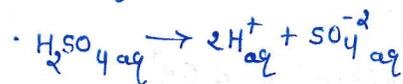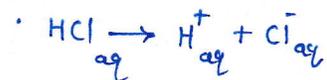# IONIC EQUILIBRIUM

## Arrhenius concepts of Acids and Base
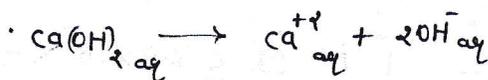
### Acid

- substance which give $H^+$ ion in water
- $HX_{aq} \longrightarrow H^+ + X^-_{aq}$
- $HCl_{aq} \longrightarrow H^+_{aq} + Cl^-_{aq}$
- $H_2SO_4\,aq \longrightarrow 2H^+_{aq} + SO_4^{-2}\,_{aq}$

### Base

- substance which gives $OH^-$ ion in $H_2O$
- $MOH_{aq} \longrightarrow m^+_{aq} + OH^-_{aq}$
- $NaOH_{aq} \longrightarrow Na^+_{aq} + OH^-_{aq}$
- $Ca(OH)_{2\,aq} \longrightarrow Ca^{+2}_{aq} + 2OH^-_{aq}$
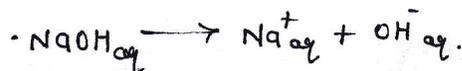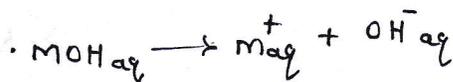
Limitation :- Applicable only to aqueous solution

Basicity of $NH_3$ is not explained (does not posses hydroxyl group)

## Bronsted-Lowry concept or Proton theory :

### Acids

- which donates $H^+$ ion or proton doner

### Base

- which accepts $H^+$ ion or proton acceptors

## Lewis-Acid & Base Theory :

### Acids

- species which accept electron pair
- Electron deficient species
- $BF_3 + NH_3 :$    $BF_3 \longleftarrow NH_3$
- $AlCl_3$, $co^{+3}$, $Mg^{+2}$ etc.

### Base

- species which donate electron pair
- electron rich species
- ex: $H_2O$, $NH_3$, $OH^-$

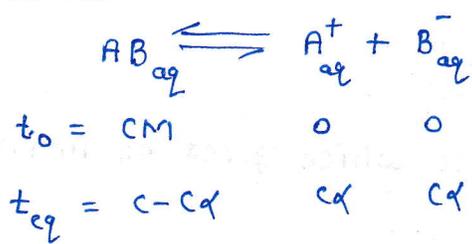## Conjugate Acid-Base pair

conjugate Acid : Add $H^+$

conjugate Base : Remove $H^+$

$OH^-$ : conjugate acid : $H_2O$

$NH_4^+$ : conjugate Base : $NH_3$

if Bronsted acid is strong then its conjugate base is weak & vice versa.

# ionization constant :

$$AB_{aq} \rightleftharpoons A^+_{aq} + B^-_{aq}$$

$$t_0 = CM \qquad 0 \qquad 0$$

$$t_{eq} = c - c\alpha \qquad c\alpha \qquad c\alpha$$

$$K_{eq} = K_1 = \frac{[A^+][B^-]}{[AB]} = \frac{c^2\alpha^2}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$
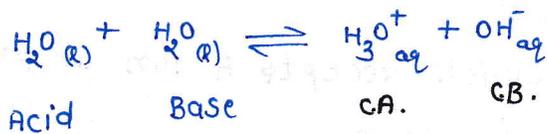
$K_1 = K_a$ : For weak acid

$K_1 = K_b$ : For weak Base

# Neglation Theory :

$$K_1 = \frac{c\alpha^2}{1-\alpha} \begin{cases} \text{if } \frac{K_1}{c} \leq 6.4 \times 10^{-3} \longrightarrow 1-\alpha \approx 1 \quad \text{therefore } K_1 = c\alpha^2 \\ \\ \text{if } \frac{K_1}{c} > 6.4 \times 10^{-3} \longrightarrow 1-\alpha \neq 1 \quad \text{therfore } K_1 = \frac{c\alpha^2}{1-\alpha} \begin{array}{l} \text{solve} \\ \text{quadratic} \end{array} \end{cases}$$

