Chapter 2

Ionic Equilibrium

→ The dynamic equilibrium between dissociated ions and undissociated electrolyte molecule in its aqueous solution is called ionic equilibrium.

When an electrolyte is dissolved in water, it dissociates into two types of ions. One type of ion carries positive charge (cation) and another carries negative charge (anion).

Let us consider an electrolyte AB, which dissociates as follows.

$$AB \rightleftharpoons A^+ + B^-$$

The forward reaction is called ionization reaction and backward reaction is called association reaction.

When weak electrolyte is taken, then undissociated electrolyte molecule dissociates into ions and at the same time the ions unite together to form molecule. Thus equilibrium is established btn. undissociated electrolyte molecule and its dissociated ions in its aqueous solution, which is dynamic in nature. Such type of equilibrium is called ionic equilibrium. The dynamic nature of ionic equilibrium means that, some electrolyte molecules dissociate into ions and at the same time same amount of ions combine together to form molecules.

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Classification of Electrolytes

On the basis of ionization substance, ~~elec~~ substance are classified into 2 types
- Electrolytes
- non-electrolytes

Electrolytes → ionize when dissolved in water
→ conduct electricity in its aqueous or molten state
→ NaCl, NaOH, HCl, HCOOH, H_2SO_4, NH_4Cl etc.

Non Electrolytes → do not ionize when dissolved in water
→ Benzene, ether, CCl_4, $CHCl_3$, kerosene etc.

On the basis of extent of ionization, electrolytes are classified into two types.

1) **Strong Electrolytes** → ionize completly when dissolved in water.
→ NaCl, NaOH, KCl, H_2SO_4, NH_4Cl etc.

2) **Weak Electrolytes** → ionize partially when dissolved in water.
→ NH_4OH, HCOOH, CH_3COOH, H_2S etc.

Ionization of strong and weak electrolyte.

The process of ionization in weak electrolyte is reversible. When weak electrolyte is dissolved in water, it dissociates into ions and at the same time, ions combine to form molecule. The equilibrium is dynamic in nature. Let us consider that an electrolyte AB is dissolved in water,

$$AB \longleftrightarrow A^+ + B^-$$

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The dynamic nature of equilibrium between electrolyte molecule AB and its dissociated ions is characterized by a constant called as dissociation constant or ionization constant (Keq) which can be written as follows.

i.e. $$K_{eq} = \frac{[A^+][B^-]}{[AB]}$$

For strong electrolyte, there is occureence of irreversiable reaction between electrolyte molecule and its ions. Due to the absence of dynamic equilibrium, Keq cannot be calculated.

In addition the process of ionization is incomplete, only a fraction of molecules dissolved in water are ionized. It is called degree of dissociation or degree of ionization

Degree of Ionization (α)

The fraction of molecules dissociated into ions is called degree of ionization or degree of dissociation. It is denoted by (α). mathematically,

$$\alpha = \frac{\text{No. of molecules ionized}}{\text{Total no of molecules dissolved}}$$

Also, $$\alpha = \frac{\text{amount that dissociates}}{\text{Initial concentration } (x)}$$

so, amount that dissociate $= \alpha x$

Initial concentration $= c\alpha$

value of α ranges from 0 to 1

value nearer to 1 → strong electrolyte

value nearer to 0 → weak electrolyte.

Ionization of weak electrolyte

Ostwald's diluation law. VVIMP

- The variation of degree of ionization with diluation is called ostwald's dilution law.
- Arrhenius observed for the first time that there is existence of dynamic equilibrium between electrolyte.
- so, Law of mass action can be applied to this dynamic equilibrium.
- Ostwald applied law of mass action to the dynamic equilibrium for the first time in 1888 and the mathmatical outcome is called Ostwald's diluation law.

Let us consider an electrolyte AB, which ionizes as follows.

i.e. $AB \longleftrightarrow A^+ + B^-$

The dissociation constant or ionization constant (K_{eq}) for the above reaction can be calculated as

$$keq = \frac{[A^+][B^-]}{[AB]} \quad \text{-------} \quad (1)$$

If the initial concentration is 'c' mole/litre and α be the degree of ionization, Then

	AB	$\rightleftharpoons$ A^+	$+$ B^-
Initially	c	0	0
At equilibrium	$c-c\alpha$	$c\alpha$	$c\alpha$

substituting the values in eqn (1) we get

$$K = \frac{c\alpha \cdot c\alpha}{c-c\alpha} = \frac{c\alpha \cdot c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha} \quad \text{---} \quad (ii)$$

* **For weak electrolyte,**

$\alpha << 1$. so, $1-\alpha = 1$

Then $K = C\alpha^2$ [∵ From (II)]

$\alpha = \sqrt{\frac{K}{C}}$ # ——— (III)

Thus,
ODL states that, " Degree of ionization / dissociation is inversly porpotional to the square root of the concentration or directily porpotional to the square root of diluation."

