IONIC EQUILIBRIUM

INTRODUCTION

The earliest classification of substances into acids and bases was bases upon the characteristic properties possessed by each one of them. For example,

Acid was defined as a substance whose aqueous solution possesses the following characteristic properties:

(i) conducts electricity,

(ii) reacts with active metals like zinc, magnesium etc. to give hydrogen,

(iii) turns blue litmus red.

(iv) has a sour taste.

(v) whose acidic properties disappear on reaction with a base.

Base was defined as a substance whose aqueous solution possessed the following characteristic properties:

(i) conducts electricity,

(ii) reacts with active metals like zinc, magnesium etc. to give hydrogen,

(iii) turns red litmus blue,

(iv) has a bitter taste

(v) whose basic properties are destroyed on reaction with an acid.

The above definitions of acids and bases are called operational definitions as they are based certain operations (i.e. tests) to be performed on the substances. However, these have been replaced by conceptual definitions (put forward by Arrhenius, Bronsted-Lowry and Lewis) which go into the causes of the observed behavior, based upon structure and composition of the substances.

Arrhenius Concept (1884)

(a) **Acid:-** According to this concept, those substances which produce free H^+ ions in aqueous solution are called acid.

Example HCl, HNO_3, H_2SO_4, H_3PO_4, H_2CO_3, H_2S, CH_3COOH etc.

$$HCl + H_2O \xrightarrow{\quad} H^+(aq.) + Cl^-(aq.)$$

$$H_2SO_4 + H_2O \xrightarrow{\quad} 2H^+(aq.) + SO_4^{-2}(aq.)$$

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^-(aq.) + H^+(aq.)$$

(b) **Base :-** Those substances which produce free OH^- ions in aqueous solution are called base.

Example $NaOH$, KOH, $Cs(OH)$, $Rb(OH)$, NH_4OH, $Ba(OH)_2$, $Ca(OH)_2$, $Al(OH)_3$ etc.

$$NaOH + H_2O \xrightarrow{\quad} Na^+ (aq.) + OH^- (aq.)$$

$$Ba(OH)_2 + H_2O \xrightarrow{\quad} Ba^{+2} (aq.) + 2OH^- (aq.)$$

(c) **Nature of water :-** According to this concept nature of water is neutral and act as a solvent.

(d) **Neutralisation Reaction :-** Those reactions in which acid and base react together to form water molecule are called neutralisation reactions.

i.e. $Na^+ + OH^- + H^+ + Cl^- \xrightarrow{\quad} NaCl + H_2O$

$H^+ + OH^- \xrightarrow{\quad} H_2O$

(e) **Strength of acids and bases :-** This concept explains the strength of acids and bases depending upon the basis of degree of ionisation.

Example For strong electrolytes $\alpha \simeq 100\%$

For weak electrolytes $\alpha < 100\%$

(f) **Advantage :-** This concept explains the acids and bases practically. i.e. To find out the pH, ionisation constant, hydrolysis constants, heat of neutralisation etc.

(g) **Disadvantage :-**

It explains the behaviour of acids and bases only in aqueous (water) solvents.

Illustrations

Illustration Gaseous hydrogen chloride is a very poor conductor of electricity but a solution of hydrogen chloride in water is a good conductor. This is due to the fact that :-

(1) Water is a good conductor of electricity

(2) Hydrogen chloride ionises in water

(3) A gas cannot conduct electricity but a liquid can

(4) HCl does not obey Ohm's law where as the solution does

Solution (2)

Illustration Which is acid in the following pairs according to Arrhenius concept ?

(1) HCl(g) and HCl (aq) (2) $CH_3COOH(l)$ and $CH_3COOH(aq)$

Solution (1) HCl(aq.) (2) $CH_3COOH(aq.)$

Bronsted-Lowry Concept (1923)

It is based upon the exchange of proton.

(a) Acid :- According to this concept those substances which have tendency to donate the proton (H^+) by any method in any solvent are called acids.

Example (i) Neutral molecules - HCl, HNO_3, H_2SO_4, H_2CO_3, H_2S, CH_3COOH, H_3PO_3 etc.

(ii) Anions - HS^-, HCO_3^-, HSO_4^-, $H_2PO_4^-$, HPO_4^{-2}, H_2O etc.

(iii) Cations - NH_4^+, H_3O^+, PH_4^+, $CH_3COOH_2^+$ etc.

$[Al(H_2O)_6]^{+3}$, $[Ag(H_2O)_2]^{+1}$, $[Fe(H_2O)_6]^{+3}$ etc.

Ex. 1 $HCl\text{ (Acid)} + H_2O\text{ (Solvent)} \longrightarrow H_3O^+ + Cl^-$

Ex.2 $HS^-\text{ (Acid)} + H_2O\text{ (Solvent)} \longrightarrow H_3O^+ + S^{-2}$

Ex.3 $NH_4^+\text{ (Acid)} + H_2O\text{ (Solvent)} \longrightarrow NH_3 + H_3O^+$

Ex.4 $[Al(H_2O)_6]^{+3}\text{ (Acid)} + H_2O\text{ (Solvent)} \longrightarrow [Al(H_2O)_5OH]^{+2} + H_3O^+$

(b) Base :- Those substances which have tendency to accept the proton by any method in any solvent are called the bases.

(1) HS^-, HCO_3^-, HSO_4^-, $H_2PO_4^-$, HPO_4^{-2}, O^{-2}, SO_4^{-2}, CO_3^{-2}, Cl^-, Br^-, I^-, CN^- etc.

(2) NH_3, RNH_2, R_2NH, R_3N, $C_6H_5NH_2$, C_5H_5N, $H_2N\text{-}NH_2$ etc.

Example (i) $HS^-\text{ (Base)} + H_2O\text{ (Solvent)} \longrightarrow H_2S + OH^-$

(ii) $NH_3\text{ (Base)} + H_2O\text{ (Solvent)} \longrightarrow NH_4^+ + OH^-$

(iii) $CO_3^{-2}\text{(Base)} + H_2O\text{ (Solvent)} \longrightarrow HCO_3^- + OH^-$

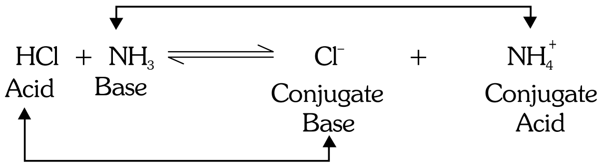
(c) Nature of water :- According to this concept nature of water is amphoteric or amphiprotic i.e. water can act as both acid and base.

(i) $HCl\text{ (Acid)} + H_2O\text{ (Base)} \longrightarrow Cl^- + H_3O^+$

(ii) $NH_3\text{ (Base)} + H_2O\text{ (Acid)} \longrightarrow NH_4^+ + OH^-$

(d) Neutralisation Reaction :- According to this concept those reaction in which acid and base react together and convert into their respective conjugate acid and base are called neutralisation reactions.

Example



$$\underset{\text{Acid}}{HCl} + \underset{\text{Base}}{NH_3} \rightleftharpoons \underset{\text{Conjugate Base}}{Cl^-} + \underset{\text{Conjugate Acid}}{NH_4^+}$$

(e) Strength of acids and bases :- This concept explain the strength of acid and base depending upon the basis of relative tendency to accept or donate the proton.

(i) $HClO_4$
(ii) HI
(iii) HBr
(iv) H_2SO_4
(v) HCl
(vi) HNO_3
(vii) H_3O^+
(viii) HSO_4^-
(ix) H_3PO_4
(x) HF
(xi) CH_3COOH
(xii) H_2CO_3
(xiii) H_2S
(xiv) NH_4^+
(xv) HCN
(xvi) C_6H_5OH
(xvii) H – OH
(xviii) C_2H_5–OH
(xix) $C_6H_5NH_2$
(xx) NH_3
(xxi) R–NH_2
(xxii) CH_4
(xxiii) H_2

Example

(i)	HCl Strong acid	+	H_2O Strong base	$\rightleftharpoons$	Cl^- Weak base	+	H_3O^+ Weak acid
(ii)	CH_3COOH Weak acid	+	H_2O Weak base	$\rightleftharpoons$	CH_3COO^- Strong base	+	H_3O^+ Strong acid
(iii)	NH_3 Weak base	+	H_2O Weak acid	$\rightleftharpoons$	NH_4^+ Strong acid	+	OH^- Strong base
(iv)	HCl Weak acid	+	CH_3COOH Weak base	$\rightleftharpoons$	Cl^- Strong base	+	$CH_3COOH_2^+$ Strong acid
(v)	HCl Strong acid	+	NH_3 Strong base	$\rightleftharpoons$	Cl^- Weak base	+	NH_4^+ Weak acid
(vi)	CH_3COOH Strong acid	+	NH_3 Strong base	$\rightleftharpoons$	CH_3COO^- Weak base	+	NH_4^+ Weak acid

POINTS TO REVISE

Types of Solvent

(a) Protogenic or acidic solvent :- They have a tendency to generate or donate the protons.
Example CH_3COOH, HCl, HNO_3, H_2SO_4 etc.

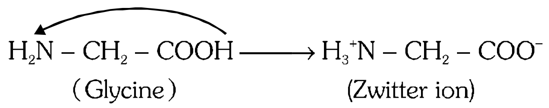
(b) Protophilic or basic solvent :- They have a tendency to accept the protons.
Example NH_3, CH_3OH, RNH_2 etc.

(c) Amphiprotic or amphoteric solvents :- They have the tendency to accept or donate the protons or they are either protophilic or protogenic.
Example H_2O, HS^-, HSO_4^-, HCO_3^- etc.

(d) Aprotic solvents :- They neither donate nor accept the protons.
Example C_6H_6, CCl_4, $CHCl_3$, BrF_3, NO_2, $COCl_2$ etc.

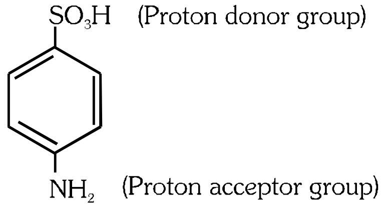
(e) Ampholyte solvents-Those solvents in which the same molecule acts as proton donor and proton acceptor.

Example (i)



$$\underset{\text{(Glycine)}}{H_2N - CH_2 - COOH} \longrightarrow \underset{\text{(Zwitter ion)}}{H_3^+N - CH_2 - COO^-}$$

(ii)



(Sulphanilic acid)

(f) Advantage :-

(i) It explain the behaviour of acids and bases in any type of solvent.

(ii) It explain the stability of proton (H^+).

(g) Disadvantage :-

(i) It does not explain the acid and base practically.

(ii) It does not explain acidic behaviour of aprotic acid. (SO_2, SO_3, CO_2, $AlCl_3$, $SiCl_4$ etc.)

