3. IONIC EQUILIBRIA

3.1 Introduction : The equilibrium between ions and unionized molecules in solution is called ionic equilibrium. T[redacted]f

electrolyte : The substances which give rise to ions when dissolved in water are electrolytes. T[redacted]se

Types of electrolyte

3.2.1 Strong electrolyte : The electrolytes ionizing completely or almost completely are strong electrolytes. For example : strong acids, strong bases and salts.

For example HCl , H_2SO_4 , NaOH , KOH

NaCl , KBr , AgCl

3.2.2 Weak electrolyte : The electrolytes which dissociate to a smaller extent in aqueous solution are weak electrolytes. Weak acids and weak bases belong to this class.

For example CH3COOH , H-COOH , NH4OH , Cu(OH)2

3.2.3 Degree of dissociation ($\propto$) : The degree of dissociation of an electrolyte is defined as a fraction of total number of moles of the electrolyte that dissociates into its ions when the equilibrium is attained. It is denoted by symbol $\propto$ and given by

$$\propto = \frac{\text{number of moles dissociated}}{\text{total number of moles}} \quad \ldots\ldots (3.1)$$

$$\text{Percent dissociation} = \propto \times 100 \quad \ldots\ldots (3.2)$$

Acids and Bases :

Arrhenius theory of acids and bases

Acid : Acid is a substance which contains hydrogen and gives rise to $H^{\oplus}$ ions in aqueous solution. For example :

$$HCl\ (aq) \xrightarrow{water} H^{\oplus}(aq) + Cl^{\ominus}(aq)$$

$$CH_3COOH(aq) \underset{}{\overset{water}{\rightleftharpoons}} CH_3COO^{\ominus}(aq) + H^{\oplus}(aq)$$

Base : Base is a substance that contains OH group and produces hydroxide ions ($OH^{\ominus}$) ions in aqueous solution. For example,

$$NaOH\ (aq) \longrightarrow Na^{\oplus}(aq) + OH^{\ominus}(aq)$$

$$NH_4OH(aq) \rightleftharpoons NH_4^{\oplus}(aq) + OH^{\ominus}(aq)$$

Bronsted - Lowry theory

Acid : Acid is a substance that donates a proton ($H^{\oplus}$) to another substance.

Base : Base is a substance that accepts a proton ($H^{\oplus}$) from another substance.

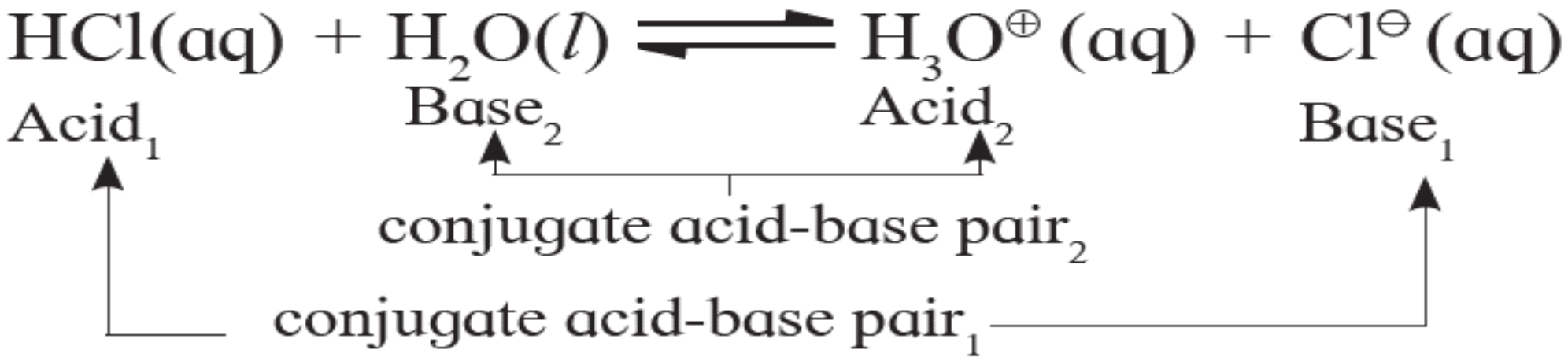
For example :

$$HCl + NH_3 \rightleftharpoons NH_4^{\oplus} + Cl^{\ominus}$$

Acid, Base, Acid, Base.

