Chapter - 3 Acid Base theory

Various theories were put forward by different chemists. These theories are based on the configuration or the inner structure of acids and bases. A few theories are :

1. Arrhenius theory
2. Bronsted Lowry theory
3. Lewis theory

1. Arrhenius theory of Acids and Bases :-

⇒ Postulates :

(i) Acids are those substances which produce H^+ ions (Protons) in aqueous solution.

Ex:- $HCl_{(g)} \xrightarrow{Water} H^+_{(aq)} + Cl^\ominus_{(aq)}$

$CH_3COOH_{(l)} \xrightarrow{Water} H^+_{(aq)} + CH_3COO^\ominus_{(aq)}$

Other examples are : HNO_3, H_2SO_4 etc.

(ii) Bases are those substances which provide $OH^\ominus$ ions in aqueous solution.

Ex:- $NaOH_{(s)} \xrightarrow{Water} Na^\oplus_{(aq)} + OH^\ominus_{(aq)}$

$NH_4OH \underset{}{\overset{Water}{\rightleftharpoons}} NH_4^\oplus{}_{(aq)} + OH^\ominus_{(aq)}$

Other examples are : KOH, $Ca(OH)_2$, $Al(OH)_3$ etc.

(iii) Neutralisation of an acid and a base is based on the key reaction between $H^\oplus$ ions and $OH^\ominus$ ions to form water molecules and the reaction is called neutralisation reaction.

Ex:- $HCl + NaOH \longrightarrow NaCl + H_2O$

(Acid) (Base) (Salt) (Water)

It may be represented as :

$H^\oplus_{(aq)} + OH^\ominus_{(aq)} \longrightarrow H_2O_{(l)}$

(from acid) (from base)

(iv) Higher is the degree of dissociation, higher is the acidic or basic nature of the substance.

(v) During electrolysis of an aqueous solution of an acid, $H^{\oplus}$ ions proceed to the cathode and negative ions to the anode. Thus,

$$HCl_{(g)} \xrightarrow{water} H^{\oplus}_{(aq)} + Cl^{\ominus}_{(aq)}$$

At cathode : $2H^{\oplus}_{(aq)} + 2e \longrightarrow H_{2(g)}$

At anode : $2Cl^{\ominus}_{(aq)} - 2e \longrightarrow Cl_{2(g)}$

⇒ Limitations :

(i) Nature of hydrogen ion and hydroxyl ion. It has been found that H^+ ions donot exist in aqueous solution. It combines with H_2O, as soon as its formation to give hydronium ion ($H_3\overset{+}{O}$).

$$H^{\oplus} + H-\ddot{O}-H \longrightarrow H_3\overset{\oplus}{O}$$ or

hydronium ion

(ii) The theory fails to explain the acidic and basic properties of substances in solvents other than water.

(iii) It fails to explain the acidic properties of substances like CO_2, SO_2, SiO_2, P_2O_5, BF_3, $AlCl_3$ etc. which donot contain hydrogen.

(iv) It also fails to explain the basic nature of substances like NH_3, PH_3, Na_2O, K_2O, CaO etc. which donot contain OH group.

(v) It fails to explain the neutralisation reactions in the absence of water. We know following neutralisation which takes place even in the absence of water.

$$\underset{(Base)}{CaO_{(s)}} + \underset{(Acid)}{SO_{2(g)}} \longrightarrow \underset{(Salt)}{CaSO_{3(s)}}$$

$$NH_{3(g)} + HCl_{(g)} \longrightarrow NH_4Cl_{(s)}$$

Such reactions donot involve the combination of H^+ ions and $OH^{\ominus}$ ions to produce water, which should occur as per Arrhenius theory.

2. Bronsted - Lowry theory of Acids and Bases :-

⇒ Postulates : According to this concept ;

(i) Acid is a substance (molecule or ion) which has a tendency to accept a proton (H^+ ion) to any other substance.

Ex:- $HCl \rightleftharpoons H^{\oplus} + Cl^{\ominus}$

$H_3O^{\oplus} \rightleftharpoons H^{\oplus} + H_2O$

$HSO_4^{\ominus} \rightleftharpoons H^{\oplus} + SO_4^{2-}$

Similarly HNO_3, H_2SO_4, CH_3COOH, H_2O, H_2S, $NH_4^{\oplus}$, $HCO_3^{\ominus}$ etc. are acids.

(ii) A base is a substance (molecule or ion) which has a tendency to accept a proton (H^+ ion) from any other substance.

Ex:- $NH_3 + H^{\oplus} \rightleftharpoons NH_4^{\oplus}$

$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^{\ominus}$

$H_2O + H^+ \rightleftharpoons H_3O^{\oplus}$

Similarly RNH_2, $CN^{\ominus}$, $HS^{\ominus}$, $NO_2^{\ominus}$, $HSO_4^{\ominus}$, HPO_4^{2-}, etc. are bases.

In short, an acid is a proton donor, while a base is a proton acceptor. An acid or a base may be a neutral molecule, cation or an anion.

(iii) A substance can only act as an acid if there is another substance to accept its proton and vice-versa.