Lewis Concept (1939)

(a) Lewis Acid :- According to this concept those species which have self tendency to accept the lone pair of electrons are called acids. i.e. Lewis acid is an electron pair acceptor (electrophilic).

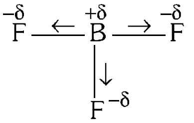
$H^+ + :\ddot{\underset{\cdot\cdot}{O}}{}_{\times}^{\cdot}H^- \longrightarrow H:\ddot{\underset{\cdot\cdot}{O}}{}_{\times}^{\cdot}H$

Acid Base

Classification of Lewis Acids :-

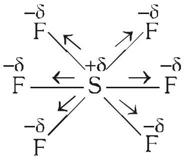
(i) Compounds whose central atom have an incomplete octet (electron deficient)

Example BF_3, BBr_3, BCl_3, BI_3, $B(CH_3)_3$, $B(OH)_3$, $AlCl_3$, $GeCl_3$ etc.

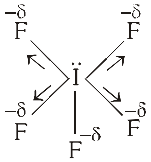


(ii) Compounds whose central atom have vacant d-orbitals and can accept one or more pair of lone electrons.

Example SF_4, SF_6, $SnCl_2$, $SnCl_4$, PX_3, PX_5, GeX_4, TeX_4, IF_5, IF_7, etc.



SF_6

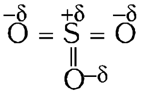


IF_5

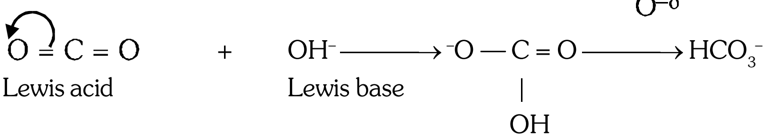
(iii) Molecules with a multiple bond between atoms of different electronegativities.

Example CO_2, SO_2, SO_3 etc.

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



$\overset{-\delta}{O} = \underset{\underset{O^{-\delta}}{\|}}{\overset{+\delta}{S}} = \overset{-\delta}{O}$



$O = C = O + OH^- \longrightarrow {}^-O - \underset{\underset{OH}{|}}{C} = O \longrightarrow HCO_3^-$

Lewis acid Lewis base

$SO_3 + H_2O \longrightarrow H_2SO_4$

Lewis acid Lewis base

(iv) **Cations :-**

Example Ag^+, Na^+, Li^+, Al^{+3}, Be^{+2}, Mg^{+2}, I^+, Cl^+, H^+ etc.

False cations :- Example NH_4^+, H_3O^+, $CH_3COOH_2^+$, PH_4^+ etc.

Example $Ag^+ + 2 : NH_3 \rightleftharpoons [Ag\,(:NH_3)_2]^+$

$Cu^{+2} + 2\,(:H_2O)_2 \longrightarrow [Cu\,(:H_2O)_4]^{+2}$

(v) Elements which have six electrons in their outermost shell or valence shell.

O–Family (O, S, Se, Te) Po – Radioactive element

$SO_3^{-2} + \ddot{\underset{\cdot\cdot}{O}}: \longrightarrow [SO_3 \longrightarrow O]^{-2}$

Base Acid

(b) Lewis Base :- Those species which have self tendency to donate the lone pair of electrons are called bases. i.e. a base is an electron pair (lone pair) donor (nucleophile).

Classification of Lewis Bases

(i) Those species whose central atom have lone pair of electrons and have self tendency to donate them –

Example $\ddot{N}H_3$, $R-\ddot{N}H_2$, $R_2-\ddot{N}H$, $C_6H_5-\ddot{N}H_2$, $C_5H_5-\ddot{N}$, $H_2\ddot{N}-\ddot{N}H_2$,

$H-\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}-H$, $R-\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}-H$, $R-\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}-R$, $R-\overset{\bullet\bullet}{\underset{\bullet\bullet}{S}}-R$, $R-\overset{\bullet\bullet}{\underset{\bullet\bullet}{S}}-H$, etc.

Explain :- $\underset{+I}{R} \xrightarrow{} \overset{-\delta}{O} \xleftarrow{} \underset{+I}{R}$ (Electron density on O, increases due to +I effect)

(ii) **Anions** –

Example O^{-2}, SO_4^{-2}, CO_3^{-2}, Cl^-, Br^-, F^-, I^-, N^{-3}, P^{-3}, NO_3^-, S^{-2}, CN^-, etc.

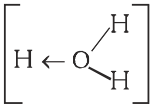
(c) Nature of water :- According to this concept nature of water is basic i.e. water is a base.

(d) Neutralisation Reaction :- According to this concept those reactions in which acid and base react together to form a co-ordinate bond between them are called neutralisation reactions.

Example

$$\underset{\text{Lewis acid}}{F_3B} + \underset{\text{Lewis base}}{\ddot{N}H_3} \rightarrow [F_3B \leftarrow NH_3]$$

$$H^+ + \ddot{N}H_3 \rightarrow [H \leftarrow NH_3]^+ \rightarrow NH_4^+$$

$H^+ + H_2\ddot{O} \rightarrow$  $\rightarrow H_3O^+$

$$Ag^+ + 2\ddot{N}H_3 \rightarrow [H_3\ddot{N} \rightarrow Ag \leftarrow \ddot{N}H_3]^+ \rightarrow [Ag(NH_3)_2]^+$$

(e) Strength of acids and bases :- This concept explain the strength of acids and bases depending upon the basis of self tendency. To accept or donate the lone pair of electrons (e^-).

Example SO_2 < SO_3 (Strong acid)

(f) Advantage :-

(a) This concept explains the acid and base without any solvent.

(b) This concept explains those acids and bases which are not explained by other concepts.

(g) Disadvantage :-

(a) This concept fails to explain the acid and base practically.

(b) According to this concept forming of co-ordinate bond in neutralisation reaction of acid and base is a slow process, whereas neutralisation reaction of acids and bases is actually fast process.

(c) This concept fails to explain the real acids and bases

Example HCl, HNO_3, H_2SO_4, NaOH, KOH, etc.

- All the lewis bases are bronsted bases but all the lewis acids are not bronsted acids.
- All Arrhenius acids are Bronsted acids but it is not so for bases.

POLYACIDIC BASE AND POLYBASIC ACIDS

(a) Polyacidic Base

$$Al(OH)_3 \rightleftharpoons Al^{+3} + 3OH^- \longrightarrow K_b$$

$$Al(OH)_3 \rightleftharpoons [Al(OH)_2]^{+1} + OH^- \longrightarrow K_{b_1}$$

$$[Al(OH)_2]^{+1} \rightleftharpoons [Al(OH)]^{+2} + OH^- \longrightarrow K_{b_2}$$

$$[Al(OH)]^{+2} \rightleftharpoons Al^{+3} + OH^- \longrightarrow K_{b_3}$$

$K_b = K_{b_1} \times K_{b_2} \times K_{b_3}$

taking –log on both sides

$pK_b = pK_{b_1} + pK_{b_2} + pK_{b_3}$

i.e. $\boxed{K_{b_1} > K_{b_2} > K_{b_3}} \quad \Rightarrow \quad \boxed{pK_{b_1} < pK_{b_2} < pK_{b_3}}$

(b) Polybasic Acid

$H_3PO_4 \rightleftharpoons 3H^+ + PO_4^{-3} \longrightarrow K_a$

$H_3PO_4 \rightleftharpoons H_2PO_4^{-1} + H^+ \longrightarrow K_{a_1}$

$H_2PO_4^{-1} \rightleftharpoons HPO_4^{-2} + H^+ \longrightarrow K_{a_2}$

$HPO_4^{-2} \rightleftharpoons PO_4^{-3} + H^+ \longrightarrow K_{a_3}$

$K_a = K_{a_1} \times K_{a_2} \times K_{a_3}$

taking –log on both sides

$pK_a = pK_{a_1} + pK_{a_2} + pK_{a_3}$

$\boxed{K_{a_1} > K_{a_2} > K_{a_3}} \quad \Rightarrow \quad \boxed{pK_{a_1} < pK_{a_2} < pK_{a_3}}$

Formulae :

(i) $\ln x = \log_e x = 2.303 \log_{10} x = 2.303 \log x$

(ii) $\log (x \times y) = \log x + \log y$

(iii) $\log \left(\frac{x}{y}\right) = \log x - \log y$

(iv) $\log x^y = y \log x$

Ex. (i) $\log 6 = \log (2 \times 3)$
$= \log 2 + \log 3$
$= 0.3010 + 0.4771 = 0.7781$

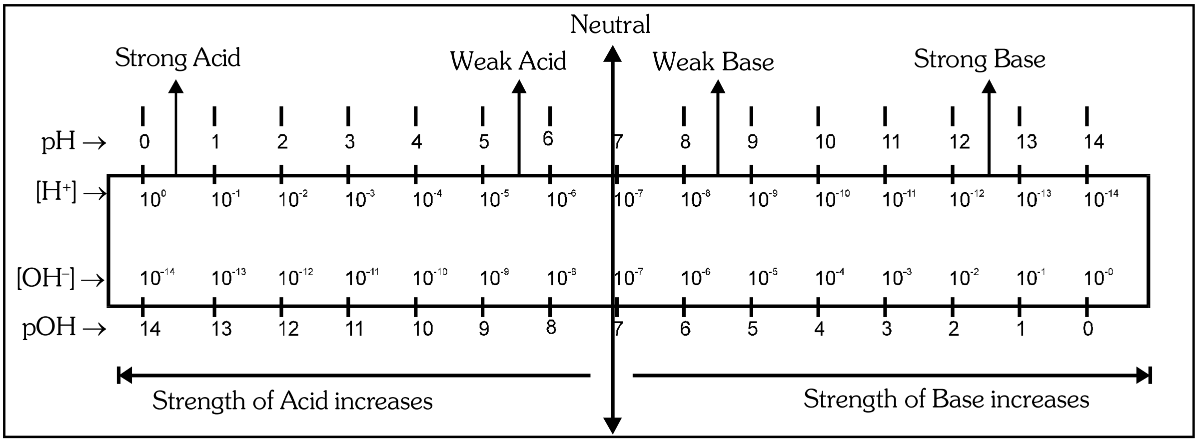
(ii) $\log 30 = \log (3 \times 10)$
$= \log 3 + \log 10$
$= \log 0.4771 + 1 = 1.4771$

(iii) $\log 1000 = \log 10^3$
$= 3 \log 10 \quad = 3 \times 1 = 3$

A. Some values of Log :

log 1 = 0
log 2 = 0.3010
log 3 = 0.4771
log 4 = 0.6020
log 5 = 0.699
log 6 = 0.7781
log 7 = 0.8451
log 8 = 0.9030
log 9 = 0.9542
log 10 = 1
log 11 = 1.04
log 100 = 2
log 1000 = 3

pH scale at 25°C



Some terms which are used in ionic equilibrium : **Antilog** : Antilog (x) = 10^x

Ex. Antilog (2) = $10^2 = 100$
Antilog (0.3010) = $10^{.3010} = 2$
Antilog [log (2)] = Antilog (0.3010) = 2

pH - Scale : Given by – **Sorenson**

pH Scale is called Sorenson scale.

pH scale is a measuring scale used to measure strength of acid and base and its value is equal to $-\log[H^+]$

i.e. $\quad pH = -\log[H^+] = \log \frac{1}{\left[H^+\right]}$

Ex. $[H^+] = 10^{-3}$
$pH = -\log 10^{-3} = +3 \log 10 = 3$

Conclusion :

If $pH = x$ then $[H^+] = 10^{-x}$ or Vice versa
i.e. If $[H^+] = 10^{-x}$ then $pH = x$

pOH → It is equal to $-\log [OH^-]$ i.e. $pOH = -\log [OH^-] = \log \frac{1}{[OH^-]}$

Ex. If $X = \frac{a}{b}\times 10^{-c}$, then find pX ?