If 1 mole of an electrolyte is dissolved in V litre of the solution Then, we can write. since $C = N/V$ no of mole.

$c = 1/V$

Then $\alpha = \sqrt{K \times V}$ [From (III)] ——— (IV)

This equation (IV) is the Final Form of ODL For weak electrolyte.

* For strong electrolyte, $\alpha \approx 1$ so $1-\alpha \approx 0$

Limitations of ODL

→ not applicable For strong electrolytes

Note:- On analysing trend, about ~9marks is asked From this chapter (1LAQ worth 8 marks + 1 mcq)

Read carefully !!!

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Theories of Acid and Base:

1) Arrhenius theory of Acid and Base. [water-ion system]

Depending upon the nature of ion produced when a substance is dissolved in water, He defined acid and base as follows.

- **Acid** → Those substances which produce H^+ ion when dissolved in water Eg:- HCl, HNO_3, H_2SO_4 etc.
- **Base** → Those substances which produces OH^- ion when dissolved in water. Eg:- $NaOH$, KOH, NH_4OH etc.

* Limitations of Arrhenius Theory of Acid & Base.

- → Free H^+ & OH^- doesnot exist in water because of their high reactivity.
- → limited to aquous medium only.
- → Considered water as the only solvent.
- → It fails to explain the acidic nature of non-metallic oxides like CO_2
- → Fails to explain the basic nature of metallic oxide like Na_2O.
- → Fails to explain the acidic nature of salt like $AlCl_3$, $FeCl_3$, BF_3 etc.

Bronsted-Lowry concept [Proton donor-acceptor system]

→ This concept is more advanced concept than Arhenius concept because it is not limited to the water as the only solvent. This concept defines acid and base on the basis of tendency of a substance to donate or accept proton during rxn. So this concept is also called as proton donor-acceptor system.

Acids $\longrightarrow$ Proton donor (H^+)
Base $\longrightarrow$ proton acceptor

Eg:- $HCL + H_2O \longrightarrow H_3O^+ + Cl^-$ So, $HCL \rightarrow$ acid, $H_2O \rightarrow$ Base.

accepts H^+ ($H_2O \rightarrow H_3O^+$)
donates H^+ ($HCL \rightarrow Cl^-$)

conjugate acid-base pair.

The pair of acid and base which are inter-conversible to each other either by donating or by accepting proton are called conjugate acid-base pair.

They differ only by one proton (H^+)

Eg:- $\underset{A}{HCL} + \underset{B}{NH_3} \longleftrightarrow \underset{A}{NH_4^+} + \underset{B}{CL^-}$

$\underset{(A)}{HCL} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} \underset{(B)}{CL^-}$ $\qquad$ $\underset{(base)}{NH_3} \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} NH_4$ (Acid)

Some conjugate acid-base pair.

Acid	Base	Acid	Base
HCL	Cl	H_2CO_3	HCO_3^{--}
H_2SO_4	HSO_4^-	HCO_3	CO_3^{--}
H_3O^+	H_2O	NH_4^+	NH_3
HSO_4^-	SO_4^{--}	H_2O	OH
CH_3COOH	CH_3COO^-		

$\rightarrow$ From this, relative strength of acid and base can be determined.

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Q) Find the conjugate acid – base pair of

a) $NH_3 \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} NH_4$
(Base) (Acid)

b) $HSO_4^- \overset{H^+}{\rightleftharpoons} H_2SO_4$
(base) (Acid)

c) $H_2O \overset{H^+}{\rightleftharpoons} H_3O^+$
(base) (acid)

d) $HS \overset{H^+}{\rightleftharpoons} H_2S$
(base) (acid)

e) $HCO_3^- \overset{H^+}{\rightleftharpoons} H_2CO_3$
(base) (Acid)

Limitations of Bronsted - Lowry concept.

- It fails to explain the acidic nature of non metallic oxides like CO_2 and basic nature of metallic oxides like Na_2O.
- It also fails to explain the acidic nature of salt like $AlCl_3$, BF_3, $FeCl_3$ etc.
- It also fails to explain the ~~acidic nature of salt~~ ~~H~~ acid – base reaction in which there is no transfer of proton. Eg.

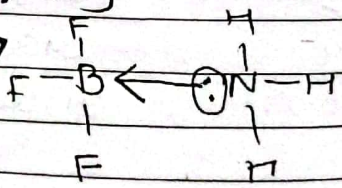
$CaO + SO_3 \longrightarrow CaSO_4$

Lewis concept of acid & base [1923]

(Electron pair donor – acceptor system)

→ { Acid — e^- acceptor
  { Base — e^- donor.

LA + LB $BF_3 + NH_3 \longrightarrow$



This is the most advanced concept to define the acid and base on the basis of tendency of a substance to accept or donate electron pair. so it is called as electron pair donor acceptor system.

