CONTENT

Chapters **Page No.**

SECTION – A

SECTION – B

SECTION – C

SECTION – D

SECTION – A

1

SOME BASIC CONCEPTS OF CHEMISTRY

LEARNING OBJECTIVES

- Chemistry and its Importance
- Classification of Matter
- Chemical Equations
- Stoichiometry ; Calculations Based on Chemical Equations
- Concept of Limiting Reagent

1.1 CHEMISTRY AND ITS IMPORTANCE

Man has been exposed to the changing surrounding over since he came into existence. He has been very curious to know about his surroundings and to study and rationalize the events occurring around him. This curiosity has led him to collect information through experiments and observations. It has also been responsible for the research activities of various people all over the world through ages. It was quite essential to systematize and arrange the knowledge gained like this for the benefit of mankind. This knowledge is referred to as science. **Science** may, thus, be defined as *systematized knowledge gained by mankind through observations and experimentation.* Science has been further classified into *different* branches due to its enormous expansion and diversified fields. *Chemistry* is one of the most important disciplines of science. **Chemistry** may be defined as the branch of science ***which deals with the study of matter, its composition, its properties and the changes which it undergoes in composition as well as in energy during various processes.*** Chemistry has been further divided into different branches depending upon specialize fields of study. The various branches of chemistry are

I. **Inorganic Chemistry.** This branch deals with the study of compounds of all other elements except carbon. It mainly deals with the study of minerals found in the crust of the earth.

II. **Organic Chemistry.** This branch deals with the study of carbon compounds especially hydrocarbons and their derivatives.

III. **Physical Chemistry.** This branch deals with the explanation of fundamental principles governing various chemical phenomena. It is basically concerned with the laws and theories of different branches of chemistry.

IV. **Industrial Chemistry.** This branch deals with the chemistry involved in industrial processes.

V. **Analytical Chemistry.** This branch deals with the qualitative and quantitative analysis of various substances.

VI. **Bio-chemistry.** This branch deals with the chemical changes going on in the bodies of living organisms ; plants and animals.

VII. **Nuclear Chemistry.** This branch deals with the study of nuclear reactions, such as nuclear fission, nuclear fusion, transmutation processes, etc.

In addition to above branches there are other branches of chemistry developed in recent years. These include, *pharmaceutical chemistry, geo-chemistry, agricultural chemistry, medicinal chemistry, solid state chemistry etc.*

Importance of Chemistry

Chemistry plays very significant role in almost all walks of life. Our daily life involves the use of many chemical products and many chemical changes although we are unaware of them. Some of the major contributions of chemistry to the life in modern word are as given below:

1. Chemistry in medicines. Modern chemical discoveries have done a lot to eradicate diseases and to improve health.
Some important contributions of chemistry in the field of medicines are development of

- *Life saving drugs* like **taxol** and **cisplatin** (used in cancer therapy); **azidithy-midine** (AZT) used for AIDS victims.
- *Prophylatics, i.e.,* disease preventing screen and vaccines.
- *Anaesthetics* and *antiseptics.*
- *Disinfectants* and *germicides.*

2. Chemistry in industry. Chemistry plays an important role in almost all industrial processes. Some important examples are manufacture of:

- *Synthetic fibers* like rayon, nylon, dacron, orlon, etc.,
- *Plastics* like bakelite, teflon, polythene, etc.,
- *Paints, varnishes, enamels, dyes*, etc.,
- *Cement, glass* and *ceramics* and *extraction of metals* like silver, magnesium, gold iron, etc.

3. Chemistry in agriculture. The major contribution of chemistry in the field of agriculture is the use of:

- *Chemical fertilizers* like urea, ammonium sulphate, calcium nitrate, etc., for the better yields of crops.
- *Insecticides* such as D.D.T., gammexane, methoxychlore, etc., for the protection of crops from insects and in the safe storage of foodgrains.
- *Presevatives* like sodium benzoate, sodium metabisulphate and salicylic acid for better preservation of food and check its wastage.

4. Chemistry in comfort, convenience and pleasure. In every walk of life the chemistry has been the poineer contributor towards the happiness of man. It has helped us in getting a number of amenities. Some examples are :

- *Domestic requirements* such as paper, fabrics, soaps, cosmetics, oils, flavouring essences, dyes and perfumes.
- *Air conditioning.* To keep efficient in all seasons we make use of air-conditioning. In this we use chemical substances like liquid ammonia or liquid sulphur dioxide.

5. Chemistry and energy resources. The energy resources of the world are *petroleum, coat, wood, nuclear fuels.* The reserves of coal and petroleum are being exhausted at a fast speed. Therefore, attempts are being made by chemists to utilize the *nuclear energy* and *solar energy* for meeting our requirements. Hydrogen from sea water may provide an inexhaustible source for future energy needs.

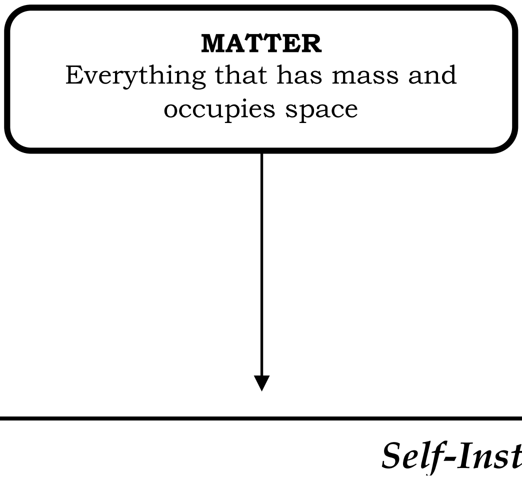
1.2 CLASSIFICATION OF MATTER

In our daily life, we come across many objects, the knowledge about which can be gained by one or more of our senses like sight, touch, hearing, taste and smelling. These objects possess mass, occupy space and may have different shapes, sizes and colours. All these objects constitute matter. **Matter** may thus, be defined as **anything that occupies space, possesses mass, offers resistance and can be felt by one or more of our senses.** Some examples of matter are, water, air, metals, plants, animals, etc. Thus, matter has countless forms. The matter can be classified into different categories depending upon its physical or chemical nature. In this unit we shall discuss about the classification of matter on the basis of chemical nature of substances.

Chemical Classification of Matter

This classification of matter is based upon chemical composition of various substances. According to this matter can be classified into two major categories, *pure substances* and *mixtures.* Pure substances can be further divided into two types, elements and compounds. Mixtures are also of two types, homogeneous mixtures and heterogeneous mixtures.

The classification of matter is summarised in Fig. 1.1.



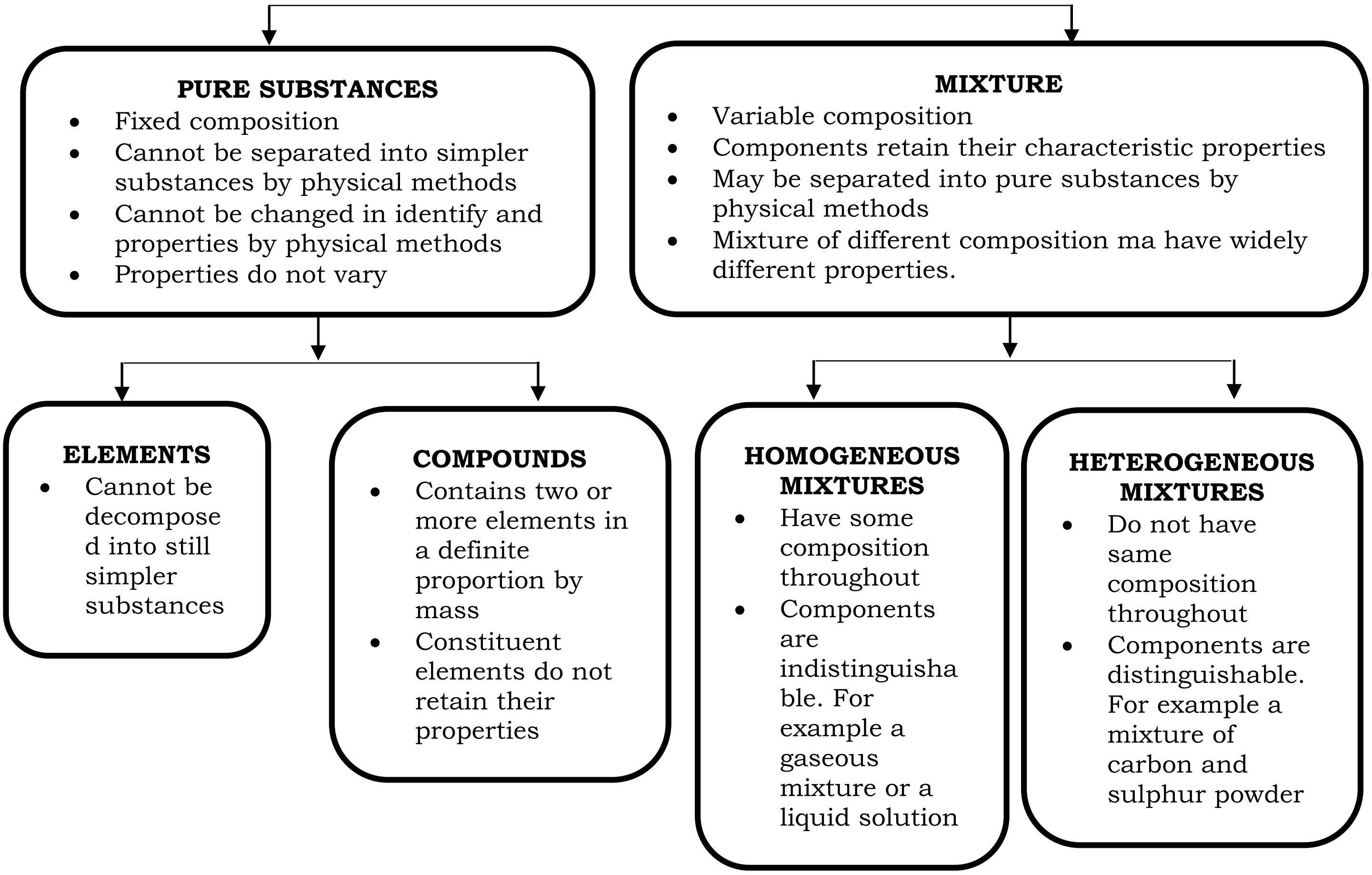


Fig. 1.1. Classification of matter

Elements

Lavoisier, the French chemist, carried out quantitative studies of many reactions by determining the masses or reactants and products. On the basis of his studies he classified pure substances into elements and compounds. A substance which could be decomposed into simpler substances by some reaction was classified as a compound while a substance which could not be split up into still simpler substances was referred to as element.

Lavoisier showed that when mercuric calx (mercuric oxide) is heated it changes into mercury and oxygen.

Mercuric oxide → Mercury + Oxygen.

Thus, mercuric oxide is a compound. Mercury and oxygen, on the other hand, could not be further decomposed into simpler substances. Therefore, mercury and oxygen elements.

An **element** may, thus, be defined as a ***pure substance which can neither be decomposed into nor built from simpler substances by any physical or chemical method.***

The above definition, however, is not in agreement with the facts that some of the elements have been synthesized by modern techniques like transmutation. In the light of discovery of atom as a fundamental unit of matter, an ***element*** may be defined as a ***pure substance made of only one kind of atoms.***

There are only 114 elements known so far. Out of 114 elements 92 occur in nature whereas the remaining have been artificially prepared. All the elements do not exist in equal abundance. Some elements like silicon, oxygen, aluminium, iron, carbon, hydrogen, calcium etc., occur more commonly. Over 90 per cent of human body is composed of only three elements namely, carbon, hydrogen and oxygen. Major portion of the earth is made up of only five elements : oxygen, silicon, aluminium, iron and calcium. List of some common elements alongwith their symbols is given in Table 1.1.

Table 1.1. Some Common Elements

Elements	Symbols	Elements	Symbols
Aluminium	AI	Oxygen	O
Arsenic	As	Phosphorus	P
Barium	Ba	Sulphur	S
Bromine	Br	Zine	Za
Calcium	Ca	(*Symbols and Latin names)*	
Carbon	C	Antimony *(Stibium)*	Sb
Chlorine	CI	Copper *(Cuprum)*	Cu
Chromium	Cr	Gold *(Aurum)*	Au
Cobalt	Co	Iron *(Ferrum)*	Fe
Fluorine	F	Lead *(Plumbum)*	Pb
Hydrogen	H	Mercury *(Hydrogyrum)*	Hg
Iodine	I	Potassium *(Kalium)*	K
Magnesium	Mg	Silver *(Argentum)*	Ag
Manganese	Mn	Sodium *(Natrium)*	Na
Nitrogen	N	Tin *(Stannum)*	Sn
Nickel	Ni	Tungsten *(Walfram,* a German name)	W

Elements can be further divided into following types:

a. **Metals.** These are generally solids and have characteristics such as *hardness, malleability, ductility, high tensile strength, lustre and ability to conduct heat and electricity.* Copper, iron, aluminium, silver, zine, etc., are common examples.

b. **Non-metals.** These are generally, *non-lustrous, brittle, poor conductors of heat and electricity.* Sulphur phosphorus, nitrogen, hydrogen, oxygen, etc., are common examples.

c. **Metalloids.** These elements have characteristics common to metals as well as non-metals. Arsenic, tin, bismuth, antimony are common examples.

