IONIC EQUILIBRIUM

★ **ELECTROLYTES :** Compounds which dissociate into ions, when dissolved in water are called Electrolytes. e.g. NaCl, HCl, CH_3COOH, H_2O, etc.

★ **STRONG ELECTROLYTES :** Compounds which get dissociated completely into ions in aqueous solution are called Strong electrolytes. e.g. Strong acids : HCl, HNO_3, H_2SO_4, and strong bases : NaOH, KOH, etc.

★ **WEAK ELECTROLYTES :** Compounds which get ionized slightly into ions in aqueous solution are called Weak electrolytes.e.g.Weak acids : CH_3COOH, HCN, C_6H_5OH and Weak bases : NH_3, N_2H_4, $C_6H_5NH_2$, etc.

Que : Explain Self - Ionisation of water.

Ans :

➙ If sensitive Instrument is used, it is observed that water conducts electrical current to a small extent. Therefore water is a very **WEAK ELECTROLYTE**. This indicates that water is slightly dissociated into ions.

➙ The formation of $H^+_{(aq)}$ and $OH^-_{(aq)}$ ions in small concentrations by the dissociation of water is called **SELF - IONIZATION** of water.

➙ There exists an equilibrium between undissociated $H_2O_{(l)}$ molecules and ions ($H^+_{(aq)}$ and $OH^-_{(aq)}$) formed due to dissociation. Thus,

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} \text{ and } OH^-_{(aq)}$$

NOTE : The number of water molecules attached to H^+ is uncertain. Therefore hydrogen ion is represented by either $H^+_{(aq)}$ or $H_3O^+_{(aq)}$.

Que : What is meant by Ionic Product of Water ? Derive the equation for it. ***[MARCH'99] (3 MARKS)***

Ans :

➙ Self-ionization of water can be represented as :

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

➙ The equilibrium constant of this reaction is expressed as under :

$$K = \frac{[H^+][OH^-]}{[H_2O]_{(\ell)}}$$

→ Suppose at 25°C, 1 litre (1000 gms) of water is taken,

→ Concentration of water = $\frac{\text{No. of Moles of water}}{\text{Litre of Water}} = \frac{1000\text{gm}/18\text{gm/mole}}{1\text{L}} = 55.55\text{M}$

→ Concentration of undissociated water ($H_2O_{(l)}$) = 55.55 M

$K = \frac{[H^+][OH^-]}{[H_2O]_{(\ell)}}$ **[Ionization of water takes place slightly hence concentration of undissociated water is almost equal to original concentration (C_o)]**

$\therefore K_{eq} \times 55.55 = [H^+][OH^-]$ ..... (1)

→ K_w is known as **IONIC PRODUCT OF WATER**. The value of K_w at 25°C is 1×10^{-14}.

➙ Self - ionization of water is an **endothermic reaction,** this increase in temperature of water shifts the equilibrium in the **forward direction**. Therefore, the concentrations of $H^+_{(aq)}$ and $OH^-_{(aq)}$ in water increase with the rise in temperature and hence K_w increases with increase in temperature of water.

→ Now at 25°C

$K_w = 1 \times 10^{-14}$ ..... (1)

$\therefore 1 \times 10^{-14} = [H^+]^2 = [OH^-]^2$

[$\because$ $H^+_{(aq)}$ and $OH^-_{(aq)}$ are formed in 1 : 1 mole ratio due to self-ionization of water, $[H^+] = [OH^-]$ in equation (1)]

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

➙ Thus in pure water $[H^+] = [OH^-]$, hence pure water is **neutral**.

Que : Discuss the ionization of electrolytes in aqueous solutions.

Ans :

➙ **IONIZATION :** The process of forming ions from molecules of compound in aqueous solution.

➙ **DEGREE OF IONIZATION :** The fraction of dissolved compound ionized. e.g. 0.08 mole of a compound dissolved in water and 0.02

mole of it is ionized, the degree of ionization of the compound is 0.02 / 0.08 = 0.25 ***[MARCH'97]***

➤ Compounds producing ions in aqueous solutions are of two kinds

(1) IONIC SOLIDS :

→ Compounds having ions as their constituents in solid state e.g. NaCl. Such compounds are known as **Ionic solids**. When such solids dissolve in water, ions are not formed but the ions which are held firmly in their positions in the lattice, of the compound are set free e.g.

$$Na^+Cl^-_{(s)} \longrightarrow Na^+_{(aq)} + Cl^-_{(aq)}$$

→ Though ionic solids are completely ionized, their concentrated solutions contain some ion-pairs, e.g. Na^+Cl^-. Such ion pairs **do not conduct electric current** as they are electrically neutral.

→ Thus two kinds of processes occur in **concentrated aqueous solutions** of strong electrolytes.

(i) A process producing ions capable of conducting electric current,

(ii) inspite of ionization process which has occurred in aqueous solution, a process of forming ion pairs incapable of conducting electric current.