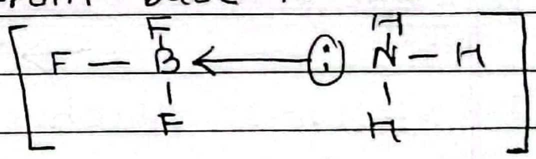
According to Lewis concept,

Acid is the substance which can ~~donate~~ accept electron pair and base is substance which can donate electron pair.

Lewis Acid :- $AlCl_3$, BF_3, $FeCl_2$, H^+, Ag^+, Cu^{++} etc.

Lewis Base :- H_2O, NH_3, ether, alcohoal, CN, OH, Cl etc.

Lewis Acid has electron deficient centre. and Lewis Base has electron rich centre. After the reaction of LA and LB there is formation of co-ordinate covalent bond which directs from base to acid.

$NH_3 + BF_3 \longrightarrow$ 

$[BF_3 NH_3]$

Limitations of Lewis concept

→ This concept excludes ionization step. So ~~release~~ relative strength of acid and base cannot be determined.

→ This concept is too simple and general that it includes all the reactions in which there is formation of coordinate covalent bond occurs.

Autoionization of water.

→ The process in which two water molecules interact to each other to form hydroxyl ion and hydronium ion is called auto ionization of water.

water is an amphoteric solvent i.e. proton can be transferred from one water molecules to the another molecule. During one water molecule to another molecule. During this process, OH^- ion and H_3O^+ ion are formed as product. This process is called autoionization of water.

i.e. $H_2O + H_2O \longleftrightarrow OH^- + H_3O^+$
(Bronsted acid) (Bronsted base)

Ionic Product of water (Kw)

→ The product of concentration of ions which are obtained during the autoionization of water is called ionic product of water. It is denoted by (kw). It is also called as water dissociation constant.

Let us consider the autoionization of water
i.e. $H_2O \longleftrightarrow H^+ + OH^-$ (simply).

From law of mass action, the dissociation constant can be calculated as

$$K_{eq} = \frac{[H^+][OH^-]}{[H_2O]} \quad \text{------------ (1)}$$

Water is a very weak electrolyte, so, it's concn doesnot change during the reaction. so concn of water can be taken as constant. Hence the above expression can be written as follows:

i.e. $K_{eq} \times [H_2O] = [H^+][OH^-]$

or, $K_w = [H^+][OH^-]$ where K_w is the ionic product of water. (Ionic product of water can be defined as the product of concn of H^+ and OH^- ion at given temp)

At 25°C $K_w = 1.0 \times 10^{-14}$

The value of $[H^+]$ and $[OH^-]$ in the solution determines the nature of soln. In neutral soln, the concn of H^+ ion = concn of OH^- ion. so the ionic product of water can be written as

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

$$\text{or, } 1.0 \times 10^{-14} = [H^+][OH^-]$$

For neutral soln

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

$$\text{so, } K_w = [H^+][H^+]$$

$$\text{or, } 1.0 \times 10^{-14} = 2[H^+]$$

$$\text{or, } [H^+] = 1.0 \times 10^{-7}\ M = [OH^-]$$

At 37°c $K_w = 2.5 \times 10^{-14}$ ← Body Temp.

* For Acidic soln $[H^+] > [OH^-]$

$[H^+] > 1.0 \times 10^{-7}$ M

* For basic soln $[H^+] < [OH^-]$

$[OH^-] > 1.0 \times 10^{-7}$ M

Dissociation constant of acid (Ka) & Pka

→ Ka is the acid dissociation constant and pka is simply the negative logarithm of this constant.

→ Expressed in mole / litre

Acid dissociate as follows:

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

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

→ Large ka value indicates strong acid because it means the acid is largly (completly) dissociated into ions.

→ Large ka also means, the formation of product in the reaction is favored.

→ ka value for most of weak acid ranges from 10^{-7} to 10^{-14}.

Negative logarithm of acid dissociation constant (ka) is called (pka)

i.e $pKa = -\log Ka$ #

smaller pka → stronger acid → range (2–14)

Dissociation constant of base (Kb) & (pKb)

- Kb is the base dissociation constant and pKb is simply the negative logarithm of this constant. (mole/ltr)
- Base dissociates as :

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

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

- large value of Kb indicates a strong base because it means the base is largly dissociated into ions.
- large Kb also means formation of product in the reaction is favored.
- Again,

Negative logarithm of base dissociation constant (Kb) is called pKb.

i.e $pK_b = -\log K_b$

smaller the pKb, stronger will be the base.

pH

{potentz → potential
H → Hydrogen ion}

- The acidity & basicity of a soln can be expressed in terms of pH.
- The negative logarithm of hydrogen ion concentration expressed in molarity is pH.

i.e. $pH = -\log [H^+]$

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

- Magnitude of pH determines nature of soln.

