6. ACIDS AND BASES

Synopsis:

- Based on apparent properties, Robert Boyle classified the substance into acids and bases.

Acids	Bases
1. Sour to taste	Bitter to taste
2. Turn blue litmus to red	Turn red litmus to blue
3. Neutralise bases	Neutralise acids
4. Liberate H_2 gas on reaction with metals	They are soapy to touch
5. Aqueous solutions are good conductors	Aqueous solutions are good conductors
6. They decompose metal carbonates and bicarbo-nates to liberate CO_2	

- According to Lavoiser all acids must contain oxygen. But dray proved that all acids must contain Hydrogen but not oxygen.
  Eg: HCl, HBr, HI, HF etc,.
- The chemical behaviour of acids and bases is explained by following three theories.
  1) Arrhenius theory
  2) Bransted - lowery theory
  3) Hewis theory
- **Bronsted – Lowery theory of Acids and bases:**
  This is also called protonic theory .
  Acid : which donates proton
  Eg: HCl, H_2SO_4, HNO_3 etc.
  Base : which accepts proton
  Eg: NH_3, PH_3, N_2H_4, $R - NH_2$ etc.
- Bronsted acid could be a neutral molecule , anion, cation.
  Neutral molecule $\rightarrow$ HCl, HNO_3, H_2SO_4 etc.
  Cations $\rightarrow$ H_3O^+, NH_4^+
  Anions $\rightarrow$ HSO_4^-, HCO_3^-, $H_2PO_4^-$, $H(PO_4)^{2-}$, $H_2(PO_3)^-$ Bronsted base could be neutral, cation or anion
  Neutral $\rightarrow$ NH_3 , PH_3, N_2H_4 etc.
  anions $\rightarrow$ CN^-, Br^-, I^-, OH^- etc.
  Cations $\rightarrow$ $[Al(H_2O)_5OH)]^{2+}$, $[Fe(H_2O)_5OH]^{2+}$
- **Neutralisation :**
  It involves transfer of proton from acid to base and formation of conjugate acid – base pair.
  1) $\underset{A_1}{HCl} + \underset{B_2}{H_2O} \rightleftharpoons \underset{B_1}{Cl^-} + \underset{A_2}{H_3O^+}$
  2) $\underset{B_1}{NH_3} + \underset{A_2}{H_2O} \rightarrow \underset{A_1}{NH_4^{\oplus}} + \underset{B_2}{OH^-}$
  3) $\underset{B_1}{NH_3} + \underset{A_2}{HCl} \rightarrow \underset{A_1}{NH_4^+} + \underset{B_2}{Cl^-}$
- Amphoteric or Amphiprotic substance : The act as both acids and base because they donate proton and accept proton.
  Eg : H_2O

- **Conjugate acid – base pairs :**

  The acid base pair which differs by a proton is called conjugated acid base pair.

  Acid $-\ H^{\oplus}$ = conjugate base

  Base + $H^{\oplus}$ = conjugate acid

  Eg :

Acid	**Base**
HCl	Cl^-
H_2SO_4	HSO_4^-
HSO_4^-	SO_4^{2-}
H_2S	HS^-
C_2H_2	$CH \equiv C^-$
CH_4	CH_3^-
$[Al(H_2O)_6]^{3+}$	$[Al(H_2O)_5OH]^{2+}$
$[Fe(H_2O)_6]^{3+}$	$[Fe(H_2O)_5OH]^{2+}$
H_2	H^-
H	e^-

- In any conjugate acid base pair, if the acid is stronger , the base is weak and if base is stronger , the acid is weak.

  Eg:

  1. HCl is strong acid, Cl^- is weak conjugate base.
  2. CH_3COOH is weak acid $CH_3COO^-$is strong base
  3. NH_3 is weak base, NH_4^+ strong acid
  4. $HClO_4$ is strongest acid, ClO_4^- weak base

- List of conjugate acid base pairs in a particular order of strength.

	Acid	**Base**
[Decreases acidic strength]		
1.	$HClO_4$	ClO_4^-
2.	HI	I^-
3.	HBr	Br^-
4.	H_2SO_4	HSO_4^-
5.	HCl	Cl^-
6.	HNO_3	NO_3^-
7.	H_3O^+	H_2O
8.	HSO_4^-	SO_4^{2-}
9.	H_3PO_4	$H_2PO_4^-$
10.	HF	F^-
11.	CH_3COOH	CH_3COO^-
12.	H_2CO_3	HCO_3^-
13.	HCN	CN^-
14.	NH_4^+	NH_3
15.	H_2O	OH^-

