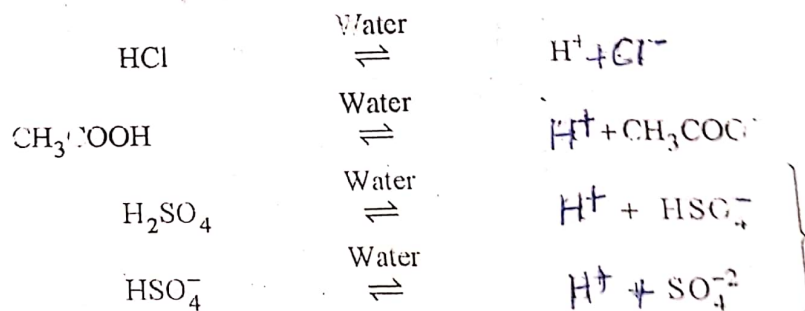## 4.8   ARRHENIUS CONCEPT OF ACIDS AND BASES

In the light of the behaviour of electrolytes in solution, Arrhenius provided a well-defined basis for the concept of acids and bases.

ACIDS: According to him, an acid may be defined as *a hydrogen containing substance which gives H^+ ions in aqueous solution*. Obviously the presence of ionisable hydrogen is an essential feature of all acids; Thus

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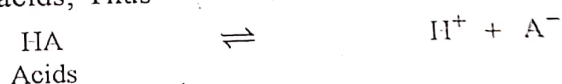
Acids

This definition could easily explain why the substances such as HCl, CH_3COOH, H_2SO_4 and H_3PO_4 etc. are recognised as acids, since each of them furnishes hydrogen ions in solution. For instance:

$$HCl \xrightleftharpoons{Water} H^+ + Cl^-$$

$$CH_3COOH \xrightleftharpoons{Water} H^+ + CH_3COO^-$$

$$H_2SO_4 \xrightleftharpoons{Water} H^+ + HSO_4^-$$

$$HSO_4^- \xrightleftharpoons{Water} H^+ + SO_4^{-2}$$

It should be noted that acids like H_2SO_4 and H_3PO_4 which contain two or more ionisable hydrogen atoms dissociate in more than one stage giving H^+ ions in each case.

The common characteristics of acids such as sour taste, turning blue litmus red, reaction with bases to from salt and H_2O were attributed to the presence of H^+ ions in aqueous solution.

BASES: A similar concept was put forward for bases. *A base is defined as a substance which contains one or more hdyroxyl groups and furnishes hydroxyl (OH)⁻ ions in aqueous solution.*

$$BOH \text{ (Base)} \quad \underset{}{\overset{Water}{\rightleftharpoons}} \quad B^+ + OH^-$$
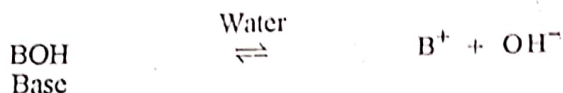
Thus, all commonly known bases such as NaOH, KOH, NH_4OH ionizes in aqueous solution to give OH^- ions.

$$NaOH \quad \overset{Water}{\rightleftharpoons} \quad Na^+ + OH^-$$

$$KOH \quad \overset{Water}{\rightleftharpoons} \quad K^+ + OH^-$$
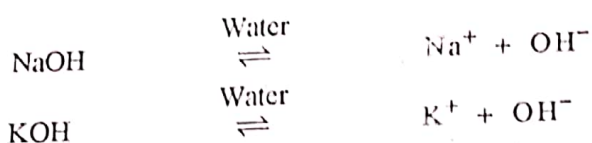
The hydroxyl ion is responsible for the basic properties exhibited by the bases.

Nature of hydrogen ion in aqueous solution

According to Arrhenius, an acid gives H^+ ions in aqueous solution. But a hydrogen ion is only a free proton which has a very small size and an extremely high charge density. It is very strongly attracted by the negative end of water molecules and as a result it gets very readily hydrated or attracted to water molecules. Therefore, it is not very appropriate to speak of the formation of free H^+ ions or protons in solution. On the other hand, the H^+ ion always exists in solution in the more stable hydrated from, H_3O^+, known as *hydronium ion* or hydrated proton.

$$H^+ + H_2O \longrightarrow H_3O^+$$
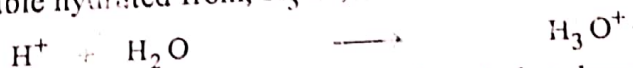
In fact, even this may be an over-simplification. It has been suggested recently that hydrated proton may not be as simple as H_3O^+. Rather it may be further hydrated to form species such as $H_9O_4^+$. But in the absence of any definite evidence about the exact number of water molecules involved, the hydronium ion is commonly represented as H_3O^+ or $H^+(aq)$ or $H_3O^+(aq)$.