Sol. $pX = -\log X = -\log\left(\frac{a}{b}\times 10^{-c}\right)$

$pX = -\left[\log\frac{a}{b} + \log 10^{-c}\right] = -[\log a - \log b - c]$

$\boxed{pX = c + \log b - \log a}$

According to conductivity substances are of two types :

(1) **Non-Conductor -** Those substances which do not show the flow of current or electricity.

Ex. Non - metals, plastic, rubber, wood etc.

Exception – Graphite is a non-metal but show conductivity due to motion of free electrons.

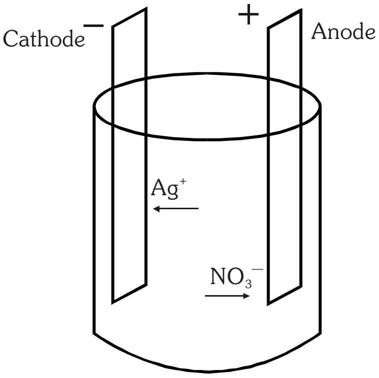
(2) **Conductors –** Those substances which show conductivity or flow of current are called conductors and these are of two types :

(a) **Metallic conductor –** Those conductor which show conductivity due to motion of free electrons.

Ex. All metals, Graphite

(b) **Ionic conductors –**

Those conductor which show conductivity due to movement of free ions. Ions are in free state in the solutions of ionic compounds. On passing electric current through the solution, ions move towards oppositely charged electrodes, i.e., the cation moves towards cathode (negative electrode) and the anion moves towards anode (positive electrode). Due to this reason, they are called cations and anions respectively. The current flows through the solution due to the movement of the ion Movement of ions through the solution of electrolyte ($AgNO_3$) towards oppositely charged electrodes.



According to strength, ionic conductors are of two types –

(1) **Strong electrolytes –** Those ionic conductors which are **completely ionized in aqueous solution** are called as strong electrolytes.

For strong electrolyte the value of degree of ionisation is 100% i.e. $\alpha = 1$

Ex. (a) Strong acid → H_2SO_4, HCl, HNO_3, $HClO_4$, HBr, HI

(b) Strong base → KOH, NaOH, $Ba(OH)_2$, CsOH, RbOH

(c) All Salts → NaCl, KCl, $CuSO_4$..........

(2) **Weak electrolytes –** Those electrolytes which are **partially ionized in aqueous solution** are called as weak electrolytes. For weak electrolytes the value of α is less than one.

Ex. (a) Weak acids → HCN, CH_3COOH, HCOOH, H_2CO_3, H_3PO_3, H_3PO_2, $B(OH)_3$, etc.

$B(OH)_3 \downarrow H_3BO_3$ (Boric acid)

(b) Weak bases → NH_4OH, $Cu(OH)_2$, $Zn(OH)_2$, $Fe(OH)_3$, $Al(OH)_3$ etc.

ARRHENIUS CONCEPT :

(a) According to Arrhenius when an electrolyte dissolves in water it splits up into two oppositely charged particles i.e. cation and anion.

(b) In an electrolytic solution (Aqueous solution of electrolyte), total +ve charge is equal to total –ve charge i.e. solution is electrically neutral.

⇒ In an electrolytic solution number of +ve ions may or may not be equal to the number of negative ions.

(c) Properties of an electrolytic solution are defined by its ions.

Ex. Blue colour of $CuSO_4$ aqueous solution is due to Cu^{+2} ion (dark blue colour)

(d) When electric current is pass in aqueous solution of electrolyte then cation shows migration towards cathode where as anion shows migration towards anode.

(e) When a weak electolyte is dissolved in water an equilibrium is set up between unionized moles and ionized moles.

This condition of the reversible ionic reaction is known as ionic equilibrium. $AB\ (Aq.) \rightleftharpoons A^{+}(Aq.) + B^{-}(Aq.)$

According to L.M.A.

Ionisation constant $K = \frac{[A^{+}][B^{-}]}{[AB]}$

OSTWALD'S DILUTION LAW

⇒ Ostwald dilution law is applicable only for weak electrolytes.

Statement : According to Ostwald when solution of weak electrolyte is diluted then degree of ionisation of solution is increased, is called dilution law.

Let	$AB\ (Aq.) \rightleftharpoons$	$A^{+}(Aq.) +$	$B^{-}(Aq.)$
Initial concentration	C	0	0
Degree of ionisation (α)	$(C - C\alpha)$	$(C\alpha)$	$(C\alpha)$

According to L.M.A.

Ionisation constant $K = \frac{[A^{+}][B^{-}]}{[AB]}$; $K = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^{2}}{(1-\alpha)}$

If $\alpha <<<< 1$ then $1 - \alpha \simeq 1$

$$K = C\alpha^{2} \quad \text{or} \quad \alpha = \sqrt{\frac{K}{C}} \quad (K = \text{constant, At constant temperature})$$

$$\alpha \propto \frac{1}{\sqrt{C}} \qquad (C \propto \frac{1}{V}) \qquad \alpha \propto \sqrt{V}$$

volume ≡ dilution $\alpha \propto \sqrt{\text{dilution}}$ by dilution law

dilution ↑ α ↑

At infinite dilution, $\alpha = 100\%$

Thus for weak electrolytes the degree of ionisation is directly proportional to square root of dilution or inversely proportional to square root of concentration. This law is known as Ostwald Dilution Law.

POINTS TO REVISE

- At infinite dilution the value of α becomes equal to one.
- The value of concentration should be in terms of normality for calculation of pH.

Application of Ostwald's Dilution Law : $\boxed{K = C\alpha^{2}}$

(a) For mono basic weak acid (HA)

(i). Ionisation constant (K_a)

	$HA \rightleftharpoons$	H^{+} +	A^{-}
Initial concentration	C	0	0
At equilibrium	C – Cα	Cα	Cα

If degree of ionisation is α

(b) For mono acidic weak base (BOH)

Ionisation constant (K_b)

	$BOH \rightleftharpoons$	B^{+} +	OH^{-}
Initial concentration	C	0	0
At equilibrium	C – Cα	Cα	Cα

If degree of ionisation is α

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

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

∵ $\alpha <<<< 1$ ∴ $(1 - \alpha) \approx 1$

∴ $K_a = C\alpha^2$

$$K_b = \frac{[B^+][OH^-]}{[BOH]} = \frac{C\alpha \times C\alpha}{C - C\alpha}$$

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

∵ $\alpha <<<< 1$ ∴ $(1 - \alpha) \approx 1$

∴ $K_b = C\alpha^2$

Where

$K_a \rightarrow$ Ionisation constant of weak acid
$K_b \rightarrow$ Ionisation constant of weak base
} Both K_a and K_b depends only on temperature

(ii). $[H^+]$ (Concentration of H^+)

$[H^+] = C\alpha$ ....(1)

$K_a = C\alpha^2$ or $\alpha = \sqrt{\frac{K_a}{C}}$ ....(2)

from Eq. (1) and (2) $[H^+] = C \times \frac{\sqrt{K_a}}{\sqrt{C}}$

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

(iii). $pH = -\log [H^+]$

put the value of $[H^+]$

$$pH = -\log(\sqrt{K_a \times C}) = -\log(K_a \times C)^{1/2}$$

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

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

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

In summary :

1. $K_a = C\alpha^2$
2. $[H^+] = C\alpha = \sqrt{K_a \times C}$
3. $pH = -\log [H^+]$

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

$[OH^-]$ (Concentration of OH^-)

$[OH^-] = C\alpha$ ....(1)

$K_b = C\alpha^2$ or $\alpha = \sqrt{\frac{K_b}{C}}$ ....(2)

from Eq. (1) and (2) $[OH^-] = C \times \frac{\sqrt{K_b}}{\sqrt{C}}$

$[OH^-] = \sqrt{K_b \times C}$

$pOH = -\log [OH^-]$

put the value of $[OH^-]$

$$pOH = -\log(\sqrt{K_b \times C}) = -\log(K_b \times C)^{1/2}$$

$$pOH = -\frac{1}{2}[\log K_b + \log C]$$

$$pOH = -\frac{1}{2}\log K_b - \frac{1}{2}\log C$$

$$pOH = \frac{1}{2}pK_b - \frac{1}{2}\log C$$

1. $K_b = C\alpha^2$
2. $[OH^-] = C\alpha = \sqrt{K_b \times C}$
3. $pOH = -\log [OH^-]$

or $pOH = \frac{1}{2}pK_b - \frac{1}{2}\log C$

Limitation of Ostwald Dilution Law :

It is not applicable for strong electrolytes.

Factors affecting the Value of Degree of ionisation :

(1) Temperature → On increasing temperature, ionization increases so α increases because dissociation is endothermic process.

(2) Dilution → $\alpha \propto \sqrt{V}$ so on dilution, α increases.

(3) Nature of electrolytes

(i) Strong electrolytes $\alpha = 100\%$ (ii) Weak electrolytes $\alpha < 100\%$

(4) Nature of solvent

If Dielectric constant μ of solvent increases then the value of α increases.

$H_2O \rightarrow \mu = 81$

$D_2O \rightarrow \mu = 79$

$C_6H_6 \rightarrow \mu = 2.5$

$CCl_4 \rightarrow \mu = 0$

Mixing of ions :

(a) Common ion effect	**(b) Odd ion effect**
When a strong electrolyte having a common ion, is mixed with weak electrolyte then the degree of ionisation ($\propto$) of weak electrolyte is decreased. This effect is called common ion effect.	When a strong electrolyte having a odd ion, is mixed with weak electrolyte then the degree of ionisation ($\propto$) of weak electrolyte is increased. This effect is called odd ion effect.