→ A process giving rise to ions capable of conducting electric current is described as **'DISSOCIATION'.**

→ A process which denotes the formation of ions capable and incapable (ion-pairs) of conducting electric current is described as **'IONIZATION'.**

➤ **(2) POLAR COMPOUNDS :**

→ Some **molecular compounds** dissociated into ions, when they dissolve in water.

→ Such compounds have **polar bonds** between parts producing positive ion and negative ion.

→ This **polar bond breaks** in aqueous medium and the atom having higher electronegativity acquires one unit of **negative charge** and the atom having lower electronegativity acquires one unit of **positive charge**.

★ IONIZATION OF WEAK ELECTROLYTES (ACIDS AND BASES)

➙ **Strong electrolytes** like HCl, HNO_3, NaOH, KOH ionize completely in their aqueous solutions.

➙ **Weak electrolytes** like CH_3COOH,NH_3 ionize slightly in their aqueous solutions. Therefore, there exists an equilibrium between ions and unionized molecules in aqueous solutions of weak electrolytes. This kind of **ionization process is reversible** and is shown by ⟺ sign in the equation e.g.

1. $CH_3COOH_{(aq)} + H_2O_{(l)} \iff CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$
2. $HCOOH_{(aq)} + H_2O_{(l)} \iff HCOO^-_{(aq)} + H_3O^+_{(aq)}$
3. $ClCH_2COOH_{(aq)} + H_2O_{(l)} \iff ClCH_2COO^-_{(aq)} + H_3O^+_{(aq)}$
4. $C_6H_5CH_2COOH_{(aq)} + H_2O_{(l)} \iff C_6H_5CH_2COO^-_{(aq)} + H_3O^+_{(aq)}$
5. $C_6H_5OH_{(aq)} + H_2O_{(l)} \iff C_6H_5O^-_{(aq)} + H_3O^+_{(aq)}$
6. $HCN_{(aq)} + H_2O_{(l)} \iff CN^-_{(aq)} + H_3O^+_{(aq)}$

1. $NH_{3\,(aq)} + H_2O_{(l)} \iff NH_4^+{}_{(aq)} + OH^-_{(aq)}$
2. $CH_3NH_{2\,(aq)} + H_2O_{(l)} \iff CH_3NH_3^+{}_{(aq)} + OH^-_{(aq)}$
3. $(CH_3)_2NH_{(aq)} + H_2O_{(l)} \iff (CH_3)_2NH_2^+{}_{(aq)} + OH^-_{(aq)}$
4. $N_2H_{4\,(aq)} + H_2O_{(l)} \iff N_2H_5^+{}_{(aq)} + OH^-_{(aq)}$
5. $C_6H_5NH_{2\,(aq)} + H_2O_{(l)} \iff C_6H_5NH_3^+{}_{(aq)} + OH^-_{(aq)}$
6. $(C_6H_5)_2NH_{(aq)} + H_2O_{(l)} \iff (C_6H_5)_2NH_2^+{}_{(aq)} + OH^-_{(aq)}$

➙ The **equilibrium constant** of an equilibrium between ions of weak acid and unionized **weak acid** is expressed as K_a.

➙ The equilibrium constant for **weak base** is denoted as K_b.

NOTE : K_a= Ionization constant of an weak acid.
K_b= Ionization constant of an weak base.

Que : Derive the equation for K_a when weak acid is dissolved in water.

OR

Derive the relation between K_a (Ionization constant) and the concentration C_o of a Weak acid in water. [MARCH 96,97]

(3 MARKS)

➙ Following equilibrium exists in the aqueous solution of weak acid HA :

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

➙ The equilibrium constant K of this equilibrium can be given by

$$K = \frac{[H_3O^+][A^-]}{[HA]\ [H_2O]_{(\ell)}} \quad \ldots\ldots\ldots (1)$$

➙ Here the decrease in concentration of water due to the dissolution of acid is negligible in comparison with the concentration of pure water. Therefore $[H_2O]$ in the above equation can be regarded as constant combining this constant concentration term with K, a new constant K_a is written as under.

$$K\ [H_2O]_{(\ell)} = K_a = \frac{[H_3O^+][A^-]}{[HA]} \quad \ldots\ldots\ldots (2)$$

→ where K_a is ionisation or dissociation constant of weak acid.

➙ As only slight amount of acid dissociates into ions in such solutions, the concentration of undissociated acid approximately equal to initial concentration C_o of the acid. Moreover, the concentrations of positive ions and negative ions are equal (neglecting H_3O^+ produced by self - ionisation of water) i.e. $[H_3O^+] = [A^-]$

$$\therefore K_a = \frac{[H_3O^+][H_3O^+]}{C_o}$$

$$\therefore K_a \cdot C_o = [H_3O^+]^2$$

$$\therefore [H_3O^+] = \sqrt{K_a \cdot C_o}$$

NOTE : Here $[H_3O^+]$ produced by self - ionisation of water is negligible, hence it is not considered.