16. NH_3 NH_2^-
17. OH^- O^{2-}
18. CH_4 CH_3^-

- Strength of bronsted acids and bronsted bases will depend on the ability to donate or to accept proton.
- **Strong acids :** which have more ability to donate protons.
  Eg: $HClO_4$, HCl, H_2SO_4
- **Weak acids** : which have less tendency to donate proton.
  Eg: HF, CH_3COOH, H_2CO_3, HCN
- Among Hydracids HCN is the weakest acid
- **Strong bases :** which have greater tendency to accept protons
  Eg: OH^-, CH_3COO^-, CH_3^- etc.
- Weak bases $\rightarrow$ which have less tendency to accept the proton.
  Eg: Cl^-, ClO_4^-, Br^-, I^-, NH_3…..etc.
- **Levelling effect :** The strength of stronger acids like $HClO_4$, H_2SO_4, HCl, HNO_3 will become equal to the strength of H_3O^+ ion in presence of H_2O. This is called levelling effect
  $HClO_4 \approx H_2SO_4 \approx HCl \approx HNO_3 = H_3O^+$
- Similarly the strength of stronger bases like NaOH, KOH, CsOH will become equal to the strength of OH^- ion in presence of H_2O
  $NaOH \approx KOH \approx CsOH = OH^-$
- This levelling effect of acids is due to greater proton accepting tendency of H_2O and instantly conversion into H_3O^+ therefore the real strength cannot be determined.
- The acids like $HClO_4$, H_2SO_4 etc. cannot be determined in a levelling solvent like H_2O.
- Therefore the strongest acid that can exist in water is H_3O^+ and the strongest base that can exist is OH^- ion.
- In a solvent like glacial acetic acid, the real strength of acids can be determined because of poor tendency to accept protons. Therefore acetic acid is differentiating solvent and the strongest acid that can exist in acetic acid solvent is $HClO_4$.
- In acetic acid, $HClO_4 > H_2SO_4 > HCl > HNO_3$
- **Types of solvents:** Based on proton donating or proton accepting tendency, solvents are classified into 4 types by bronsted lowery solvents.
  1) Protophilic solvents : which accept proton
     Eg : H_2O, NH_3 , ether , C_2H_5OH etc.
     Protophilic solvents will increase acidic strength and decrease the basic strength.
  2) Photogenic solvents : which donate H^+
     protogenic solvents will decrease the acidic strength and increase the basic strength.
  3) Amphiprotic solvents : which donates and accept proton
     Eg : H_2O, C_2H_5OH
  4) Aprotic solvents: which neither donates nor accepts proton.
  Eg : CCl_4, $CHCl_3$, C_6H_6, Acetone

  Merits of Bronsted – Lowery theory :
  1) It could explain acid base behaviour in non – aqueous solvents also .
     Eg: liquid SO_2, liquid NH_3
  2) It could explain the basic nature of substances like NH_3.
  3) It could explain the acidic nature of HCl gas.

4) It is more generalized than Arrhenius theory.

- **Limitations of Bronsted – Lowery theory :**

1) This theory explains behaviour of acids only when there is a base (or) It explains behaviour of base only when there is a acid. (Acid base pairs must be present)

2) It fails to explain the acidic nature of electron deficient compound like BF_3, $AlCl_3$ etc.

- **Lewis theory of acids – bases :**

Acid : which accepts electron pair.

- All electrophiles are Lewis acids
- Lewis acid must contain suitable vacant orbitals.

Eg: BF_3, BCl_3, $AlCl_3$, H^+, Ag^+ etc.

Base : which donates e^- pair.

- All nucleophiles are Lewis bases
- Lewis base must contain 1 or more lone pairs of electrons.

Eg: $\ddot{N}H_3, \ddot{P}H_3, R-\ddot{N}H_2$,

$\ddot{N}H_2-\ddot{N}H_2$,OH^-, Cl^-, $H_2\ddot{O}$

Neutralisation: It involves formation of coordinate covalent bond by the transfer of e^- pair form base to acid.

$H_3\ddot{N} + BF_3 \rightarrow [H_3N \rightarrow BF_3]$

$H_2\ddot{O} + H^{\oplus} \rightarrow [H_2O-H]^+$ or $H_3O^{\oplus}$

$H_3\ddot{N} + H^{\oplus} \rightarrow [H_3N-H]^+$ or $NH_4^{\oplus}$

$Cl^- + AlCl_3 \rightarrow [Cl-AlCl_3]^-$ or $AlCl_4^-$

- **Types of Lewis acids :**

1) All simple cations :

Eg : H^+, Ag^+, Li^+, Cu^{2+}, Co^{3+}, Al^{3+} etc.

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

2) Electron deficient molecules :

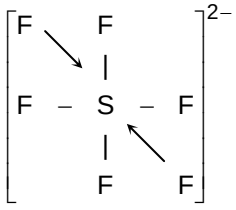
Eg: BF_3, BCl_3, BBr_3, BI_3, $AlCl_3$, $GaCl_3$ etc.