Common ion : On mixing CH_3COONa with CH_3COOH solution

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

(On mixing) $CH_3COONa \longrightarrow CH_3COO^- + Na^+$; $[CH_3COO^-]$ increases so $[H^+]$ decreases respectively.

Odd ion : On mixing, NaOH with CH_3COOH solution

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

(On mixing) $NaOH \longrightarrow Na^+ + OH^-$

Due to odd ion effect $H^+ + OH^- \rightarrow$ Water

EXPLANATION OF WATER

a. Nature of water is neutral. $[H^+] = [OH^-]$ $[=10^{-7}M$ (at 25°C)$]$

i.e. at 25°C $pH = 7$ and $pOH = 7$

$\therefore \quad pH = pOH$

b. No. of H_2O moles in 1 litre water $= \dfrac{1000}{18} = 55.5$ moles

c. Molar concentration of $H_2O = 55.5 \text{ mol L}^{-1}$

d. Number of H_2O molecules in 1 litre water $= 55.5\ N_A$ (N_A= AVOGADRO'S NUMBER)

e. Concentration of H^+ and OH^- ions in 1 litre water

$[H^+] = 10^{-7} \text{ mol L}^{-1}$ and $[OH^-] = 10^{-7} \text{ mol L}^{-1}$

f. No. of H^+ and OH^- ions in 1 litre water

No. of H^+ ions $= 10^{-7}N_A$ and No. of OH^- ions $= 10^{-7}\ N_A$

g. In water (Number of H_2O molecules : Number of H^+ ions)

$= 55.5\ N_A : 10^{-7}\ N_A$

$= 55.5 \times 10^7 : 1$

i.e. one H^+ ion is obtained from $55.5 \times 10^7\ H_2O$ molecules

h. Degree of ionisation of water (α) :

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

According to Ostwald's dilution law

$[H^+] = c\,\alpha$

$$\alpha = \frac{10^{-7}}{55.5} = 1.8 \times 10^{-9}$$

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

Hence, water is a very weak electrolyte.

i. K (Ionisation constant of water) :

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

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

$$K = \frac{10^{-7} \times 10^{-7}}{55.5} \quad \text{or} \quad \boxed{K = 1.8 \times 10^{-16}}$$

j. Ionic product of water K_w :

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

$$K = \frac{[H^+].[OH^-]}{[H_2O]}$$

$K \times [H_2O] = [H^+]\,[OH^-]$

Since, dissiociation takes place to a very small extent, $[H_2O]$ may be regarded as constant.

Thus, the product $K.[H_2O]$ gives another constant which designated as $K_{w.}$. So,

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

At 25°C – $K_W = 10^{-7} \times 10^{-7} = 10^{-14}$

$K\,[H_2O] = K_W \Rightarrow \boxed{K_W > K}$ (always)

Various forms of K_W

(a) $K_W = [H^+]\,[OH^-]$ for water $[H^+] = [OH^-]$

(b) $K_W = [H^+]^2$

(c) $K_W = [OH^-]^2$

(d) $K_W = [H_3O^+]\,[OH^-]$

(e) $K_W = [H_3O^+]^2$ $\{\underset{\text{Hydronium ion}}{[H_3O^+]} = \underset{\text{Proton}}{[H^+]}\}$

- **Relation in between pH and pOH :**

$K_W = [H^+]\,[OH^-]$

taking –log on both sides

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

$$\boxed{pK_w = pH + pOH}$$

- Nature of water is neutral so,

  [pH = pOH]

$pK_W = pH + pH$	$pK_W = pOH + pOH$
$2pH = pK_W$	$2\ pOH = pK_W$
$pH = \frac{pK_W}{2}$	$pOH = \frac{pK_W}{2}$

$$\boxed{pH = pOH = \frac{pK_W}{2}}$$

At 25°C, $K_W = 10^{-14}$ or $pK_W = 14$ $\therefore$ $pH + pOH = 14$ or $pH = pOH = 7$

k. Effect of temperature :-

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

Ionization of water is endothermic process so, on increasing temperature α increases or $[H^+]$ and $[OH^-]$ increases or $[H^+][OH^-]$ increases i.e. K_w increases means pH decreases or pOH decreases.

$T\uparrow = \alpha\uparrow = [H^+]\,[OH^-]\uparrow = K_W\uparrow \Rightarrow pK_W\downarrow$

At 25° C, $K_W = 10^{-14}$

At 90° C, $K_W = 10^{-12}$

Parameters	**At 25°C**	**At 90°C**
K_W	10^{-14}	10^{-12}
pK_W	14	12
$pH = \frac{pK_w}{2} = pOH$	7	6
$[H^+] = [OH^-] = \sqrt{K_W}$	10^{-7}	10^{-6}
$pH + pOH = pK_W$	14	12

POINTS TO REVISE

- On increasing temperature, both $[H^+]$ and $[OH^-]$ increases equally so water remains neutral but neutral pH changes from 7 to 6 at 90°C.

Illustrations

Illustration Dissociation constant of water at 25° C is

(1) $10^{-14} \times (55.5)^{-1}$ (2) $10^{-7} \times (18)^{-1}$ (3) $10^{-14} \times (18)^{-1}$ (4) $10^{-7} \times (55.4)^{-1}$

Solution **Ans. (1)**

Illustration What should be the number of H^+ ions in 1 mL of distilled water, if the number of H^+ ions in 1 L is 6.023×10^{16}?

Solution Number of H^+ ions in 1 mL distilled water = $\frac{6.023 \times 10^{16}}{1000} = 6.023 \times 10^{13}$

SALTS, TYPES OF SALT AND CONJUGATE THEORY

(A) **SALT :** Salts are regarded as compounds made up of positive and negative ions. The positive part comes from a base while negative part from an acid. Salts are ionic compounds.

i.e. A compound formed by the combination of acid and base is known as salt.

Acid + Base $\rightarrow$ Salt + Water; $\Delta H = -ve$

$HCl + NaOH \rightarrow NaCl\ (Salt) + H_2O$

(B) TYPES OF SALT

(a) Normal/general salts :– The salts formed by the loss of all possible protons. (replaceable hydrogen ions as H^+) are called normal salts. Such a salt does not contain either a replaceable hydrogen ion or a hydroxyl (OH^-) group.

Ex.: $NaCl$, $NaNO_3$, K_2SO_4, $Ca_3(PO_4)_2$, Na_2HPO_3, NaH_2PO_2 etc.

(b) Acid salts :– Salts formed by incomplete neutralisation of poly basic acids are called acid salts. Such salts still contain one or more replaceable hydrogen ions (H^+).

Ex.: $NaHCO_3$, $NaHSO_4$, NaH_2PO_4, Na_2HPO_4 etc.

(c) Basic salts :– Salts are formed by incomplete neutralisation of poly acidic base are called basic salts. Such salts still contain one or more hydroxyl ion group.

Ex.: $Zn(OH)Cl$, $Mg(OH)Cl$, $Fe(OH)_2Cl$, $Bi(OH)_2Cl$ etc.

(d) Double salts :– The addition compounds formed by the combination of two simple salts are termed double salts. Such salts are stable in solid state only i.e. when dissolved in water they break into simple ions.

Ex.: $FeSO_4.(NH_4)_2SO_4.6H_2O$, $K_2SO_4.Al_2(SO_4)_3.24H_2O$ etc.

(Ferrous ammonium sulphate) (Potash alum)

(e) Complex salts :– These salts when dissolved in water give complex ions. Complex ions are stable in solid state as well as in solutions.

Ex.: $K_4[Fe(CN)_6]$, $[Co(NH_3)_6]SO_4$, $[Ag(NH_3)_2Cl$ etc.

(f) Mixed salts :– The salts which furnishes more than one type of cations or more than one type of anions when dissolved in water are called mixed salts.

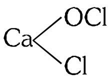
These are formed by the neutralisation of more than one acids and bases.

Ex. (i)

$$\underset{\text{acid}}{H_2SO_4} + \underset{\text{base}}{NaOH} \longrightarrow \underset{\text{acidic salt}}{NaHSO_4} + H_2O$$

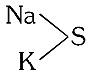
$$\underset{\text{acidic salt}}{NaHSO_4} + \underset{\text{base}}{KOH} \longrightarrow \underset{\text{(mixed salt)}}{NaKSO_4} \longrightarrow \underset{\text{(more than two radicals)}}{Na^+\,K^+\,SO_4^{-2}}$$

(ii)



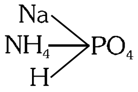
$Ca\begin{cases}OCl\\Cl\end{cases}$

(iii)



$\begin{matrix}Na\\K\end{matrix}\Big>S$

(iii)



$\begin{matrix}Na\\NH_4\\H\end{matrix}\Big>PO_4$

(a) Types of general salts :

(i) SASB (ii) SAWB (iii) WASB (iv) WAWB

(C) Conjugate acid-base pair :

(i) Conjugate acid-base pairs means difference between two species of only one H^+ ion.

(ii) When an acid loses a proton, the residual part of it has a tendency to regain a proton. Therefore it behaves as a base.

$$\underset{\substack{\text{Weak acid}\\(K_a = 1.85 \times 10^{-5})}}{CH_3COOH} \rightleftharpoons \underset{\substack{\text{Conjugate strong base}\\\text{(acceptor ion)}}}{CH_3COO^-} + H^+$$

$$\underset{\substack{\text{Weak base}\\(K_b = 1.85 \times 10^{-5})}}{NH_4OH + H^+} \rightleftharpoons NH_4OH_2^+ \longrightarrow \underset{\substack{\text{Conjugate strong acid}\\\text{(acceptor ion)}}}{NH_4^+} + H_2O$$

$$\underset{\text{Strong acid}}{HCl} \longrightarrow H^+ + \underset{\substack{\text{Conjugate weak base (spectator ion)}\\\text{Accepting tendency of } H^+ \simeq 0}}{Cl^-}$$

$$\underset{\text{Strong base}}{NaOH + H^+} \longrightarrow NaOH_2^+ \longrightarrow \underset{\substack{\text{Conjugate weak acid}\\\text{(spectator ion)}}}{Na^+} + H_2O$$

Note : Strong acids have weak conjugate bases while weak acids have strong conjugate bases. Similarly, strong bases have weak conjugate acids while weak bases have strong conjugate acids.

(D) Relation between conjugate acid-base pair :–

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

Acid — conjugate base

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

Base — conjugate acid

CH_3COOH **acid**	**CH_3COO^-** **conjugate base**
$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$	$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$
$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$ ...... (i)	$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$ ..... (ii)

In both the reactions H_2O in excess quantity so active mass of H_2O is one.