a) pH = 7 (neutral)
b) pH > 7 (basic)
c) pH < 7 (acidic)

pOH

German word
{potentz → potential
OH → hydroxyl ion}

- The acidity and basicity of a solution can be expressed in terms of pOH.
- The negative logarithm of hydroxyl ion concn expressed in molarity is called pOH.

pOH = 7 (neutral)
pOH > 7 (acidic)
pOH < 7 (basic)

pH Scale

- It is the scale which is used to compute the pH values of different solution.
- In pH scale, the pH values are arranged in ascending order from left to right in b/n 0 to 14.
- The [H+] concn are arranged in descending order from left to right b/n ($10^{0} - 10^{-14}$ M)

pH	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
$[H^+]$	10^{0}	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14}

← Acidic character increases | Neutral | Basic character increases →

Relation btn pH & pOH

→ The ionic product of water can be written as,

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

Taking log on both sides we get,

$$\log(K_w) = \log\{[H^+][OH^-]\}$$

Taking (−ve) sign at both sides

$$-\log(K_w) = -\log[H^+] + \{-\log[OH^-]\}$$

At 25°C, $K_w = 1.0\times10^{-14}$

so, $-\log(1.0\times10^{-14}) = -\log[H^+] + \{-\log[OH^-]\}$

or, $14 = pH + pOH$

$$\therefore pH + pOH = 14$$

For strong acid & base, $pH = -\log[N]$

For weak acid & base, $pH = -\log[H^+] = -\log C\alpha$
$= -\log\sqrt{K_a C}$

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

Show that, $pH + pOH = pKw$

→ The ionic product of water can be written as, $Kw = [H^+][OH^-]$

Taking log on both sides

$$\log Kw = \log\{[H^+][OH^-]\}$$

or, $\log Kw = \log[H^+] + \log[OH^-]$

or, $-\log Kw = -\log[H^+] + \{-\log[OH^-]\}$

or, $pKw = pH + pOH$ #

Common ion Effect.

→ Supression of degree of dissociation of weak electrolyte by the addition of strong electrolyte having one ion common is called common ion effect.

Eg:- The dissociation of NH_4OH is supressed by the addition of NH_4Cl. This can be explained on the basis of Le-chatelier's principle as follows :

$$\underset{\text{(weak base)}}{NH_4OH} \longleftrightarrow NH_4^+ + OH^- \text{ (partially)}$$

NH_4Cl is a strong electrolyte and it ionizes almost completly in its aqueous solution. as :

$$NH_4Cl \longleftrightarrow NH_4^+ + Cl^- \text{ (completely)}$$

When NH_4Cl is added to the aqueous soln of NH_4OH. so according to Le-chatelier's principle the reaction shifts backward. due to increase in concn of NH_4^+ ion (product).

so, NH_4^+ ion and OH^- ion combines to form NH_4OH. Hence the degree of dissociation of NH_4OH (weak electrolyte) is suppressed. This effect is common-ion effect.

It decreases solublity of weak electrolyte

Application of common-ion effect.

- purification of salt
- precipitation of soap etc.

Solublity product.

In case of sparingly soluable ionic salt in its saturated solution, dynamic equilibrium exists btn. undissociated salt molecules and its dissociated ions. so law of mass action can be applied to this dynamic equilibrium to calculate ionization constant (Keq).

Let us consider a sparingly soluable salt AB which ionizes as follows in its saturated soln.

$$AB \rightleftharpoons A^+ + B^-$$

Applying law of mass action.

$$Keq = \frac{[A^+][B^-]}{[AB]}$$

$$Keq \cdot [AB] = [A^+][B^-]$$

or $Ksp = [A^+][B^-]$

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- This new constant Ksp is called solublity product or solublity product constant. and is equal to the product of ionization constant and the conc^n of sparingly soluable ionic salt in its saturated solution. It is dependent upon tempeature.

- For the salt OF A_xB_y type, the solublity product can be written as follows:

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

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

- Soublity product can also be defined as the product OF molar conc^n OF its ion in saturated solution, each conc^n raised to the power equal to the stoichiometric coeFFicient OF ions in a balanced equation.

- Similarly, Ionic product is the product OF conc^n. of ions in all types OF soln.

  ksp only in saturated soln.

For AB type of salt.

$$AB \rightleftharpoons A^+ + B^-$$

1M	1M	1M
'S' M	'S' M	'S' M

$$k_{sp} = [A^+][B^-]$$

$$= S \times S$$

$$K_{sp} = S^2$$

For AB_2 salt.

$$AB_2 \rightleftharpoons A^{+2} + 2B^{-1}$$

'S'M 'S'M 2'S'M

$$\therefore K_{sp} = [A^{+2}][B^-]^2$$
$$= [S][2S]^2$$
$$= S \times 4S^2$$

or, $K_{sp} = 4S^3$

For, A_2B_3 salt

$$A_2B_3 \rightleftharpoons 2A^{+3} + 3B^{-2}$$

1'M' 2m 3M

'S' 2S 3S.

$$K_{sp} = [A^{+3}]^2 [B^{-2}]^3$$
$$= [2S]^2 \cdot [3S]^3$$
$$= 4S^2 \cdot 27S^3$$

$K_{sp} = 108 S^5$

Application of Common ion effect & solublity product principle.

a) Precipitation of sulphides of group II and IIIB basic radicals. $[H_2S]$

→ Both group II and IIIB metal ions precipitate out in the form of metal sulphide.