# ionization constant of water & its ionic product

water act as acid as well as base

$$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{aq} + OH^-_{aq}$$

Acid    Base    CA.    CB.

$$K_1 = \frac{[H_3O^+][OH^-]}{[H_2O]}$$

$K_1 = $ Dissociation constant

$K_w = $ ionic product of water

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

Experimental : $[H^+] = [OH^-] = 10^{-7} M$    at 298 K

$$K_w = [H^+][OH^-] = 10^{-7} \times 10^{-7} = 10^{-14}$$

$K_w \leftarrow$ Temperature dependent

# ostwald dilution law :-

According to this law degree of ionization of weak electrolyte is directly proportional to square root of dilution (vol $\uparrow$) and inversely proportional to sq. root of concentration

$$\alpha = \frac{K}{\sqrt{c}} \quad , \qquad \alpha = K\sqrt{dilution}$$

## common ion effect :

when strong electrolyte is added to weak electrolyte having common ion then degree of ionization of weak electrolyte decreases.

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

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

concentration of common ion $\uparrow$. so reaction will shift backward.

## PH - Scale

$$P = -\log$$

$$PH = -\log[H^+] \qquad : \quad H^+ = 10^{-PH}$$

$$POH = -\log[OH^-] \qquad : \quad OH^- = 10^{-POH}$$

$$pK_a = -\log K_a$$

$$pK_b = -\log K_b \qquad \begin{cases} pKW = -\log 10^{-14} \\ pKW = 14 \text{ at } 25°C \end{cases}$$

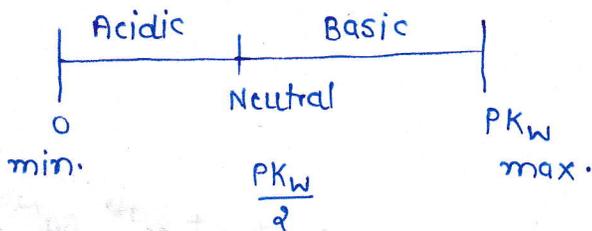$$pK_W = -\log K_W$$

## Relation b/w PH & POH :

$$K_W = [H^+][OH^-] \qquad \longrightarrow \text{at all temp}$$

$$-\log K_W = -\log H^+ - \log OH^-$$

$$pK_W = PH + POH \qquad \text{at all temp.}$$

$$14 = PH + POH \qquad \text{at } 25°C$$

## PH - Scale :

```
        Acidic      |      Basic
      |-------------+-------------|
      |          Neutral          |
      0                          PKw
     min.          PKw           max.
                   ---
                    2
```

## PH - cases

1. strong Acid or strong Base

2. Mixture of strong Acid or strong Base

3. salt hydrolysis

4. Buffer solution

strong monoprotic acid & Base :

Ex: HCl, NHO$_3$ , NaOH, KOH

$PH = -\log H^+$

$POH = -\log OH^-$

if $\dfrac{H^+}{OH^-} < 10^{-6} M$ then, we can't calculate PH directly by this formula we

have to consider $H^+$ ion concentration from water also

## PH of mixture :-

case-1 : PH of mixture of two or more strong acid solution

$$N_1V_1 + N_2V_2 \cdots\cdots N_nV_n = NV$$

acid① Acid② - - - .

$$N_m = \dfrac{N_1V_1 + N_2V_2 \cdots}{V_T} = [H^+]$$

case-2 : PH of mixture of two or more strong Base solution

$$N_1V_1 + N_2V \cdots\cdots = N_TV_T$$

$$N_T = [OH^-]$$

case3 : PH of a mixture of strong Acid and strong Base solution

$$\left(N_1V_1 + N_2V_2 \cdots\cdots\right)_{Acid} - \left(N_1V_1 + N_2V_2 \cdots\cdots\right)_{Base} = N_TV_T$$

$$N_T = H^+ \text{ or } OH^- \text{ or } 0$$

$$\begin{cases} N_T \oplus ve \text{ then } N_m = H^+ \\ N_T \ominus ve \text{ then } N_T = OH^- \\ N_T \cdot \text{---} \text{ then } N_T = 7 \end{cases}$$