Compound

A **compound** may be defined as ***a pure substance which can be decomposed into simpler substances by some suitable chemical technique. A compound is formed by combination of two or more elements in a definite proportion by mass.***

For example, water is a compound of hydrogen and oxygen elements and, these elements are present in water in the ratio of 1 : 8 by mass. Similarly, carbon and oxygen in carbon dioxide are present in the ratio of 3 : 8 by mass.

When a compound is formed, the constituent elements lose their properties. For example, *hydrogen* is combustible, *oxygen* is supporter of combustion but *water* which is a compound of hydrogen and oxygen is neither combustible nor supporter of combustion rather it extinguishes fire.

It may be noted that there are innumerable number of compounds although the number of elements constituting them are only 114. The compounds may further be classified broadly into two categories:

I. **Organic compounds.** Carbon element is the essential constituent of these compounds. They are originally obtained from living sources, i.e., animals and plants. Some examples are oils, fats, proteins etc.

II. **Inorganic compounds.** These compounds find their origin from non-ling sources such as minerals and rocks. Common salt, marble, gypsum, etc., are some examples.

Mixture

Mixtures may be defined as ***the substances which are made up of two or more pure substances. They can possess variable composition and can be separated into constituent components by some suitable physical means.*** For example, crude oil is a mixture of large number of different substances which can be separated by carrying out thorough fractional distillation. Mixtures are of two types, *homogeneous mixtures* and *heterogeneous mixtures.* **Homogeneous mixtures** *are the mixtures which have same composition throughout. These mixtures are also known as solutions.* The components of such a mixture cannot be seen even under a microscope, Some examples of homogeneous mixtures are air, gasoline, sea water, brass, coloured glass, ete. **Heterogeneous mixtures** *are the mixtures which have different composition in different parts.* In other words, components of such a mixture are not distributed uniformly. The components of a heterogeneous mixture can be observed with naked eyes or with the help of a microscope. Some examples of heterogeneous mixtures are sand and iron filings, sand and water, mud, etc.

1.3 CHEMICAL EQUATIONS

Brief representation of the chemical change in terms of symbols and formulae of the reactants and products is called a **chemical equation.**

When zinc reacts with hydrochloric acid, zinc chloride and hydrogen are produced.

Zinc + Hydrochloric acid → Zinc Chloride + Hydrogen

If symbols and formulae of various reactants and products are used, the above reaction may be represented as

$$Zn + HCl \rightarrow ZnCl_2 + H_2$$

However, we know from Dalton's atomic theory that atoms are neither created nor destroyed during chemical changes, therefore, the number of atoms of various elements should be equal on the reactant side and product side.

Equations (such as 1.1) in which no attempt has been made to equalize the number of atoms of various elements on both the sides are called **skeleton equations.**

In order to equalize the number of atoms of various elements the various species are multiplied with appropriate numbers. This process is called balancing of a chemical equation. Equation 1.1 can be balanced by multiplying HCl with 2.

$$Zn + 2HCI \rightarrow ZnCl_2 + H_2$$

A chemical equation in which the number of atoms of each element is equal on the reactant side and the product side is called a **balanced equation.**

Essentials of a Chemical Equation

A chemical equation must fulfil the following conditions:

a. *It should represent a true chemical change, i.e.,* if a reaction is not possible between certain substances, it cannot be represented by a chemical equation.
b. It should be balanced.
c. *It should be molecular, i.e.*, all the species should be represented in their molecular form. For example, elementary gases like hydrogen, oxygen, etc. should be represented as H_2 and 0_2.

Information Conveyed by a Chemical Equation

In order to understand the information conveyed by the chemical equation, consider the chemical reaction between nitrogen and hydrogen gases to form ammonia gas. The chemical equation for the reaction is as follows:

$\mathbf{N_2}$	+	$\mathbf{3H_2}$	→	$\mathbf{2NH_3}$
1 molecule		3 molecules		2 molecules

Multiply throughout by Avogadro's constant (6.02×10^{23})

6.02×10^{23}	$3 \times 6.02 \times 10^{23}$	$2 \times 6.02 \times 10^{23}$
N_2 molecule	H_2 molecule	NH_2 molecule
1 mol of nitrogen	3 mol of hydrogen	2 mol of ammonia

Convert mol into mass by multiplying with respective molar masses

28g of nitrogen	3 × 2 g of hydrogen	2 × 17 g of ammonia

Convert mol into volume at S.T.P. by multiplying with 22.4 L

22.4 L of N_2 at S.T.P.	3×22.4 L of H_2 at S.T.P.	2×22.4 L of NH_3 at S.T.P.

From the above discussion it follows that a chemical equation has both qualitative as well as quantitative significance.

1. **Qualitatively,** a chemical equation tells us the names of the various reactants and products
2. **Quantitatively,** it expresses
   a. The relative number of molecules of the reactants and products taking part in the reaction
   b. The relative number of moles of reactants and products.
   c. The relative masses of reactants and products.
   d. The relative volumes of gaseous reactants and products.

As an illustration, let us consider the following example:

$$2H_2 + 0_2 \rightarrow 2H_20$$

1. **Qualitatively,** it tells us that hydrogen and oxygen react to form water.
2. **Quantitatively,** it conveys the following information:
   a. Two molecules of hydrogen react with one molecule of oxygen to form two molecules of water.
   b. Two moles of hydrogen react with one mole of oxygen to form two moles of water.
   c. 4 g of hydrogen react with 32 g of oxygen to form 36 g of water.
   d. Two volumes of hydrogen react with one volume of oxygen to form two volumes of water vapours.

The chemical equation can be made more informative by incorporating the following changes :

a. The physical states of reactants and products can be indicated by using the abbreviations: (s) for solid, (l) for liquid, (g) for gas and (aq) for aqueous solution. For example,

$$Zn(s) + 2HCl\ (aq) \rightarrow ZnCl_2\ (aq) + H_2\ (g)$$

b. In order to indicate the strength of acid or base dil for dilute or cone for concentrated is written before the formula of acid or base.

$$Zn(s) + 2 \text{ dil } HCl\ (aq) \rightarrow ZnCl_2\ (aq) + H_2\ (g)$$

c. The reaction conditions, such as presence of catalyst, temperature, pressure, etc., may be written above the arrow between the reactants and products.

$$2SO_2(g) + O_2\ (g) \xrightarrow{V_2O_5,\ 775\ K} 2SO_3\ (g)$$

d. Heat change taking place during the reaction may be expressed in any of the following two ways:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) + 93.6\ kJ$$

or

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)\ ;\ \Delta H = -\ 93.6\ kJ.$$

Balancing of Chemical Equations

The balancing of chemical equations is based upon the law of conservation of mass and Dalton's atomic theory. According to Dalton's atomic theory atom is the smallest unit of an element that takes part in chemical reactions and that during chemical reactions atoms are neither created nor destroyed. Therefore, the number of atoms of each element should remain same before and after the reaction. During balancing the symbols and formulae of various species given in the equation are multiplied with appropriate numbers. The simple equations can be balanced by **Hit and trial** method. The following points should be kept in mind while balancing the chemical equations by this method:

1. If elementary gases like hydrogen, oxygen, etc., are involved in the equation, these are represented in their atomic form in the beginning and after balancing, the equation is changed to molecular form.
2. The formula which contains maximum number of elements is selected first and the stoms present in it are balanced.
3. If the above step fails, the atoms of that element which occurs at minimum number of places are balanced first. Atoms of the element which occurs at maximum number of places are balanced last of all.
4. While balancing the chemical equation, the chemical formula of any compound should not be changed for the sake of convenience because each compound has a fixed chemical formula.

In order to understand the application of above points let us consider, the reaction between iron and steam to form magnetic oxide and hydrogen. The skeleton equation for the reaction may be written as

$$Fe + H_2O \rightarrow Fe_30_4 + H_2$$

Changing the elementary substance hydrogen to atomic form, we get

$$Fe + H_2O \rightarrow Fe_30_4 + H$$

Selecting the compound Fe_3O_4, which has largest number of atoms, there are 3 atoms of Fe on right hand side, so Fe on left hand side is multiplied by 3. To balance oxygen H_2O is multiplied by 4. In 4 molecules of H_2O there are 8 atoms of H which are equalized by multiplying H on right hand side by 8. Thus, the balanced equation in atomic form will be

$$3Fe + 4H_2O \rightarrow Fe_30_4 + 8H$$

In order to convert the equation into molecular form, 8 atoms of H are written as 4 molecules

$$3Fe + 4H_2O \rightarrow Fe_30_4 + 4H_2$$

As another example, consider the decomposition of potassium chlorate, on heating, into potassium chloride and oxygen. The skeleton equation for the change may be written as

$$KCIO_3 \rightarrow KCI + O_2$$

Changing the elementary gas oxygen into atomic state, we get

$$KCIO_3 \rightarrow KCI + O$$

Selecting $KClO_3$, containing maximum number of atoms, potassium and chlorine atoms are already balanced. In order to balance o atoms, on the right hand side is multiplied by 3 and we get balanced chemical equation in atomic form.

$$KCIO_3 \rightarrow KCI + 3O$$

To change the equation into molecular form multiply the above equation by 2.

$$2KCIO_3 \rightarrow 2KCI + 3O_2$$

This is the balanced molecular equation.

Balancing of Equations by Partial Equation Method

The Hit and Trial method is quite successful in balancing the simple chemical equations, but the equations in which the some element is involved in the more number of compounds, cannot be easily balanced by this method. In such cases the partial equation method is more successful. The partial equation method involves the following steps:

i. Different probable steps are written for the given chemical equation. The chemical equations for probable steps are called partial equations.
ii. Each partial equation is separately balanced by hit and trial method.
iii. In order to cancel out the intermediate species (not involved in the final equation), the partial equation are multiplied by suitable integers.
iv. Partial equations are, then added to give final balanced equation.
v.

Let us apply these steps to balance the following chemical equation:

$$I_2, + HNO_3 \rightarrow NO_2 + HIO_3 + H_20$$

Probable steps for the equation are:

$$HNO_3 \rightarrow NO_2 + H_2O + O$$
$$I_2 + 0 \rightarrow I_20_5$$
$$I_20_5 + H_20 \rightarrow HIO_3$$

Balance the individual partial equations

$$2HNO_3 \rightarrow 2NO_2 + H_20 + 0$$
$$I_2 + 50 \rightarrow I_20_5$$
$$I_20_5 + H_20 \rightarrow 2HIO_3$$

In order to cancel out intermediate species, O multiply the first equation by 5 and add partial equations.

$$[2HNO_3 \rightarrow 2NO_2 + H_20 + 0] \times 5$$
$$I_2 + 50 \rightarrow I_20_5$$
$$I_20_5 + H_20 \rightarrow 2HIO_3$$
$$I_2 + 10HN_3 \rightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

1.4 STOICHIOMETRY ; CALCULATIONS BASED ON CHEMICAL EQUATIONS

We know that the chemical equation tells us the quantitative relationship between the reactants and the products. This quantitative information can be utilized to carry out variety of calculations which are required many a times, to assess the economic viability of a chemical process. Calculations based on the quantitative relationship between the reactants and the products are also referred to as **stoichiometry.** The term stoichiometry is derived from Greek words Stoicheion meaning element and metron meaning measure. Stoichiometry is, therefore, that area of chemistry and chemical technology on which determination of quantities of reactants and products of chemical reaction is based. In order to solve the problems based on chemical calculations the following steps, in general, are quite helpful.

i. Write the balanced chemical equation.
ii. From the chemical write the molar ratio between the given and required substance.
iii. Covert these moles into the desired parameters such as mass or volume.
iv. Calculate the final result by applying unitary method.

SOLVED EXAMPLE ON STOICHIOMETRY

Example 1.1. How many grams of oxygen (O_2) are required to completely react with *0.200 g* of *hydrogen* (H_2) to yield water (H_20) ? Also calculate the amount of water formed. *(AT. Mass H = 1; O = 16).*
Solution. The balanced equation for the reaction is

$$\begin{array}{ccccc} 2H_2 & + & O_2 & \rightarrow & 2H_2O \\ 2\text{ mol} & & 1\text{ mol} & & 2\text{ mol} \\ 4\text{ g} & & 32\text{ g} & & 36\text{ g} \end{array}$$

Now, 4g of H_2 require oxygen = 32g

0.200 g of H_2 require oxygen $= \frac{32}{4} \times 0.200 =$ **1.60 g**

Again, 4 g of H_2 produce H2O = 36 g

0.200 g of H_2 produce H2O $= \frac{32}{4} \times 0.200 =$ **1.80 g**

Example 1.2. What volume of oxygen at S.T.P. can be produce by 6.125 g of potassium chlorate according to the reaction $2\ KCIO_3 \rightarrow 2KCI + 3O_2$
Solution. The given chemical equation is :

$$\begin{array}{ccccc} 2KCIO_3 & \rightarrow & 2KCI & + & 3O_2 \\ 2\text{ mol} & & 2\text{ mol} & & 3\text{ mol} \\ 2 \times 122.5\text{ g} & & & & 3 \times 22.4\text{ L at S.T.P.} \end{array}$$

Now 245 g of $KCIO_3$ produce oxygen at S.T.P. = 3 × 22.4 L

6.125 g of $KCIO_3$ produce oxygen $= \frac{3 \times 22.4}{245} \times 6.125 =$ **1.68 L at S.T.P.**

SUMMARY

- **Matter.** Anything that occupies space and has mass.
- **Element.** A pure substance which can neither be decomposed into nor built from simpler substances by any physical or chemical method. It contains only one kind of atoms.
- **Compound.** A pure substance which can be decomposed into simpler substance by some suitable chemical method. It contains only one kind of molecules.
- **Mixture.** A substance obtained by simple mixing of two or more pure substances
- **Chemical Equation.** Representation of a chemical change in terms of symbols and formulae of the reactants and products.