$BF_3 < BCl_3 < BBr_3 < BI_3$

$BF_3 + \ddot{F}^- \rightarrow [F_3B-F]^-$ or BF_4^-

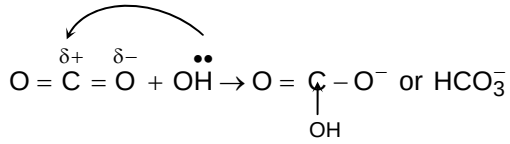
- 3) Molecules which can extend octet configuration:

Eg: SiF_4 , $SiCl_4$, $SnCl_4$, SF_4, $SFCl_4$, $TeCl_4$ etc.

$SiF_4 + 2\,F^- \rightarrow$  or SiF_6^{2-}

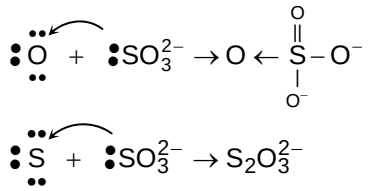
- 4) Molecules with multiple bonds in between atoms of different electronegativities

Eg : CO_2, SO_2, SO_3, NO_2, N_2O_5, Cl_2O_7, P_2O_5



- 5) Molecules in which the central atom with sextet configuration

  Eg : S, O, Se……..



- Types of Lewis bases :

  All simple anions :

  Eg : Cl^-, P^- , Br^-, OH^-, CN^- etc.

  $SiCl_4 + 2Cl^- \rightarrow SiCl_6^{2-}$

- Molecules with lone pairs :

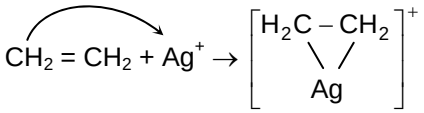
  Eg : $\ddot{N}H_3, \ddot{P}H_3, \ddot{N}_2H_4, R-\ddot{N}H_2, R-\ddot{O}H, H_2\ddot{O}$,

  $R-\ddot{O}-R$, $R_2\ddot{S}$ etc.

  $\ddot{N}H_3 + H^+ \rightarrow [H_3N \rightarrow H]^+$ or NH_4^+

- Molecular multiple bonds in between similar atoms:

  Eg: $CH_2 = CH_2$, CH≡ CH, pyridine , **:** NO, : CO



- **Draw backs of Lewis theory :**

  1) It will not consider popular acids like $HClO_4$, HNO_3, H_2SO_4 as they do not form co-ordinate covalent bond.

  2) It fails to explain the catalytic activity of H^+.

  3) Lewis acid base neutralisation is very slow as it involves formation of co-ordinate covalent bond but actually neutralisation reactions are very fast.

  4) It fails to explain strength of acids and bases.

  5) It fails to explain the simple neutralisation reactions where H^+ is involved.

IONISATION OF ACIDS AND BASES AND DEGREE OF IONISATION

- Acids which donate protons are generally known as protonic acids. These are represented as HX

  The compounds which contain OH^- ions are generally known as bases and represented by BOH

  When acids are dissolved in water, they ionised into H^+ and X^-

  $HX \xrightarrow{H_2O} H^+ + X^-$

  When bases are dissolved in water they ionised into B^+ and OH^-

  $BOH^- \xrightarrow{H_2O} B+$

  This process in known as ionisation same time referred to as dissociation

The extent of hydrolysis is more for strong acids and strong bases (100% ionisation)

The extent of hydrolysis is less for weak acids and weak bases

The process of ionisation is an equilibrium process

HX $\overset{H_2O}{\rightleftharpoons}$ $H^+ + X^-$ ---------(1)

BOH $\overset{H_2O}{\rightleftharpoons}$ $B^+ + OH^-$-------(2)

The dissociation constant of acid

Ka = $\frac{[H^+][X^-]}{[HX]}$ (based on the equation(1))

The dissociation constant of base or base ionisation constant

Kb = $\frac{[B^+][OH^-]}{[BOH]}$ (based on the equation(2))

For any weak acid:

HX $\rightleftharpoons$ $H^+ + X^-$

C(1- α) C α C α

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

1. $\mathrm{Ka} = \mathrm{C}\alpha^2$
2. $\alpha = \sqrt{\mathrm{Ka}/\mathrm{C}}$
3. $\left[\mathrm{H}^+\right] = \mathrm{C}\alpha$
4. $\left[\mathrm{H}^+\right] = \sqrt{\mathrm{Ka}\times\mathrm{C}}$
5. $\mathrm{P}^{\mathrm{H}} = \frac{1}{2}\mathrm{P}^{\mathrm{Ka}} - \frac{1}{2}\log\mathrm{C}$

α = degree of ionization of acid

C = molar concentration of acid

Ka = ionisation constant of acid

For any weak base:

1. $\mathrm{K_b} = \mathrm{C}\alpha^2$
2. $\alpha = \sqrt{\mathrm{K_b}/\mathrm{C}}$
3. $\overline{\mathrm{O}}\mathrm{H} = \mathrm{C}\alpha$
4. $\left[\overline{\mathrm{O}}\mathrm{H}\right] = \sqrt{\mathrm{K_b}\times\mathrm{C}}$
5. $\mathrm{P}^{\mathrm{OH}} = \frac{1}{2}\mathrm{P}^{\mathrm{K_b}} - \frac{1}{2}\log\mathrm{C}$
6. $\mathrm{P}^{\mathrm{H}} = 14 - \mathrm{P}^{\mathrm{OH}}$

α = degree of ionisation of base

C = molar concentration of base

K_b = ionisation constant of base

- **Comparison of acid – base theories :**

  1) All Arrhenius acids are bronsted lowery acids but all bronsted lowery bases are not Arrhenius bases.

  Eg: $HCl_{(aq)} \rightarrow$ It is Arrhenius acid as it gives H^+ and bronsted lowery acid as it donates proton.

  $NH_3 \rightarrow$ It is bronsted lowery base because it accepts proton but it is not Arrhenius base as it will not give OH^-.

- 2) All bronsted lowery bases are Lewis base but Lewis acids need not be bronsted lowery acids.

  Eg: $N\overset{\bullet\bullet}{H}_3 \rightarrow$ It is Bronsted lowery base because it accepts proton and it is Lewis base because it donates e^- pair.

  $BF_3 \rightarrow$ It is Lewis acid as it accepts electron pair but it is not bronsted lowery acid as it will not donate proton.

- **Ionic product of water :**

  Pure water is weak electrolyte that is just one molecule out of 556 millions of water molecules will ionise.

- Ionisation of water :

  $H_2O \rightleftharpoons H^+ + OH^-$ (or)

  $2H_2O \rightleftharpoons H_3O^+ + OH^-$

  By applying law of mass action to the above ionisation reaction.

  $K = \frac{[H^+]\,[OH^-]}{[H_2O]}$ (or) $\frac{[H_3O^+]\;[OH^-]}{[H_2O]^2}$

  since the molar concentration of $[H_2O]$ is practically a constant and therefore

  K or $K_\omega = [H^+]\,[OH^-]$

  $K_\omega \rightarrow$ ionic product of water.

- K_ω is defined as the product of molar concentration of H^+ and OH^- ions.
- At 25^0C, $K_\omega = 1 \times 10^{-14}$ mol^2 / lit^2.
- "with an increase in temperature the value of k_ω increase as the extent of ionisation of water increases"
- At a given temperature the value of K_ω remains constant for any given dilute aqueous solution. i.e. neutral (or) acidic (or) basic.

  In pure water (or) neutral aqueous solution.

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

  $[H^+] = 10^{-7}$ mol/lit

  $[OH^-] = 10^{-7}$ mol / lit

  $K_\omega = 1 \times 10^{-14}$ mol/ lit

  In acidic solution :

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

  $[H^+] > 10^{-7}$

  $[OH^-] < 10^{-7}$

  $K_\omega = 10^{-14}$

  In basic solution

  $[OH^-] > 10^{-7}$

  $[H^+] < 10^{-7}$

  $K_\omega = 10^{-14}$

- At 90^0C the concentration of H_3O^+ ions is 10^{-6} mole/ lit in pure water. The value of K_w is

Pure $H_2O \rightarrow [H_3O^+] = [OH^-]$

$1 \times 10^{-6} = 1 \times 10^{-6}$

$\therefore K_w = 1 \times 10^{-12}\ mol^2 / lit^2$

- p^H of solutions:

  It was introduced by Sorensen to calculate lower concentrations of H^+ ion.

- p^H is –ve logarithm of H^+ ion concentration.

  p^H is logarithmic reciprocal of H^+ ion concentration.

  P^H is the negative power rised on ten in order to express H^+ ion concentration.

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

  $p^H = \log \frac{1}{[H^+]}$

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

  Even OH^- ion concentration can be expressed on p^H scale.

  $p^{OH} = -\log(OH^-)$

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

  For any dilute solution; $[H^+]\ [OH^-] = 10^{-14}\ mol^2/\ litre^2$

  $P^{K_w} = p^H + p^{OH} = 14$

- Other similar expressions:

  $p^{OH} = -\log[OH^-]$

  Similarly

  $p^{k_a} = -\log k_a$

  $p^{k_b} = -\log k_b$

  $p^{k_\omega} = -\log k_\omega$

  $p^k = -\log k$

  $p^M = -\log[M^+]$ $\quad M^+ \rightarrow$ metal ion concentration

  p^H scale $1 \xrightarrow{\text{acids}} 7 \xrightarrow{\text{bases}} 14$

  neutral

- The maximum concentration of H^+ ion that could be expressed on p^H scale is 0.1 M. When $[H^+] = 0.1$; $p^H = 1$. If $[H^+]$ = more than 0.1 p^H is less than 1