Limitations of Arrhenius Concept

Soon after Arrhenius had proposed his concept of acids and bases, it was realized, that his concept has a limited scope only. This is because it attributes all acidic and basic properties to the formation of hydrogen and hydroxyl ions *in aqueous solution only*. However; there are substances such as NH_3, CaO etc. which do not contain the hydroxyl group but can still act as bases since they are known to neutralise acids. Similarly, there are substances such as carbon dioxide which cannot by themselves dissociate to form hydrogen ions but even then act as acids in aqueous solution.

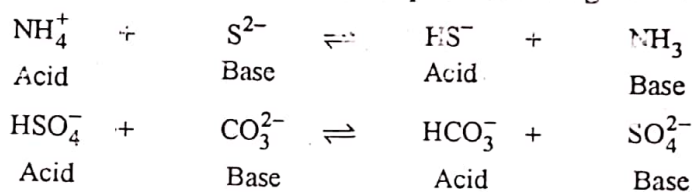## 4.8.1 Bronsted-Lowry Concept of Acids and Bases

In view of the limitations of Arrhenius concept, Bronsted and Lowry proposed more general definition for acids and bases. According to their concept *an acid is a substance (molecular or ionic) which has a tendency to donate a proton.* On the other hand, *a base is a substance (molecular or ionic) that has a tendency to accept a proton from any other substance.* For example, the behaviour of HCl and H_3COOH in water is shown below:

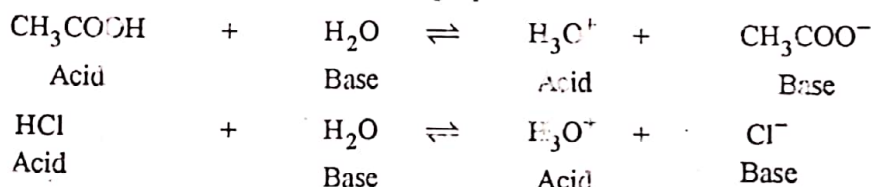$$HCl + H_2O \rightleftharpoons Cl^- + H_3O^+$$

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$
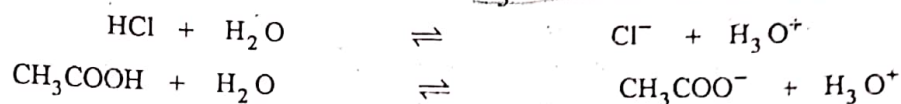
As HCl donates a proton to water, hence HCl is an acid. On the other hand, H_2O accepts a proton from HCl, hence H_2O is a base. Similarly H_3COOH donates a proton to H_2O and acts as an acid, whereas H_2O accepts a proton and acts as a base.

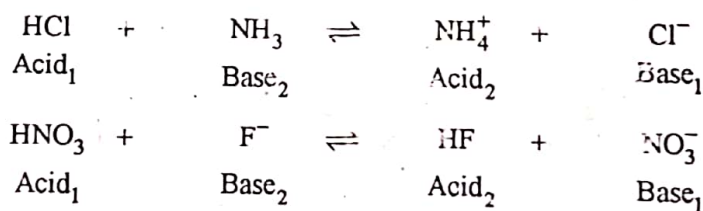The main features of Bronsted–Lowry concept are given as under:

1. An acid–base reaction involves the transference of a proton from a proton donor (acid) to a proton acceptor (base). Thus this concept is also called **proton transfer theory of acids and bases.**

2. Not only molecules but ions are also capable of acting as acids and bases. For example,

$$\underset{\text{Acid}}{NH_4^+} + \underset{\text{Base}}{S^{2-}} \rightleftharpoons \underset{\text{Acid}}{HS^-} + \underset{\text{Base}}{NH_3}$$

$$\underset{\text{Acid}}{HSO_4^-} + \underset{\text{Base}}{CO_3^{2-}} \rightleftharpoons \underset{\text{Acid}}{HCO_3^-} + \underset{\text{Base}}{SO_4^{2-}}$$

3. For an acid to act as a proton donor, a base (proton acceptor) must be present to receive proton. For example, acetic acid or HCl acts as an acid in water but not in benzene because benzene does not accept proton.
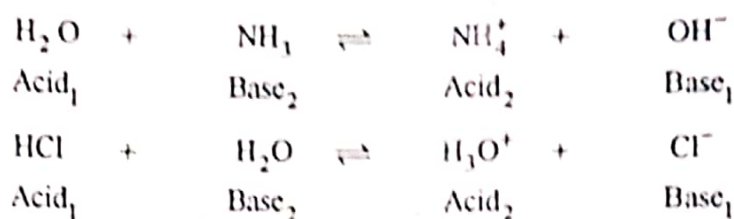
$$\underset{\text{Acid}}{CH_3COOH} + \underset{\text{Base}}{H_2O} \rightleftharpoons \underset{\text{Acid}}{H_3O^+} + \underset{\text{Base}}{CH_3COO^-}$$

$$\underset{\text{Acid}}{HCl} + \underset{\text{Base}}{H_2O} \rightleftharpoons \underset{\text{Acid}}{H_3O^+} + \underset{\text{Base}}{Cl^-}$$