➙ This formula indicates the concentration of H_3O^+ produced by ionisation of weak acid.

Que : Derive the equation for K_b when the weak base NH_3 (or $C_6H_5NH_2$, $C_2H_5NH_2$, N_2H_4, CH_3NH_2 etc.) is dissolved in water.

OR

Derive the relation between the K_b and the concentration C_o of the weak base (NH_3). **[October 97] (3 marks)**

Ans :

➙ Following equilibrium exists in the aqueous solution of weak base NH_3

$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

➙ The equilibrium constant :

$$K = \frac{[NH_4^+][OH^-]}{[NH_3]\ [H_2O]_{(\ell)}}$$

➙ Here the decrease in concentration of water due to the dissolution of base is negligible in comparison with the concentration of pure water. Therefore, $[H_2O]_{(l)}$ in the above equation is regarded constant. Combining this constant concentration term with K, a new constant K_b is,

$$K\ [H_2O]_{(\ell)} = K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

→ where K_b is ionisation constant or dissociation constant of weak acid.

➙ As weak base $[NH_3]$ ionizes slightly in such solutions, the concentration of unionized base in aqueous solution is nearly equal to the initial concentration C_o.Moreover $[NH_4^+] = [OH^-]$, as the concentration of OH^- produced by self-ionization of water is negligible.

$$K_b = \frac{[OH^-][OH^-]}{C_o}$$

$$\therefore\ K_b \cdot C_o = [OH^-]^2$$

$$\therefore\ [OH^-] = \sqrt{K_b \cdot C_o}$$

➙ This formula indicates $[OH^-]$ produced by ionization of weak base.

Que : Derive the equation of ionization constant for the aqueous solution of dimethyl amine. [October 98] (3 marks)

➙ Importance of K_a & K_b :

➙ Higher the value of K_a, stronger the acid.

➙ Higher the value of K_b, stronger the base.

Que : Write a note on pH scale.

➙ Sorenson devised a new scale to express concentration of $H^+_{(aq)}$ in aqueous solution. This new scale is known as pH scale.

➤ **pH scale :**

→ **Definition :** "Negative logarithm of the molarity of the H_3O^+ ion in aqueous solution is called **pH**.

$$pH = -\log [H_3O^+] \text{ ..... (4)}$$

→ **Definition :** "Negative logarithm of the molarity of the OH^- ion in aqueous solution is called **pOH.**

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

➤ If the **concentration** of H_3O^+ in solution **decreases, pH** of the solution **increases.**

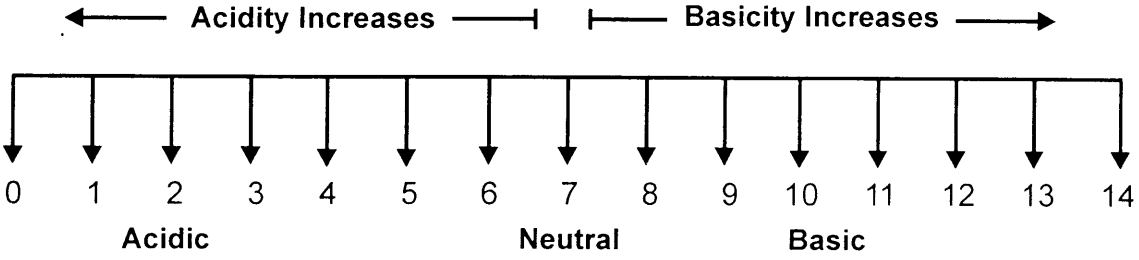
➤ **Values of pH and pOH at 25°C**

→ 1. For pure water : $[H_3O^+] = [OH^-] = 1X10^{-7}$ M
pH = pOH = $-\log(1X10^{-7}) = 7.0$

→ 2. For acidic solutions : $[H_3O^+] > 1X10^{-7}$ M & $[OH^-] < 10^{-7}$ M
pH < 7 & pOH > 7

→ 3. For basic solutions : $[H_3O^+] < 1X10^{-7}$ M & $[OH^-] > 10^{-7}$ M
pH > 7 & pOH < 7

→ 4. For any aqueous solution : pH + pOH = 14
pH scale can be represented as under :



★★ **DETERMINATION (CALCULATION) OF pH :**

➤ In the aqueous solution of **strong acid,** concentration of strong acid is equal to the concentration of H_3O^+ in solution. Hence pH value can be calculated directly from the concentration of strong acid.

➤ In the aqueous solution of **strong base,** concentration of strong base is equal to the concentration of OH^- in the solution. Hence pOH value can be calculated directly from the concentration of strong base. From this pH can be calculated.