  [no provision for less than 1 on scale]

- The maximum concentration of OH^- ion that could be expressed on p^H scale is 1M. When $[OH^-]$ =1M; $p^{OH} = 0$; $p^H = 14$ if $[OH^-]$ = more than 1M; $p^{OH} < 0$ and $p^H > 14$ [no provision for more than 14 on p^H scale]
- P^H scale is applicable for dilute solutions.
- With increase in the concentration of $[H^+]$, p^H value decreases, p^{OH} value increases.
- With increase in the $[OH^-]$ the p^H value increases, and p^{OH} value decreases.
- With increase in temperature p^H value decreases. At higher temperature, the extent of ionisation increases and H^+ ion concentration increases. There fore p^H value decreases.

  Similarly OH^- ion concentration also increases and p^{OH} decreases and thus the entire p^H scale contracts.
- If $[H^+]$ ion concentration is increased by 10^n times p^H value decreases by n units.
- If $[H^+]$ ion concentration is decreased by 10^n times p^H value increases by n units.
- If acid solution is diluted by 10^n times, p^H value increases by n units.

- If basic solution is diluted by 10^n times, p^H value decreases by n units.
- **P^H of weak acids and weak bases :**

  Ionisation of weak acid(HA) :

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

  C 0 0

  $C - C\alpha \quad C\alpha \quad C\alpha$

  $K_a = \frac{C\alpha.C\alpha}{C - C\alpha} = \frac{\alpha^2 C}{(1-\alpha)} = \alpha^2 C$ ($\because$ α is very less)

  $K_a = \alpha^2 C$; $\alpha^2 = K_a / C$

  $\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{K_a.V} = \left(\frac{1}{c} = v\right)$

  Ostwald's law of dilution explains the variation of degree of ionisation with concentration. The degree of ionisation is inversely proportional to its square root of its concentration (or) directly proportional to square root of its dilution.

  $[H^+] = C\alpha$

  $[H^+] = C\sqrt{\frac{k_a}{C}}$; $[H^+] = \sqrt{K_a.C}$

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

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

- Ostwald's law of dilution is applicable for weak electrolytes (weak acid and weak base) it is not applicable to strong electrolytes because they completely ionise at moderate concentration.
- The behaviour of strong electrolytes is explained by Debye – Huckel's theory.

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

  $p^H = \frac{1}{2}p^{k_a} - \frac{1}{2}\log C$

- **Ionisation of weak bases (MOH) :**

  $MOH \rightleftharpoons M^+ + OH^-$

  C 0 0

  $(C - C\alpha)\ C\alpha\ C\alpha$

  $K_b = \frac{C\alpha \times C\alpha}{C - C\alpha}$

  $K_b = \frac{\alpha^2 C}{(1-\alpha)}$ ($\because$ α is very less)

  $K_b = \alpha^2 C$; $\alpha^2 = \frac{K_b}{C}$

  $\alpha = \sqrt{\frac{K_b}{C}} \Rightarrow \alpha = \sqrt{K_b.v}\ \left(\frac{1}{c} = v\right)$

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

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

  $-\log[OH]^- = -\frac{1}{2}\log K_b - \frac{1}{2}\log C$

$$p^{OH} = \frac{1}{2}p^{K_b} - \frac{1}{2}\log C$$

$$p^{H} = K_w - p^{OH}$$

$$p^{H} = k_w - \frac{1}{2}p^{K_b} + \frac{1}{2}\log C$$

For weak acids :

$$[H^+] = C\alpha\ ;\ [H^+] = \sqrt{K_{a.}C}$$

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

For weak bases :

$$[OH^-] = C\alpha\ \textbf{;}\ [OH^-] = \sqrt{K_b.C}$$

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

For strong acids ; $[H^+]$ = N of acid

For weak acids ; $[H^+]$ < N of acid

For strong bases; $[OH^-]$ = N of base

For weak bases; $[OH^-]$ < N of base

- **Buffers :** The solutions which maintain constant p^H value on addition of acid or base.
- Resisting change in p^H value on adding acid or base to a buffer is called Buffer action.
- Buffers posses reserve acidity and reserve alkality. Reserve acidity will nullify the effect of added base and reserve basicity will nullify the effect of added acid.
- Blood buffer is H_2CO_3 + $NaHCO_3$.

  Types of buffers:

  1) Acid buffers: It is the mixture of weak acid and it's salt of strong base.

     CH_3COOH + CH_3COONa

     H_2CO_3 + $NaHCO_3$

     Tetra boric acid + Borax $\rightarrow$ [p^H > 7]

     H_3PO_4 + NaH_2PO_4

     The p^H of acid buffers is usually less than 7 but not always.

  2) Basic buffers: It is mixture of weak base and its salt of strong acid.