- **Balanced Chemical Equation.** A chemical equation in which the number of atoms of each element is equal on the reactant side and the product side.
- **Essential of a Chemical Equation**
  - ✓ It should represent a true chemical change.
  - ✓ It should be balanced.
  - ✓ It should be molecular.
- **Stoichiometry.** It refers to the quantitative relationship between various species (reactants and product) involved in a reaction.

REVIEW QUESTIONS

1. What are the main difference between
(i) Element and Compound (ii) Compound and Mixture

2. Classify the following substances into elements, compound and mixtures. In case of mixture. In case of mixture indicate whether the mixture is homogeneous or heterogeneous.
(i) Iodized table salt (ii) Steel (iii) Smoke
(iv) 22-Carat gold (v) Mercury (vi) Brass
(vii) Diamond (viii) Sucrose (ix) Dry Ice
(x) Aerated drinks (xi) Sodium chloride (xii) Distilled Water.

3. Gum power is a mixture of sulphur, charcoal and potassium nitrate (KNO_3). How would you separate it into its constituents?
Hint. *Sulphur is soluble in CS_2 and is insoluble in water, KNO_3 is soluble in water. Charcoal is insoluble in both water as well as CS_2.*

4. How would you separate each of the following from a mixture with water?
(i) Charcoal (ii) Sugar (iii) Petrol

5. Classify the following substances as elements, compounds and mixtures. In case of mixtures clearly indicate whether the mixture is homogeneous of heterogeneous.
(i) Gasoline (ii) Tap Water (iii) Milk
(iv) Air (v) Sand (vi) Wood.

6. How would separate the following mistures?
(i) Salt and Water
(ii) Glass powder, iron filling and suger
(iii) Ammonium chloride and sodium chloride
(iv) KCI and I_2.

7. (i) What are the essential of a chemical equation?
(ii) What is the information conveyed by a chemical equation?

8. Balance the flowing equations:
(i) $Fe + H_2O \rightarrow Fe_3O_4 + H_2$
(ii) $Fe_2(SO_4)_3 + NH_3 + H_2O \rightarrow Fe(OH)_3 + (NH_4)_2SO_4$
(iii) $KMnO_4 + H_2SO_4 \rightarrow K_2SO_4 + MnSO_4 + H_2O + O_2$
(iv) $K_2Cr_2O_7 + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O + O_2$
(v) $I_2 + HNO_3 \rightarrow HIO_3 + NO_2 + H_2O$
(vi) $FeSO_4 + H_2SO_4 + HNO_3 \rightarrow Fe_2(SO_4)_3 + NO + H_2O$
(vii) $Zn + HNO_3 \rightarrow Zn(NO_3)_2 + N_2O + H_2O$.

9. What do you understand by the exam?
(i) Limitation reagent (ii) Molar solution.

10. 0.6 mol of Cu_2S is roasted in excess of oxygen to yield Cu and SO_2, according to reaction.

$$Cu_2S + O_2 \rightarrow 2Cu + SO_2$$

Calculate the mass of Cu formed.

2

STRUCTURE OF ATOM

LEARNING OBJECTIVES

- Introduction
- Discovery of the Electron – Cathode Rays
- Anode Rays or Canal Rays
- Rutherford's Nuclear Model of Atom
- Discovery of the Neutron
- Atomic Number and Mass Number
- Nature of Electromagnetic Radiations
- Particle Nature of Electromagnetic Radiation – Planck's Quantum Theory
- Atomic Spectrum
- Bohr's Model for Hydrogen Atom
- The Dual Nature of Matter
- Heisenberg's Uncertainty Principle
- Quantum Mechanical Model of Atom
- Quantum Numbers
- Shapes of Orbitals
- Pauli's Exclusion Principle
- Rules for filling or Orbitals in an Atom
- Electronic Configurations of Atoms
- Valence Bond Theory (VBT)
- Concept of Hybridisation
- Modern Periodic Law
- Long Form of Periodic Table
- IUPAC Nomenclature for Elements with Atomic Number, Z > 100
- Division of Periodic Table into *s*-, *p*-, *d*- and *f*- blocks on the Basis of Electronic Configurations.

2.1 INTRODUCTION

In the fifth century B.C. the Greek Philosopher Democritus proposed that all matter consists of very small indivisible particles called *atoms* (meaning uncuttable or indivisible). These earlier ideas were mere speculations and did not have any experimental basis. It was in 1808 that an English scientist, John Dalton formulated a precise definition of the indivisible building blocks of matter that are known as atoms. However, he did not say anything about internal structure of atoms and assumed atoms to be structure less particles. This concept of atom as structure less particles could not explain how atoms of different elements differ from one another; and also why and how atoms of different elements combine with one another. However, by the end of 19th century it was discovered that atoms consist of subatomic particles such electrons, protons and neutrons. The **protons** are positively charged particles and are present in the nucleas of the atom. The **electrons** are negatively charged particles and are present in the extra-nuclear part of the atom. The **neutrons** are neutral particles and are present in the nucleus along with the protons. Most of the mass of the atom is concentrated in the nucleus. In this unit, we shall discuss various development's which led to the evolution of model for the internal structure of atom.

2.2 DISCOVERY OF THE ELECTRON – CATHODE RAYS

Much of the information about electron is obtained from the study of cathode rays, which were discovered by Julius Plucker in 1859 during the experiments with gas discharge tubes. A discharge tube is long glass tube, such as shown in Fig. 2.1. This tube is fitted with metal electrodes on either and across which high voltage can be applied. The tube is also connected to a vacuum pump for controlling the pressure of gas inside the discharge tube.

When the gas pressure inside the discharge tube is one atmosphere, no electric current flows through the tube. If the pressure is reduced to about 10^{-2} atmospheres and a potential difference of about 10000 volts is applied to the electrodes, an electric current flow and at the same time light is emitted by the gas. The neon lights (reddish orange) used in advertising signs operates in the way. The colour of the light depends upon the nature of the gas in the discharge tube. If the gas pressure is reduced to 10^{-4} atmospheres, the emission of light ceases, instead the tube glows (fluoresces) with a *faint greenish light.* Further investigations revealed that the fluorescence was caused due to the bombardment of the walls of the tube by rays emanating from cathode. These rays were called **cathode rays** because they started from cathode and ended at anode. These rays were found to consist of negatively charged material particles, called **electrons.**

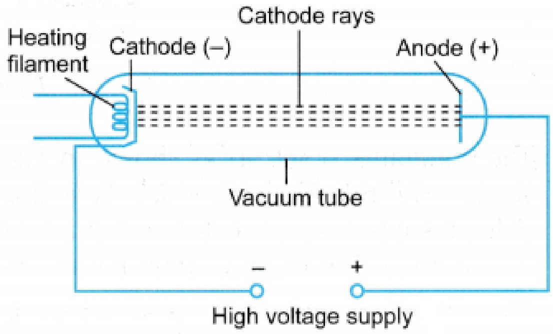


Fig. 2.1 Cathode rays

Properties of Cathode Rays

The cathode rays possess the following properties:

1. *Cathode rays travel in straight lines.* An object placed in the path of cathode rays casts a sharp shadow (Fig. 2.2). It shows that cathode rays travel in straight lines
2. *Heating effect.* When cathode rays are focused on a thin metal foil, it gets hented up to incandescence.
3. *Cathode rays consist of material particles.* This was indicated by the fact that a light paddle wheel placed in the path of cathode rays starts rotating.

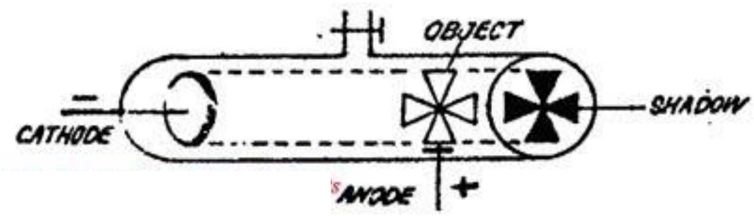


Fig. 2.2 An object placed in the path of cathode rays casts a sharp shadow

4. *Effect of electric field.* When electric field is applied to a stream of cathode rays, they get deflected towards positive plate. It showed that cathode rays themselves are negatively charged.
5. *Effect of magnetic field.* When magnetic field is applied, perpendicular to the path of cathode rays, they get deflected in the direction expected for negative particle. This further confirmed that cathode rays are negatively charged.
6. On striking against walls of the discharge tube *cathode rays produce faint greenish fluorescence.*
7. *Cathode rays ionize the gas through which they pass.*
8. *Cathode rays produce X-rays* when they are made to fall on metals such as tungsten, copper, etc.
9. *They can penetrate through thin metal foils.*
10. *The charge to mais ratio (elm) for the particles in the cathode is independent of the nature of the gas taken in the discharge or the nature of the cathode.*

The above mentioned properties of cathode rays indicated that they consist of a fast-moving stream of negatively charged material particles. These particles were named electrons by J.J. Thomson.

Determination of Change to Mans Ratio (e/m) of Electrons

Sir J. Thomson studied the deflection of cathode rays under the simultaneous application of electric and magnetic fields, applied perpendicular to each other (Fig. 23). It is possible to adjust the two fields so that the cathode rays strike the fluorescent screen at the same position as they do when neither field is applied. From the magnitudes of electric held and magnetic field thus applied it is possible to calculate changes *(e)* to mana *(m)* ratio of the electrons. ***The value of e/m was found to be 1.76 × 10^8 Cg^{-1} or 1.76 × 10^{11} C kg^{-1}.*** *The e/m ratio for the particles in the cathode rays was found to be same irrespective of the nature of cathode or the nature of the gas taken in the discharge tube, thus showing that the* ***electrons are universal constituent of all matter.***

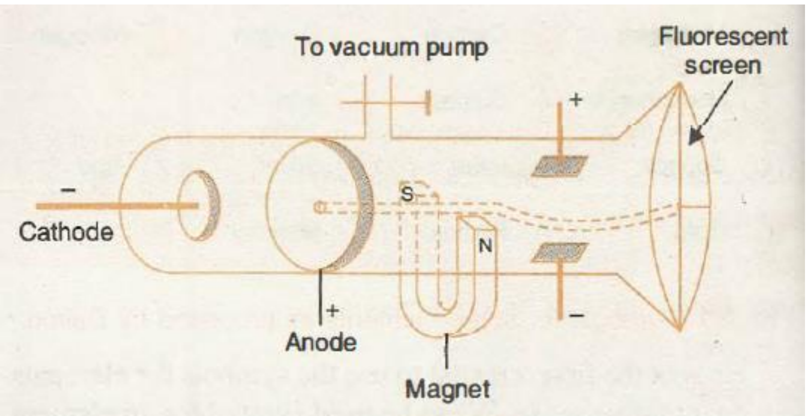


Fig. 2.3 Cathode rays deflected though magnetic and electric fields.

The charge *(e)* on an electron was determined by R.A. Milikan in 1909 by *oil drop experiment.*

The charge on the electron is found to be **1.602 × 10^{-19} C.** This is taken as one unit negative charge.

Mass of the Electron

By combining the elm ratio and charge (e) of the electron, it is possible to calculate mass of the electron.

Thomson experiment: $e/m = 1.76 \times 10^8$ C/g
Milikan experiment: $e = 1.602 \times 10^{-19}$ C/electron

Mass of the electron, $$m = \frac{e}{e/m} = \frac{1.602 \times 10^{-19}\ \text{C/electron}}{1.76 \times 10^{8}\ \text{C/g}}$$

$$= 9.11 \times 10^{-28}\ \text{g/electron}$$
$$= 9.11 \times 10^{-31}\ \text{kg/electron}$$

The mass of electron is very small and is approximately 1/1837 times the mass of an atom of hydrogen.

From the above discussion it follows that:

An electron is a fundamental particle of atom carrying one unit negative charge and having mass nearly equal to 1/1837th of mass of an atom of hydrogen.

2.3 ANODE RAYS OR CANAL RAYS

Goldstein, in 1886, discovered the existence of a new type of rays in the discharge tube. He used a perforated cathode (Fig. 2.4) in the discharge tube. On passing the electric discharge at low pressure he observed a new type of rays streaming behind the cathode. These rays were named **anode rays or canal rays.**

Further investigations of these rays showed that they consist of positively charged material particle.