➟ From the concentration of **weak acid,** and its K_a value, molar concentration of H_3O^+ can be calculated which is used to calculate pH value.

➟ From the concentration of **weak base,** and its K_b value, molar concentration of OH^- can be calculated, which is used to calculate pOH and thereby pH can be calculated.

➟ **pH** can be measured **accurately** by **pH meter**.

➟ **Approximate value** of **pH** of solution can be determined by using pH paper of indicator.

★★ **pH OF CONCENTRATED SOLUTION :**

➟ Usually pH values of most of solutions are in the range 1 - 14.

➟ However, if $[H_3O^+]$ is less than 0.1 M, pH would be less than one e.g. pH of 1 M HCl solution is near to zero and pH of 2 M HCl is less than zero. So pH is not generally useful to **express concentration of concentrated** solution.

➟ In concentrated solution neutral solution neutral ion - pairs are formed. Morever, there is proximity of ions. Hence concentrated solution behave **non - ideally.**

➟ As a result the actual concentration of H_3O^+ in solution having high molarity cannot be calculated on the basis of molarity of solution. Hence correct pH values of concentrated solution are not obtained.

★★ **USEFULNESS OF pH :**

1. pH scale **magnifies small values** of concentration of H_3O^+.
2. The extent of **acid - base titration** can be demonstrated graphically by using pH scale.
3. The useful pH range of **acid - base indicator** can be explained using pH scale.

Que : Write the operational definition of an acid and a base. (Robert Boyle theory)

Ans :

➟ An **Acid** 1. is sour in taste. 2. Turns blue litmus red.
3. Is neutralised by alkali. 4. Evolves $H_{2(g)}$ when reacts with metals.

➤ A **Base** 1. Is bitter in taste. 2. Turns red litmus blue.
3. Is neutralised by acid.

Que : Discuss different theories put forward to explain acid - base reactions.

★★ 1. ARRHENIUS THEORY OF ACID - BASE : (1880 - 1890)

➤ **Definition :** The substance which **produce H^+** when dissolved in water is acid and the substance which **produce OH^-** when dissolved in **water is base**.

➤ He attributed properties of acids to H^+ and properties of bases to OH^-

➤ It was believed that these compounds **dissociated reversibly** into ions in aqueous solutions and therefore, their aqueous solutions **showed electrical conductivity and chemical reactivity.**

➤ **Limitations : [Q. Give reasons - Arrhenius theory of acid-base has met some difficulties] [MARCH 99] (1.5 Marks)**

→ 1. This theory does **not** explain the **form of H^+** (proton) in aqueous solutions.

→ 2. Some compounds do **not** have **hydroxyl ions (OH^-)** in the formulae; yet they **behave** like as **base**.
e.g. $NH_{3(g)}$, behaves like a base in its reaction with $HCl_{(g)}$. Similarly Na_2CO_3 does not have OH^- but **behaves** as **base**.

→ 3. This theory does not explain the role of water.

➤ **Usefulness** : This theory is useful to **compare relative strengths** of different **acids and bases.**

Que : Write Lowry - Bronsted theory of Acids and Bases, explain giving two examples and write a note on conjugate acid and conjugate base. (March 98)

Ans :

★★ LOWRY BRONSTED THEORY OF ACIDS AND BASES (1925) :

➤ **Definition :** "**Acids** were compound which **donated protons and bases** were compound which **accepted protons** during reactions".

➤ According to this definition, an acid-base reaction is a process in which **proton transfer** occurs, e.g.

$$\underset{\text{Acid-1}}{HA_{(aq)}} + \underset{\text{Base-2}}{H_2O_{(l)}} \Longleftrightarrow \underset{\text{Acid-2}}{H_3O^+_{(aq)}} + \underset{\text{Base-1}}{A^-_{(aq)}}$$

Proton Donor	Proton Acceptor		Proton Donor	Proton Acceptor
$HCl_{(aq)}$	+ $H_2O_{(l)}$	$\Longleftrightarrow$	$H_3O^+_{(aq)}$	+ $Cl^-_{(aq)}$
$CH_3COOH_{(aq)}$	+ $H_2O_{(l)}$	$\Longleftrightarrow$	$H_3O^+_{(aq)}$	+ $CH_3COO^-_{(aq)}$
$HNO_{3(l)}$	+ $H_2O_{(l)}$	$\Longleftrightarrow$	$NO_3^-{}_{(aq)}$	+ $H_3O^+_{(aq)}$
$H_2SO_{4\,(l)}$	+ $2H_2O_{(l)}$	$\Longleftrightarrow$	$SO_4^{-2}{}_{(aq)}$	+ $2H_3O^+_{(aq)}$
$H_2O_{(l)}$	+ $H_2O_{(l)}$	$\Longleftrightarrow$	$H_3O^+_{(aq)}$	+ $OH^-_{(aq)}$
$H_2O_{(l)}$	+ $NH_{3(g)}$	$\Longleftrightarrow$	$OH^-_{(aq)}$	+ $NH_4^+{}_{(aq)}$

➙ From above illustrations it can be said that a reaction between acid and base produce a base and a acid.