→ But the ksp of group II sulphides is very less than gr. IIIB metal sulphide

$[As^{3+}]$ $[Sb^{3+}]$ Cu^{2+}, Hg^{2+}, Pb^{2+}

→ So, to decrease the ksp, HCL gas is passed along H_2S to decrease conc^n of sulphide ion due to common ion effect.

Gr. II metals → Cu^{++}, Hg^{++}, Pb^{++}, Sb^{3+}, As^{3+}, Sn^{2+}
Gr. IIIB metals → Co^{++}, Ni^{++}, Zn^{++}, Mn^{++}

$$HCL \longrightarrow H^+ + CL^-$$
$$H_2S \longrightarrow 2H^+ + S^{-2}$$

common ion.

- This cause decrease in concn of sulphide ion, which then decreases Ionic product.
- This decreased IP only exceeds the ksp of gr. II metal sulphides but not gr. IIIB metal sulphides. So group II metals precipitated.

Here, Role of HCL is imp.

Solublity product principale

It states that, " For the precipitation to occur, ionic product value must exceed solublity product value.

i.e. IP > Ksp.

Kip < Ksp, the soln is unsaturated
Kip = Ksp, the soln is saturated
Kip > Ksp, the soln is super saturated

b) precipitation of hydroxides of group IIIA basic radicals.

- Both group IIIA (Fe^{3+}, Al^{3+}, Cr^{3+}) and Group V metal ions precipitate out in the form of metal hydroxide However the solublity product of Group IIIA metals hydroxide. is less than group V metal hydroxide
- When NH_4Cl is added along with NH_4OH then the concentration of hydroxide ion in solution is decreases due to. common ion effect.

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$
$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

common ion.

- This decrease in concn of hydroxide ion causes decrease in ionic product.
- This decreased ionic product exceed the solubility product (Ksp) of only group IIIA metal hydroxide but not group V metal hydroxide.
- So only group IIIA metal hydroxide are precipated leaving group V metal ions in the soln.

Group IV (Zn^{++}, Co^{++}, Ni^{++}, Mn^{++})

- For the precipitation of group IV redicals (as a sulphide) high concn of S^{--} ion is to be obtained. This is done by adding double volume of NH_4Cl followed by NH_4OH before adding H_2S gas in the original solution.
- The role of NH_4Cl is to supress the degree of ionization of NH_4OH to maintain a low concn of OH^- ions.

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$
$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

- This low concn of OH^- ions prevents precipitation of hydroxides of group IIB metals ion. The presence of OH^- ions further increases ionization of H_2S as OH^- consumes H^+ to form H_2O.

$$H_2S \rightleftharpoons 2H^+ + S^{2-} \text{ (high concn)}$$
$$H^+ + OH^- \longrightarrow H_2O$$

- This lead to an increase in the concn of S^{--} so that the IP exceeds the solublity product and only group.

IV radicals get precipitated.

$$Zn^{++} + H_2S \xrightarrow[NH_4OH]{NH_4Cl} ZnS\downarrow + 2H^+$$

white ppt.

Buffer solution and its application

➤ The solution which can resist change in pH value even after the addition of small amount of acid or base to it is called buffer solution.

Eg:- Blood ($p^H = 7.35$) maintained by the mixture of H_2CO_3 and HCO_3.

➤ The tendency of buffer solution to resist change in pH value after the addition of acid or base is called buffer action. The buffer action of buffer solution is due to the consumption of H^+ or OH^- ions from acid or base by buffer solution.

Types of Buffer Solution:-

i) Acidic buffer solution:- The buffer solution whose pH value is lesser than 7 is called acidic buffer solution. It is prepared by mixing equimolar conc^n of solution of weak acid and its salt of strong base. For eg:-

CH_3COOH & CH_3COONa ($p^H = 4.74$)

ii) Basic buffer solution:- The buffer solution whose pH is more than 7 is called acidic buffer solution. It is prepared by mixing equimolar conc^n of solution of weak base and its salt of strong acid. Eg:

NH_4OH & NH_4Cl (pH = 9.1)

Henderson's Equation.

i) For acidic buffer, $pH = pKa + \log \frac{[salt]}{[acid]}$

ii) For basic buffer, $pOH = pKb + \log \frac{[salt]}{[base]}$

Applications of buffer solution.

→ In, industries for manufacture of paper, dyes, paints etc.