4. Whenever an acid and a base reacts another pair of acid–base is formed e.g.,

$$\underset{\text{Acid}_1}{HCl} + \underset{\text{Base}_2}{NH_3} \rightleftharpoons \underset{\text{Acid}_2}{NH_4^+} + \underset{\text{Base}_1}{Cl^-}$$

$$\underset{\text{Acid}_1}{HNO_3} + \underset{\text{Base}_2}{F^-} \rightleftharpoons \underset{\text{Acid}_2}{HF} + \underset{\text{Base}_1}{NO_3^-}$$

5. **Amphoteric compounds:** Certain molecules and ions may exhibit both acidic or basic behaviour under the appropriate conditions. Such species are known as amphiprotic or amphoteric. For example, water may lose a proton to a base such as NH_3 or gain a proton from an acid such as HCl and so it is classified as amphiprotic.

$$H_2O \ + \ NH_3 \ \rightleftharpoons \ NH_4^+ \ + \ OH^-$$
$$\text{Acid}_1 \qquad \text{Base}_2 \qquad \text{Acid}_2 \qquad \text{Base}_1$$

$$HCl \ + \ H_2O \ \rightleftharpoons \ H_3O^+ \ + \ Cl^-$$
$$\text{Acid}_1 \qquad \text{Base}_2 \qquad \text{Acid}_2 \qquad \text{Base}_1$$

Species like HSO_3^-, HS^-, HCO_3^- are amphoteric in nature.

6. Water has a dual character. It can behave as a base in presence of acid (say HCl) and as an acid in presence of a base (say NH_3) as shown above. Its dual behaviour can be represented as:

$$H_2O \ + \ H_2O \ \rightleftharpoons \ H_3O^+ \ + \ OH^-$$
$$\text{Acid}_1 \qquad \text{Base}_2 \qquad \text{Acid}_2 \qquad \text{Base}_1$$

7. All Bronsted acids are Arrhenius acids but Bronsted bases are not Arrhenius bases. Bronsted acids are proton donors. In other words, it releases proton to some substance acting as base. Arrhenius acids also release H^+ ions (protons) in aqueous solutions. Thus Bronsted acids are Arrhenius acids. But Bronsted bases are proton acceptors, whereas Arrhenius bases should release OH^- ions in aqueous solution. A Bronsted base may or may not have OH^- ions.

Conjugate acid-base pairs

When an acid loses a proton, it forms what is called conjugate base of the acid. For example,

Acid		Proton		Conjugate base
HCl	$\rightarrow$	H^+	$+$	Cl^-
CH_3COOH	$\rightarrow$	H^+	$+$	CH_3COO^-
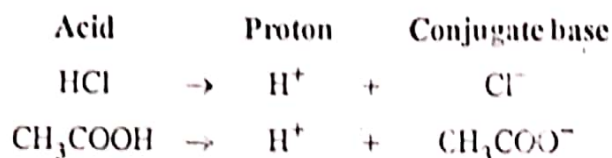
When a base accepts a proton, it forms what is called the conjugate acid of the base. For example,

| Base		Proton		Conjugate acid
H_2O	$+$	H^+	$\rightarrow$	H_3O^+
NH_3	$+$	H^+	$\rightarrow$	NH_4^+
CO_3^{2-}	$+$	H^+	$\rightarrow$	HCO_3^-
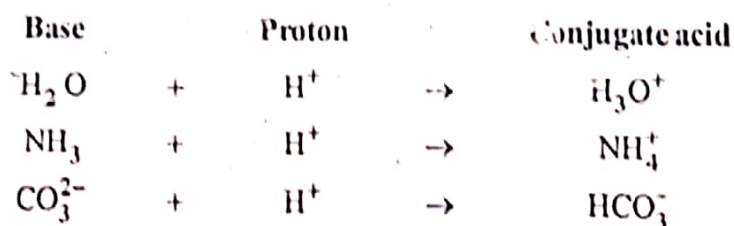
Now an acid does not form its conjugate base unless a second base (Base_2) is present to accept a proton. When the second base (Base_2) accepts the proton, it forms its conjugate acid, i.e., Acid_2. For example,

$$HCl \ + \ H_2O \ \rightleftharpoons \ H_3O^+ \ + \ Cl^-$$

In the forward reaction, HCl donates a proton and thus behaves as an acid, water accepts a proton and thus behaves as a base. In the reverse reaction, H_3O^+ donates a proton to chloride ion and thus H_3O^+ is an acid while Cl^- is a base. Such pairs of substances which are

formed from one another by gain or loss of a proton are known as **conjugated acid–base pairs.** Thus hydrochloric acid is a conjugate acid of chloride ion while water is a conjugate base of hydronium ion.