Now multiply the equation (i) and (ii) $K_a \times K_b = [H^+][OH^-]$

we know $[H^+] \times [OH^-] = K_W$ (Ionic product of water) $\boxed{K_a \times K_b = K_w}$

Taking –log on both sides $\boxed{pK_a + pK_b = pK_w}$

we know that for water at 25°C, $K_W = 10^{-14}$ or $pK_W = 14$

So $\boxed{K_a \times K_b = 10^{-14}}$ or $\boxed{pK_a + pK_b = 14}$

Above relation is applicable only for conjugate acid-base pairs.

HYDROLYSIS OF SALTS

Salt hydrolysis is defined as the process in which water reacts with cation or anion or both of a salt to change the concentration of H^+ and OH^- ions of water.

Salt hydrolysis is reverse process of neutralization.

Water + Salt $\rightleftharpoons$ Acid + Base ; $\Delta H = +ve$

(A) Hydrolysis of strong acid and strong base [SA – SB] types of salt –

Ex. $NaCl$, $BaCl_2$, Na_2SO_4, $KClO_4$, $BaSO_4$, $NaNO_3$, KBr, KCl etc.

$Na^+ + Cl^- + H_2O \longrightarrow Na^+ + OH^- + H^+ + Cl^-$

$H_2O \rightleftharpoons H^+ + OH^-$ (It is not salt hydrolysis)

(i) Hydrolysis of salt of [SA – SB] is not possible as both cation and anion are not reactive.

(ii) Aqueous solution of these type of salt is neutral in nature. (pH = pOH = 7)

(iii) pH of the solution is 7.

(iv) No effect on litmus paper.

(B) Hydrolysis of strong acid and weak base [SA - WB] types of salt –

Ex. $CaSO_4$, NH_4Cl, $(NH_4)_2SO_4$, $Ca(NO_3)_2$, $ZnCl_2$, $CuCl_2$, $CaCl_2$, $AgCl$, AgI, $AgNO_3$ etc

$NH_4Cl + H_2O \rightleftharpoons \underset{WB}{NH_4OH} + \underset{SA}{HCl}$

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

$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$

(i) In this type of salt hydrolysis, cation reacts with H_2O therefore called as cationic hydrolysis. The cation of the salt which has come from weak base is reactive.

(ii) Solution is acidic in nature as $[H^+]$ is increased.

(iii) pH of the solution is less than 7.

(iv) Solution turns blue litmus paper red.

K_h = Hydrolysis constant
K_W = Ionic product of water
K_a = Ionisation constant of acid
K_b = Ionisation constant of base
h = Degree of hydrolysis
C = Concentration of salt (concentration of ions)

(a) Relation between K_h , K_W and K_b

$$B^+ + H_2O \rightleftharpoons BOH + H^+$$

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

Hydrolysis constant $[K_h]$

$$K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]} \qquad ....(1)$$

For weak Base $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$$K_b = \frac{\left[NH_4^+\right]\left[OH^-\right]}{\left[NH_4OH\right]} \qquad ....(2)$$

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

$$K_W = [H^+]\,[OH^-] \qquad ....(3)$$

Now mutiplying Eq. (1) and (2) = Eq. (3)

$$\frac{\left[NH_4OH\right]\left[H^+\right]}{\left[NH_4^+\right]} \times \frac{\left[NH_4^+\right]\left[OH^-\right]}{\left[NH_4OH\right]} = [H^+]\,[OH^-]$$

i.e. $K_h \times K_b = K_W$

$$\boxed{K_h = \frac{K_W}{K_b}} \qquad ....(4)$$

(b) Degree of hydrolysis – Represented by h

	$NH_4^+ + H_2O$	$\rightleftharpoons$ NH_4OH	+ H^+
Initial concentration of salt	C	0	0
	C – Ch	Ch	Ch

$$K_h = \frac{\left[NH_4OH\right]\left[H^+\right]}{\left[NH_4^+\right]} = \frac{Ch \times Ch}{C - Ch} = \frac{C^2h^2}{C(1-h)} = \frac{Ch^2}{(1-h)}$$

Since h <<<< 1 then $(1 - h) \approx 1$

$$\therefore \quad \boxed{K_h = Ch^2} \qquad ....(5)$$

$$h^2 = \frac{K_h}{C} \quad \Rightarrow \quad h = \sqrt{\frac{K_h}{C}} \qquad ....(6)$$

$$\therefore \quad K_h = \frac{K_W}{K_b} \quad \Rightarrow \quad h = \sqrt{\frac{\frac{K_W}{K_b}}{C}}$$

$$h = \sqrt{\frac{K_W}{K_b \times C}} \qquad ....(7)$$

(c) pH of the solution : $pH = -\log [H^+]$

$[H^+] = Ch = C\sqrt{\dfrac{K_W}{K_b \times C}} \quad \Rightarrow \quad [H^+] = \sqrt{\dfrac{K_W \times C}{K_b}}$ ....(8)

taking – log on both sides

$-\log [H^+] = -\log \sqrt{\dfrac{K_W \times C}{K_b}} \quad \Rightarrow \quad pH = -\log \left(\dfrac{K_W \times C}{K_b}\right)^{1/2}$

$$pH = -\frac{1}{2}\ [\ \log K_W + \log C - \log K_b\ ]$$

$$pH = -\frac{1}{2}\ \log K_W - \frac{1}{2}\ \log C - \frac{1}{2}\ (-\log K_b)$$

$$pH = \frac{1}{2}pK_W - \frac{1}{2}\log C - \frac{1}{2}pK_b$$

$\boxed{pH = 7 - \frac{1}{2}pK_b - \frac{1}{2}\log C}$ ....(9)

(C) Hydrolysis of weak acid and strong base [WA – SB] types of salt –

Ex. CH_3COONa, $HCOONa$, KCN, $NaCN$, K_2CO_3, $BaCO_3$, K_3PO_4 etc.

$$CH_3COONa + H_2O \rightleftharpoons \underset{WA}{CH_3COOH} + \underset{SB}{NaOH}$$

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

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

(i) In this type of salt hydrolysis, anion reacts with water therefore called as anionic hydrolysis. The anion of the salt which has come from weak acid is reactive.

(ii) Solution is basic in nature as $[OH^-]$ increases.

(iii) pH of the solution is greater than 7.

(iv) Solution turns red litmus paper blue.

(a) Relation between K_h , K_W and K_a

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

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} \qquad ....(1)$$

For weak acid

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

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \qquad ....(2)$$

For water

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

$$K_W = [H^+][OH^-] \qquad ....(3)$$

Now multiply eq. (1) × eq. (2) = eq. (3)

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

$$K_h \times K_a = K_W$$

$$\boxed{K_h = \frac{K_W}{K_a}} \qquad \text{........(4)}$$

(b) Degree of hydrolysis (h) :

$$CH_3COO^- \; + \; H_2O \rightleftharpoons CH_3COOH \; + \; OH^-$$

Initial concentration of salt $\quad C \qquad 0 \qquad 0$

$\quad C - Ch \qquad Ch \qquad Ch$

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = \frac{Ch \times Ch}{C - Ch} = \frac{C^2h^2}{C(1-h)}$$

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

Since $\quad h <<<< 1 \quad$ then $\quad (1 - h) \approx 1$

$$\therefore \quad \boxed{K_h = Ch^2} \qquad \text{........(5)}$$

$$h^2 = \frac{K_h}{C} \quad \text{or} \quad h = \sqrt{\frac{K_h}{C}} \qquad \text{........(6)}$$

$$\boxed{h = \sqrt{\frac{K_W}{K_a \times C}}} \qquad \text{........(7)}$$

(c) pH of the solution

$[OH^-] = Ch$

$$[OH^-] = C \times \sqrt{\frac{K_W}{K_a \times C}} \quad \text{or} \quad [OH^-] = \sqrt{\frac{K_W \times C}{K_a}} \qquad \text{........(8)}$$

taking – log on both sides

$$-\log[OH^+] = -\log\left(\frac{K_w.C}{K_a}\right)^{1/2}$$

$$pOH = -\frac{1}{2}\,[\log K_W + \log C - \log K_a]$$

$$pOH = \frac{1}{2}\,pK_W - \frac{1}{2}\,pK_a - \frac{1}{2}\,\log C \quad \text{or} \quad pOH = 7 - \frac{1}{2}\,pK_a - \frac{1}{2}\,\log C$$

$\because \quad pH + pOH = 14$

$pH = 14 - pOH$

$$\therefore \quad pH = 7 + \frac{1}{2}\,pK_a + \frac{1}{2}\,\log C \qquad \text{........(9)}$$

(D) Hydrolysis of weak acid and weak base (WA - WB) type of salt :

Ex. CH_3COONH_4, $AgCN$, NH_4CN, $CaCO_3$, $[NH_4]_2CO_3$, $ZnHPO_3$ etc.

$$CH_3COONH_4 + H_2O \rightleftharpoons \underset{WA}{CH_3COOH} + \underset{WB}{NH_4OH}$$

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

(i) Maximum hydrolysis occurs of the salt of (WA – WB) as both the cation and anion are reactive.

(ii) Solution is almost neutral but it may be acidic or basic depending upon the nature of acid base

(iii) pH of the solution is near to 7.