→ In analytical chemistry and bacteriological research

→ In food and pharmaceutical industries as a preservative.

→ In biological process to maintain the pH of blood about 7.4

* plasma consists of H_2CO_3 and $NaHCO_3$.
* The mechanism of buffer action on blood is ;

OH^- → H_2O ; H^+ → H_2CO_3

$$H_2CO_3 \longleftrightarrow 2H^+ + CO_3^{--}$$

$$NaHCO_3 \longleftrightarrow Na^+ + HCO_3^-$$

pH of blood remains constant from 7.38 – 7.42 even during metabolic reaction after eating/drinking acidic or basic foods.

acid add गर्यो भने → H_2CO_3

Base add गर्यो भने → H_2O →

Selection of Indicators

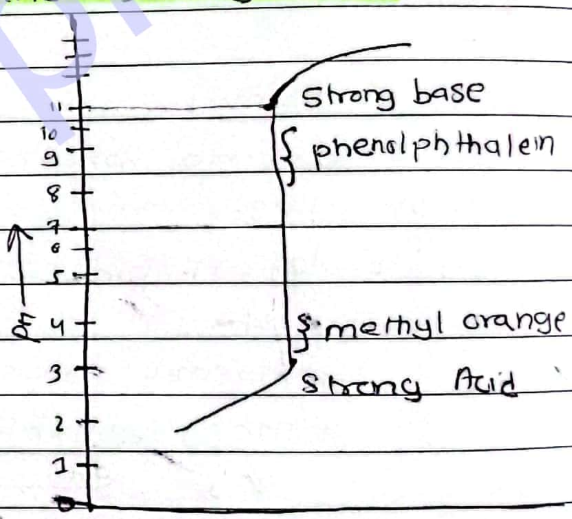
Qn) Define indicator. How is indicator selected for a particular titration?

→ Indicators are the substance that changes it's colour at different pH values to indicate that the titration is completed.

Methods for selection of indicators

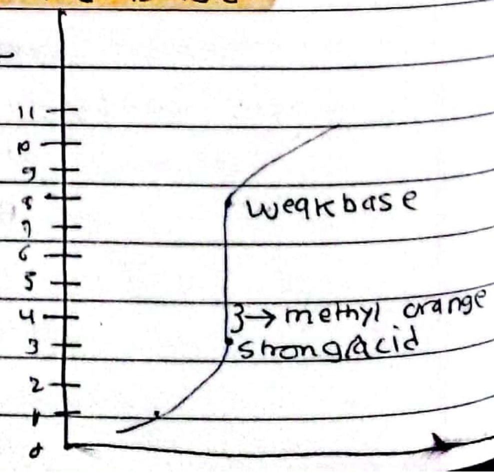
a) **Titration of strong Acid and strong base.**

→ In the titration of strong Acid (HCl) and strong base (NaOH), the step rise of curve occurs at pH from 3 to 11. Any indicator capable of changing it's colour b/n 3 to 11 is suitable indicator. In this titration methyl orange (3.2 – 4.4) & phenolphthalein (8 – 10) are used as indicator.



b) **Titration of strong acid and weak base.**

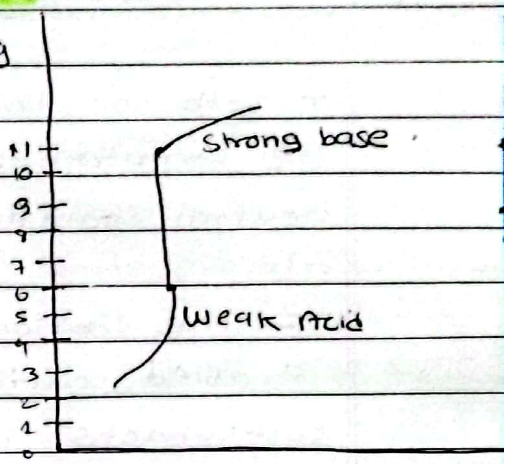
→ In titration of strong Acid (HCL) & weak base (NH_4OH), the step rise of the curve occurs from 3 to 8. And methyl orange (3.2–4.4) is used as indicator.



methyl red – 4.2 to 6.3

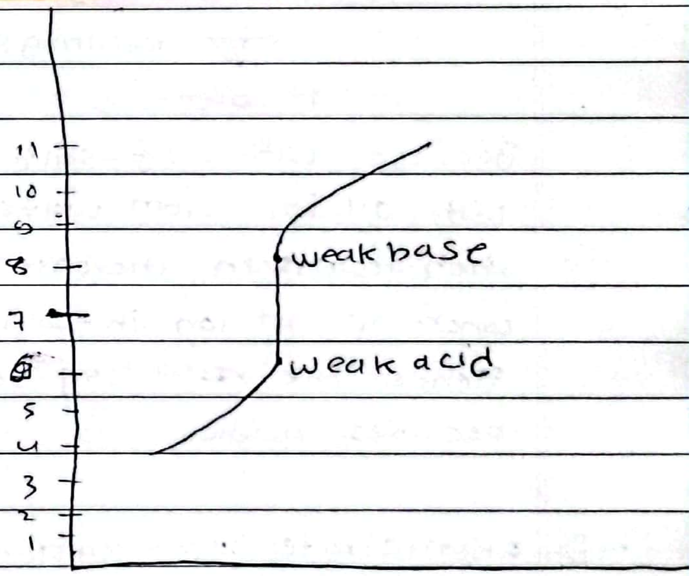
c) Titration of weak Acid and strong base.