     NH_4 OH + NH_4Cl

     Glycine + Glycine hydro chloride

  3) Normal salt of weak acid and its acidic salt

     Na_2CO_3 + NaH CO_3

     Na_3PO_4 + Na_2HPO_4

  4) Salt of weak acid and weak base

     Eg : CH_3COONH_4 ; $HCOONH_4$

  5) Ampholytes Amino acids proteins **:**

     Which of the following can act as buffer

- **Action of Acid buffers:**

  Eg : CH_3COOH + CH_3COONa

  Acetic acid mostly remains as unionised and sodium acetate is almost completely ionised. Therefore the components present in the above buffer are

$(CH_3COOH + CH_3COO^- + Na^+)$

If little strong acid (H^+) is added to the above buffer, the added strong acid will convert into weak acid. Thus the effect is nullified.

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

If little strong base (OH^-) is added to buffer, the added strong base is converted into water (H_2O). Thus the effect of added base is nullified.

$CH_3COOH + H^- \rightarrow CH_3COO^- + H_2O$

Thus acid buffer can resist change in p^H on addition of little amount of acid or little amount of base.

In the above buffer the reserve acidity is due to CH_3COOH and reserve basisity is due to CH_3COO^-.

- **Action of Basic buffer :**

  Eg : $NH_4OH + NH_4Cl$

  NH_4OH ionizes to very small extent and NH_4Cl being a salt ionizes completely. Therefore the components present in the above buffer are $[NH_4OH + NH_4^+ + Cl^-]$

  The reserve acidity of the above buffer is due to NH_4^+ and reserve bascity is due to NH_4OH.

- If strong acid $[H^+]$ is added to buffer, it is converted into H_2O

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

- If strong base $[OH^-]$ is added to buffer, it will convert into weak base

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

  Thus an acid buffer or a basic buffer can maintain constant p^H value by adding acid as well as base.

- P^H of Buffers : [Henderson's equation]

  Deriving p^H expression for Acid buffer :

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

  (weak acid)

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

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

$$[A^-] = K_a\left[\frac{\text{Acid}}{\text{Salt}}\right]$$

$[\because$ most of the A^- concentration comes from salt $]$

By applying – log on both sides.

$$-\log[H^+] = -\log K_a - \log\left[\frac{\text{Acid}}{\text{salt}}\right]$$

$$p^H = p^{K_a} - \log\left[\frac{\text{Acid}}{\text{salt}}\right]$$

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

- Deriving p^H expression for basic buffer :

  $BOH \rightleftharpoons B^+ + OH^-$

  (weak base)

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

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

$$[OH^-] = K_b \left[\frac{base}{salt}\right]$$

[$\because$ most of the B^+ concentration come from salt]

By applying – log on both sides

$$-\log[OH]^- = -\log K_b - \log\left[\frac{base}{salt}\right]$$

$$p^{OH} = p^{K_b} - \log\left[\frac{base}{salt}\right]$$

$$p^{OH} = p^{K_b} + \log\left[\frac{salt}{base}\right]$$

$$p^H = 14 - p^{OH}$$

$$p^H = p^{K_\omega} - p^{K_b} - \log\left[\frac{salt}{base}\right]$$

$$\left.\begin{aligned} p^H &= p^{K_a} + \log\left[\frac{salt}{acid}\right] \\ p^{OH} &= p^{K_b} + \log\left[\frac{salt}{base}\right] \end{aligned}\right\} \text{[Henderson's equation]}$$

- **Buffer capacity :**

  It is the capacity of a buffer to resist change in p^H by adding acid or base.

- A good buffer shows only a slight change in p^H on addition of acid or base.
- Buffer capacity is defined as the number of moles of acid or base added per litre of buffer to cause the change in its p^H by one unit

  (or)

  Buffer capacity is the ratio of number of moles of acid or base added per litre of buffer to the change in p^H

  Buffer capacity =

$$\frac{\text{no.of mole of acid or base added per litre of buffer}}{\text{change in } p^H}$$

- p^H range of buffer :

  It is the range of p^H values where a buffer can effectively resist the change in p^H on adding acid or base.
- For an acid buffer the p^H range.

$$p^H = p^{K_a} \pm 1$$

  For example P^{K_a} of CH_3COOH + CH_3COONa buffer is 4.5. Therefore it functions effectively between p^H values 3.5 and 5.5.
- The p^H range of basic buffer.

$$p^{OH} = p^{K_b} \pm 1$$

- Buffer capacity will maximum if p^H=p^{Ka}:[salt] =[acid]

  Buffer capacity will be more if the components are taken in higher concentrations.
- Any buffer has a definite p^H values. The p^H of buffer does not change on long standing.
- The p^H of buffer does not change on dilution.