Some of the characteristic **properties of anode rays are:**

1. Anode rays travel in straight lines.
2. Anode rays consist of material particles.
3. Anode rays are deflected by electric Geld towards negatively charged plate. *This indicate that they are positively charged.*

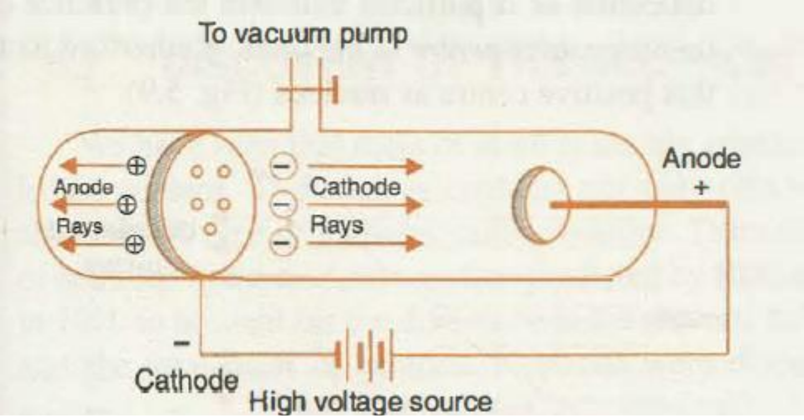


Fig. 2.4 Canal rays

4. When a magnetic field is applied in a direction perpendicular to the path of anode rays, they get deflected in the direction expected for positive particles. *This further indicates that they are positively charged.*
5. Charge to mass ratio of the particles in the anode rays depends upon nature of the gas taken in the discharge tube.

Discovery of the Proto

As already mentioned, the charge to mass ratio of the particles in the anode rays was found to depend upon the nature of the gas in the discharge tube. It was observed that e/m ratio was maximum when hydrogen gas was taken in the discharge tube. This indicated that positive ions formed from hydrogen are lightest. These lightest positively charged particles were named **protons.** The charge and mass of the proton were determined in the same manner as the one discussed in case of electron. Charge to mass ratio for protons was found to be 9.58×10^4 C/g. Charge on proton is opposite but equal in magnitude to the charge on the electronic i.e., 1.6022×10^{-19} C. From these two observations mass of a proton works out to be 1.67×10^{-24} g or 1.673×10^{-27} kg. It is practically the same as the mass of a hydrogen atom and is about 1837 times the mass of an electron.

From the above discussion it follows that:

A proton is a fundamental particle of atom carrying one unit positive charge and having mass nearly equal to the mass of an atom of hydrogen.

2.4 RUTHERFORD’S NUCLEAR MODEL OR ATOM

Alpha Particle Scattering Experiment

Rutherford in 1911 performed an experiment which led to the downfall of Thomson's model. The experiment involved the bombardment of a thin sheet of gold (thickness - 100 nm or 10^{-5} cm) by α-particles. These particles were obtained in the form of a narrow beam by passing through a slit in a lead plats. A circular fluorescent screen coated with zinc sulphide (ZnS) was placed around the foil to detect the deflnection suffered by α-particles as shown in Fig. 2.5. Whenever an a-particle struck the screen a tiny flash of light was produced at that point.

Rutherford observed that:

(i) *Most of the α-particles (nearly 99%) passed through the gold foil underflected.*

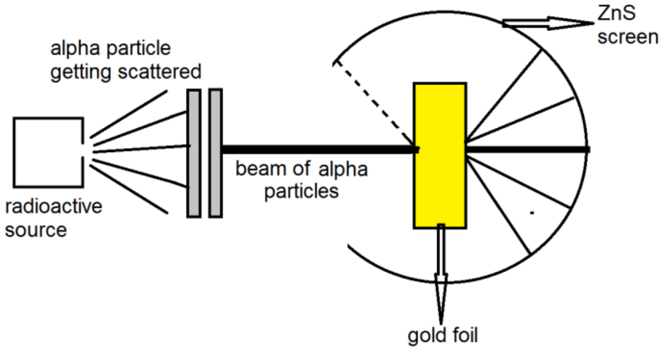


Fig. 2.5 Rutherford’s scattering experiment

(ii) Some of the particles were deflected by small angles.

(iii) A very few c-partie (1 in 20000) were either deflected by very large angles or were actually reflected back along their path.

In order to explain the observations of d-particle scattering experiment Rutherford assumed that the solid gold foil consists of layers of individual atoms which are touching each other so that there is hardly any empty space between them. As such the α-particles striking the gold foil must pass through the atoms. Rutherford explained his observations as follows:

(i) Since most of the α-particles pass through the foil undeflected, it indicates that the most of the space in an atom is empty.

(ii) α-particles being positively charged and having considerable mass could be deflected only by some heavy, positively charged centre. The small angle of deflection of α-particles indicated the presence of a heavy positive centre in the atom. Rutherford named this positive centre as **nucleus** (Fig. 2.6).

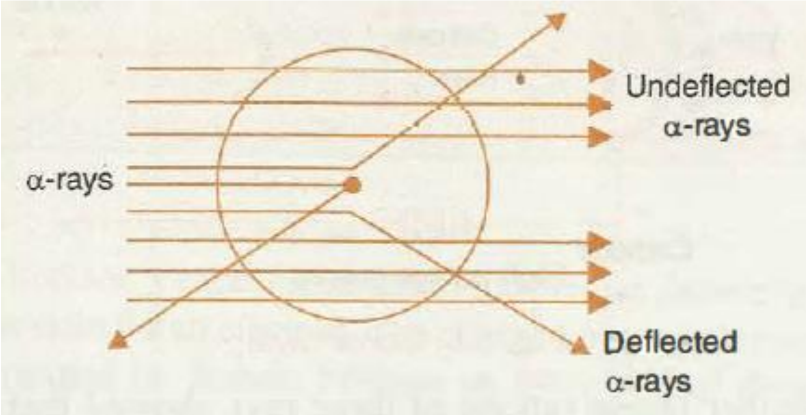


Fig. 2.6.

(iii) α-particles which make hend-on collision with heavy positive centre are deflected through large angles. Since the number of such a particles is verysmall, *the space occupied by the heavy positive centre must be very small.*

Rutherford’s Nuclear Model of Atom

On the basis of cattering experiment Rutherford put forward nuclear model of atom. Main points of this model are:

1. Most of the most and all the position charge of an atom is concentrated in a very small region called **nucleus.** *Size of the nucleus is extremely small as compared with the size of the atom.* Radius or the nucleus is of the order of 10^{-15} m, whereas radius of towns in of the order of 10^{-10} m.
2. *The positive charge on the nucleus is due to protons. The magnitude of the charge on the nucleus is different for atoms of different elements.*
3. *The nucleus is surrounded by electrons which are revolving around it at very high speeds. The electrostatic force of attraction between electrons and the nucleus is balanced by the centrifugal force acting on the revolving electrons.*
4. *Total negative charge on the electrons is equal to the total positive charge on the nucleus so that atom on the whole is electrically neutral.*

5. *Most of the space inside an atom is empty.*

Nuclear model of atom can be compared with the solar system. In an atom electrons revolve around the nucleus in just the same way the planets revolve around the sun. Due to this comparison revolving electrons are sometimes called planetary **electrons** and Rutherford's nuclear model of atom is known **planetary model of atom.**

Failure of Rutherford's Model

Rutherford model failed in view of electromagnetic theory given by Maxwell. According to this theory a charged particle when accelerated emits energy in the form of electromagnetic radiation. According to Rutherford's model, electrons are revolving around the nucleus. This means, electrons would be in a state of acceleration all the time. Since electrons are charged particles, therefore, electron revolving in an orbit should continuously emit radiations. As a result of this, it would slow down and would no longer be able to withstand the attractive force of the nucleus. Hence, it would move closer and closer to the nucleus and would finally fall in the nucleus by following a spiral path (Fig. 2.7). This means atom should collapse. But actually we know atom is stable. Thus, ***Rutherford's model failed to explain stability of atoms.***

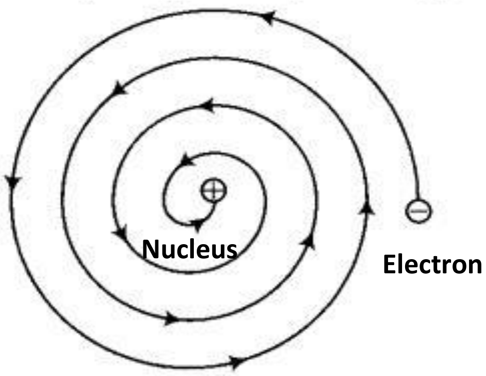


Fig. 2.7 Gradual decrease in the radius of orbit.

Another drawback of Rutherford's model is that it does not explain the distribution of electrons around the nucleus and does not tell us anything about their energies.

Rutherford's model also failed to explain the existence of certain definite lines in the hydrogen spectrum. If the electron were to continuously lose energy, as discussed above, the atomic spectrum of hydrogen would have been continuous.

2.5 DISCOVERY OF THE NEUTRON

We have seen that mass of atom is mainly concentrated in the nucleus. The nucleus contains not only protons but also another type of particles called neutrons. Neutrons were discovered by James Chadwick in 1932. He bombarded a thin foil of beryllium with fast moving α-particles and observed that highly penetrating rays consisting of neutral particles were produced.

These neutral particles were found to have mass 1.675×10^{-27} kg and were named neutrons.

From the above discussion it follows that:

A neutron is a subatomic particle carrying no charge and having mass 1.675×70^{-7} kg which is almost equal to that of a hydrogen atom.

The mass of the atom is largely due to protons and neutrons in the nucleus of the atom.

Except for the hydrogen ntom, the atoms of all other elements contain all the three fundamental particles electrons, protons and neutrons. The atom of hydrogen contains only one proton and one electron.

The properties of the three fundamental particles of atoms are summarized in Table 2.1.

Table 2.1. Properties of Fundamental Particles of Atoms

Particles	Symbol	Relative Charges	Absolute charges (C)	Mass (kg)	Mass (amu)	Approximate Mass (amu)
Electron	*e*	-1	-1.6022×10^{-19}	9.10939×10^{-31}	0.00054	0
Proton	*p*	+1	$+1.6022 \times 10^{-19}$	1.67262×10^{-27}	1.00727	1
Neutron	*n*	0	0	1.67493×10^{-27}	1.00867	1

2.6 ATOMIC NUMBER AND MASS NUMBER

Atomic Number

In 1913, H.G.J. Moseley devised an experiment to find out positive change on the bodies of an atom. He calculated the charge on the nucleus from the frequencies or wavelengths of the X-rays emitted by the different elements. ***The number of unit positive charges on the nucleus of an***

atom of the element is called atomic number of the element. Since positive charge on the nucleus is due to protons and each proton carries one unit positive charge, therefore, atomic number of an element is equal to the number of protons in the nucleus of its atom. Further, in an atom number of protons is equal to the number of electrons. Hence atomic number is also equal to the number of electrons in an atom of the element. Thus, ***atomic number of an element is equal to the number of protons in the nucleus of its atom or the number of extra-nuclear electrons***. Generally, it is denoted by the letter Z.

Atomic Number (Z) = Number of protons
= Number of electrons

Mass Number

It has already been stated that mass of an atom is mainly concentrated in the nucleus. In the nucleus there are protons and neutrons. From this it follows that mass of an atom is mainly due to protons and neutrons. Protons and neutrons are collectively called nucleons. Total number of protons and neutrons in the nucleus is called mass number of the atom. It is generally represented by the letter A.

Mass Number (A) = **Number of protons + Number of neutrons**
= Number of nucleons.

Calculation of Number of Electrons, Protons and Neutrons

From the knowledge of atomic number and mass number of an element it is possible to calculate number of electrons, protons and neutrons in an atom of the element. For example, atomic number and mass number of aluminium are 13 and 27 respectively. Number of electrons, protons and neutrons in an atom of it can be calculated as under:

Number of protons = Atomic number = 13
Number of electrons = Atomic number = 13
Number of neutrons = Mass number - Atomic number
= 27 - 13 = 14

In case of ions, the number of protons and neutrons remains the same as in the atoms, however, the number of electrons changes. This is due to the reason that an ion is formed either by the addition or by the removal of one or more electrons from the neutral atom.

For example, Mg^{2+} ion is formed by the removal of two electrons from Mg atom.

$$Mg - 2e - Mg^{2+}$$

Therefore, Mg^{2+} ion has two electrons less than the number of electrons in Mg atom. Knowing that the atomic number and mass number of Mg are 12 and 24, respectively, the number of electrons, protons and neutrons in Mg^{2+} ions may be calculated as under:

Number of protons = Atomic number = 12
Number of electrons = Atomic number - 2 = 10
Number of neutrons = Mass number - Atomic number
= 24 - 12 = 12

Similarly, a negative ion is formed by addition of one or more electrons to the neutral atom For example, pl-ion (phosphide ion) is formed by addition of three electrons to a phosphorus atom.

$$P + 3e^{-} \rightarrow P^{3-}$$

Knowing that atomic number of phosphorus is 15 and mass number is 31, the number of electrons, protons and neutrons in phosphide ion may be calculated as under:

Number of protons = Atomic number = 16
Number of electrons = Atomic number + 3 = 18
Number of neutron = Mass number – Atomic Number
= 31 – 15 = 16.