For WA - WB types of salt :

Terms	$K_a > K_b$	$K_b > K_a$	$K_a = K_b$
1. Hydrolysis	Cationic-anionic	Anionic-cationic	Neutral hydrolysis
2. Nature	Acidic	Basic	Neutral
3. pH	pH < 7	pH > 7	pH = 7

(a) Relation between K_h, K_W, K_a and K_b

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

$$K_h = \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]} \qquad ....(1)$$

For weak base

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

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \qquad ....(2)$$

For weak acid

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

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \qquad ....(3)$$

For water

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

$$K_W = [H^+][OH^-] \qquad ....(4)$$

Multiply Eq. (1) ×Eq. (2) ×Eq. (3) = Eq. (4)

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

$$K_h \times K_b \times K_a = K_W$$

$$\boxed{K_h = \frac{K_W}{K_a \times K_b}} \qquad ....(5)$$

(b) Degree of hydrolysis (h) –

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

	CH_3COO^-	NH_4^+	CH_3COOH	NH_4OH
Initial concentration of salt	C	C	0	0
	C – Ch	C – Ch	Ch	Ch

$$K_h = \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]} = \frac{Ch \times Ch}{(C - Ch)(C - Ch)} = \frac{C^2h^2}{C(1-h) \times C(1-h)}$$

Since $h <<<< 1$ then $(1 - h) \approx 1$

$$\therefore \quad \boxed{K_h = h^2} \qquad \text{.......(6)}$$

$$\text{or} \quad h^2 = \frac{K_W}{K_a \times K_b} \quad \text{or} \quad \boxed{h = \sqrt{\frac{K_W}{K_a \times K_b}}} \qquad \text{.......(7)}$$

(c) pH of the solution

from equation (3)

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

$$[H^+] = \frac{K_a \times [CH_3COOH]}{[CH_3COO^-]} = \frac{K_a \times Ch}{C - Ch} = \frac{K_a \times h}{1 - h}$$

Since $h <<<< 1$ then $(1 - h) \approx 1$

$[H^+] = K_a \times h$ [Now put the value of h from eq. (5)]

$$= K_a \times \sqrt{\frac{K_W}{K_a \times K_b}}$$

$$\boxed{[H^+] = \sqrt{\frac{K_W \times K_a}{K_b}}} \qquad \text{.......(8)}$$

taking – log on both sides $-\log [H^+] = -\log \left(\frac{K_W \times K_a}{K_b}\right)^{1/2}$

$$pH = -\frac{1}{2} [\log (K_w \times K_a) - \log K_b]$$

$$pH = -\frac{1}{2} [\log K_W + \log K_a - \log K_b]$$

$$pH = -\frac{1}{2} [\log K_W] - \frac{1}{2} [\log K_a] - \frac{1}{2} [-\log K_b]$$

$$pH = +\frac{1}{2} pK_W + \frac{1}{2} pK_a - \frac{1}{2} pK_b$$

$$\boxed{pH = 7 + \frac{1}{2} pK_a - \frac{1}{2} pK_b} \qquad \text{.......(9)}$$

POINTS TO REVISE

- Degree of hydrolysis, pH of weak acid and weak base [WA – WB] type salts do not depend on the concentration of salt.
-

	SA SB salts	SA WB salts	WA SB salts	WA WB salts
1.	Neutral solution	Acidic solution	Basic solution	Almost neutral solution
2.	No hydrolysis	Cationic hydrolysis	Anionic hydrolysis	Hydrolysis by both cation and anion
3.	–	$K_h = \frac{K_W}{K_b}$	$K_h = \frac{K_W}{K_a}$	$K_h = \frac{K_W}{K_a \times K_b}$
4.	–	$h = \sqrt{\frac{K_W}{K_b.C}}$	$h = \sqrt{\frac{K_W}{K_a.C}}$	$h = \sqrt{\frac{K_W}{K_a.K_b}}$
5.	–	$\left[H^+\right] = C.h = \sqrt{\frac{K_W.C}{K_b}}$	$\left[OH^-\right] = C.h = \sqrt{\frac{K_W.C}{K_a}}$	$\left[H^+\right] = K_a.h = \sqrt{\frac{K_W.K_a}{K_b}}$
6.	–	$pH = 7-\frac{1}{2}\ pK_b - \frac{1}{2}\log C$	$pH = 7+\frac{1}{2}\ pK_a + \frac{1}{2}\log C$	$pH = 7+\frac{1}{2}\ pK_a - \frac{1}{2}\ pK_b$

SOLUBILITY AND SOLUBILITY PRODUCT (K_{sp})

(A) SOLUBILITY

(a) Definition At constant temperature the maximum number of moles of solute which can be dissolved in a solvent to obtain 1 litre of solution (i.e. saturated solution) is called solubility.

$$S(M) = \frac{\text{Number of moles of solute}}{\text{Volume of solution (L)}} \qquad S = \frac{x}{M_w \times V_L}\ \text{mol L}^{-1}$$

$$S_{g/\ell} = S_M \times \text{molar mass}$$

POINTS TO REVISE

- Solubility does not depend on amount of substances and volume of solution where as depends on the following–
  - (i) Temperature
  - (ii) Presence of common ion
  - (iii) Nature of solvent (Molecular wt. of AgCl = 143.5)
    (Molecular wt. of $BaSO_4$ = 233)
- Solubility can be expressed in terms of molarity.

(B) SOLUBILITY PRODUCT(K_{sp}) :

When a sparingly soluble salt such as AgCl is put into water, a very small amount of AgCl dissolves in water and most of the salt remains undissolved in its saturated solution.

- The salt AgCl is an electrolyte, its dissociation occurs in solution. Hence, the quantity of AgCl that dissolves in water dissociates into Ag^+ and Cl^- ions. Thus, in the saturated solution of AgCl an equilibrium exists between undissolved solid AgCl and its ions, Ag^+ and Cl^- ions.

$$AgCl_{(s)} \underset{\text{Precipitation}}{\overset{\text{Dissolution}}{\rightleftharpoons}} Ag^+_{(aq)} + Cl^-_{(aq)}$$

according to law of mass action $K = \frac{[Ag^+].[Cl^-]}{[AgCl]}$

Since, the concentration of undissolved solid AgCl is constant. Thus, the product K.[AgCl] gives another constant which is designated as Ksp.

So, $K.[AgCl] = [Ag^+].[Cl^-]$ $\therefore$ $K_{sp} = [Ag^+] . [Cl^-]$

At constant temperature product of concentrations of ions in a saturated solution of substance is called solubility product of that substance. (Saturated solution is that solution in which solid solute and the ions in solution remain in equilibrium with each other.

- **K_{sp} for $CaCl_2$** $CaCl_2(s) \rightleftharpoons Ca^{+2}(aq) + 2Cl^-(aq)$

Solubility product in terms of concentration of ions $K_{sp} = [Ca^{+2}]\,[Cl^-]^2$

- **K_{sp} for $AlCl_3$** $AlCl_3(s) \rightleftharpoons Al^{+3}(aq) + 3Cl^-(aq)$

  Solubility product in terms of concentration of ions $K_{sp} = [Al^{+3}]\,[Cl^-]^3$

- **General form** $AxBy(s) \rightleftharpoons xA^{+y}(aq) + yB^{-x}(aq)$

$K_{sp} = [A^{+y}]^x\,[B^{-x}]^y$

APPLICATION OF SOLUBILITY PRODUCT (K_{sp})

(A) To find out the solubility (S) :

(i) K_{sp} of AB (Mono-mono, di-di, tri-tri valency) type salt –

Ex. NaCl, $BaSO_4$, CH_3COONa, $CaCO_3$, NaCN, KCN, NH_4CN, NH_4Cl etc.

$$\begin{array}{lll} AB(s) & \rightleftharpoons A^+(aq) + & B^-(aq) \\ a & 0 & 0 \\ (a-s) & s & s \end{array}$$

$K_{sp} = [A^+]\,[B^-]$

$K_{sp} = s^2$ or $s = \sqrt{K_{sp}}$

(ii) K_{sp} of AB_2 or A_2B (Mono-di or di-mono valency) type salt –

Ex. $CaCl_2$, $CaBr_2$, K_2S, $(NH_4)_2SO_4$, K_2SO_4, K_2CO_3 etc.

$$\begin{array}{lll} AB_2(s) & \rightleftharpoons A^{+2}(aq) + & 2B^-(aq) \\ a & 0 & 0 \\ a - s & s & 2s \end{array}$$

$K_{sp} = [A^{+2}]\,[B^-]^2$

$K_{sp} = s \times (2s)^2 = s \times 4s^2 = 4s^3$

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

(iii) **K_{sp} of AB_3 or A_3B (Mono-tri or tri-mono valency) type salt –**

Ex. $FeCl_3$, $AlCl_3$, K_3PO_4 etc.

$AB_3(s)$	$\rightleftharpoons$	$A^{+3}(aq)$	+	$3B^{-}(aq)$
a		0		0
a–s		s		3s

$$K_{sp} = [A^{+3}][B^{-}]^3 = s \times (3s)^3 = 27s^4$$

$$s = \left(\frac{K_{sp}}{27}\right)^{1/4}$$

(iv) **K_{sp} of A_2B_3 or A_3B_2 (Di-tri or tri-di valency) type salt**

Ex. $Al_2(SO_4)_3$, $Ba_3(PO_4)_2$ etc.

$A_2B_3(s)$	$\rightleftharpoons$	$2A^{+3}(aq)$	+	$3B^{-2}(aq)$
a		0		0
a–s		2s		3s

$$K_{sp} = [A^{+3}]^2[B^{-2}]^3 = 2s \times 2s \times 3s \times 3s \times 3s = 108s^5$$

$$s = \left(\frac{K_{sp}}{108}\right)^{1/5}$$

(v) **General form :**

$A_xB_y(aq)$	$\rightleftharpoons$	$xA^{+y}(aq)$	+	$yB^{-x}(aq)$
a		0		0
a–s		xs		ys

$K_{sp} = [A^{+y}]^x \,.\, [B^{-x}]^y$

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

(B) Condition of precipitation /Ionic product (IP or Q_{sp}) :

- Ionic product (IP) of an electrolyte is defined in the same way as K_{sp}. The only difference is that ionic product expression contains the initial concentration of ions or the concentration at any time whereas the expression of K_{sp} contains only equilibrium concentration. Thus, for AgCl.

  $Q_{sp} = IP = [Ag^+]_i\,[Cl^-]_i$ and $K_{sp} = [Ag^+]_{eq}.[Cl^-]_{eq}$
- Ionic product changes with concentration but K_{sp} does not. K_{sp} is applicable for saturated solution of the sparingly soluble electrolyte.
- To decide whether an ionic compound will precipitate, its K_{sp} is compared with the value of ionic product. The following three cases arise :

  (i) $Q_{sp} < K_{sp}$: The solution is unsaturated and precipitation will not occur.

  (ii) $Q_{sp} = K_{sp}$: The solution is saturated and solubility equilibrium exists.

  (iii) $Q_{sp} > K_{sp}$: The solution is supersaturated and hence precipitation of the compound will occur.

  Thus, a salt is precipitated when its ionic product exceeds the solubility product of the salt.

(C) Common ion effect on solubility :

Important point :- Solubility of substances always decreases in the presence of common ion. According to Le-Chatelier's principle on increasing common ion concentration equilibrium shifts in backward direction until the equilibrium is re-established so, the solubility of substances decreases but K_{sp} remains same because it is an equilibrium constant which depends only on temperature.