For example: HCl gas acts as an acid in water and not in benzene. The reason is that water can take up its proton while benzene cannot.

(iv) Whenever an acid reacts with a base, we get another pair of acid and base. For example, HCl reacts with water (base) to form $H_3O^{\oplus}$ (acid) and $Cl^{\ominus}$ (base).

$$\underset{\text{Acid}_1}{HCl} + \underset{\text{Base}_1}{H_2O} \rightleftharpoons \underset{\text{Acid}_2}{H_3O^{\oplus}} + \underset{\text{Base}_2}{Cl^{\ominus}}$$

Conjugate Acid-Base Pair.

(v) The paire of acid and base which differ by a proton (H^+ ion) is called Conjugate acid-base paire.

$$Acid - H^+ \longrightarrow \text{Conjugate base}$$

$$Base + H^+ \longrightarrow \text{Conjugate acid}$$

Note:- Some conjugate acid-base Paires are given below:

Acid	Conjugate base	Base	Conjugate acid
HCl	$Cl^{\ominus}$	Br^-	HBr
H_2SO_4	HSO_4^-	$CN^{\ominus}$	HCN
HS^-	S^{2-}	O^{2-}	OH^-
$NH_4^{\oplus}$	NH_3	NH_3	$NH_4^{\oplus}$
H_2O	$OH^{\ominus}$	H_2O	$H_3O^{\oplus}$

(vi) Stronger is an acid weaker is its conjugate base and vice-versa

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^{\ominus}$$

(Strong acid) (Weak base)

(vii) The substance such as H_2O, HS^-, HCO_3^-, HPO_4^{2-}, HSO_4^-, etc. which act as both acid (Proton donor) as well as base (proton acceptor) are called amphoteric substances.

⇒ **Limitations**:-

(i) It fails to explain the acidic nature of the substances, such as SiO_2, CO_2, SO_2, BF_3, $AlCl_3$, $FeCl_3$ etc. which cannot donate H^+ ion and the basic nature of the substances, such as Na_2O, K_2O, CaO, MgO etc. which cannot accept H^+ ion.

(ii) It fails to explain the reaction between some acids and bases which donot give another Paire of acid and base.

Ex:- $HCl + NaOH \longrightarrow NaCl + H_2O$

3. Lewis theory or Electronic concept of Acids and Bases :-

G.N. Lewis (1923) gave new definitions to 'acid' and 'base' taking into account their electronic configurations. According to this theory

An acid is defined as any substance that can accept a pair of electrons while a base is any substance which can donate a pair of electrons.

In other words, acids are electron acceptors while bases are electron donors.

⇒ A Lewis acid may be of following types :-

(a) All cations e.g. $CH_3^{\oplus}$, H^+, Cu^{2+}, Ag^+, Ca^{2+}, Fe^{3+} etc.

(b) Neutral molecules having ~~one or more lone pairs of electrons~~, eg. electron deficient atoms e.g. $FeCl_3$, $ZnCl_2$, SO_3, $AlCl_3$, BF_3 etc.

(c) Molecules having atoms which can accomodate more electrons in the vacant d-orbitals in the valency shell.

e.g. $SiCl_4$, SiF_4 etc.

(d) The molecules having multiple bonds between atoms of different electro-negativities. e.g. CO_2 ($O=C=O$), SO_2 etc.

⇒ A Lewis base may be of the following types :-

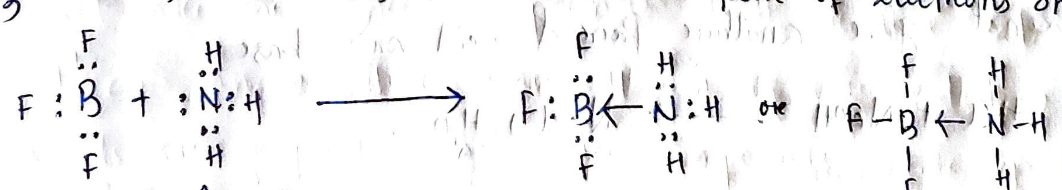
(a) All negative ions are Lewis bases e.g. $OH^{\ominus}$, CN^-, $CH_3COO^{\ominus}$, Cl^-, Br^-, CO_3^{2-} etc.

(b) Neutral molecules having one or more lone pairs of electrons, e.g. $\ddot{N}H_3$, $R\ddot{N}H_2$, $H_2\ddot{O}:$, $\ddot{P}H_3$ etc.

* **Acid - base reactions :-**

According to this concept, whenever an acid and a base react, a co-ordinate bond is formed.