In general, each acid base reaction involves two pairs of acids and bases as shown below:

Bronsted Acid + Bronsted Base = Conjugate Acid + Conjugate Base
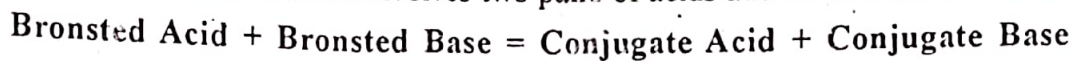
This is illustrated with the following examples:

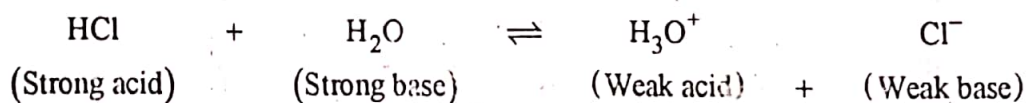| Bronsted Acid		Bronsted Base		Conjugate Acid		Conjugate Base
HCl	+	H_2O	$\rightleftharpoons$	H_3O^+	+	Cl^-
HCl	+	NH_3	$\rightleftharpoons$	NH_4^+	+	Cl^-
H_2O	+	CO_3^{2-}	$\rightleftharpoons$	HCO_3^-	+	OH^-
H_2O	+	H_2O	$\rightleftharpoons$	H_3O^+	+	OH^-

Polyprotic acid

Some acids can furnish two or more protons. These are called polyprotic acid, e.g. H_2SO_4 is a diprotic acid while H_3PO_4 is a triprotic acid. These acids always dissociate in stages. Each stage furnishes only one proton so that Bronsted concept is applied to each stage of dissociation of such acids. For example dissociation of H_3PO_4 takes place in three stages:

Conjugate Acid		Conjugate Base		Conjugate Acid		Conjugate Base
H_3PO_4	+	H_2O	$\rightleftharpoons$	H_3O^+	+	$H_2PO_4^-$
$H_2PO_4^-$	+	H_2O	$\rightleftharpoons$	H_3O^+	+	HPO_4^{2-}
HPO_4^{2-}	+	H_2O	$\rightleftharpoons$	H_3O^+	+	PO_4^{3-}

Relative Strengths of Conjugate Acids and Bases

It is observed that if an acid is strong its conjugate base is weak and vice versa. For example, HCl is a strong acid, its conjugate base, Cl⁻ ion, is a weak base.

$$HCl \quad + \quad H_2O \quad \rightleftharpoons \quad H_3O^+ \qquad Cl^-$$
(Strong acid)   (Strong base)   (Weak acid)   +   (Weak base)

On the other hand, acetic acid is a weak acid but its conjugate base, acetate ion, is a strong base.

$$CH_3COOH \quad + \quad H_2O \quad \rightleftharpoons \quad CH_3COO^- \qquad H_3O^+$$
(Weak)   (Weak)   (Strong)   +   (Strong)
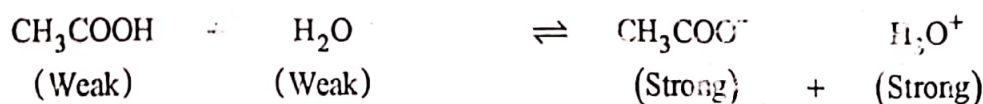
Limitation of Bronsted-Lowry Theory

The theory fails to explain acid-base reactions in which no proton transfer takes place, e.g., the reaction:

$$CaO \quad + \quad SO_3 \quad \longrightarrow \quad CaSO_4$$

involves the neutralisation of basic oxide (CaO) with acidic oxide (SO_3) to form a salt ($CaSO_4$) without any transfer of proton between them.

Similarly, reactions taking place in non-aqueous solvents cannot be explained by this theory, e.g.:

$$SO_2 \quad + \quad SO_2 \quad \rightleftharpoons \quad SO^{2+} \quad + \quad SO_3^{2-}$$
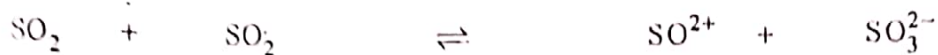
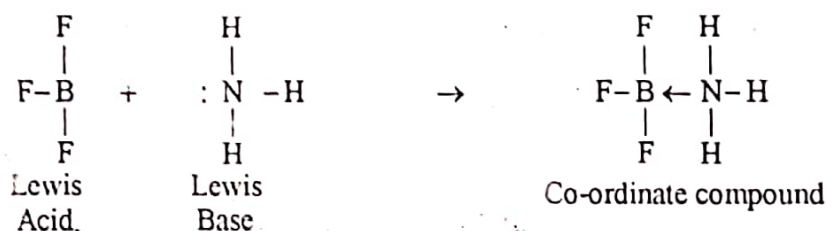## 4.8.2 Lewis Concept of Acids and Bases

The Arrhenius as well as Bronsted-Lowry concepts limit classification of acid as substances which contain hydrogen. But G.N. Lewis put forward a more general concept which does not require hydrogen to be an essential constituent of all acids. According to Lewis, *an acid is a substance which can accept a pair of electrons while a base is a substance which can donate a pair of electrons to form a coordinate or dative bond.*

In other words, a base is an electron donor while an acid is an electron acceptor. This is the most fundamental of acid-base concepts and includes all other concepts.