POINTS TO REVISE

*● **Group precipitation of Salt**

Group	Radicals	Condition for precipitation (Group reagent)	Forms of precipitation
Zero	NH_4^+	………..	………..
First	$Pb^{+2}, Hg^{+1}, \left(Hg_2^{+2}\right), Ag^+$	By mixing of dilute HCl	Chloride $AgCl, Hg_2Cl_2, PbCl_2$
Second II(A)	$Pb^{+2}, Cu^{+2} Hg^{+2}, Cd^{+2}, Bi^{+3}$	H_2S gas passed in the presence of acidic medium	Sulphide $PbS, HgS, CuS, CdS, SnS, SnS_2, As_2S_3, Sb_2S_3, Bi_2S_3$
Second II(B)	$As^{+3}, Sb^{+3}, Sn^{+2}, Sn^{+4}$		
Third	$Al^{+3}, Cr^{+3}, Fe^{+3}$	NH_4OH mixed in the presence of NH_4Cl	Hydroxide $Al(OH)_3, Fe(OH)_3, Cr(OH)_3$
Fourth	$Zn^{+2}, Ni^{+2}, Mn^{+2}, Co^{+2}$	H_2S gas passed in presence of basic medium	Sulphide MnS, CoS, NiS, ZnS
Fifth	$Ba^{+2}, Sr^{+2}, Ca^{+2}$	$(NH_4)_2CO_3$ mixed in the presence of NH_4Cl	Corbonate $BaCO_3, SrCO_3, CaCO_3$
Sixth	Na^+, K^+, Mg^{+2}	By mixing of Na_2HPO_4	Hydrogen phosphate ($MgHPO_4$)

- Hg^{+1} (us) → Unstable in aqueous solution.

  [Stable in dimer form (Hg_2^{+2}) ⇒ Hg_2Cl_2]

  $$\begin{array}{lcl} Hg_2Cl_2 & \rightleftharpoons & Hg_2^{+2} + 2Cl^- \\ S & & S \quad\quad 2S \end{array}$$

  $K_{sp} = [Hg_2^{+2}]\,[Cl^-]^2$

  $= (S)\,(2S)^2$

  $\boxed{K_{sp} = 4S^3}$

- Hg^{+2} (ic) → $HgCl_2$ → stable in aqueous solution

  $$\begin{array}{lcl} HgCl_2 & \rightleftharpoons & Hg^{+2} + 2Cl^- \\ S & & S \quad\quad 2S \end{array}$$

  $\boxed{K_{sp} = 4S^3}$

- For precipitation of II group, H_2S gas is passed in acidic medium to decrease S^{-2} concentration by common ion effect. So that ionic product of cations of group II and S^{-2} ions exceed the solubility product of their corresponding metal sulphides. Therefore only the cations of group II gets precipitated. But the sulphides of the cation of the other groupes (III, IV & V) are not precipitated under these conditions because their solubility products are quite high.

  When H_2S gas is directly passed through solution then IVth group is also precipitated with IInd group.

  $$H_2S \rightleftharpoons 2H^+ + S^{-2}$$

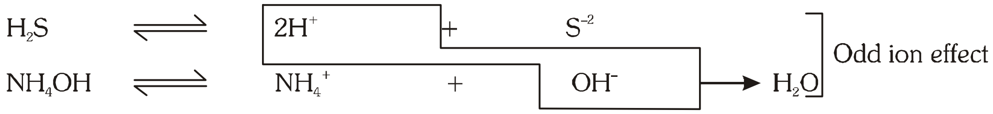
  $Ksp_{II} < Ksp_{IV} <$ [radicals of IInd and IV group] $[S^{-2}]$

When H_2S gas pass in acidic medium $[H^+]$ then only IInd group radicals are precipitated.

$H_2S \rightleftharpoons 2H^+ + S^{-2}$

Ksp_{II} < [radicals of IInd and IV group] $[S^{-2}]$ < Ksp_{IV}

- For precipitation of group III, NH_4OH is added in the presence of NH_4Cl to decrease the concentration of OH^- by common ion effect so that ionic product of cations of group III and hydroxides ions exceed the solubility product of their corresponding metal hydroxides and only group III cations will precipitated. On the other hand cations of group IV, V and VI, which require large concentration of OH^- due to their high solubility product, will not be precipitated.
- In IV group, H_2S gas is passed in basic medium to increase S^{-2} ion concentration by odd ion effect, so that the ionic product of cations of group IV and S^{-2} ions exceed the solubility product of their corresponding metal sulphide and hence gets precipitated.



So $[S^{-2}]\uparrow$

Ksp_{IV} < [Radicals of group IV] $[S^{-2}]$

(D) Precipitation of soap and salt (NaCl)

(i) Precipitation of NaCl (common salt) :

For the precipitation of NaCl, HCl gas passed in saturated solution of NaCl to increase the concentration of Cl^- ion by common ion, so ionic product of concentration of Na^+ and Cl^- ion becomes more than Ksp of NaCl and NaCl easily precipitated.

Saturated solution of NaClNaCl $\rightleftharpoons Na^+ + Cl^-$

$Ksp = [Na^+][Cl^-]$

By passing HCl gas $HCl \longrightarrow H^+ + Cl^-$

due to common ion $Ksp < [Na^+][Cl^-]\uparrow$

(ii) Precipitation of soap :

For precipitation of soap, NaCl mixed in saturated solution of soap to increase the concentration of Na^+ ion by common ion. So ionic product of concentration of Na^+ and strearate ions is more than Ksp of soap and soap is easily precipitated.

Ex. $C_{17}H_{35}COONa$ (Sodium stearate)

Saturated solution of $C_{17}H_{35}COONa$ ⇒ $C_{17}H_{35}COONa^+ \rightleftharpoons C_{17}H_{35}COO^- + Na^+$

$Ksp = [C_{17}H_{35}COO^-][Na^+]$

By mixing NaCl solution $NaCl \longrightarrow Na^+ + Cl^-$

due to common ion $Ksp < [C_{17}H_{35}COO^-][Na^+]\uparrow$

FEW IMPORTANT POINTS

(A) Isohydric solution – If different–different solution has same pH are called isohydric solution.

Sp. point :– Isohydric conditions for two given weak acids HA_1 and HA_2 which has concentration C_1 and C_2 and ionisation constants are Ka_1 and Ka_2 respectively.

Then $[H^+]_1 = \sqrt{Ka_1 C_1}$ and $[H^+]_2 = \sqrt{Ka_2 C_2}$

According to given condition for isohydric solution pH of different solution is same.

Hence $[H^+]_1 = [H^+]_2$

$$\sqrt{Ka_1 C_1} = \sqrt{Ka_2 C_2}$$

$\boxed{Ka_1C_1 = Ka_2C_2}$ or If n = 1 mole then $\boxed{\frac{Ka_1}{V_1} = \frac{Ka_2}{V_2}}$ $\because$ $\boxed{C \propto \frac{1}{V}}$

(B) Relative strength of Acids :– It indicates that how many times an acid is stronger than the other acid.

We know $\boxed{\text{Strength of acid } \propto [H^+]}$

If there are two weak acids HA_1 and HA_2 which has concentration C_1 and C_2, degree of ionisation α_1 and α_2 and ionisation constants Ka_1 and Ka_2 respectively then ratio of their strength of acids.

We know $[H^+] = C\alpha = \sqrt{KaC}$

$$\text{So } \frac{\text{Strength of weak acid } HA_1}{\text{Strength of weak acid } HA_2} = \frac{[H^+]_1}{[H^+]_2} = \frac{C_1\alpha_1}{C_2\alpha_2} = \frac{\sqrt{Ka_1C_1}}{\sqrt{Ka_2C_2}}$$

If $C_1 = C_2$

$$\boxed{R.S. = \frac{\text{Strength of weak acid } HA_1}{\text{Strength of weak acid } HA_2} = \sqrt{\frac{Ka_1}{Ka_2}} = \frac{\propto_1}{\propto_2}}$$

Thus the relative strength of two acids of equimolar concentration can be compared by taking square root of the ratio of their ionisation constants.

pH

1. INTRODUCTION

pH of some important substance :-

(i)	Blood	⟶	7.4
(ii)	Tear	⟶	7.4
(iii)	Gastric Juice	⟶	1 to 3
(iv)	Soft drink	⟶	2 to 4
(v)	Acidic rain	⟶	6
(vi)	Milk	⟶	6.3 to 6.6
(vii)	Water	⟶	7

2. TYPES OF pH

(i) pH of SA and SB. $[H^+] = C$, $[OH^-] = C$

(ii) pH of WA and WB. $[H^+] = C\alpha$, $[OH^-] = C\alpha$

(iii) pH of very dilute solution. (Consider H^+ & OH^- of H_2O also)

(iv) pH of salt solution.

(a) SA SB Type Salt (always 7)
(b) SA WB Type Salt (< 7)
(c) WA SB Type Salt (> 7)
(d) WA WB Type Salt (Almost 7)

3. pH of mixture of acid and base.

(a) pH of mixture of strong acids :

$N_1V_1 + N_2V_2 + N_3V_3 + \ldots\ldots\ldots\ldots\ldots\ldots = NV$

V = Volume of final solution $= V_1 + V_2 + V_3 + \ldots\ldots\ldots$

N = Normality of final solution = $[H^+]$ in final solution.

(b) pH of mixture of strong base :

$N_1V_1 + N_2V_2 + N_3V_3 + \ldots\ldots\ldots\ldots\ldots\ldots = NV$

V = Volume of final solution = $V_1 + V_2 + V_3 + \ldots\ldots\ldots$

N = Normality of final solution = $[OH^-]$ in final solution.

(c) pH of mixture of strong acids and strong bases :

For acid :

$$N_1V_1 + N_2V_2 + N_3V_3 + \ldots\ldots\ldots\ldots\ldots\ldots = (NV)_{Acid}$$

For base :

$$N_1V_1 + N_2V_2 + N_3V_3 + \ldots\ldots\ldots\ldots\ldots\ldots = (NV)_{Base}$$

(i) If $(NV)_{Acid} > (NV)_{Base}$ then solution is acidic.

$NV = (NV)_{Acid} - (NV)_{Base}$ and

$[H^+] = N$

(ii) If $(NV)_{Base} > (NV)_{Acid}$ then solution is basic.

$NV = (NV)_{Base} - (NV)_{Acid}$ and

$[OH^-] = N$

(iii) If, $(NV)_{acid} = (NV)_{base}$ then solution is neutral.

(d) p^H of mixture of (WA + SB); when equivalent of WA > SB]

pH of mixture of (SA + WB); When equivalent of WB > SA]

$\Downarrow$

gives rise to concept of buffer solution

BUFFER SOLUTION

(A) Definition : A solution which resist the change in pH and pH does not change significantly on addition of small amount of strong acid or strong base is called buffer solution.

(B) Properties of buffer solution :

- **(i)** The pH of buffer solution does not change appreciably upon the addition of small amount of either strong acid or strong base.
- **(ii)** The pH of buffer solution does not depend on the volume of solution. Hence, solution can be diluted without change in pH.
- **(iii)** The pH of buffer solution remains constant even if it is kept for a long time.

(C) Buffer solutions are used in

(a) Qualitative analysis of mixture

(b) Quantitative analysis of mixture

(c) Digestion of food

(d) Preservation of food and fruits.

(e) Agriculture and dairy product preservation.

(f) Industrial process such as manufacture of paper, dyes inks, paints, drugs etc.