Example 2.1. *An ion with mass number 37 possesses one unit of negative charge. If the contains 11.1% more neutrons than the electrons, find the symbol of the ion.*

Solution. Since the ion carries one unit negative charge, it means that in the ion the number of electrons is one more than the number of protons.

Total number of electrons and neutrons in the ion = 37 + 1 = 38

Let the number of electrons in the ion be = x

Number of neutrons in the ion = $\frac{x \times 111.1}{100} = 1.111x$

∴ Total number of electrons and neutrons in the ion = $x + 1.111x = 2.111x$

$$2.111x = 38$$
$$x = \frac{38}{2.111} = 18$$

∴ Number of electrons in the ion = 18

Number of protons in the ion = 18 – 1 = 17

Thus, atomic number of the element is 17 which corresponds to chlorine.

∴ Symbol of the ion is $^{37}_{17}\text{Cl}^{-}$

2.7 NATURE OF ELECTROMAGNETIC RADIATIONS

Wave Theory of Radiations

Light is an important from of energy. According to Newton's corpuscular theory it was considered as a stream of particles called corpuscles of light. This theory could successfully explain phenomena of reflection and refraction but failed to explain phenomena of diffraction and interference. Therefore, corpuscular theory was discarded and it was replaced my Maxwell's wage theory of light. According to this theory, light is transmitted in the form of electromagnetic waves. These waves are associated with oscillating electric field and magnetic field.

These two fields are perpendicular to each other and also to the direction of propagation as shown in Fig. 2.8.

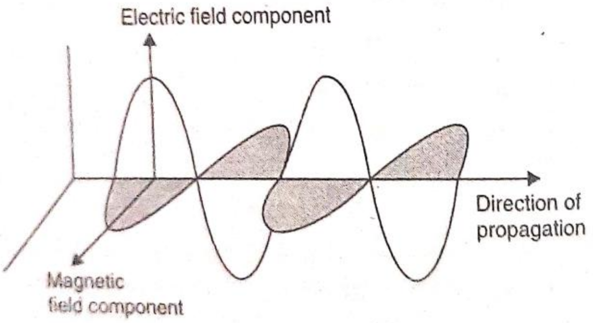


Fig 2.8. Electromagnetic wave.

In order to characterize these waves following parameters are used:

1. Wavelength. It may be defined as the distance between two neighbouring crests or thoughts of the wave as shown in Fig. 2.9. It is represented by Greek letter λ (lambda) and is generally measured in Angstrom units (A) of nanometers (nm).

$$1 \text{ Å} = 10^{-10} \text{ m}$$
$$1 \text{ nm} = 10^{-9} \text{ m.}$$

In addition, the following units are also sometimes used.

picometer, pm = 10^{-12} m
microns, μ = 10^{-6} m
millimicron, mμ = 10^{-9} m

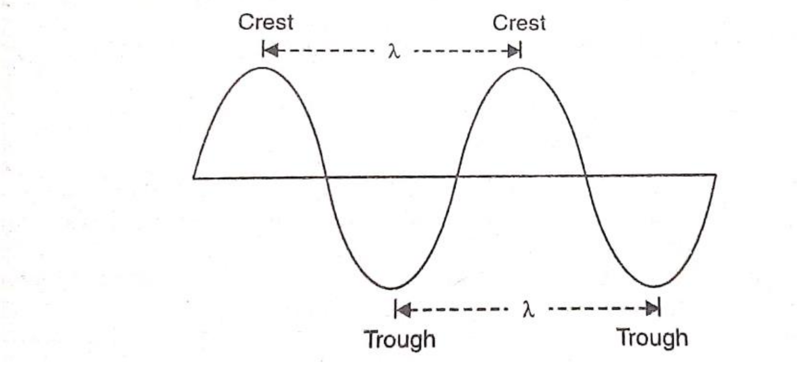


Fig 2.9. Propagation of wave motion

2. Frequency. It may be defined as the number of waves which pass through a particular poin in one second. It is represented by Greek litter ν (nu). Its unit are:

Cycles per Second (cps) or **Hertz** (Hz)

$$1 cps = 1 Hz$$

$$1 kHz = 10^3 Hz$$

$$1 MHz = 10^6 Hz$$

3. Velocity. The distance travelled to a wave in one second is called velocity of the wave. It is denoted by letter c. the frequency (v) and wavelength (λ) are related to velocity (c) by the following relation:

$$c = \nu\lambda \text{ or } \nu = \frac{c}{\lambda}$$

Velocity of all electromagnetic radiations in space or in vacuum is same and is equal to 3×10^8 m/sec.

4. Wave number. It may be defined as the number of wavelengths per unit length. It is equal to the inverse of wavelength. It is denoted by $\bar{\nu}$. Its unit is the reciprocal of wavelength unit. It is generally expressed as cm^{-1} or m^{-1}.

$$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}$$

5. Amplitude. It is the height of a crest or depth of a trough of a wage. It is generally expressed by the latter 'a'. The amplitude of a wave determines the intensity of radiation.

The electric and magnetic components of an electromagnetic wave have the same wavelength, frequency, speed and amplitude but they vibrate in two mutually perpendicular planes.

Electromagnetic Spectrum

The different electromagnetic radiations have different wavelengths. The visible light in the presence of which out eye can see contains radiations having wave length between 400nm – 750nm. Different colours in the visible light correspond to radiations of different wavelengths. In addition to visible light there are so many other electromagnetic radiations, such as X-rays, ultraviolet rays. Infra-red rays, microwaves and radiowaves.

Arrangement of all the electromagnetic radiations in the increasing order of their wavelengths or decreasing order of their frequencies is called electromagnetic spectrum.

Different regions of electromagnetic spectrum are identified by different names. Complete electromagnetic spectrum, is shown in Fig. 2.10.

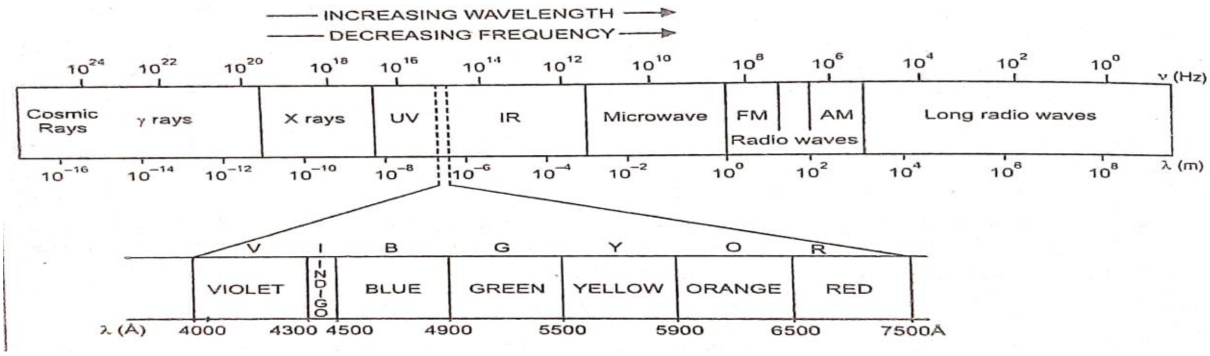


Fig. 2.10. Complete electromagnetic spectrum

The various types of electromagnetic radiations have different energies and are being used for different as listed below in Table 2.2.

Table 2.2. Some Applications of Electromagnetic Waves

Name (Hz)	Frequency	Wavelength (m)	Uses
Gamma rays	10^{20} to 10^{21}	10^{-12}	Cancer treatment
X-rays	10^{17} to $10^{19.}$	10^{-10}	Medical “pictures”, materials testing
Ultraviolet	10^{15} to 10^{16}	10^{-7}	Germicidal lamps
Visible	10^{13} to 10^{14}	10^{-6}	Illumination
Infrared	10^{12} to 10^{13}	10^{-4}	Heating
Microwave	10^{9} to 10^{11}	10^{-2}	Cooking, radar
Radio frequency	10^{5} to 10^{8}	10^{2}	Signal transmission

SOLVED EXAMPLES BASED ON RELATIONS
$c = \nu\lambda$ AND $\nu = c\,\bar{\nu}$

Example 2.2. Yellow light emitted from a sodium lamp has a wavelength (λ) of 580 nm. Calculate frequency (ν) and wave number ($\bar{\nu}$) of the yellow light.

Solution. Wavelength of the radiation λ = 580 nm

$$= 580 \times 10^{-9}\text{ m} = 5.80 \times 10^{-7}\text{ m}$$

Velocity of radiation, $c = 3 \times 108$ m/s

$$c = \nu\lambda$$

Frequency $\nu = \frac{c}{\lambda} = \frac{3 \times 10^{8}\text{ ms}^{-1}}{5.80 \times 10^{-7}\text{ m}} = \mathbf{5.17 \times 10^{14}\ s^{-1}}$

Wave number $\bar{\nu} = \frac{1}{\lambda} = \frac{1}{5.80 \times 10^{-7}\text{ m}} = \mathbf{1.72 \times 10^{6}\ m^{-1}}$

Example 2.3. The wage number of a beam of light is 400 cm^{-1}. What is the wave-length of the light in nanometers? Also find out frequency of the light.

Solution. Calculation of wavelength

$$\bar{\nu} = 400\text{ cm-1}$$

$$\bar{\nu} = \frac{1}{\lambda}$$

or $\lambda = \frac{1}{\lambda} = \frac{1}{\lambda}\text{ cm} = 2.5 \times 10^{-3}\text{ cm}$

$$= 2.5 \times 10^{-3} \times 10^{7}\text{ nm} = \mathbf{2.5 \times 10^{4}\ nm.}$$

Calculation of frequency

$$c\,\lambda$$

$$\nu = \frac{c}{\lambda} = c\,\bar{\nu}\ 3 \times 10^{10}\text{ cm s}^{-1} \times 400\text{cm} = \mathbf{1.2 \times 10^{13}\ s^{-1}}$$

2.8 PARTICLE NATURE OF ELECTROMAGNETIC RADIATION-PLANCK'S QUANTUM THEORY

The failure of the classical electromagnetic theory of radiation to explain the phenomenon of photoelectric effect led Max Planck (1901) to propose a new theory known as **Quantum theory of radiation.** The main points of this theory are:

1. **Radiant energy is emitted or absorbed not continuously but discontinuously in the form of small packets of energy called quanta.**

Each wave packet or **quantum** is associated with definite amount of energy. In case of light, the quantum of energy is often called **photon.**

2. **The amount of energy associated with a quantum of radiation is proportional to the frequency of radiation.**

$$E \propto \nu$$

or $$\mathbf{E = h}\nu$$

where h is a constant known as **Planck's constant** and is equal to **6.625 * 10^{-34} joule-sec.**

The energy of a photo of light in terms of wavelength λ and velocity of light, c is given as

$$\mathrm{E} = h\nu$$

$$\mathrm{E} = h\frac{c}{\lambda} \qquad (\therefore c = \nu\lambda; \quad \nu = c/\lambda)$$

3. **A body can emit or absorb energy only in terms of the integral multiples of quantum, i.e.,**

$$\mathrm{E} = nh\nu \qquad \text{where } n = 1, 2, 3, 4, \ldots$$

This means that a body can emit or absorb energy has $h\nu$, $2h\nu$, $3h\nu$, $4h\nu$ … but it cannot emit or absorb energy in fractional values of $h\nu$ such as $1.5h\nu$ or $2.5h\nu$.

SOLVED EXAMPLES BASED ON PLANCK'S QUANTUM THEORY

Example 2.4. Calculate and compare the energies of two radiations, one with a wavelength of 400 nm and the other with 800 nm.

Solution. $$\mathrm{E} = h\nu = h \times \frac{c}{\lambda}$$

$$\mathrm{E}_1 = \frac{6.6 \times 10^{-34}\ \mathrm{Js} \times 3 \times 10^{8}\ \mathrm{ms}^{-1}}{400 \times 10^{-9}\mathrm{m}} = 4.95 \times 10^{-19}\ \mathrm{J}$$

$$\mathrm{E}_2 = \frac{6.6 \times 10^{-34}\ \mathrm{Js} \times 3 \times 10^{8}\ \mathrm{ms}^{-1}}{800 \times 10^{-9}\mathrm{m}} = 2.48 \times 10^{-19}\ \mathrm{J}$$

$$\frac{\mathrm{E}_1}{\mathrm{E}_2} = \frac{4.95 \times 10^{-19}\ \mathrm{J}}{2.48 \times 10^{-19}\ \mathrm{J}} = 2$$

or $\mathbf{E_1 = 2E_2}$

Energy of the radiation with a wavelength 400 nm is twice that of the radiation of wavelength 800 nm.

Example 2.5. Find energy of each of the photons which (i) correspond to light of frequency 3×10^{15} Hz (ii) have wavelength of 0.50 A.