A base according to Lewis, is any substance with one or more lone pairs of electrons. It may be a neutral molecule such as: NH_3 or a negative ion such as: CN^- ion. It may be noted that any substance which can donate a pair of electrons can easily accept a proton. This means that a Lewis base is a Bronsted base.
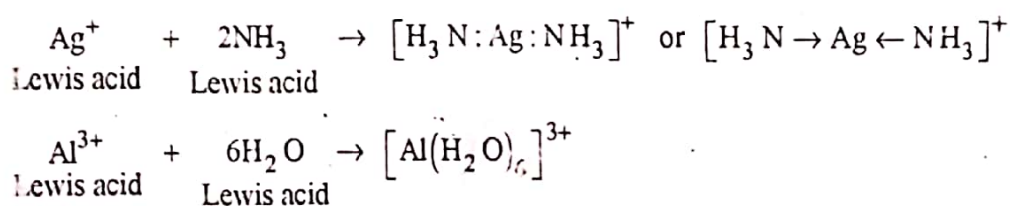
Examples of Acid–base reactions:

(i) The molecule of a Lewis acid with a central atom having incomplete octet, and a Lewis base with one or more unshared pairs of electrons, BF_3 and $AlCl_3$ are examples of Lewis acids of this type.

$$
\begin{array}{ccccc}
\text{F} & & \text{H} & & \text{F}\quad\text{H} \\
| & & | & & |\quad\ | \\
\text{F--B} & + & :\text{N --H} & \rightarrow & \text{F--B} \leftarrow \text{N--H} \\
| & & | & & |\quad\ | \\
\text{F} & & \text{H} & & \text{F}\quad\text{H} \\
\text{Lewis} & & \text{Lewis} & & \text{Co-ordinate compound} \\
\text{Acid.} & & \text{Base} & &
\end{array}
$$

(ii) The molecule of a Lewis acid containing multiple bonds, e.g., SO_3 has multiple bonds. It is not an Arrhenius or Bronsted acid. It is a Lewis acid and neutralizes bases.

$$
\underset{\text{Lewis base}}{Ca^{2+} O^{2-}} \quad + \quad \underset{\text{Lewis acid}}{SO_3} \quad \rightarrow \quad \left[SO_4^{2-} \right] Ca^{2+}
$$
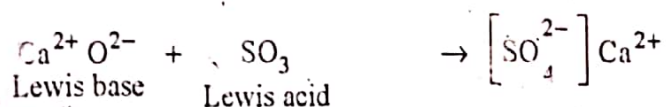
(iii) **Simple cations:** Simple cations like Al^{3+}, $Ag+$, act, as lewis acids, because they have empty orbitals in their outermost energy levels.

$$
\underset{\text{Lewis acid}}{Ag^+} \quad + \quad \underset{\text{Lewis acid}}{2NH_3} \quad \rightarrow \quad \left[H_3 N : Ag : NH_3 \right]^+ \text{ or } \left[H_3 N \rightarrow Ag \leftarrow NH_3 \right]^+
$$

$$
\underset{\text{Lewis acid}}{Al^{3+}} \quad + \quad \underset{\text{Lewis acid}}{6H_2O} \quad \rightarrow \quad \left[Al(H_2O)_6 \right]^{3+}
$$

(iv) The molecule of a Lewis acid having central atom with empty d-orbitals. Sn in $SnCl_4$ has empty d- orbitals which are used up to make $SnCl_4$ a Lewis acid, the base is a negative ion, Cl^-, F^-.

$$SnCl_4 + 2Cl^- \rightarrow SnCl_6^{2-}$$
$$\text{Lewis} \quad \text{Lewis}$$
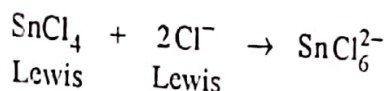
Limitations of Lewis concept:

1. It is very general and includes all the co-ordination compounds and reactions. Protonic acids do not form co-ordinate bond with bases.

2. Acid-base reactions are quite fast. But the reactions taking place forming co-ordinate compound are very slow. Thus it does not fit in normal acid-base concept.

3. The catalytic action of acids in different reactions is due to H^+ ions. Lewis acid may not contain hydrogen, so, they cannot act as catalysts.

4. The essential requirement or the main feature of Lewis concept of acid is the formation of co-ordinate bond with bases. However, protonic acids (H_2SO_4, HCl) do not form co-ordinate bond with bases. This is against Lewis theory.