Applications of buffers :

1) Buffers are used in various chemical industries
2) Buffers are used in various enzyme catalyses reaction.
3) used in softening of hard water.
4) used in various research programmes.
5) used in chemical analysis. [precipitation of radicals]

- **Salt of Hydrolysis :**

$$\text{Acid + base} \underset{\text{salt hydrolysis}}{\overset{\text{neutralisation}}{\rightleftharpoons}} \text{salt} + H_2O$$

Salt hydrolysis is endothermic because t is reverse of neutralisation.

- The reaction of the salt with water to produce acid or base or both is called salt hydrolysis.
- Salt hydrolysis is of three types.

1) Cationic hydrolysis : Cation of the salt reacts with water to produce H^+ ions.

Eg: NH_4Cl, NH_4NO_3, $[NH_4]_2SO_4$, $AlCl_3$ etc.

In these salts cation is stronger because it is the conjugate of weak base therefore they undergo cationic hydrolysis.

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

2) Anionic Hydrolysis : Anion of the salt reacts with water to produce OH^-.

Eg: CH_3COONa, $HCOOK$, Na_2CO_3, etc.

In these salts anion is stronger as it is the conjugate of weak acid.

Eg: CH_3COONa^+ :

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

3) Cationic and Anionic hydrolysis : Both cation and anion of the salt react with water to produce H^+ and OH^- ions. Therefore the solution is neutral.

Eg: CH_3COONH_4, $HCOONH_4$, $Al(CH_3COO)_3$

In these salts both cation and anion are stronger because they are the conjugates of weak base and weak acid respectively.

Eg: $CH_3COONH_4^+$:

$CH_3OO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$

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

there are four types of salts depending on the nature of acid and base involved in the titrations.

- **Salt of strong acid and weak base :**

Eg: NH_4Cl, NH_4NO_3, $(NH_4)_2SO_4$, $AlCl_3$, $MgCl_2$, $Al_2(SO_4)_3$ etc,…

- These salts undergo cationic hydrolysis to produce H^+ ions.
- Their aqueous solution is acidic and p^H is less than 7.
- Their aqueous solution will turn blue litmus to red and they can be used for titrating against bases.

Eg: $NH_4^+Cl^-$

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

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

$$K.[H_2O] = \frac{[NH_4OH]\,[H^+]}{[NH_4^+]}$$

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

Ionisation of

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

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

Ion product of water = $k_\omega = [H^+]\,[OH^-]$

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

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

The degree of hydrolysis of the salt is inversely proportional to the square root of its molar concentration.

$$\alpha = \sqrt{\frac{K_b}{C}} \Rightarrow \sqrt{\frac{K_w}{K_b.C}}$$

$[H^+] = C\alpha$

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

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

Appling – log on both sides

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

$$p^H = \frac{1}{2}p^{Kw} - \frac{1}{2}p^{K_b} - \frac{1}{2}\log C$$

- **Salt of weak acid and strong base :**

Eg: CH_3COONa, $HCOOK$, Na_2CO_3, $NaHCO_3$, Na_3PO_4, Na_2HPO_4, KCN etc.

Anionic hydrolysis : CH_3COONa

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

$$K = \frac{[CH_3COOH][OH^-]}{[CH_3OO^-]\;\;[H_2O]}$$

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

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

Ionisation of CH_3COOH :

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

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

ionic product of water : $K_w = [H^+]\,[OH^-]$

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

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

The degree o hydrolysis of these salts is also inversely proportional to the square root of its concentration.

$$\alpha = \sqrt{\frac{k_h}{C}} \Rightarrow \sqrt{\frac{k_w}{k_a.C}}$$

$$\left[OH^-\right] = C\sqrt{\frac{K_w}{K_a.C}} \Rightarrow \sqrt{\frac{K_w.C}{K_a}}$$

applying – log on both sides

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

$$p^{OH} = \frac{1}{2}p^{K_w} - \frac{1}{2}p^{K_a} - \frac{1}{2}\log C$$

- aqueous solution of these salts are basic they undergo anionic hydrolysis because the anion of the salt is stronger as it is the conjugate of weak acid.

  $[OH^-]$ is produced and solution is basic.

- **Salt of weak acid and weak base :**

  Eg: CH_3COONH_4, $HCOONH_4$, NH_4CN, $Al(CH_3COO)_3$ etc…

- The aqueous solution of these salts is all most neutral and p^H is all most equal to 7.
- The nature of the salt solution actually depends on K_a and K_b values of acid and base.

  i) If $K_a = K_b$, solution is exactly neutral.

  Eg: CH_3COONH_4

  K_a of CH_3COOH = K_b of NH_4OH

  ii) If $K_a > K_b$, solution is acidic

  Eg: $HCOONH_4$

  K_a of $HCOOH > K_b$ of NH_4OH

  iii) If $K_a < K_b$, solution is basic

  Eg: $Mg(CN)_2$

  K_b of $Mg(CN)_2 > K_a$ of HCN

- These salts will undergo both cationic and anionic hydrolysis to produce both H^+ and OH^- ions.