➙ An acid produces conjugate base by giving up proton and a base produces a conjugate acid by gaining a proton.

→ i.e. Any Acid - H^+ = conjugate base & base + H^+ = conjugate acid.

★★ CONJUGATE ACID - BASE : [MARCH 96, 98, OCTOBER 96, 97]

➙ "The pair of acid-base having difference of one proton is known as conjugate acid-base."

➙ According to this theory :

→ 1. Strong acid has high tendency to give up proton so its conjugate base will be weak.

→ 2. Strong base has high tendency to accept proton, so its conjugate acid will be weak.

[Q. Complete $\underset{\text{(Acid-1)}}{H_3ASO_4} + 2H_20\ (1) \Longleftrightarrow \_\_\_]$ (March 99) (1 mark)

➙ This theory helps us

→ 1. To measure the strength of different acids i.e. tendency to donate protons, water is selected as a base. On the basis of this quantitative expression of tendency to loose proton by acid is given by **K_a value.**

→ 2. To measure the strength of different acids i.e. tendency to accept protons, water is selected as a base. On the basis of this quantitative expression of tendency to accept proton by base is given by **K_b value.**

➙ **Limitations :**

→ 1. According to this theory, proton transfer is essential, otherwise reaction is not considered as acid-base reaction. But in fact there are some acid - base reaction in which proton transfer does not take place e.g. $\underset{\text{Acid}}{BF_3} + \underset{\text{Base}}{F^-} \longrightarrow BF_4^-$

→ 2. This theory does not cover the reactions taking place in absence of solvent.

★★ LEWIS THEORY OF ACID - BASE : (1923)

➙ **Definition :** 'Acid is a compound which accept electron pair during reaction and base is a compound which donates and electron pair during reactions'.

e.g.

Acid		Base		
$Ag^+_{(aq)}$	+	$2NH_{3\,(aq)}$	$\Longleftrightarrow$	$Ag(NH_3)_2^+{}_{(aq)}$
BF_3	+	F^-	$\Longleftrightarrow$	BF_4^-
BF_3	+	NH_3	$\Longleftrightarrow$	$F_3B \longleftarrow NH_3$
$Ag^+_{(aq)}$	+	$2CN^-_{(aq)}$	$\Longleftrightarrow$	$Ag(CN)_2^-{}_{(aq)}$

→ In above reactions, NH_3, F^- and CN^- donate electron pair hence they are Lewis base while Ag^+ and BF_3 accept electron pair hence they are Lewis acids.

→ Thus reactant acting as Lewis acid may be cation or electron deficient molecule (e.g. Ag^+, Cu^{+2}, BF_3) and a reactant act as a lewis base may be anion or a molecule having non-bonding electron-pair with the atom (e.g. NH_3, F^-, CN^-, OH^-, Cl^-, NH_2^-)

[October 98]

★★ ILLUSTRATION OF LEWIS ACID - BASE REACTION : (Explain Hydration) [October 98] (2 Marks)

➙ 1. When salt is dissolved in water, ions formed in solution become hydrated. This process of hydration is an acid - base reaction. e.g. Lewis acid base reaction between Na^+ and H_2O as under :

$$\underset{\text{LewisAcid}}{Na^+} + \underset{\text{LewisBase}}{6H_2O} \Longleftrightarrow [Na(H_2O)_6]^+$$

Similarly, $\underset{\text{LewisAcid}}{Cl^-} + \underset{\text{LewisBase}}{6H_2O} \Longleftrightarrow [Cl(H_2O)_6]^-$

➙ 2. Ions and molecules acting as **ligands** in the formation of complex salts are **Lewis Bases** and **metal ions** bonding to ligands in the formation of complex salts are Lewis Acids.

★★ **REASONING :**

➙ Lowry Bronsted bases are Lewis bases, Lowry Bronsted acids are **Lewis acids**.

➙ All Lewis bases donate electron pair and owing to non-bonding electron pair Lewis bases can accept proton, hence can be considered as Lowry bronsted base. e.g. NH_3, Cl^-, OH^- etc. are Lewis bases as well as Lowry Bronsted bases.

➙ Lewis acids accept electron pair during reaction. But some of those cannot donate proton, hence cannot be considered as Lowry - Bronsted acids e.g. H_2O, BF_3, Ag^+ etc accept electron pair, hence they are Lewis acid, but BF_3 and Ag^+ cannot donate protons, hence they are not Lowry - Bronsted acid.

➙ Thus, **all Lowry - Bronsted bases are Lewis bases and all Lowry Bronsted acids are Lewis acids but all Lewis acids are not Lowry - Bronsted acids.**

Que : Write a note on Acid - base titrations and pH scale.