Solution. (i) $E = h\nu$

$$= 6.63 \times 10^{-34} \text{ Js} \times 3 \times 10^{15} \text{ s}^{-1}$$

$$= 1.989 \times 10^{-18} \text{ J}$$

(ii) $E = h\nu = \frac{hc}{\lambda}$

$$= \frac{6.6 \times 10^{-34} \text{ Js} \times 3 \times 10^{8} \text{ ms}^{-1}}{0.50 \times 10^{-10} \text{m}}$$

$$= \mathbf{3.98 \times 10^{-15}\ J.}$$

2.9 ATOMIC SPECTRUM

When an element is excited by some method such as by heating, by passing electric current or by passing electric discharge, the atoms of the element emit electromagnetic radiations of definite frequencies. The arrangement of these radiations in the order of increasing wavelength or decreasing frequencies is called **emission spectrum** of the element. Since the radiations in the spectrum are emitted due to energy changes taking place in the atoms, this spectrum is also known as **atomic spectrum.**

The instrument used for obtaining a spectrum is called spectroscope or spectrograph. In the spectroscope light is passed through a prism and the emergent light is observed. It is a well-established fact that ray of light undergoes deviation when passed through a prism. The angle of deviation is directly proportional to the frequency of radiation. Thus, if we pass a beam of radiations having different frequencies through a prism, these radiations undergo unequal deviation and get arranged in order of decreasing frequencies. For example, a beam of ordinary light splits up into seven colour (VIBGYOR) after passing through the prism. **This phenomenon of splitting of a beam of light into radiations of different frequencies after passing through the prism is called dispersion and the pattern of radiations obtained after dispersion of beam is called spectrum.**

In case of dispersion of sunlight, the seven colours obtained change from violet to red without any discontinuity, which means each colour blends into the other. Such a spectrum is called **continuous spectrum.**

In continuous spectrum, the radiations corresponding to all the wavelengths (within a certain range) are present.

On the other hand, atomic spectra of most of the elements consist of a number of bright lines separated by dark bands. That is why atomic spectrum is also known as **line spectrum.** The various lines in the line spectrum correspond to the radiations of different wavelengths, emitted by the excited element. The lines in the line spectrum of an element are characteristic of the atoms of the element. Therefore, **atomic spectrum of an element can be used to identify the element and is sometimes called fingerprint of its atoms.**

Elements like rubidium (Rb), caesium (Cs), indium (In), scandium (Sc), etc. were discovered when their minerals were analysed by spectroscopic methods. The element helium was discovered in the sun by study of spectrum of sunlight.

Absorption Spectrum

When a beam of continuous light is passed through a tube containing vapours or solution of the substance and the transmitted light is analysed with the help of a spectrometer, it is observed that the spectrum obtained contains a number of dark lines in otherwise continuous spectrum. These dark lines appear due to the absorption of radiations of corresponding wavelengths by the substance. The dark lines in the absorption spectrum of a substance appear at the same position as the bright lines in the emission spectrum of the substance. For example, emission spectrum of sodium has two bright lines in the yellow region of 589.0 nm and 589.6 nm whereas its absorption spectrum has two dark lines corresponding to the same wavelengths. Generally more lines are observed in the emission spectrum than in its absorption spectrum Therefore, absorption spectrum is taken if simplification of the spectrum is desirable.

The study of emission or absorption spectra is called **spectroscopy.**

Hydrogen Spectrum.

The atomic spectrum of hydrogen has proved quite helpful in the development of atomic structure. It can be obtained by passing the light being emitted from the discharge tube containing hydrogen at low pressure, through the spectrograph as shown in Fig. 2.11.

When an electric discharge is passed through hydrogen gas its molecules dissociates into hydrogen atoms. The excited hydrogen atoms, thus produced, emit electromagnetic radiation of discrete frequencies.

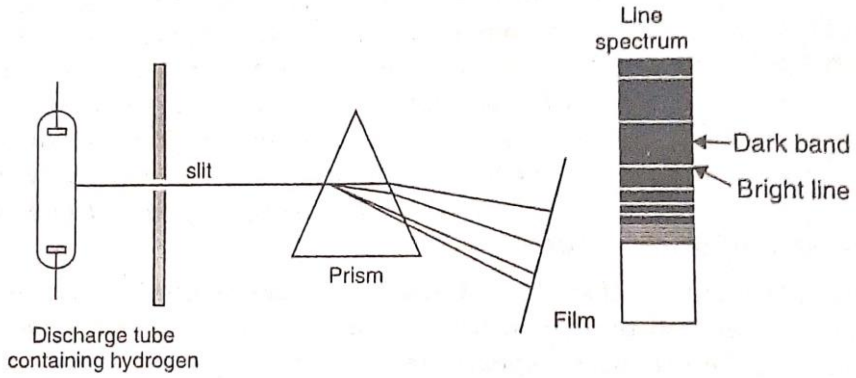


Fig. 2.11. Emission spectrum of hydrogen

The spectrum obtained consists of a large number of sharp lines. Each line corresponds to a particular frequency of light emitted by hydrogen atoms. Lines in the emission spectrum of hydrogen are present in ultraviolet, visible and infra-red regions. While the lines in the ultraviolet and visible regions can be directly obtained on photographic plate, the lines in the infra-red region are detected by other method.

The lion in the emission spectrum of hydrogen are classified into five series as follows:

(i) **Lyman Series** ... Ultraviolet region

(ii) **Balmer Series** ... Visible region

(iii) **Paschen Series** ... Infra-red region

(iv) **Brackett Series** ... Infra-red region

(v) **Pfund Series** ... Infra-red region

The complete spectrum of hydrogen is shown in Fig. 2.12.

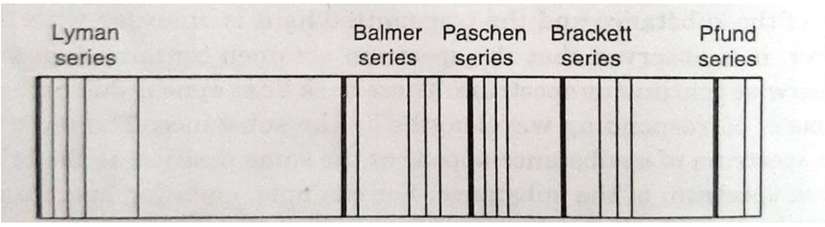


Fig. 2.12. Atomic spectrum of hydrogen

Balmer showed in 1885 that if the spectral lines are expressed in terms of wave numbers (inverse of wavelengths), then the lines in the visible region (Balmer series) obey the formula,

$$\bar{\nu} = 109,677\left(\frac{1}{2^2}-\frac{1}{n^2}\right)\ \text{cm}^{-1}$$

Where n is an integer equal to or greater than 3 i.e., $n = 3, 4, 5$ .....

Later on, Rydberg gave a more general formula which is applicable to all the series in the hydrogen spectrum.

$$\bar{\nu} = 109{,}677 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{cm}^{-1}$$

where n_1 and n_2 are integers, such that $n_2 > n_1$. For a particular series n_1 is constant.

For Lyman Series $n_1 = 1$, $n_2 = 2, 3, 4.....$

For Balmer Series $n_1 = 2$, $n_2 = 3, 4, 5.....$

For Paschen Series $n_1 = 3$, $n_2 = 4, 5, 6.....$

For Bracket Series $n_1 = 4$, $n_2 = 5, 6, 7.....$

For Pfund Series $n_1 = 5$, n_2 $6, 7, 8....$

The value 109,677 cm^{-1} is called **Rydberg constant** for hydrogen.

SOLVED EXAMPLES BASED ON RYDBERG FORMULA

Example 2.6. What is the wavelength of light emitted when the electron in a hydrogen atom undergoes transition from the energy level with $n = 4$ to the energy level with $n = 2$?

Solution. According to Rydberg's formula,

$$\bar{\nu}\ \text{cm}^{-1} = 109{,}677 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

In the present case $n_2 = 4$ and $n_1 = 2$

$$\bar{\nu} = 109{,}677 \left(\frac{1}{(2)^2} - \frac{1}{(4)^2}\right) = 109{,}677 \times \frac{3}{16} = 20564\ \text{cm}^{-1}$$

$$\lambda = \frac{1}{\bar{\nu}} = \frac{1}{20564}\ \text{cm}$$

$$= 4.86 \times 10^{-5}\ \text{cm} = 4.86 \times 10^{-5} \times 10^{7}\ \text{nm}$$

$$= \mathbf{486\ nm.}$$

2.10. BOHR'S MODEL FOR HYDROGEN ATOM

In order to overcome the shortcomings of Rutherford's model, Neils Bohr (1913) proposed a new model of hydrogen atom based upon quantum theory of radiations. This model could explain quantitatively the general features of structure of hydrogen atom and its spectrum. Main points of this model are:

1. The electron in the hydrogen atom revolves around the nucleus only in certain selected circular orbits. These orbits are associated with definite energies and are also called **energy shells or energy levels.** These are numbered us 1, 2, 3, 4 ......etc., or designed as K, L, M, N ..... etc. shells (Fig. 2.13).

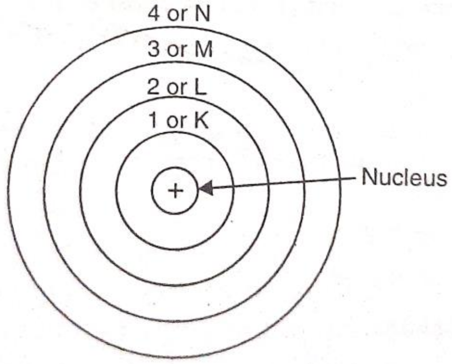


Fig. 2.13. Bohr's orbits

2. Only those orbits are permitted in which the angular momentum of the electron is a whole number multiple $\frac{h}{2\pi}$ of where h is Planck's constant. That is, angular momentum of the electron,

$$mvr = n\frac{h}{2\pi}, \text{ where } n = 1, 2, 3, \ldots n,$$

where, m is the mass of the electron

v is the velocity of the electron and

r is the radius of the orbit.

In other words, **angular momentum of electrons in an atoms in quantized,**

3. As long as the electron remains in a particular orbit, it does not lose or gain energy. This means that energy of an electron in a particular orbit remains constant. That is why, there orbits are also called **stationary states.**

4. When energy from some external source is supplied to the electron, it may Jump some higher energy level by absorbing a definite amount of energy (equal to the difference in energy between the two energy levels). When the electron jumps back to the lower energy level it radiates same amount of energy in the form of a photon of radiation such that

$$\Delta E = E_2 - E_1 = hv$$

$$v = \frac{E_2 - E_1}{h}$$

where υ is the frequency of the radiation emitted when electron jumps from the energy level having energy E, to the energy level having energy E_1.

According to Bohr's model, energy of the electron in an atom is quantized. **Quantization means that a quantity cannot vary continuously to have any arbitrary values but can change only discontinuously to have some specific values.**

Successes of Bohr's Model

The main successes of Bohr's model are:

1. Bohr's model could explain the stability of an atom.

According to Bohr's model, an electron revolving in a particular orbit cannot lose energy. The electron can lose energy only if it jumps to some lower energy level. If no lower energy level is vacant then electron will keep on revolving in the same orbit without losing energy and hence it explains the stability of atom.J

2. Bohr's theory helped in calculating energy of an electron in a particular orbit of hydrogen.

On the basis of various postulates of Bohr's model, it is possible to derive

mathematical relation for energy of an electron in nth orbit of hydrogen. 'The expression is,

$$E_n = -k^2 \frac{2\pi^2 me^4}{n^2 h^2}$$

where, m = mass of the electron

e = charge on the electron

h = Plancks' constant

k = Coulomb's law constant.

The value of Coulomb’s law constant is 9.00×10^9 J.m/C^2

Substituting the value of m, e, h, π and k in the above expression, we get

$$E_n = -\frac{2.178 \times 10^{-18}}{n^2} \text{ J/atom} = -\frac{13.595}{n^2} \text{ eV/atom} = -\frac{1312}{n^2} \text{ kJ/mole}$$

As is clear from the expression of energy of an electron in various orbits, as the electrons mover more and more come to the nucleus E_n becomes Inrge in absolute value and more and more negative. The most negative energy value is for the first orbit (n - 1). This is the most stable orbit. When the electron is present in this orbit, it is said to be in **ground state.** The higher orbits have greater energy than the first orbit. When the electron is present in any of the higher orbit ($n > 1$) it is said to be in **excited state.**

NEGATIVE VALUE OF ELECTRONIC ENERGY FOR HYDROGEN ATOM

If we observe the expression for energy of the electron in various orbits of hydrogen and hydrogen like species we find that the energy of the electron has a negative sign for all possible orbit Now let us understand why electronic energy has negative sign for hydrogen and hydrogen like systems.

When an electron in at infinite distance from the nucleus, there is no force of attraction between the electron and the nucleus. Therefore, energy of the electron at infinity in arbitrarily assumed to be zero. When the electron moves closer to the nucleus it does so by itself under the attractive force or the nucleus in doing so, it consumes or spends some of its energy. Therefore, energy of the electron becomes less than zero. That is why energy of the electron in an atom in negative. As the electron moves closer to the nucleus, energy of the electron become more and more negative. The electron has the most negative energy when it is in the first orbit ($n = 1$) of hydrogen atom. This is known as the **ground state** will hydrogen atom.