(i) BF_3 behaves as an acid as boron atom in its electron deficient. $\ddot{N}H_3$ acts as a base as there is a lone pair of electrons on nitrogen atom



(Acceptor) Acid (Donor) Base

(ii) H^+ ion is a Lewis acid and NH_3 is a Lewis base. They react to form ammonium ion by co-ordinate linkage as follows:

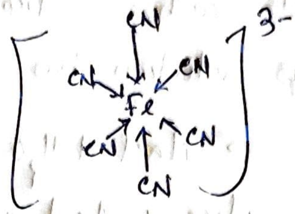
$$\ddot{N}H_3 + H^{\oplus} \longrightarrow H_3N \rightarrow H^{\oplus}$$

(Donor) Base (Acceptor) Acid — Ammonium ion

(iii) Fe^{3+} ion (Lewis acid) reacts with $CN^{\ominus}$ ion (Lewis base) and $Ag^{\oplus}$ (Lewis acid) reacts with NH_3 (Lewis base) as follows:

$$Fe^{3+} + 6CN^- \longrightarrow$$

Lewis acid Lewis base



Co-ordinate Complex

$$Ag^+ + 2NH_3 \longrightarrow [H_3N \rightarrow Ag \leftarrow NH_3]^+$$

Lewis acid Lewis base

⇒ **Limitations :-**

(i) It fails to explain the relative strengths of acids and bases as it does not consider ionisation.

(ii) It fails to explain the acidic nature of well known acids like HCl, HNO_3, H_2SO_4 etc. which cannot accept electrons, also the basic nature of well-known bases like NaOH, KOH etc. which cannot donate electrons.

(iii) According to this theory, an acid reacts with a base with the formation of a dative bond but no such bond is formed when HCl reacts with NaOH or H_2SO_4 with KOH etc.

(iv) Acid-base reactions are fast and instantaneous, but the formation of a dative bond is a slow process.

(v) Acids show catalytic activity in many reactions because H^+ ions are furnished by them. But the Lewis theory does not permit any such property.

* Neutralization of Acids and Bases :-

When an aqueous solution of an acid is added to an aqueous solution of a base, a chemical reaction occurs, resulting in the formation of a salt and water. This process is called acid - base neutralisation. Neutralization reaction may take place as follows:

1. Neutralisation between a Strong Acid and a strong Base :

A strong acid reacts with a strong base to form a simple one normal salt. Its aqueous solution has a pH of about 7 and is neutral.

Ex:- $HCl + NaOH \longrightarrow NaCl + H_2O$.

2. Neutralision between a strong Acid and a weak Base ;

A strong acid reacts with a weak base to form a acidic salt. Its aqueous solution has a $pH < 7$ and the solution is acidic.

Ex:- $HCl + NH_4OH \longrightarrow NH_4Cl + H_2O$

3. Neutralisation between a Weak Acid and a strong Base ;

A weak acid reacts with a strong base to form a basic salt. Its aqueous solution has a $pH > 7$ and is alkaline.

Ex:- $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

4. Neutralisation between a weak Acid and a Weak Base :

A weak acid reacts with a weak base to form a salt which may be acidic, basic or neutral depending upon the relative proportion of H^+ and $OH^\ominus$ ions in solution.

Ex:- $CH_3COOH + NH_4OH \longrightarrow CH_3COONH_4 + H_2O$

* SALTS :-

⇒ Definitions :- ① Salts are the compounds formed by the neutralisation reaction between acids and bases.

or: ② Salts are the ionic compounds which produce cation other than H^+ and anion other than OH^- in aqueous solution.

or : ③ Salts are regarded as ionic compounds made up of positive and negative ions. The positive part comes from a base while negative part from an acid.

⇒ **Types of Salts :-**

Salts may be classified into the following types:

1. **Normal salts** :- The salt obtained by the complete replacement of all the replaceable hydrogen atoms of an acid by metal atoms is called a normal salt. These salts are obtained by the reaction between strong acids and strong bases.

Ex:- $NaCl$, K_2SO_4, Na_2SO_4, $Ca_3(PO_4)_2$ etc.

2. **Acidic salts** :- The salt obtained by the incomplete neutralisation of polybasic acids is called an acidic salt. These types of salts still contain one or more replaceable hydrogen atoms.

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

Thus,

$$HSO_4^{\ominus} + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$$

$$H_2PO_4^{\ominus} + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-}$$

3. **Basic salts** :- These are the salts obtained by the incomplete neutralisation of poly acidic bases. Such salts still contain one or more 'OH' groups.

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

4. **Double salts** :- These are the molecular addition compounds formed by the combination of two simple salts. Such salts are stable only in the solid state. These salts retain the properties of constituents in aqueous solution and give the test of all the constituent ions when dissolved in water.

Ex:- $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ [Potash alum], $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ [Mohr's salt] etc.

5. **Complex salts** :- These are the compounds formed by the combination of simple salts which are stable in solid state as well as in solution. The properties of complex salts are different from their constituents and do not give the test of all the constituent ions in aqueous solution.

Ex:- $K_4[Fe(CN)_6]$, $[Cu(NH_3)_4]SO_4$ etc.

6. **Mixed salts** :- These are the salts which furnish more than one cation or more than one anions when dissolved in water.

Ex:- Bleaching powder ($CaOCl_2$), $NaKSO_4$, $NaNH_4HPO_4$ etc.

e.g.: $CaOCl_2 \xrightarrow{Water} Ca^{2+} + OCl^{\ominus} + Cl^{\ominus}$