TYPES OF BUFFER SOLUTION

(A). Simple buffer solution

(B). Mixed buffer solution :- (i) Acidic buffer solution (ii) Basic buffer solution

(A) Simple buffer solution :- Aqueous solution of weak acid-weak base (WA – WB) types of salt.

Ex. CH_3COONH_4, NH_4CN, $AgCN$ etc.

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

pH does not depend on concentration.

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

Buffer Action :

Case 1

When mixing of acid [H^+]

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

$$NH_4OH + H^+ \rightleftharpoons NH_4^+ + H_2O$$

Case 2.

When mixing of base [OH^-]

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

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

(B) Mixed buffer solution :

(i) Acidic buffer solution :- The solution in which weak acid and its conjugate base are present.

OR

Aqueous solution of mixture of weak acid and salt of same weak acid with any strong base is called acidic buffer solution.

Ex. $\underset{\text{WA}}{CH_3COOH} + \underset{\text{WASB}}{CH_3COONa}$

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

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

$$\left[\underset{\text{WA}}{CH_3COOH} + \underset{\text{C Base}}{CH_3COO^-}\right] + Na^+ \text{ (Spectator ion)}$$

BUFFER ACTION :-

Case 1. If a small amount of acid is added to the buffer solution. The H^+ ions of the acid react with CH_3COO^- ions and produce CH_3COOH and most of the added H^+ ions are consumed so there is no appreciable change in pH.

$$CH_3COO^-_{(aq)} + H^+ \rightleftharpoons CH_3COOH_{(aq)}$$

Case 2. If small amount of base is added to the buffer solution, the OH^- ions are consumed by CH_3COOH.

$$CH_3COOH_{(aq)} + OH^-_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H_2O_{(\ell)}$$

So, there is no appreciable change in pH.

(a) pH of acidic buffer solution :

$\underset{\text{Acid}}{CH_3COOH} + \underset{\text{Salt}}{CH_3COONa}$

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

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

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

or $$[H^+] = \frac{Ka[CH_3COOH]}{[CH_3COO^-]} = \frac{Ka[\text{Acid}]}{[\text{Conjugate base}]}$$

taking –log on both sides

$$pH = pKa - \log\frac{[\text{Acid}]}{[\text{Conjugate base}]} \text{ or } pH = pKa + \log\frac{[\text{Conjugate base}]}{[\text{Acid}]}$$

Henderson's equation :

$$\boxed{pH = pKa + \log\frac{[\text{Salt}]}{[\text{Acid}]} \text{ or } \frac{[\text{Conjugate base}]}{[\text{Acid}]}}$$

- $[\text{Conjugate base}]_{eq} \simeq [\text{Salt}]$ because CH_3COO^- mainly comes from salt since dissociation of CH_3COOH in presence of CH_3COONa is appreciably decreased.
- $[\text{Acid}]_{aq} \simeq$ initial concentration of acid since it is almost unionised in presence of salt due to common ion effect.

(b) pH range of acidic buffer solution : It depends on pK_a of acid and ratio of salt to acid concentrations.

$$[CH_3COOH] \quad : \quad [CH_3COONa] \quad \Rightarrow \quad pH = pKa + \log\frac{[CH_3COONa]}{[CH_3COOH]}$$

(i) If, $\quad 1 \quad : \quad 10 \quad \Rightarrow \quad pH = pKa + \log\frac{10}{1} = pKa + 1$

(ii) If, $\quad 10 \quad : \quad 1 \quad \Rightarrow \quad pH = pKa - 1$

So pH range

$$\boxed{pH = pKa \pm 1}$$

(c) Maximum buffer action condition of acidic buffer solution :

$[CH_3COOH] \quad : \quad [CH_3COONa]$

$$1 \quad : \quad 1 \quad \Rightarrow \quad pH = pK_a + \log\frac{1}{1}$$

$$\boxed{pH = pKa}$$

(ii) Basic buffer solution :

Definition : The solution in which weak base and its conjugate acid are present. OR

Aqueous solution of mixture of weak base and salt of same weak base with any strong acid is called basic buffer solution.

Ex. $NH_4OH + NH_4Cl$

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

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$

$$\left[\underset{\text{W.B.}}{NH_4OH} + \underset{\text{C.acid}}{NH_4^+}\right] + Cl^- [\text{Spectator ion}]$$

BUFFER ACTION :-

Case 1. If a small amount of the acid is added to the buffer solution, the H^+ ions are consumed by NH_4OH.

$$NH_4OH_{(aq)} + H^+_{(aq)} \rightleftharpoons NH^+_{4(aq)} + H_2O_{(\ell)}$$

So there is no appreciable change in pH.

Case 2. If small amount of base is added to the buffer solution, the OH^- ions react with NH_4^+ ions to produce NH_4OH.

$$NH^+_{4(aq)} + OH^-_{(aq)} \rightleftharpoons NH_4OH_{(aq)}$$

Hence most of the added OH^- ions are consumed. so there is no appreciable change in pH.

(a) pOH of basic buffer solution :

$$[\underset{\text{Base}}{NH_4OH} + \underset{\text{Salt}}{NH_4Cl}]$$

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

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$

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

taking –log on both sides $\quad pOH = pK_b + \log\frac{[NH_4^+]}{[NH_4OH]}$

Henderson's equation :

$$\boxed{pOH = pK_b + \log\frac{[\text{Salt}]}{[\text{Base}]} \text{ or } \frac{[\text{Conjugate acid}]}{[\text{Base}]}}$$

(b) pOH range of basic buffer solution : It depends on pK_b of base and ratio of salt to base concentrations.

$[NH_4OH] \; : \; [NH_4Cl] \; \Rightarrow \; pOH = pK_b + \log\frac{[NH_4Cl]}{[NH_4OH]}$

(i) If, $1 : 10 \Rightarrow pOH = pK_b + 1$

(ii) If, $10 : 1 \Rightarrow pOH = pK_b - 1$

So, pOH range : $\boxed{pOH = pK_b \pm 1}$

(c) Maximum buffer action condition of basic buffer solution :

$NH_4OH : NH_4Cl$

$1 : 1$

$$\boxed{pOH = pK_b}$$

BUFFER CAPACITY

Definition :-

(i) It is defined as the number of moles of strong acid (or strong base) added to one litre of a buffer solution to change its pH by one unit.

(ii) It measures the effectiveness of a buffer.

(iii) Larger the value of buffer capacity more resistant is the solution to pH change.

$$\text{Buffer capacity} = \frac{\text{Number of moles of acid or base added per litre}}{\text{Change in pH of buffer solution}}$$

INDICATOR

(A) Definition :- An indicator is a substance that undergoes change in its colour to show end point of an acid-base titration.

- Titration involves neutralization of an acid and base.

(B) Types of indicators :

(a) Acidic indicator (HIn)

Ex. Phenolphthalein (HPh)

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

(b) Basic indicator (InOH)

Ex. Methyl orange (MeOH)

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

OSTWALD THEORY OF INDICATORS

(i) According to this theory, all the indicators are weak organic acid or base.

(ii) Every indicator has light colour in its unionised form and dark colour in ionised form.

(iii) Every indicator has one colour in acidic medium and an altogether different colour in basic medium due to common ion effect and odd ion effect.

Ex. Acidic indicator [HPh]

Case 1. $\text{HPh} \rightleftharpoons \text{H}^+ + \text{Ph}^-$

In acidic medium $[\text{H}^+]$ $[\text{HPh}] > [\text{Ph}^-]$

Colourless due to common ion effect.

Case 2. $\text{HPh} \rightleftharpoons \text{H}^+ + \text{Ph}^-$

In basic medium $[\text{OH}^-]$ $[\text{Ph}^-] > [\text{HPh}]$

Pink colour due to odd ion effect.

(a) pH of acidic indicator -

$$\text{HIn} \rightleftharpoons \text{H}^+ + \text{In}^-$$

$$K_a \text{ or } K_I = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]}$$

$$[\text{H}^+] = \frac{K_I[\text{HIn}]}{[\text{In}^-]}$$

Taking – log on both sides

$$\text{pH} = \text{p}K_I - \log[\text{HIn}] + \log[\text{In}^-]$$

$$\text{pH} = \text{p}K_I + \log\frac{[\text{In}^-]}{[\text{HIn}]} \qquad \boxed{\text{pH} = \text{p}K_I + \log\frac{[\text{Ionised form}]}{[\text{Unionised form}]}}$$

(b) pOH of basic indicator -

$$\text{InOH} \rightleftharpoons \text{In}^+ + \text{OH}^-$$

$$K_b \text{ or } K_I = \frac{[\text{In}^+][\text{OH}^-]}{[\text{InOH}]} \qquad \boxed{\text{pOH} = \text{p}K_I + \log\frac{[\text{Ionised form}]}{[\text{Unionised form}]}}$$

(c) pH range of indicators :

Indicators show colour change for a certain pH range not at a definite pH which is called pH range of indicator.

(i) pH range of acidic indicator :

$[\text{HIn}]$: $[\text{In}^-]$

1 : 10

10 : 1 $\boxed{\text{pH} = \text{p}K_I \pm 1}$

(ii) pOH range of basic indicator :

$[\text{InOH}]$: $[\text{In}^+]$

1 : 10

10 : 1 $\boxed{\text{pOH} = \text{p}K_I \pm 1}$

(iii) Neutral condition for indicators (No working condition)

For acidic indicator			For basic indicators		
[HIn]	:	$[In^-]$	[InOH]	:	$[In^+]$
1	:	1	1	:	1
$\boxed{pH = pK_I}$			$\boxed{pOH = pK_I}$		

S.No.	Name of indicator	Colour in acidic medium	Colour in basic medium	Working pH range of indicators
1.	Methyl orange (MeOH)	Orange red	Yellow	3.1 to 4.5
2.	Methyl red	Red	Yellow	4.2 to 6.2
3.	Phenol red	Yellow	Red	6.2 to 8.2
4.	Phenolphthalein (HPh)	Colourless	Pink	8.2 to 10.2

ACID-BASE TITRATION

S.No.	Type of titration	pH range of titration	Suitable indicators
1.	SA/SB.	3 – 11	All indicators (MeOH, HPh etc.)
2.	SA/WB	3 – 7	Methyl orange (MeOH) and methyl red
3.	WA/SB	7 – 11	Phenolphthalein (HPh)

Important points of titration :

(i). Titration is always possible in two opposite solution. (i.e. one is acidic and other is basic).

(ii). For any titration only that indicator is suitable if their working pH range is in pH range of titration.

(iii). At the end point of titration equivalents of acids and bases are always same.

(iv). At the euivalence point, nature of solution depends on the type of titration.

SA/SB - Neutral (pH = 7)
SA/WB - Acidic
WA/SB - Basic
WA/WB - Any one possible