Conjugate acid-base pair

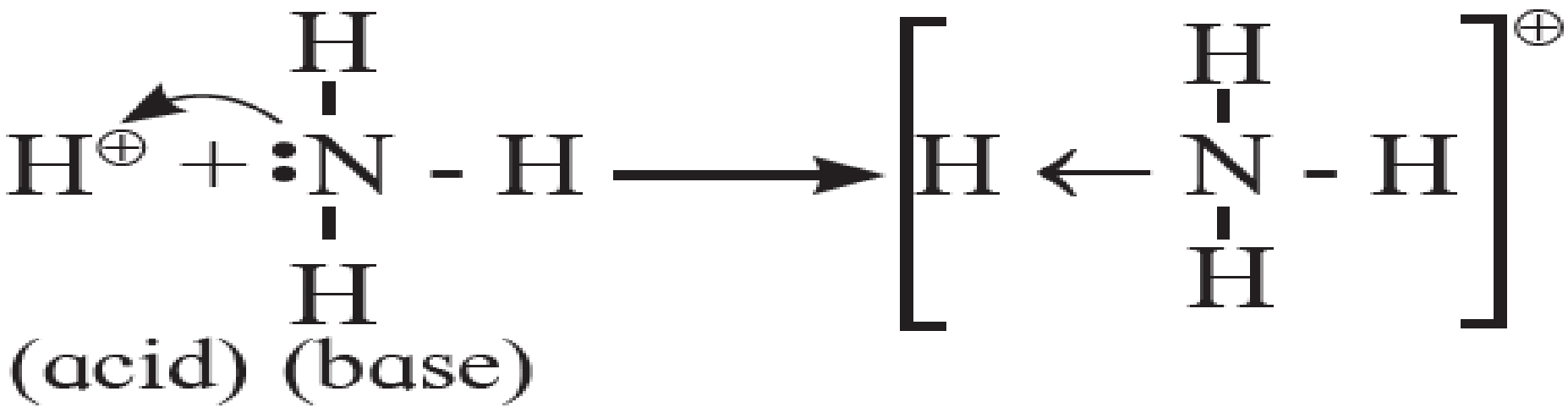
[redacted] A pair of an acid and a base differing by a proton is said to be a **conjugate acid-base pair**.

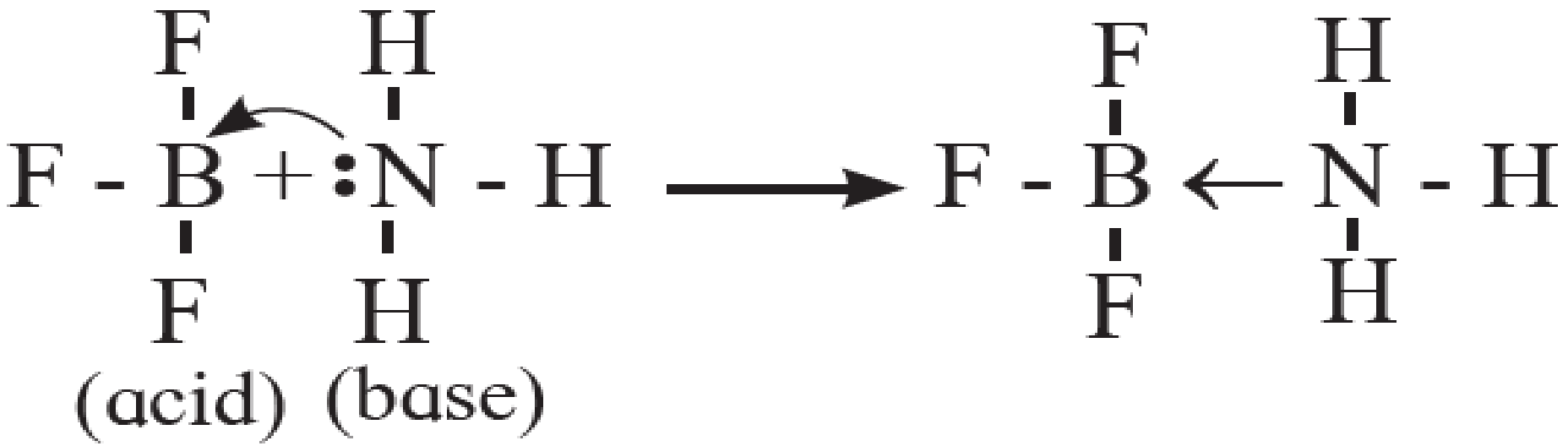


3.3.3 Lewis theory :

Acid : Any species that accepts a share in an electron pair is called Lewis acid.