➢ In a titration of weak Acid & strong base, the step rise of the curve occurs from 6 to 11. And phenolphthalein (8–10) is used as indicator.



d) Titration of weak Acid and weak base.

➢ In titration of weak acid and weak base, the step rise of the curve occurs from 6 to 8. And here neither methyl orange nor phenolphthalein is used. In this case, conductometric titration is done.



Salt Hydrolysis

The reaction of either cation or anion or both of the salt with water, which results in the formation of either acidic or basic or very rarely neutral solution is called **salt hydrolysis**

If the cation of the salt reacts with water, it is called cationic hydrolysis and if the anion of salt reacts with water, it is called anionic hydrolysis.

Cationic hydrolysis
↓ Resulting soln
Acidic

Because cation of salt reacts with OH^- ion from water which results in increase in concn of H^+ ion in solution. Hence the resulting soln becomes acidic.

Anionic hydrolysis
↓ Resulting soln
Basic

Because anion of salt reacts (combines) with H^+ ion from water which results in increase in concentration of OH^- ion in soln. Hence resulting soln becomes basic

→ If the rate of cationic hydrolysis becomes equal to the rate of anionic hydrolysis, then **resulting soln becomes neutral**.

→ **Salt hydrolysis is reverse of neutralization reaction.** During neutralization rxn, H^+ ion from acid reacts with OH^- ion from base which results in formation of water molecule. But in salt hydrolysis, water molecule dissociates into H^+ and OH^- ion.

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Depending upon the nature of interaction btn. salt and water, salts are classified into 4 types, which are

a) salt of strong acid and weak base.

Strong acid :- H_2SO_4, HCl, HNO_3,

weak base :- $Fe(OH)_3$, NH_4OH, $Ag(OH)$

like NH_4Cl, $CuSO_4$, $FeCl_3$ etc. are the salts of strong acid and weak base. When this type of salt is dissolved in water, the resulting soln becomes acidic due to cationic hydrolysis.

$$HCl + NH_4OH \longrightarrow NH_4Cl + H_2O$$

NH_4Cl ionizes as, $NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$

H_2O ionizes as, $H_2O \rightleftharpoons H^+ + OH^-$

The NH_4^+ ion from salt combines with OH^- ion from water to form NH_4OH and Cl^- combines with H^+ ion from water to form HCL.

i.e. $NH_4^+ + OH^- \leftrightarrow NH_4OH$ (partially ionized)

$H^+ + Cl^- \rightleftharpoons HCl$ (completely ionized)

NH_4OH being weak base ionizes partilly and gives small concn of OH^- ion in solution. HCl is a strong acid which is almost completely ionized to give large amount of H^+ ion so resulting salt will be acidic in nature

Numerical Problems Based on Solublity Product

1) If the solublity of AgCl is $0.1435\ gL^{-1}$, Find its solublity product.

→ Solution :- Here,

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

$$\quad S \qquad\qquad S \qquad S$$

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

$$= S \times S = S^2.$$

$$\text{solublity of AgCl} = 0.1435\ gL^{-1}$$

$$= \frac{0.1435}{143.5}\ mol.L^{-1}.$$

$$= 10^{-3}\ mol\ L^{-1}$$

$$\text{Now, } K_{sp} \text{ of AgCl} = S^2$$

$$= [10^{-3}]^2$$

$$= 10^{-6}$$

Salt of weak acid and strong base

like Na_2CO_3, CH_3COONa, $HCOONa$ etc are the salts of weak acid and strong base, when this type of salt is dissolved in water, ~~H+ ion~~ the resulting soln becomes basic due to anionic hydrolysis. Eg: Na_2CO_3.

$$Na_2CO_3 \rightleftharpoons 2Na^+ + CO_3^{--}$$
$$H_2O \rightleftharpoons H^+ + OH^-$$

Na^+ ion combines with OH^- ion from water

$$Na^+ + OH^- \rightleftharpoons NaOH \text{ (completely ionized).}$$

CO_3^{-} ion combines with H^+ ion from water

$$2H^+ + CO_3^{--} \rightleftharpoons H_2CO_3 \text{ (partially ionized)}$$

Here concn of OH^- > concn of H^+ so resulting soln will be basic in nature.