3. Bohr's model could explain the atomic spectrum of hydrogen.

According to Bohr's model, electron in an atom can have only certain definite energy levels. When the electron is present in lowest possible energy level, it is said to be in ground state. When energy is supplied from some external source, the electron may absorb energy and jump to some higher energy level. The electron in such a state is said to be in excited state. The excited state is unstable and therefore, the electron has tendency to come back to the ground state. When the electron jumps back to lower energy levels, it gives out energy in the form of n quantum equal to the difference of energies between the two energy levels. If E_1 and E_2 are the energies of lower and higher energy levels respectively, then frequency (v) of the radiation emitted is given by the following relation:

$$E_2 - E_1 = h\upsilon \text{or} \qquad \upsilon = \frac{E_2 - E_1}{h}$$

where h is Planck’s constant.

According to Bohr's model, in n hydrogen atom (or in any other atom) E_2 and E_1 can have only certain definite values. From this, it follows that can have only certain fixed values. Thus, Bohr's model explains why there are certain discrete lines in the spectrum of hydrogen. **Bohr's model also accounts for the existence of so many lines in hydrogen spectrum.**

In hydrogen atom there is one electron which is present in first orbit in ground state. When energy is supplied, such as by passing electric discharge, this electron may be excited to some higher energy level. Since in a sample of hydrogen there are large number of atoms, the electrons in different atoms absorb different amounts of energies and are excited to different higher energy levels. For example, the electron in some atom may jump to third energy level while in others it may be raised to fourth energy level and so on. Now, from excited states the electron may return to ground state in one or more jumps.

For example, let us consider the electron present in the fourth energy level (n = 4) of different hydrogen atoms. In some atoms it may come to ground state (n = 1) by direct jump while in some other it may first jump to second energy level (n = 2) and then to first energy level (n = 1), while in still others it may come to group state via third (n = 3) and second energy levels (n = 2) as illustrated in Fig. 2.14.

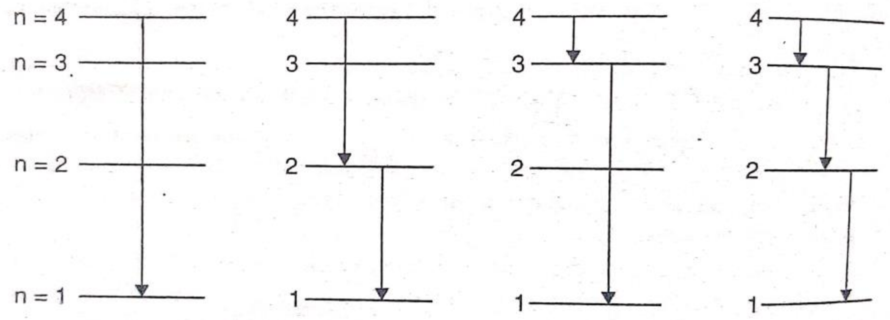


Fig. 2.14. Different routes to the ground state from fourth energy level.

These different downwards jumps are associated with different amount of energies and hence result in the emission of radiations of different wavelengths which appear as different lines in the hydrogen spectrum. **Since large number of different type of downward transitions take place simultaneously in a sample of hydrogen, therefore, large number of lines are obtained in emission spectrum of hydrogen.**

The lines which arise due to the transitions from higher energy levels to first energy level are grouped ns **Lyman Series.** Similarly, the lines obtained as a result of transitions of electrons from higher energy levels to second, third, fourth and fifth energy levels give rise to **Balmer, Paschen, Brackett** and **Pfund** series respectively as illustrated in Fig. 2.15.

Lyman series	From n = 2, 3, 4, 5 ...... to n = 1
Balmer series	From n = 3, 4, 5, 6 ...... to n = 2
Paschen series	From n = 4, 5, 6, 7 ...... to n = 3

Brackett series	From n = 5, 6, 7, 8 ……. to n = 4
Pfund series	From n = 6, 7, 8, 9 …… to n = 5.

Bohr was able to calculate frequencies and wavelengths of various lines in the atomic spectrum of hydrogen.

Suppose an electron from an higher orbit having $n = n_2$ jumps to a lower level having $n = n_1$ in hydrogen atom. As a result of this transition, the electron emits energy equal to ΔE in the form of a photon radiation.

$\Delta E = En_2 - En_1$

$$= \left(\frac{-2.18 \times 10^{-18}\,\mathrm{J}}{n_2^2}\right) - \left(\frac{-2.18 \times 10^{-18}\,\mathrm{J}}{n_1^2}\right) = 2.18 \times 10^{-18}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \mathrm{J/atom}$$

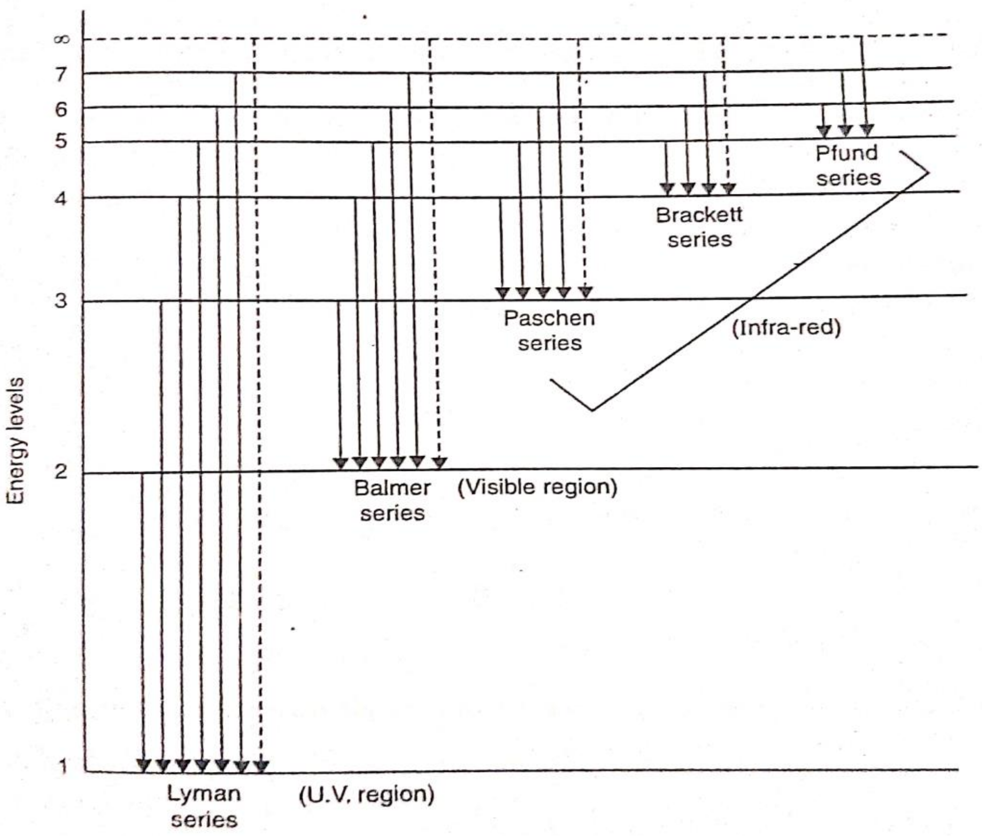


Fig. 2.15. Generation of various spectral series in hydrogen spectrum

The frequency of the emitted photon is related to ΔE as:

$$\Delta E = h\upsilon$$

or $$\upsilon = \frac{\Delta E}{h} = \frac{2.18 \times 10^{-18}}{h} = \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \text{s}^{-1}$$

$$\upsilon = \frac{2.18 \times 10^{-18}\ \text{J}}{6.626 \times 10^{-34}\ \text{J.s}} = \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$\boxed{\upsilon = 3.29 \times 10^{15} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \text{s}^{-1}}$$

The wage number, $\bar{\upsilon}$ of the radiation may be calculated as under:

$$\bar{\upsilon} = \frac{\upsilon}{c} = \frac{3.29 \times 10^{15}\ \text{s}^{-1}}{3 \times 10^{10}\ \text{cm s}^{-1}} = \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$\boxed{\bar{\upsilon} = 109677 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \text{cm}^{-1}}$$

or $$\boxed{\bar{\upsilon} = 109677 \times 10^{7} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \text{m}^{-1}}$$

This expression is same as deduced by Rydberg from experimental data.

SOLVED EXAMPLE BASED ON HYDROGEN SPECTRUM

Example 2.7. Applying Bohr's model calculate the wavelength of the radiation emitted when an electron in a hydrogen atom makes a transition from fourth energy level to first energy level.

Planck's constant $h = 6{,}63 \times 10\text{-}^{34}\ Js$.

Solution.

For fourth energy level $n = 4$

For first energy level $n = 1$

Energy of fourth energy level, $E_2 = \frac{2.18 \times 10^{-18}\ \text{J}}{(4)^2}$ J/atom

Energy of first energy level, $E_1 = \frac{2.18 \times 10^{-18}\ \text{J}}{(1)^2}$ J/atom

$$\Delta E = E_2 - E_1 = -\ 2.18 \times 10^{-18} \left[\frac{1}{(4)^2} - \frac{1}{(1)^2}\right] \text{J/atom}$$

This energy is given out in the form of a single photon or quantum of radiation.

$\therefore$ $\Delta E = h\upsilon$

or $\lambda = \frac{hc}{\Delta \mathrm{E}}$

Substituting for $h = 6.63 \times 10^{-34}$ Js

and $c = 3.00 \times 10^{8}$ ms^{-1}

we get $\lambda = \frac{6.63 \times 10^{-34} \text{ Js} \times 3.100 \times 10^{8} \text{ ms}^{-1}}{2.04 \times 10^{18} \text{ J}}$

$= 9.7 \times 10^{-8}$ m = **91nm.**

Limitations of the Bohr's Model

1. Bohr's model could not explain the spectra of atoms containing more that one electron. Bohr's model could not explain even hydrogen spectrum obtained using high resolution spectroscopes. Each spectral line, on high resolution was found to consist of two closely spaced lines.
2. It was observed that in the presence of a magnetic field, each spectral line gets split up into closely spaced lines. This phenomenon known as **Zeeman Effect,** could not be explained by Bohr's model.
   Similarly, the splitting of spectral line under the effect of applied electric field (**Stark effect),** could not be explained by Bohr's model.
3. In 1923, de Broglie, the French physicist, suggested that electron, like light, has a **dual character.** It has particle as well as wave nature. Bohr had treated electron only as a particle. Thus, Bohr's model ignored dual character of electron.
4. The main objection to Bohr's theory was raised by **Heisenberg's uncertainty principle**. According to this principle, it is impossible to determine simultaneously the exact position and the momentum of a small moving particle like an electron. The postulate of Bohr that electrons move in well-defined orbits around the nucleus, therefore, is not valid. Thus, Bohr's model contradicts Heisenberg's uncertainty principle.
5. Bohr's model could not explain ability of atoms to form molecules and the geometry and shapes of molecules.

2.11. THE DUAL NATURE OF MATTER

Einstein had suggested in 1905 that light has dual nature, that is, wave nature as well as particle nature. In 1923, Louis de Broglie, the French physicist proposed that like light, matter also has dual character. It exhibits wave as well as particle nature. He even derived a relationship for the calculation of wavelength (λ) of the wave associated with a particle of mass m, moving with velocity v as given below:

$$\lambda = \frac{h}{mv} \text{ or } \lambda = \frac{h}{p}$$

where h is Planck's constant and p in momentum of the particle.

Derivation of de Broglie Relationship

The energy E of a photon of frequency υ is given by $E = h\upsilon$ …(i)

Also according to Einstein's equation, $E = mc^2$ …(ii)

where m in the mass of photon.

From equations (i) and (ii), we get $mc^2 = h\upsilon$

$$mc^2 = h \cdot \frac{c}{\lambda} \qquad \left(\because \upsilon = \frac{c}{\lambda}\right)$$

Rearranging, we get $\lambda = \frac{h}{mc}$

de Broglie pointed out that the same equation might be applied to material particle by using m for the mass of the particle instead of the mass of photon and replacing c, the velocity of the photon, by v, the velocity of the particle.

$$\boxed{\lambda = \frac{h}{mv}} \qquad \text{…(iii)}$$

Equation (iii) is called de Broglie’s equation. It may also be written as

$$\boxed{\lambda = \frac{h}{P}} \qquad \text{…(iv)}$$

where p is the momentum of the particle.

The waves associated with material particles or objects in motion are called **matter waves** or **de Broglie waves.** These waves are distinctively different from the electromagnetic waves.

It may be noted that wave character has significance only in case of submicroscopic particles such as electrons. For the objects of ordinary size wavelength of the wave associated with the object is too small because of their large mass. Therefore, wave properties of objects of ordinary size cannot be detected. On the otherhand, the wave properties of small particles, such as electrons, can be detected experimentally.

The wave nature of electrons was verified experimentally by Davisson and Germer, by carrying out diffraction experiments with a beam of fast moving electrons. The wave nature of electrons is utilized in the construction of the electron microscope which is used to photograph objects of very small size (upto 10 Å) and to study surface structure of solids. As electron microscope in a very powerful tool in scientific research because it can achieve a magnification of about 15 million times.

SOLVED EXAMPLES BASED ON de BROGLIE'S EQUATION

Example 2.8. Calculate the wavelength of a body of mass 1 mg moving with a velocity of 10 m sec^{-1}.