[March 98] (3 marks)

Ans :

➙ A titration is one of the experimental methods used in laboratories to determines the concentrations of one solution (unknown) from the known concentration of other solution (using $N_1V_1 = N_2V_2$)

➙ In acid - base titrations, a definite volume of solution (acid or base) is taken in pipette which is completely neutralised with other solution (base or acid) of burette.

➙ In order to detect the stage at which the reaction is completed two or three drops of a solution of a third reagent capable of changing its colour in the process of neutralisation, called **indicator**.

➙ By knowing volume of second solution, the unknown concentration of solution can be calculated.

➙ During acid-base titration, change in pH of the solution is very slow in the starting of reaction. But pH undergoes a large change during last stage. On the basis of large change in pH, indicator is selected in acid-base titration which can be explained as under :

Volume of Solution of NaOH added from burette	Percentage of neutralization	pH of solution of HCl taken in pipette
0.0 ml	0%	1
5.0 ml	50%	1.4
9.9 ml	99.99%	4.3
10.0 ml	100.00%	7.00(Complete neutralization)
10.1 ml	100.10%	10.7

➙ Thus, pH changes very rapidly from 4.3 to 10.70 during 99.9% - 100.1 % titration stage (phenolphthalein can be used as an indicator because useful pH range of phenolphthalein is 8 - 10)

➙ This range of pH decreases, if the concentration of HCl is less than 0.1M.Therefore, it is essential to have certain minimum concentrations of solutions used in titration; too dilute solutions cannot be titrated successfully.

[Q.What is the change in the value of pH during 99.9% - 100% acid - base titration stage] **[October 98] (1 mark)**

Que : Write a note on : HYDROLYSIS OF SALTS in aqueous solutions.

Ans :

➙ Aqueous solution of salts are either ACIDIC, BASIC OR NEUTRAL.

	SALT	SOLUTION	ILLUSTRATION
1	Strong acid - strong base	Neutral	KNO_3, Na_2SO_4, KCl
2	Strong acid - weak base	Acidic	$CuSO_4$, NH_4Cl, $FeCl_3$
3	Weak acid - strong base	Basic	Na_2CO_3, K_3PO_3,CH_3COONa
4	Weak acid - weak base	Netural	$HCOONH_4$, $(CH_3COO)_3Al$

➙ **HYDROLYSIS :** Ions formed from salts react with ions ($H^+_{(aq)}$ or $OH^-_{(aq)}$) produced from water, reaction is called **hydrolysis**.

→ **1. Hydrolysis of salt of strong base - weak acid (CH_3COONa)**

Suppose salt MA produced by a reaction between a strong base (MOH) and a weak acid (HA) is dissolved in water.

The following equilibrium exists in water.

$$H_2O_{(l)} \iff H^+_{(aq)} + OH^-_{(aq)}$$

Salt MA ionise completely in aqueous solution :

$$MA \iff M^+ + A^-$$

→ Now salt MA reacts with H_2O as under :

$$MA + H_2O_{(l)} \iff MOH + HA$$

Salt Water Strong Base WeakAcid

$$M^+_{(aq)} + A^-_{(aq)} + H_2O_{(1)} \iff M^+_{(aq)} + OH^-_{(aq)} HA$$

(Removing spectator ions)

$$A^-_{(aq)} + H_2O_{(1)} \iff HA_{(aq)} + OH^-_{(aq)}$$

→ As HA is weak acid, it ionises slightly. Therefore, the concentration of A present along with H^+ would be very low. When salt dissolves in water A^- ions are formed in large concentration. As a result, they combine with H^+ ions produced by self - ionization of water and form undissociated HA. This disturbs the equilibrium in water. As a result, according to Le chateliers's principle, the equilibrium of water shifts in the forward direction and produces more H^+ and OH^- ions. However, as H^+ are removed by A^-, the concentration of OH^- ions exceeds the concentration of H^+ ions in the new state of equilibrium and therefore solution becomes basic.

[Q. An aqueous solution of sodium formate is basic] **(March 97) (2 marks)**

→ **2. HYDROLYSIS OF strong acid (HA) and weak base (MOH) (NH_4Cl)**

→ Suppose salt MA is produced by reaction between strong acid (HA) and weak base (MOH) dissolved in water.

→ The following equilibrium exists in water

$$H_2O_{(l)} \iff H^+_{(aq)} + OH^-_{(aq)}$$

→ Salt MA ionize completely in water (aqueous solution)

$$MA \iff M^+ + A^-_{(aq)}$$

→ Now salt MA reacts with water ($H_2O_{(l)}$) as under

$$MA + H_2O_{(l)} \Longleftrightarrow MOH + HA$$

Salt **Water** **WeakBase** **StrongAcid**

$$M^+_{(aq)} + A^-_{(aq)} + H_2O_{(l)} \Longleftrightarrow MOH + H^+_{(aq)} + A^-_{(aq)}$$

(Removing spectator ions)

$$M^+_{(aq)} + H_2O_{(l)} \Longleftrightarrow MOH + OH^-_{(aq)}$$

→ As MOH is weak base, it ionizes slightly. The concentration of M^+ present along with OH^- would be very low. When salt dissolves in water M^+ are formed in large concentration which combines with OH^- to give MOH (undissociated). This reaction disturbs the equilibrium in water. When the net reaction reaches new state of equilibrium, the concentration of H^+ exceeds the concentration OH^- and the solution becomes acidic.