Salt of strong acid and strong base.

Salts like $NaCl$, KCl, Na_2SO_4 etc are salts of strong acid and strong base.

$$NaCl \rightleftharpoons Na^+ + Cl^- \qquad H_2O \rightleftharpoons H^+ + OH^-$$
$$Na^+ + OH^- \rightleftharpoons NaOH. \text{ (completely ionized)}$$

similarly, $H^+ + Cl^- \rightleftharpoons HCl$ (completely ionized).

Here concn of OH^- = concn of H^+ so resulting soln will be neutral.

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Salt of weak acid and weak base.

like, $(NH_4)_2CO_3$, CH_3COONH_4, $HCOONH_4$ etc.

$$(NH_4)_2CO_3 \rightleftharpoons 2NH_4^+ + CO_3^{--}$$

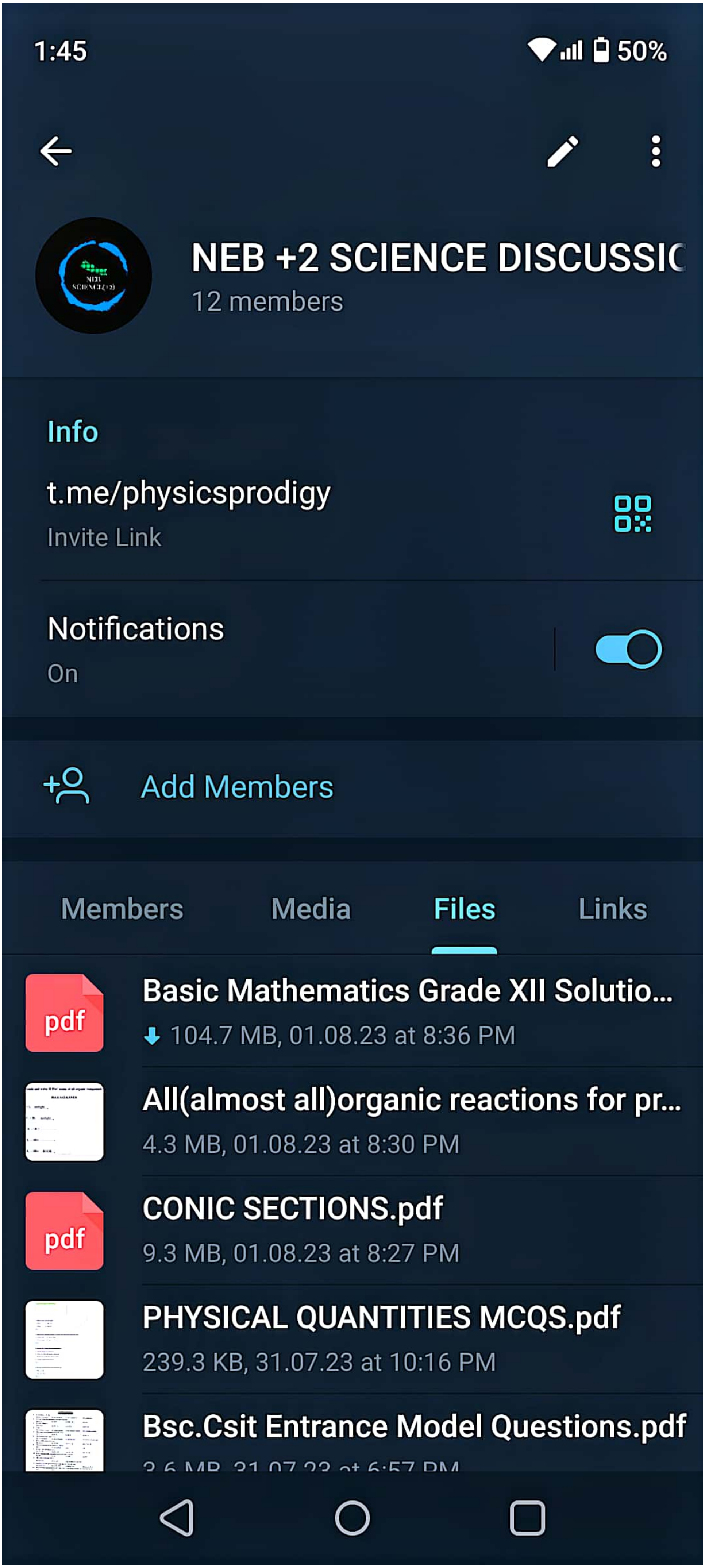
NH_4^+ combines with OH^- $\quad H_2O \rightleftharpoons H^+ + OH^-$

$$\downarrow NH_4^+ + OH^- \rightleftharpoons NH_4OH \text{ (partially ionized)}$$

CO_3^{--} combines with H^+

$$2H^+ + CO_3^{--} \rightarrow H_2CO_3 \text{ (partially) ionized}$$

Neutral salt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