Lewis – Bases are essentially Bronsted Bases because all such substances, e.g., NH_3, CN^-, etc., are also capable of accepting a proton. But Bronsted acids are not Lewis-acids.
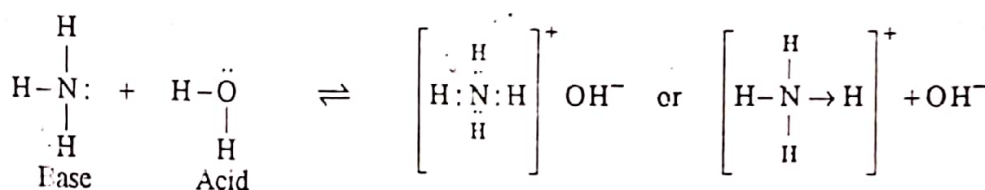

Water in the above reaction acts as Bronsted acid (donates a proton). However, water is not Lewis acid (does not accept electron pair).
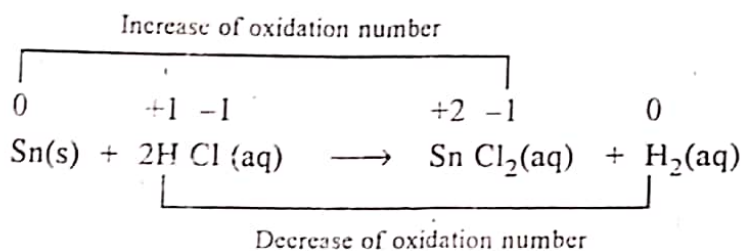
4.9 OXIDATION AND REDUCTION

Oxidation : Earlier oxidation was treated as any process involving addition of oxygen or removal of hydrogen from a substance. However, these days oxidation is defined as a process which involves the loss of electrons by a substance. Consequently, there is an increase in positive charge or decrease in negative charge of the atom or ion which undergoes oxidation. For example,

(i) *Loss of electrons resulting in an increase in positive charge*

$$Zn \longrightarrow Zn^{2+} + 2e^-$$

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$

$$Sn^{2+} \longrightarrow Sn^{4+} + 2e^-$$
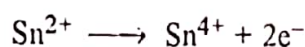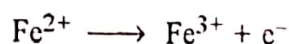
Therefore, any reaction involving charges in oxidation numbers is an oxidation reduction or Redox reaction. For example, consider the reaction

Increase of oxidation number

$$
\begin{array}{ccccc}
0 & +1 \ -1 & & +2 \ -1 & 0 \\
Sn(s) & + \ 2H \ Cl \ (aq) & \longrightarrow & Sn \ Cl_2(aq) & + \ H_2(aq)
\end{array}
$$

Decrease of oxidation number

As may be seen, Sn is converted to Sn^{2+}(aq) by losing two electron and gets oxidized. On the other hand H^+ ions gained one electron and gets reduced. It may also be seen that oxidation number of Sn increases from 0 to +2 when it gets oxidized. The oxidation number of H^+ decreases from +1 to 0 when it gets reduced. Therefore, *oxidation is an increase in oxidation number while reduction is decrease in oxidation number.* In the above reaction, HCl acts as *oxidising agent* while Sn acts as *reducing agent.*

4.10 SOLUBILITY EQUILIBRIA

When dissolved in suitable solvents electrolytes undergo dissociation to form charged chemical species known as *ions.* But this dissociation into ions seldom takes place to completion due to reversible nature of the process. In fact, the extent of dissociation is different in different cases. Electrolytes such as NaCl and HCl which are almost completely ionised into ions is called *strong. electrolyte.*

On the other hand, electrolytes such as acetic acid (CH_3COOH) where the degree of dissociation is low. Such substances which dissociate to a small extent in aqueous solution and hence conduct electricity to a small extent are called *weak electrolytes.*

In the solutions of weak electrolytes, an equilibrium is established between the ions in solution and the undissociated molecules. This is known as *ionic equilibrium.* Therefore, *ionic equilibrium is the equilibrium which is established between the undissociated molecules and the ions the solution of weak electrolytes.*

The fraction of the total number of molecules which is ionised at the equilibrium state is known as the *degree of dissociation or ionisation.* It is usually represented by the symbol α.

$$\alpha = \frac{\text{No. of dissociated molecules}}{\text{Total No. of molecules}}$$

and   Percentage dissciation $= \dfrac{\text{No. of dissociated molecules}}{\text{Total No. of molecules}} \times 100$

### Different types of Ionic Equilibria

Reactions involving ionic equilibrium may be classified as follows:

1. Equilibria involving soluble ionic compounds such as weak acids and weak bases.
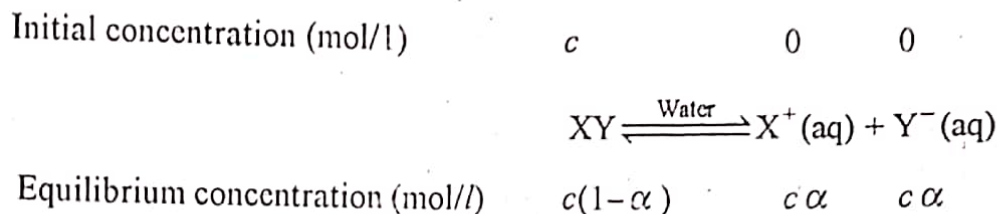2. Equilibria involving sparingly soluble ionic compounds: solubility product.