  Eg: CH_3COONH_4

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

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

$$K = \frac{[CH_3COOH]\,[NH_4OH]\,[H^+]\;[OH^-]}{[CH_3COO^-]\,[NH_4^+]\,[H_2O]^2}$$

$$K[H_2O]^2 = \frac{[CH_3COOH]\,[NH_4OH]\,[H^+]\;[OH^-]}{[CH_3COO^-]\,[NH_4^+]}$$

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

The $[H^+] = [OH^-]$ they get cancelled mutually

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

ionic product of water $K_w = [H^+]\,[OH^-]$

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

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

$$\frac{K_w}{K_a.k_b} = \frac{[H^+][OH^-][CH_3COOH][NH_4OH]}{[CH_3COO^-][H^+][NH_4^+][OH^-]}$$

$$\frac{K\omega}{K_a.k_b} = \frac{[CH_3COOH]\,[NH_4OH]}{[CH_3COO^-]\,[NH_4^+]}$$

$$K_b = \frac{K_w}{K_a.K_b}$$

- The degree of hydrolysis [α] is independent of concentration of the salt because both cation and anion of the salt are stronger as they are conjugate of weak base and weak acid respectively.

$$\alpha = \sqrt{K_h} \Rightarrow \sqrt{\frac{K_w}{K_a.K_b}}$$

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

apply - log on both sides

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

$$p^H = \frac{1}{2}p^{K_w} + \frac{1}{2}p^{K_a} - \frac{1}{2}p^{K_b}$$

$$[OH^-] = K_b \cdot \alpha$$

$$= K_b\sqrt{\frac{k_w}{k_a.k_b}} = \sqrt{\frac{k_w \times k_b}{k_a}}$$

apply – log on both sides

$$-\log[OH^-] = -\frac{1}{2}\log k_w - \frac{1}{2}\log k_b + \frac{1}{2}\log k_a \quad p^{OH} = \frac{1}{2}p^{kw} + \frac{1}{2}p^{k_b} - \frac{1}{2}p^{k_a}$$

- **Salt of strong acid and strong base :**
  Eg: NaCl, KNO_3, Na_2SO_4, $BaCl_2$, $NaClO_4$, $Ba(NO_3)_2$, $Sr.(NO_3)_2$ etc.
- These salts do not undergo hydrolysis because both anion and cation are weak as they are conjugates of strong acid and strong base respectively.
- Therefore their aqueous solutions are exactly neutral and p^H is exactly.
- **Solubility Product : -** $\left(K_{SP}\right)$
- It is the product of the molar concentration of its ions in a saturated solution of electrolyte.
- K_{SP} for a salt changes with temperature
- Solubility product of a sparingly soluble salt is given by

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

$$\therefore K_{SP} = \left[A^{+y}\right]^x.\left[B^{-x}\right]^y$$

$$Ksp = \left[xs\right]^x\left[ys\right]^y$$

- If solubility is known K_{SP} can be calculated (or) vice versa.

APPLICATIONS :

1) The concept of solubility product helps the formation of a precipitate.
   a) Ionic product < K_{SP}, no ppt is formed (unsaturated solution)
   b) Ionic product > K_{SP}, a ppt is formed (super saturated solution)
   c) Ionic product = K_{SP}, solution is saturated
2) In predicting the solubility of a sparingly soluble salt.
3) In qualitative analysis, the seperation and identifi cation of various basic radicals into different groups.
4) In purification of common salts.
5) In salting out of soap.

- For binary salts like $AgCl, AgBr$ solubility S can be calculated as $S = \sqrt{K_{SP}}$
- For ternary salt like $PbCl_2$, $Mg(OH)_2$, Ag_2CrO_4

  $S = \sqrt[3]{\frac{K_{SP}}{4}}$ (or) $S = \left(\frac{K_{SP}}{4}\right)^{1/3}$

- For salt $K_{SP} = s^2$:

  AB_2 salt $K_{SP} = 4S^3$:

  AB_3 salt $K_{SP} = 27S^4$

  A_3B_2 salt $K_{SP} = 108S^5$;Where S=Solubility

COMMON ION EFFECT :-

- The suppression of the dissociation of a weak electrolyte by the addition of strong electrolyte having common ion is called common ion effect.

  Ex : - A solution of Sodium Aectate is added to solution of Acetic acid as a result in the decrease in ionization of acetic acid due to common ion is (CH_3COO^-)

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

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

common ions

3. According to Lechatlier principle $[H^+]$, decreases P^H is increases and equilibrium shifts to left hand side.

APPLICATIONS : -

1) It is used in the controlling the H^+ ion concentration in Buffer solution.
2) The concentration of S^{2-} in the II Group or OH^- in III group of qualitative Analysis is controlled by HCl and NH_4OH on the basis of common ion effect.
3) Common ion effect is also used in the purification of common salt by passing dry HCl gas into impure salt solution