Base : Any species that donates a share in an electron pair is called Lewis base.


H
H⊕ + :N - H
H
(acid) (base)
H
H ← N - H
H
⊕


F H
F - B + :N - H
F H
(acid) (base)
F H
F - B ← N - H
F H

Amphoteric nature of water : Water has the ability to act as an acid as well as a base. Such behaviour is known as amphoteric nature of water. For example :

$$H_2O(l) + NH_3(aq) \rightleftharpoons OH^{\ominus}(aq) + NH_4^{\oplus}(aq)$$

Acid

$$H_2O(l) + HCl(aq) \rightleftharpoons H_3O^{\oplus}(aq) + Cl^{\ominus}(aq)$$

Base

H_2O acts as an acid towards NH_3 and as a base towards HCl. Therefore H_2O is amphoteric.

3.4 Ionisation of acids and bases

Strong acids and bases are almost completely dissociated in water. For example :

$$HCl\,(aq) \longrightarrow H^{\oplus}(aq) + Cl^{\ominus}\,(aq)$$

$$NaOH\,(aq) \longrightarrow Na^{\oplus}(aq) + OH^{\ominus}(aq)$$

Typical strong acids are HCl, HNO_3, H_2SO_4, HBr and HI while typical strong bases may include NaOH and KOH.

Weak acids and weak bases are partially dissociated in water. The solution of a weak

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^{\ominus}(aq) + H^{\oplus}(aq)$$

$$NH_4OH(aq) \rightleftharpoons NH_4^{\oplus}(aq) + OH^{\ominus}(aq)$$

Note that HCOOH, HF, H_2S are examples of weak acids while $Fe(OH)_3$, $Cu(OH)_2$ are examples of weak bases.

3.4.1 Dissociation constant of weak acids and weak bases :

The dissociation of a weak acid HA in water is expressed as

$$HA(aq) \rightleftharpoons H^{\oplus}(aq) + A^{\ominus}(aq)$$

The equilibrium constant called acid-dissociation constant for this equilibrium is :

$$K_a = \frac{[H^{\oplus}][A^{\ominus}]}{[HA]} \qquad \ldots\ldots\ldots\ldots (3.3)$$

Similarly the dissociation of weak base BOH in water is represented as :

$$BOH(aq) \rightleftharpoons B^{\oplus}(aq) + OH^{\ominus}(aq)$$

The equilibrium constant called base-dissociation constant for this equilibrium is,

$$K_b = \frac{[B^{\oplus}][OH^{\ominus}]}{[BOH]} \quad \text{..... (3.4)}$$

Ostwald's Dilution law:-

For weak electrolytes degree of dissociation α, is inversly proportional to square root of its concentration, or directly proportional to the square root of volume of solution.

For weak acid HA: consider one mole of weak acid HA is dissolved in $V\ dm^3$ of solution and α is degree of dissociation of this weak acid, so initial concentration of HA is $c = \frac{1\ mol}{V\ dm^3}$

Now weak acid partially dissociates into its ions and equilibrium is established between undissociated molecules HA & its ions.

$$HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}$$

	$HA_{(aq)}$	$H^+_{(aq)}$	$A^-_{(aq)}$
Initial mole	1 mole	0	0
mole at equilibrium	$(1-\alpha)$	α	α
conc. at equilibrium	$\frac{1-\alpha}{V}$	$\frac{\alpha}{V}$	$\frac{\alpha}{V}$

Dissociation constant K_a of acid

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

put the concentrations of species at equilibrium in above eq^n

$$K_a = \frac{(\alpha/V) \cdot (\alpha/V)}{\left(\frac{1-\alpha}{V}\right)}$$

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

For weak acid α is very small

$\alpha <<< 1$ & $(1-\alpha) \cong 1$

$$\therefore K_a = \frac{\alpha^2}{V} \quad \text{or} \quad K_a = \alpha^2 \cdot C$$

where c is initial conc. $\left[\because C = 1/V\right]$

$$\therefore \alpha^2 = K_a \cdot V \quad \text{or} \quad \alpha^2 = K_a/C$$

$$\alpha = \sqrt{K_a \cdot V} \qquad \alpha = \sqrt{K_a/C}$$

For weak base BOH:

Consider 1 mole is dissolved in $V dm^3$ of solution & initial concentration $C = 1/V$

if α is degree of dissociation

$$BOH_{(aq)} \rightleftharpoons B^+_{(aq)} + OH^-_{(aq)}$$

Initial mole	1	0	0
Final mole	$(1-\alpha)$	α	α
conc.	$1-\alpha/V$	α/V	α/V

Dissociation constant of weak base K_b

$$K_b = \frac{[B^+] \cdot [OH^-]}{[BOH]}$$

$$K_b = \frac{(\alpha/V) \cdot (\alpha/V)}{(1-\alpha)/V}$$

$$K_b = \frac{\alpha^2}{(1-\alpha)V} \qquad \left[\because 1 >>> \alpha \;\; \because (1-\alpha) \simeq 1\right]$$

$$\therefore K_b = \frac{\alpha^2}{V} \quad \text{or} \quad K_b = \alpha^2 \cdot C$$

$$\alpha^2 = K_b \cdot V \quad \text{or} \quad \alpha^2 = \frac{K_b}{C}$$

$$\alpha = \sqrt{K_b \cdot V} \quad \text{or} \quad \alpha = \sqrt{\frac{K_b}{C}}$$

3.5 Autoionization of water : Pure water ionizes to a very small extent. The ionization

$$H_2O\,(l) + H_2O\,(l) \rightleftharpoons H_3O^{\oplus}(aq) + OH^{\ominus}(aq)$$

The equilibrium constant (K) for the ionization of water is given by

$$K = \frac{[H_3O^{\oplus}][OH^{\ominus}]}{[H_2O(l)]^2} \qquad \ldots\ldots\ldots\ldots (3.12)$$

$$\text{or } K[H_2O]^2 = [H_3O^{\oplus}][OH^{\ominus}] \qquad \ldots\ldots\ldots\ldots (3.13)$$

$[H_2O]^2 = K'$. Substituting this in Eq. (3.13) we get,

$$K \times K' = [H_3O^{\oplus}][OH^{\ominus}] \qquad \ldots\ldots\ldots\ldots (3.14)$$

$$K_w = [H_3O^{\oplus}][OH^{\ominus}]$$

where $K_w = KK'$ is called ionic product of water. The product of molar concentrations of hydronium (or hydrogen) ions and hydroxyl ions at equilibrium in pure water at the given temperature is called ionic product of water.

$$K_w = [H_3O^{\oplus}][OH^{\ominus}]$$

$$K_w = (1.0 \times 10^{-7})\,(1.0 \times 10^{-7})$$

$$K_w = 1.0 \times 10^{-14} \qquad \text{.....(3.15)}$$

pH defined the pH of a solution as the negative logarithm to the base 10, of the concentration of $H^{\oplus}$ ions in solution in mol dm^{-3}. Expressed mathematically as

$$pH = - \log_{10}[H^{\oplus}]$$

Similarly *pOH* of a solution can be defined as the negative logarithm to the base 10, of the molar concentration of $OH^{\ominus}$ ions in solution.

Thus, $pOH = -\log_{10}[OH^{\ominus}]$ ..... (3.16)

3.6.1 Relationship between pH and pOH

The ionic product of water is

$$K_w = [H_3O^{\oplus}][OH^{\ominus}]$$

Now, $K_w = 1 \times 10^{-14}$ at 298 K and thus

$$[H_3O^{\oplus}][OH^{\ominus}] = 1.0 \times 10^{-14}$$

Taking logarithm of both the sides, we write

$$\log_{10}[H_3O^{\oplus}] + \log_{10}[OH^{\ominus}] = -14$$

$$-\log_{10}[H_3O^{\oplus}] + \{-\log_{10}[OH^{\ominus}]\} = 14$$

From Eq. (3.16) and (3.17)