In this chapter, we shall be discussing them as under:

1. **Equilibria involving soluble ionic compounds such as weak acids and weak bases.:** Let a weak electrolyte XY be dissolved in water, its ionisation may be represented as:

$$XY \xrightleftharpoons{\text{Water}} X^+(aq) + Y^-(aq)$$
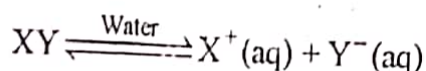
Let the original concentration of XY prior to dissociation be c moles per litre and let α be the degree of dissociation at equilibrium. Then the concentrations of the various species will be as shown below :

Initial concentration (mol/l) c 0   0

$$XY \xrightleftharpoons{\text{Water}} X^+(aq) + Y^-(aq)$$

Equilibrium concentration (mol/l) $c(1-\alpha)$ $c\alpha$ $c\alpha$

Applying the law of chemical equilibrium, we have

$$K_c = \frac{[X^+][Y^-]}{[XY]} = \frac{c\alpha \times c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

where K_c is known as *dissociation constant*. ✓

If α is very small as compared to unity, the value of $\underline{a}$ may be neglected in the denominator, i.e., $1-\alpha$ may be taken equal to 1. In that case :

$$K_c = c\alpha^2 \quad \text{or} \quad \alpha^2 = \frac{K_c}{c}$$

or

$$\alpha = \sqrt{\frac{K_c}{c}} \quad \text{or} \quad \alpha \propto \sqrt{\frac{1}{c}}$$

Thus, it may be seen that the degree of ionisation of a weak electrolyte is inversely proportional to the concentration of the solution. This means that the degree of ionisation would increase with dilution and would approach unity in very dilute solutions. This means that all electrolytes are almost completely ionised in very dilute solutions

2. **Equilibria involving sparingly soluble ionic compounds : Solubility Product:** All electrolytes dissolve in water. Substances like AgCl, $BaSO_4$, etc. which dissolve ioan extremely small extent are called sparingly soluble. When a sparingly soluble salt like AgCl is treated with water, an extremely small amount of it dissolves. The solution is, therefore, saturated with respect to AgCl although it is very very dilute. But whatever little AgCl dissolves, splits into ions and an equilibrium is set up between the undissolved AgCl and its ions. Thus, even very dilute solutions of sparingly soluble salts are saturated and there exists an equilibrium between the undissolved salt and its ions.

Let us now consider a general case of a sparingly soluble salt, say AB. When this salt is dissolved in water to get a saturated solution at a particular temperature, there exists an equilibrium between the undissolved solid salt and the ions A^+ (aq) and B^- (aq) in solution. This can be represented as :

$$AB(s) \underset{}{\overset{Water}{\rightleftharpoons}} A^+ (aq) + B^- (aq)$$

Applying the Law of Mass Action, we have :

$$K_c \approx \frac{[A^+][B^-]}{[AB]_{solid}}$$

Since the molar concentration or active mass of a solid is taken as constant (say k), we may rewrite the above equation as :

$$K_c = \frac{[A^+][B^-]}{k}$$

or
$$K \times k = [A^+][B^-] = K_{sp}$$

The constant K_{sp} is known as *solubility product*. It is equal to the product of ionic concentrations, termed as *ionic product*, for a saturated solution.

In general, for any sparingly soluble salt AxBy, which dissociates to set up the equilibrium

$$A_x B_y \rightleftharpoons xA^{y+} \, yB^{x-}$$
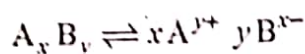
The solubility product may be expressed as :

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

where A^{y+} and B^{x-} denote the positive and negative ions respectively and x and y represent the number of these ions in the formula or the electrolyte

Thus, the solubility product of a salt at a given temperature may be defined *as the product of the concentrations of its ions, in a saturated solution, each concentration raised to a power equal to the number of times each ion occurs in the equation for the dissociation of the salt.*

It may be borne clearly in mind that both the terms ionic product and solubility product represent the product of the concentrations of the ions of the salt in the solution. But the term ionic product applies to all kinds of solutions whether unsaturated or saturated so that its value is not definite. The term solubility product, however, applies only to a saturated solution and has a definite value. It is, therefore, the ionic product of a saturated solution.

It may be noted that the K_{sp} of any electrolyte is independent of the source of the ions. However, the product of the concentration of the ions in any solution cannot be more than K_3 irrespective of the nature of the source of the ions. If the concentration of either one or both types of ions is increased so that the ionic product temporarily exceeds the solubility product the excess ions at once combine with oppositely charged ions and the solid salts separate out. Thus, the concept of solubility product fixes the relative values of ionic concentrations in a saturated solution even when the ions are furnished by different electrolytes producing the required ions.

4.10.1 Calculation of Solubility Product

The value of solubility product can be easily calculated if the concentration of ions present in saturated solutions are known as illustrated below.

Example 13. The solubility of $Mg(OH)_2$ is 1.518×10^{-4} moles per litre at 285 K. Calculate its solubility product at this temperature.

