K_b}}$ → In Case of base

$\boxed{K_h = \frac{K_w}{K_a}}$ → In Case of acid

$$pH = 7 - \frac{1}{2}(\log K_c + PK_b)$$

- In Case of Salts of WB + SA

$$pH = 7 - \frac{1}{2}(\log C + pK_b)$$

- In Case of salts of WA + SB

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

- Salts of Weak acid + weak base

$$K_h = \left(\frac{h}{1-h}\right)^2 \qquad K_h = \left(\frac{K_w}{K_a \cdot K_b}\right)$$

$$pH = 7 - \frac{1}{2}(pK_a - pK_b)$$

Buffer Solution

A Solution having constant pH is called a buffer solution.

(i) **Acidic buffer** :- A solution having weak acid along with the conjugate base in significant amount.

eg:- $CH_3COOH / CH_3COO^- \longrightarrow$ (acidic buffer)

(ii) **Basic buffer** :- A solution having weak base along with the conjugate acid in significant amount

eg:- $NH_3 / NH_4Cl \longrightarrow$ (Basic buffer)

pH Calculations for acidic buffer

$$pH = pK_a + \log\left(\frac{[salt]}{[Acid]}\right)$$

pH Calculations for basic buffer

$$pOH = pK_b + \log\left(\frac{[salt]}{[Base]}\right)$$

$$pH + pOH = 14$$

Weak polyprotic acid (H_3PO_4)

$$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+$$

Ka_1 $t=t$ $c-x$ x $x+y+z$

$$H_2PO_4^- \rightleftharpoons HPO_4^{-2} + H^+$$

Ka_2 $t=t$ $x-y$ y $y+x+z$

$$HPO_4^{-2} \rightleftharpoons PO_4^{-3} + H^+$$

Ka_3 $t=t$ $y-z$ z $z+x+y$

$$Ka_1 = \frac{(x+\cancel{y}^{\circ}+\cancel{z}^{\circ})(x)}{(c-\cancel{x})^{\circ}} = \frac{x^2}{c}$$ — (1.)

$$Ka_2 = \frac{(x+\cancel{y}^{\circ}+\cancel{z}^{\circ})(y)}{x-\cancel{y}^{\circ}}$$

$Ka_2 = y$ — ②

$$Ka_3 = \frac{(x+\cancel{y}^{\circ}+\cancel{z}^{\circ})(z)}{(y-\cancel{z})^{\circ}} = \frac{xz}{y}$$ — ③

Calculate x, y, z from ①②③; and

$[H^+] = x+y+z$ then $pH = -\log(x+y+z)$

Solubility and Solubility prod

eg:- $AgCl_{(s)} \rightleftharpoons Ag^+ + Cl^-$ ksp

s s

$Ksp = s^2$

eg:- $PbCl_2 \rightleftharpoons Pb^{+2} + 2Cl^-$

s $2s$

$Ksp = (s)(2s)^2 = 4s^3$