[Q.Write the effect of aqueous solution of $CaCl_2$ on litmus paper] (Oct 98)

OR

[Q.An aqueous solution of $FeCl_3$ is acidic.] [Oct 96] (1.5 marks)

→ **HYDROLYSIS CONSTANT (K_h) :** The equilibrium constant of hydrolysis reaction is known as hydrolysis constant (K_h).

1. For the salt formed from strong base and weak acid,

$$K_h = \frac{K_w}{K_a}$$ where, K_a = ionization constant of acid &

K_w = ionic product of water.

2. For salt formed from strong acid and weak base,

$$K_h = \frac{K_w}{K_b}$$ where, K_b = ionization constant of acid &

K_w = ionic product of water.

Que : Explain and illustrate solubility product. [March 97] (2 marks)

Ans :

➙ **SPARINGLY SOLUBLE SALTS :** Salts which form aqueous saturated solution, having less than 0.01 M concentration are called **sparingly soluble salts.** **[Oct. 96, March 98] (1mark)**

➙ If a saturated solution of such salts is in contact with a solid salt, there exists an equilibrium between the solid salt and its ions in the solution.

$MA_{(s)} \iff M^+_{(aq)} + A^-_{(aq)}$

➙ Now as the concentration of saturated solution of sparingly soluble salt is low, there is no possibility of presence of undissociated salt in the solution.

➙ DERIVATION OF SOLUBILITY PRODUCT OF SPARINGLY SOLUBLE SALTS (K_{sp}) :

→ Let MA be the sparingly soluble salt.

$MA_{(s)} \iff M^+_{(aq)} + A^-_{(aq)}$

$K = \frac{[M^+][A^-]}{[MA]_{(s)}}$ $\quad \therefore K \cdot [MA]_{(s)} = [M^+][A^-]$

$\therefore K_{(sp)} = [M^+][A^-]$

eg.

1. $AgCl_{(s)} \iff Ag^+_{(aq)} + Cl^-_{(aq)}$

$K = \frac{[Ag^+][Cl^-]}{[AgCl]_{(s)}}$ $\quad \therefore K \cdot [AgCl]_{(s)} = [Ag^+][Cl^-]$

$\therefore K_{(sp)} = [Ag^+][Cl^-]$

2. $CaF_{2(s)} \iff Ca^{+2}_{(aq)} + A^-_{(aq)}$

$K = \frac{[Ca^{2+}][F^-]^2}{[CaF_2]_{(s)}}$ $\quad \therefore K \cdot [CaF_2]_{(s)} = [Ca^{2+}][F^-]^2$

$\therefore K_{(sp)} = [Ca^{2+}][F^-]^2$

➙ SIGNIFICANCE OF K_{sp} : [March 98] (1 mark)

→ (i) From the value of K_{sp}, the condition necessary for quantitative precipitation of positive ion of the salt from its solution can be attained.

→ (ii) From the value of K_{sp}, the solubility of sparingly soluble salt can be known.

→ (iii) From the value of K_{sp} of different salts having similar formula, their solubility can be compared.

➙ EXPERIMENTAL INFORMATION ABOUT SOLUBILITY OF SALT :

→ 1. All salts of Na^+, K^+ and NH_4^+, are soluble in water.

→ 2. All nitrates are soluble in water.

→ 3. All compounds formed by bonding of inorganic negative ion with H^+ are soluble in water.

→ 4. All sulphates, except $PbSO_4$, $CaSO_4$, and $BaSO_4$, and $SrSO_4$, are soluble in water.

→ 5. All chlorides, except AgCl, $HgCl_2$ and $CuCl_2$ are soluble in water.

→ 6. Sulphides of alkali metals and alkaline earth metals are soluble in water. Sulphides of other metals (heavy) are sparingly soluble in water.

→ 7. Hydroxides of alkali metals, barium and radium are water - soluble.

→ 8. Carbonates, phosphates and sulphates of alkali metals and radium are water - soluble.

Que : Explain and illustrate : Common ion effect.

[October 96] (3 marks)

Ans :

➙ An equilibrium exists between **undissociated molecules** of weak electrolytes and its **ions**, if the electrolyte is dissolved in water. Similarly, if a saturated **solution** of a salt is in contact with the solid salt, an ionic equilibrium between the **solid salt** and its ions in the solution exist.