Solution. We know that : $Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$

It is obvious that the concentration of Mg^{2+} ions is the same as that of $Mg(OH)_2$ while that of OH^- ions is twice that of $Mg(OH)_2$.

$$[Mg^{2+}] = [Mg(OH)_2] = 1.518 \times 10^{-4} \text{ moles/litre}$$

$$[OH^-] = 2 \times [Mg(OH)_2]$$
$$= 2 \times 1.518 \times 10^{-4} = 3.036 \times 10^{-4} \text{ moles/litre}$$

Hence $K_v = [Mg^{2+}].[OH^-]^2 = [1.518 \times 10^{-4}] [3.036 \times 10^{-4}]^2 = 1.4 \times 10^{-11}$

4.10.2 Applications of Solubility Product

The concept of solubility product has been very helpful in studying the reactions involving ionic equilibria. The more important applications are discussed below :

(i)   **Calculation of Solubility.** Knowing the solubility product of a salt at a particular temperatures, its solubility can be readily calculated as explained below.

Example 14. Calculate the solubility of silver chloride in water at room temperature if solubility product of AgCl is 1.6×10^{-10}.

Solution. The solubility equilibrium may be shown as :

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$
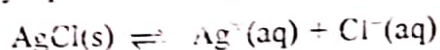
Let the solubility of silver chloride in water be c moles per litre. Therefore, the solution would contain c moles of Ag^+ ions and c moles of Cl^- ions per litre, since one mole of AgCl produces one mole each of Ag^+ and Cl^- ions. Hence, the solubility product, K_{sp} of silver chloride would be given by the expression :

$$K_{sp} = [Ag+] [Cl^-] = c \times c = c^2$$

But the actual value of solubility product is 1.6×10^{-10}

So, $c^2 = 1.6 \times 10^{-10}$

$$c = \sqrt{1.6 \times 10^{-10}} = 1.26 \times 10^{-5} \text{ moles/litre.}$$

As one mole of AgCl is equal to 143.5 g, therefore c may also be expressed as :

$$c = 143.5 \times 1.26 \times 10^{-5} \text{ g/litre} = 0.0018 \text{ g/litre.}$$

(ii)   **Predicting thePrecipitation of Reactions.** As already pointed out, the solubility product represents the upper limit of ionic product for a saturated solution of a salt and this value cannot be exceeded if the ions are to remain in solution. In other words, if the *ionic product exceeds the solubility product even momentarily, the excess ions immediately combine with oppositely charged ions and the solid salt precipitates*

...out. This serves as an importan. guiding principle in following the course of ionic reactions. For instance, let us find out what happens when 10 ml of 0.2 M solution of sodium sulphate is mixed with an equal volume of 0.1 M barium chloride solution. Will a precipitate of barium sulphate be formed or will it not be formed ?

The solubility equilibrium of $BaSO_4$ may be written as :

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$
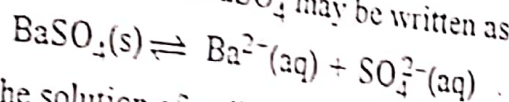
To start with, the solution of sodium sulphate contains 0.2 mole per litre of SO_4^{2-} ions while the solution of barium chloride contains 0.1 mole per litre of Ba^{2+} ions. But on mixing the two solutions, the total volume is doubled and as a result the concentration of each of the ions is reduced to one half. Therefore, the resulting solution contains 0.1 mole per litre of SO_4^{2-} ions and 0 05 mole per litre of Ba^{2+} ions.

Product of ionic concentration $= [0.1] [0.05] = 0.005 = 5 \times 10^{-3}$

But the solubility product of $BaSO_4$ is 1.0×10^{-10}

Since the ionic product far exceeds the solubility product, barium sulphate gets precipitated. In short,

- A precipitate is formed if ionic product is greater than K_{sp}.
- A solution is just saturated if ionic product is equal to K_{sp}
- A solution is unsaturated (no ppt. formed) if ionic product is less than K_{sp}.

iii) Inorganic Qualitative Analysis. The solubility product concept plays a very important role in inorganic qualitative analysis. It enables us to effect the selective precipitation of salts in different groups which forms the basis of the scheme for the analysis of cations. For example, the basis of grouping Pb^{2+}, Ag^- and Hg^+ together in group I is that their chlorides have very low solubility products. As such they are practically insoluble in water and are, therefore, readily precipitated on adding dilute hydrochloric acid to the solution of the salt.

4.10.3 Comparison of Solubility Product with Ionic Product

The main points of difference between solubility product and ionic product are listed in Table 4.2.

Table 4.2. Comparison of solubility product with ionic product

Solubility product	Ionic product
1. It is product of the concentrations of the ions of an electrolyte, each raised to the appropriate power in saturated solution.	1. It is the product of the concentration of the ions of an electrolyte each raised to the appropriate power in any solution.
2. It is applicable to only saturated solutions.	2. It is applicable to all types of solutions which may be unsaturated or saturated.