$$pH + pOH = 14 \qquad \text{.....(3.18)}$$

1) Neutral solution

$$[H^+] = [OH^-] = 1 \times 10^{-7} M$$

$$pH = 7$$

ii) Acidic solution

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

$[H^+] > 1 \times 10^{-7} M$ & $[OH^-] < 1 \times 10^{-7} M$

$pH < 7$

For e.g. pH = 6·9, 6·8, ... 6, 5, 4 .... etc

iii) Basic solution

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

& $[H^+] < 1 \times 10^{-7}$

$$pH > 7$$

for example

$$pH = 8, 9, 10 \ldots\ldots 14$$

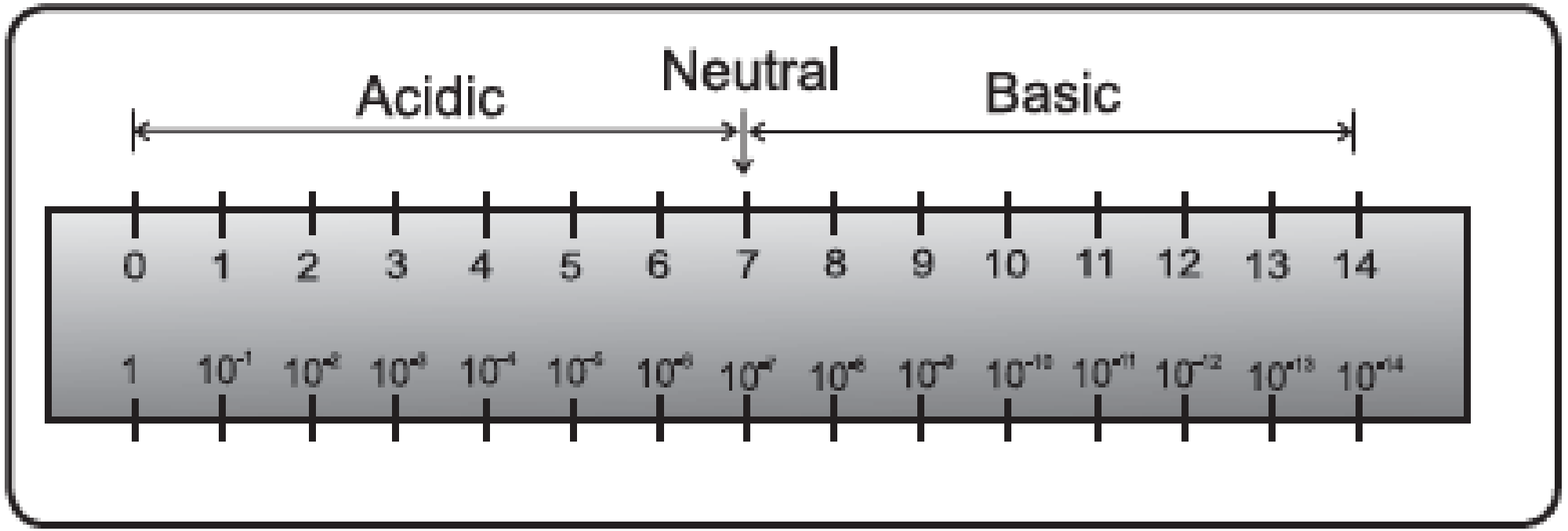


Fig. 3.1 : *pH* scale

Concentration of ions produced from strong electrolyte

$$\left[\text{ion}_{\text{conc}}\right] = \text{coefficient of ion} \times \text{initial concentration of strong electrolyte}$$

if initial concentration is C :

	H_2SO_4	$\longrightarrow$	$2H^+$	+	SO_4^{2-}
Initial concentration	C		0		0
Final conc	0		2C		C

⇒ Concentration of ion produced by dissociation of weak electrolyte

$$\left[\begin{matrix}\text{ionic}\\ \text{concentration}\end{matrix}\right] = \begin{matrix}\text{coefficient}\\ \text{of}\\ \text{ion}\end{matrix} \times \begin{matrix}\text{initial}\\ \text{concentration}\\ \text{of}\\ \text{electrolyt}\end{matrix} \times \begin{matrix}\text{degree}\\ \text{of}\\ \text{dissociation}\end{matrix}$$

e.g. $Cu(OH)_2 \rightleftharpoons Cu^{2+}_{(aq)} + 2OH^-_{(aq)}$

	$Cu(OH)_2$	$Cu^{2+}_{(aq)}$	$2OH^-_{(aq)}$
Initial conc.	C	0	0
Final conc.	$(C-\alpha C)$	αC	$2\alpha C$