➙ If **another electrolyte** having one of the ions the **same are** present in the solution, is **added** to the saturated solution, the **equilibrium** in the solution gets **disturbed**.

➙ According to the **Le - chatelier's principle**, the **reverse process** is favoured to reach the new state of equilibrium. This effect is known as **COMMON ION EFFECT.**

e.g.

1. The following equilibrium exists in aqueous solution of CH_3COOH.

$CH_3COOH_{(aq)} \Longleftrightarrow CH_3COO^-_{(aq)} + H^+_{(aq)}$ (Weak electrolyte)

➙ If CH_3COONa is added to this solution, the concentration of CH_3COO^- ion increases, as CH_3COONa is a strong electrolyte. This distrurbs the above equilibrium. i.e.

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

$CH_3COONa_{(l)} \longrightarrow Na^+_{(aq)} + \boxed{CH_3COO^-_{(aq)}}$ → Common ions

➙ To reach again the state of equilibrium some CH_3COO^- ions combine with H^+ ions and produce undissociated CH_3COOH. This effect is called **Common ion effect**.

➙ If a small amount of HCl is added to the solution, the addit ion of common ion H^+ shifts the equilibrium in the reverse direction as under:

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

$HCl_{(l)} \longrightarrow \boxed{Cl^-_{(aq)} + H^+_{(aq)}}$ → Common ions

2. The following equilibrium exists in saturated solution of AgCl (Sparingly soluble salt)

$AgCl_{(s)} \Longleftrightarrow Ag^+_{(aq)} + \boxed{Cl^-_{(aq)}}$

$NaCl_{(s)} \longrightarrow Na^+_{(aq)} + \boxed{Cl^-_{(aq)}}$ → Common ions

➙ Addition of small quantity of $NaCl_{(s)}$ to this solution increases the concentration of $Cl^-_{(aq)}$. Therefore, some of Cl^- combine with $Ag^+_{(aq)}$ (Le - Chatlier's Principle) and precipitate AgCl. Thus due to **common ion** (Cl^-) effect, **solubility of AgCl decreases.**

➙ If **$HCl_{(g)}$** is passed through saturated solution of **NaCl** the concentration of $Cl^-_{(aq)}$ increases (Common ion effect). This result in the precipitation of **$NaCl_{(s)}$** i.e. **[March 96] (2 marks)**

$NaCl_{(s)} \Longleftrightarrow Na^+_{(aq)} + \boxed{Cl^-_{(aq)}}$

$HCl_{(g)} \longrightarrow H^+_{(aq)} + \boxed{Cl^-_{(aq)}}$ → Common ions

Que : Explain application of Common ion effect.

Ans :

➙ (i) Useful in **qualitative** analysis.

➙ (ii) To **precipitate** or to decrease the solubility of salt (as discussed above). e.g.

➙ **1. Precipitation of Cu^{+2} as CuS from Cu^{+2} & Zn^{+2} solution.**

→ If $H_2S_{(g)}$ is passed through a solution containing Cu^{+2} and Zn^{+2} after adding small quantity of HCl to the solution, only CuS precipitates,

ZnS does not precipitate. The degree of ionisation decreases in presence of HCl. i.e.

$$H_2S_{(aq)} \Longleftrightarrow S^{-2}_{(aq)}$$

$$HCl_{(g)} \longrightarrow Cl^{-}_{(aq)} + \boxed{2H^{+}_{(aq)}} \longrightarrow \text{> Common Ions}$$

→ The concentration of S^{2-} ions the solution becomes **very low** under the influence of common ion (H^+). As the **solubility of CuS is very low** compared to the solubility of ZnS ($K_{sp(CuS)} < K_{sp(ZnS)}$), **only CuS** precipitates by keeping very low concentration of S^{2-} ions.

➙ 2. Precipitation of Gr. III A metal ions only using $NH_4OH + NH_4Cl$ [Oct.97)

→ To precipitate hydroxides of only Al^{+3}, Fe^{+2}, Fe^{+3} & Cr^{+3} in Gr. III A of qualitative analysis, NH_4Cl solution is added to the test solution before NH_4OH solution. As a result the following equilibrium shifts in reverse direction due to common ion NH_4^+ (Le-chatelier's principle). This decreases the concentration of OH^- to a large extent. As a result, the hydroxides of ions of Gr. III B, IV and Mg^{+2} do not precipitate in Gr. III A.

$$NH_{(4)}OH \Longleftrightarrow OH^{-} + \boxed{NH_4^{+}}$$

$$NH_{(4)}Cl \longrightarrow Cl^{-} + \boxed{NH_4^{+}} \longrightarrow \textbf{Common ions}$$

→ As the **solubilities of hydroxides of Gr. III A** are very low, only hydroxides of Gr. III A precipitate by NH_4OH in the presence of NH_4Cl.

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