Hydrolysis of salts : $\begin{cases} \text{cationic Hydrolysis from Base } (Na^+, K^+, Ca^{+2}, Ba^{+2}) \\ \text{Anionic Hydrolysis from Acid } (ClO_4^-, SO_4^{-2}, NO_3^-, Br^-, Cl^-) \end{cases}$

# Types of salt :-

① Salt of WA + SB : $CH_3COONa$ , $NaCN$ , $NaHCO_3$ , $NaHS$

② Salt of SA + WB : $NH_4Cl$ , $(NH_4)_2SO_4$ , $R NH_3Cl^-$

③ Salt of WA + WB : $CH_3COONH_4$ , $NH_4CN$ , $NH_4NO_2$

④ Salt of SA + SB : $NaCl$ , $KCl$ , $CaCl_2$

## Hydrolysis of salts and PH calculation :-

| salt | SA + SB | SA + WB | WB + SB | WA + SB |
|---|---|---|---|---|
| Hydrolysis | NO | cationic | Anionic | Both cationic + Anionic |
| Nature of solution | Neutral | Acidic | Basic | Almost Neutral |
| $K_h = \dfrac{K_W}{K_{weak}}$ | — | $\dfrac{K_W}{K_b}$ | $\dfrac{K_W}{K_a}$ | $\dfrac{K_W}{K_a \cdot K_b}$ |
| (h) Degree of Hydrolysis | — | $\sqrt{\dfrac{K_h}{c}}$ or $\sqrt{\dfrac{K_W}{K_b C}}$ | $\sqrt{\dfrac{K_h}{c}}$ or $\sqrt{\dfrac{K_W}{K_a \cdot c}}$ | $\sqrt{K_h}$ or $\sqrt{\dfrac{K_W}{K_a K_b}}$ |
| PH value | 7 | $7 - \frac{1}{2} PK_b - \frac{1}{2} \log c$ | $7 + \frac{1}{2} PK_a + \frac{1}{2} \log c$ | $7 + \frac{1}{2} PK_a - \frac{1}{2} PK_b$ |

**Buffer solution ;** solution which resist in PH value on dilution

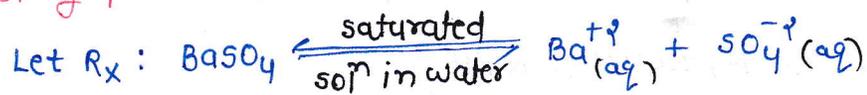- → simple Buffer :- salt of WA + WB in water : $CH_3COONH_4$ , $NH_4CN$ , $AgCN$
- → Mixed Buffer
  - → Acidic : salt of WA & its conjugation : $HCN + KCN$
  - → Basic : salt of WB & its conjugation : $NH_4OH + NH_4Cl$

## solubility of salt ;

if solubility > ·1M : soluble salt       or     ·1M to ·01M than salt is
              < ·01M : Insoluble salt              sparingly soluble salt

# solubility product :-

Let $R_X$ : $BaSO_4 \underset{\text{sol}^n \text{ in water}}{\overset{\text{saturated}}{\rightleftharpoons}} Ba^{+2}_{(aq)} + SO_4^{-2}{}_{(aq)}$

$$K_1 = \frac{[Ba^{+2}][SO_4^{-2}]}{[BaSO_4]}$$

$$K_1 (BaSO_4) = [Ba^{+2}][SO_4^{-2}]$$

$$K_{sp} = [Ba^{+2}][SO_4^{-2}]$$

$\left\{ \begin{array}{l} K_{sp} = \text{solubility product} \end{array} \right.$