3.7.1 Types of salts

These are of four types

I. Salts derived from **strong acid and strong base**. For example : NaCl, Na_2SO_4, $NaNO_3$, KCl, KNO_3.

II. Salts derived from **strong acids and weak bases**. For example : NH_4Cl, $CuSO_4$, NH_4NO_3, $CuCl_2$.

III. Salts derived from **weak acids and strong bases**. For example : CH_3COONa, KCN, Na_2CO_3.

IV. Salts derived from **weak acids and weak bases**. For example : CH_3COONH_4, NH_4CN.

⇒ Salt of strong acid & strong Base

Salt	S.B	S.A
NaCl	NaOH	HCl
Na_2SO_4	2 NaOH	H_2SO_4
$NaNO_3$	NaOH	HNO_3
KCl	KOH	HCl

⇒ Salt of weak base & strong acid

Salt	W.B	S.A
NH_4Cl	NH_4OH	HCl
$CuSO_4$	$Cu(OH)_2$	H_2SO_4
NH_4NO_3	NH_4OH	HNO_3

⇒ Salt of strong base & weak acid

Salt	S.B	W.A
CH_3COONa	NaOH	CH_3COOH
KCN	KOH	HCN
Na_2CO_3	2NaOH	H_2CO_3

⇒ Salt of weak base & weak acid

Salt	W.B	W.A
NH_4CN	NH_4OH	HCN
CH_3COONH_4	NH_4OH	CH_3COOH
NH_4F	NH_4OH	HF

3.7 Hydrolysis of salts

hydrolysis of salt. **Hydrolysis of salt is defined as the reaction in which cations or anions or both ions of a salt react with ions of water to produce acidity or alkalinity (or sometimes even neutrality).**

Salts of strong acids and strong bases

⇒ Hydrolysis of salt of strong Acid & strong base

$NaCl_{(aq)} + H_2O \rightleftharpoons NaOH_{(aq)} + HCl_{(aq)}$

(Salt) S·B S·A

In ionic form above eqn is

$Na^+_{(aq)} + Cl^-_{(aq)} + H_2O \rightleftharpoons$

$Na^+_{(aq)} + OH^-_{(aq)} + H^+_{(aq)} + Cl^-_{(aq)}$

Cancell common ions on both side

$H_2O \rightleftharpoons OH^-_{(aq)} + H^+_{(aq)}$

Neigther cation of salt, nor anion of salt reacts with water and there is no hydrolysis of salt.

$[H^+] = [OH^-]$ & $pH = 7$

Salts of strong acids and weak bases :

⇒ Salt of weak base & strong acid

$$CuSO_{4(aq)} + 2H\text{-}OH \rightleftharpoons Cu(OH)_{2(aq)} + H_2SO_{4(aq)}$$

salt — W.B — S.A

In ionic form

$$Cu^{+}_{(aq)} + SO_4^{-2}{}_{(aq)} + 2H_2O \rightleftharpoons Cu(OH)_{2(aq)} + 2H^{+}_{(aq)} + SO_4^{2-}{}_{(aq)}$$

Cancell common ions on both side of equilibrium

$$Cu^{+2}_{(aq)} + 2H_2O_{(l)} \rightleftharpoons Cu(OH)_{2(aq)} + 2H^{+}_{(aq)}$$

$$Cu^{+2}_{(aq)} + 2H_2O_{(l)} \rightleftharpoons Cu(OH)_{2(aq)} + 2H^+_{(aq)}$$

Cation of salt reacts with water

∴ Salt is hydrolysed

& excess of H^+ at equilibrium makes solution acidic

$[H^+] > [OH^-]$ & $pH < 7$

solution of $CuSO_{4(aq)}$ is acidic

Salts of weak acids and strong bases

⇒ Salt of strong base and weak acid

$CH_3COONa_{(aq)} + H_2O \rightleftharpoons CH_3COOH_{(aq)} + NaOH_{(aq)}$

salt W·A S·B

In ionic form, above equilibrium is

$CH_3COO^-_{(aq)} + Na^+_{(aq)} + H_2O \rightleftharpoons$

$CH_3COOH_{(aq)} + Na^+_{(aq)} + OH^-_{(aq)}$

Cancell common ion $Na^+_{(aq)}$ on both side

$CH_3COO^-_{(aq)} + H_2O \rightleftharpoons CH_3COOH + OH^-$

$CH_3COO^-_{(aq)} + H_2O \rightleftharpoons CH_3COOH + OH^-$

Anion of salt reacts with water

∴ salt undergoes hydrolysis, & excess OH^- at equilibrium makes solution basic

$[H^+] < [OH^-]$ & $pH > 7$ & [basic solution]

Salts of weak acids and weak bases:

i. if, $K_a > K_b$, the solution will be acidic.

ii. if, $K_a < K_b$, the solution will be basic.

iii. if, $K_a = K_b$, the solution will be neutral.

i. Salt of weak acid and weak base for which $K_a > K_b$.

NH_4F is a salt of weak acid HF (K_a = 7.2×10^{-4}) and weak base NH_4OH ($K_b = 1.8 \times 10^{-5}$). Here, K_a is greater than K_b. The salt hydrolyses as

$NH_4F_{(aq)} + H_2O \rightleftharpoons NH_4OH_{(aq)} + HF_{(aq)}$

salt w.B w.A

In ionic form above eqn is,

$$NH_4^{\oplus}(aq) + F^{\ominus}(aq) + H_2O \rightleftharpoons NH_4OH(aq) + HF(aq)$$

(weak base) (weak acid)

HF is slightly stronger acid than NH_4OH
Hence the solution of NH_4F is slightly acidic

$$NH_4^{\oplus}(aq)+2H_2O(l)\rightleftharpoons NH_4OH(aq)+H_3O^{\oplus}(aq)$$

.....(3.19)

$$F^{\ominus}(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^{\ominus}(aq)$$

.....(3.20)

The $NH_4^{\oplus}$ ions hydrolyse to a slightly greater extent than the $F^{\ominus}$ ions. That means

The solution of NH_4F is thus only slightly acidic

ii. Salt of weak acid and weak base for which $K_a < K_b$: NH_4CN is the salt of weak acid HCN ($K_a = 4.0 \times 10^{-10}$) and weak base NH_4OH ($K_b = 1.8 \times 10^{-5}$) showing that $K_a < K_b$. When NH_4CN is dissolved in water, it hydrolyses as

$NH_4CN + H_2O \rightleftharpoons NH_4OH + HCN$

(salt) W.B W.A

In ionic form above eqn is

$$NH_4^{\oplus}(aq) + CN^{\ominus}(aq) + H_2O(l) \rightleftharpoons NH_4OH(aq) + HCN(aq)$$

(weak base) (weak acid)

The base NH_4OH is stronger than the acid HCN.

in reaction (3.21). The solution of NH_4CN is, basic and turns red litmus blue.

iii. Salt of weak acid and weak base for which $K_a = K_b$.

CH_3COONH_4 is a salt of weak acid, CH_3COOH ($K_a = 1.8 \times 10^{-5}$) and weak base, NH_4OH ($K_b = 1.8 \times 10^{-5}$).

$CH_3COONH_4(aq) + H_2O \rightleftharpoons CH_3COOH(aq) + NH_4OH(aq)$

Salt — W.A — W.B

In ionic form above eqn is

$$CH_3COO^{\ominus}(aq) + NH_4^{\oplus}(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + NH_4OH(aq)$$

(weak acid) (weak base)

CH_3COOH and NH_4OH are equal in strength, hence solution of CH_3COONH_4 is neutral

3.8 Buffer solutions : Buffer solution is defined as a solution which resists drastic changes in pH when a small amount of strong acid or strong base or water is added to it.

a. Acidic buffer solution : A solution containing a weak acid and its salts with strong base is called an acidic buffer solution.

For example : A solution containing weak acid such as CH_3COOH and its salt such as CH_3COONa is an acidic buffer solution.

pH of acidic buffer is given by the equation

$$pH = pK_a + \log_{10}\frac{[\text{salt}]}{[\text{acid}]} \qquad \ldots\ldots\ldots\ldots (3.23)$$

$$\text{where } pK_a = -\log_{10}K_a \qquad \ldots\ldots\ldots\ldots (3.24)$$

and K_a is the dissociation constant of the acid.

b. Basic buffer solution : A solution containing a weak base and its salt with strong acid is the basic buffer solution.

For example : A solution containing a weak base such as NH_4OH and its salt such as NH_4Cl is a basic buffer solution.

The *pOH* of basic buffer is given by,

$$pOH = pK_b + \log_{10}\frac{[\text{salt}]}{[\text{base}]} \quad \ldots\ldots\ldots\ldots (3.25)$$

where $pK_b = -\log_{10}K_b$ ..... (3.26)and K_b is the dissociation constant for the base. Equations (3.26) and (3.25) are known to **Henderson Hasselbalch equation**.