Solution. We know = $\boldsymbol{\lambda = \frac{h}{mv}}$

Substituting the values, m = 1 mg = 10^{-6} kg, v = 10 m sec^{-1}

And $h = 6.63 \times 10^{-34}$ kg m^2 s^{-1}

$$\lambda = \frac{6.63 \times 10^{-34}\ \text{kg m}^2\ \text{s}^{-1}}{10^{-6}\ \text{kg} \times 10\ \text{ms}^{-1}} = \mathbf{6.63 \times 10^{-29}\ m.}$$

Example 2.9. Calculate the momentum of a moving particle which has a de Broglie wavelength of 200 pm.

Solution. We know, $\lambda = \frac{h}{mv}$ or $mv = \frac{h}{\lambda}$

$h = 6.63 \times 10^{-34}$ Js = 6.63×10^{-34} kg m^2 s^{-1}

λ = 200 pm = 2×10^{-10} m

Momentum,

$$mv = \lambda = \frac{6.63 \times 10^{-34}\ \text{kg m}^2\ \text{s}^{-1}}{2 \times 10^{-6}\ \text{m}} = \mathbf{3.31 \times 10^{-24}\ kg\ m\ s^{-1}}$$

2.12. HEISENBERG'S UNCERTAINTY PRINCIPLE

As already discussed electrons possess particle nature as well as wave nature. One can hardly speak of the prcise location of a wave because a wave is not located at particular point but extends in space. Thus, the wave nature of electrons puts some restriction on how precisely the position of an electron can be determined. Werner Heisenberg, the German physicist put forward this limitation in the form of **uncertainty** principle. This principle states that:

It is not possible to determine simultaneously the position and momentum of a small moving particle, such as electron, with entire certainty.

Mathematically, it may be expressed as

$$\Delta x \times \Delta p \geq \frac{h}{4\pi}$$

$$\Delta x \times m\Delta p \geq \frac{h}{4\pi}$$

or

where Δx = uncertainty in position

Δp = uncertainly in momentum

m = mass of the particle

Δv = uncertainty in velocity

h = Planck's constant.

From the above expression it is clear that the more precisely one can define the position of small particle, the less certainly one in able to define its velocity or momentum and vise-versa.

It may be emphasised that the uncertainty principle is not due to any limitation of the measuring device but is the direct consequence of dual nature of matter.

2.13. QUANTUM MECHANICAL MODEL OF ATOM

The motion of all macroscopic objects such as a filling stone, moving car, orbiting satellite, etc. can be successfully described in terms of classical mechanics, based on Newton' laws of motion. These objects have predominantly particle character. However, a microscopic object such as electron has both observable wave-like and particle-like properties. The behaviour of such particles cannot be explained on the basis of classical mechanics which is based on Newton's laws of motion. In order to explain the behavior of electrons and other microscopic particles a new branch of science called quantum mechanics was developed. **Quantum mechanics is a theoretical science that takes into account the dual nature of matter**. Quantum mechanics was developed independently in 1926 by Werner Heisenberg und Erwin Schrodinger. In the present context we shall deal with the quantum mechanics of Schrodinger.

Based on quantum mechanics now model of atom was developed during 1920's. This model is known as **quantum mechanical model.** In this model behaviour of the electron in an atom is described by an equation known as the **Schrodinger wave equation.**

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V)\,\psi = 0$$

where x, y and z are the three space co-ordinates,

m is mass of the electron,

h is the Planck's constant,

ψ (Greek letter psi) is amplitube of the elctron wave and is called **wage function.**

and $\frac{\partial^2\psi}{\partial x^2}$ refers to the second derivative of with respect of x only and so on.

The solution of Schrodinger wave equation are known as wave functions. When Schreiner wave equation is solved for hydrogen atom, several solutions are obtained Out of the coly curtain solutions are permissible. Each permitted solution* or wave function corresponds to definite energy state and is called **orbital.** Each energy state or orbital is characterized by a set of the quantum numbers, principal quantum number (n), azimuthal quantum number (l) and magnetic quantum number (m_1). Each orbital can be considered a quantum mechanical analog of the electron orbits as proposed by Bohr. The electron orbitals in atoms are called atomic orbitals while thosea molecule are called molecular orbitals. Since in an atom (or a molecule) only specific of define energy states are permitted, it implies that an electron in an atom (or a molecule) can have only certain specific values of energy. In other words, **energy of electron in an atom is quantized.**

This may also lead us to conclude on the basis of wave mechanical concepts that definite energy levels are present in an atom.

It may be mentioned here that Schrodinger wave equation cannot be solved exactly for multielectron atoms. However, certain approximate methods can be applied to obtain solutions of Schrodinger equation for such systems.

Important Features of the Quantum Mechanical Model of Atom

The main features of the quantum mechanical model of atom are:

1. The energy of electrons in atom in quantized i.e., electrons can have only certain specific values of energy in atoms.
2. The existence of quantized electronic energy states is a direct consequence of the wave properties of electrons.
3. The exact position and exact velocity of an electron in an atom cannot be determined simultaneously. Therefore, it is not possible to determine the exact trajectory of the electron in an atom. Therefore, we consider the probability of finding the electron at different positions in an atom.
4. ψ for an electron in an atom represents an atomic orbital. An orbital is associated with a definite amount of energy. Since many wave functions

are possible for an electron in an atom, there are many atomic orbitals in an atom. An orbital cannot contain more than two electrons.

5. All the information about the electron in an atom can be obtained from the orbital wave function ψ.
6. The probability of finding an electron at a point within an atom is proportional to square of the orbital wave function $|\psi|^2$ at that point. $|\psi|^2$ is known as **probability density** and is always positive.

Significance of ψ

A moving electron is associated with a wave and the wave function ψ gives the amplitude of electron wave It has got no physical significance. However, the square of ψ i.e., $|\psi|^2$ has a physical significance. Just like light radiations where square of amplitude gives the intensity of light, similarly, in electron wave. $|\psi|^2$ gives the intensity of the electron at any point. In other words, the knowledge of $|\psi|^2$ is helpful in assessing the probability of electron in a particular region. Thus, $|\psi|^2$ is called **probability density** and $|\psi|^2$ is referred to as **probability amplitude.**

Concept of Orbitals

According to Heisenberg's uncertainty principle it is not possible to determine precisely the position and momentum of an electron in the atom simultaneously. Therefore, Bohr's concept of well defined orbits is ruled out. In quantum mechanical model, we speak of probability or possibility of an electron with a particular energy being present in a certain region of space around the nucleus. The probability of finding the electron at a particular location is given by the square of wave function ($|\psi|^2$) corresponding to that location. There are certain regions around the nucleus where probability of finding the electron is high and there are certain regions where probability of finding the electron is low. The probability of finding the electron does not become zero even at large distance from the nucleus, although it may become negligible. Therefore, it is not possible to draw a boundary that will enclose the region of 100% probability. However, for the sake of simplicity we draw arbitrary boundaries which enclose he regions where probability of finding the electron is maximum (about 90- 95%). These refits of price around the nucleus where probability of finding the electron is maximum are called orbitals.

An orbital may be defined as that region of space around the nucleus where the probability of finding an electron in maximum (90-95%).

It is rather difficult to represent an orbital by a simple picture. Different methods are employed for this purpose. But the most common method is to represent an orbital as an electron cloud in terms of small dots, the intensity of dots being more in some region and less in other.

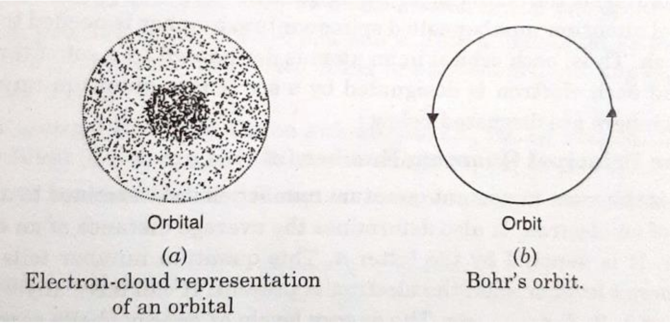


Fig. 2.16. Orbital and an orbit.

In terms of electron cloud representation, the probability of finding an electron in a particular region of space in directly proportional to the density of dots in that region.

The important differences between an orbit and an orbital are given in Table 2.3.

Table 2.3. Differences between an Orbit and an Orbital

Orbit	Orbital
1. It is well-defined circular path followed by revolving electron around the nucleus.	1. It is a region of space cannot the nucleus of the atom where the electron is most likely to be found.
2. It represents planar motion of an electron.	2. It represents three-dimensional motion of an electron around the nucleus.
3. The maximum number of electrons in an orbit is $2n^2$, where n stands for number of the orbit.	3. An orbital cannot accommodate more than two electrons.
4. Orbits are circular in shape.	4. Orbitals have different shapes, *e.g., s-orbitals* are spherically symmetrical whereas *p-orbitals* are dumb-bell shaped.
5. Orbits are non-directional in character hence they cannot explain shapes of molecules.	5. Orbitals (except s-orbitals) have directional character and hence they can amount for shapes of molecules.
6. Concept of well-defined orbit is against Heisenberg's principle.	6. Concept of orbitals is in accordance with Heisenberg's principle.

2.14. QUANTUM NUMBERS

In an atom a large number of electron orbital are permissible. These orbitals are designated by a set of numbers known as quantum numbers. In order to specify energy, size, shape and orientation of the electron orbital three quantum numbers are required. These are, principal quantum number, azimuthal quantum number and magnetic quantum number. These quantum numbers arise as a natural consequence during the solution of the Schrodinger wave equation. In order to designate the electron, an additional quantum number called spin quantum number is needed to specify spin of the electron. Thus, each orbital in an atom is designated by a set of three quantum numbers and each electron i denigrated by a set of four quantum numbers. These quantum numbers are discussed below:

1. The Principal Quantum Number (n)

This is the most important quantum number as it determines to a large extent the energy of an electron It lo determines the average distance of an electron from the nucleus. It is denoted by the letter n. This quantum number tells us in which principal energy level or shell the electron in present. It can have any whole number value such a 1, 2, 3, 4, …… etc. The energy levels or energy shells corresponding to these numbers are designated as K, L, M, N,……, etc. As the value of increases, the electron gets farther away from the nucleus and its energy increases. The higher the value of n, the higher is the electronic energy For hydrogen and hydrogen-like species, the energy and size of the orbital are determined by principal quantum number alone.

Energy of the electron in a hydrogen atom in related to principal quantum number by the following relation:

$$E_n = -k^2 \frac{2^{\pi} m e^4}{n^2 h^2} = \frac{2.18 \times 10^{-18}}{n^2} \text{ J}$$

where, m = mass of electron

e = charge on electron

h = Planck's constant

E_n = Energy of the electron in nth principal shell

n = Principle quantum number used to designate the principle shell

k = Columb's law material

This relation is similar to the expression gives by Bohr.

2. The Orbital Angular Momentum Quantum Number or Azimuthal Quantum Number *(l)*

This quantum number determines angular momentum of the electron. This is denoted by *l*. The value of giives the **sub-level** or **sub-shell** in which the electron is located. It also determines the shape of the orbital in which the electron is located. The number of sub-shells within a principal shell is determined by the value of *n* for that principal energy level. Thus, *l* nay have all possible whole number values from 0 to *n*-1 for each principal energy level. For a given value of *n*, I can have *n* alues. The various sub-levels are designated as s, p, d, *f* depending upon the value of *l* follows:

Value of 1 →	0	1	2	3	4	5	6
Designation of sub-shell →	*s**	*p*	*d*	*f*	*g*	*h*	*i*

For **n = 1,** *l* can have only one value i.e., 0. It means that an electron in first energy level can be present only in *s*-sub-shell (l = 0).

So **first energy** level bus only **one sub-shell,** i.e., 1*s*.

For n = 2, *l* can have values 0 and 1 It mean that the electron in second principal energy level may be located either in *s*-sub-shell(*l* = 0) or *p*-sub-shell (*l* = 1)

So **second energy** level has only **two sub-shells**, i.e., 2*s* and 2*p.*

For n = 3, possible values of *l* are 0, 1 and 2 This implies that an electron in third principal energy level may be present either in *s*-sub-shell (*l* = 0) or *p*-sub-shell (*l* = 1) or *d*-sub-hell (*l* =2).

So third energy level has three sub-shells, i.e., 3*s,* 3*p* and 3*d* Similarly, fourth energy level (*n* = 4) can have four sub-shells 4*s*, 4*p*, 4*d* and 4*f.*

The relation between the orbital angular momentum and azimuthal quantum number, *l* is

$$\text{Orbital Angular Momentum} = \sqrt{l(1+l)}\,\frac{h}{2\pi} = \sqrt{l(1+l)}\;n$$

Azimuthal quantum number is also known as **subsidiary quantum number.**

3. The Magnetic Quantum Number (m)

This quantum number which is denoted by m_1 refers to the different orientations of electron cloud in a particular sub-shell. These different orientations are called **orbitals.** The number of orbitals in a particular sub-shell within a principal energy level is given by the number of values allowed to m, which in turn depends on the Value of *l*. The possible values of m_1 range from + *l* through 0 to -1, thus making a total of $(2l + 1)$ values. Thus, in a subshell, the number of orbitals is equal to $(2l + 1)$.

For l = 0 (*i.e., s*-sub-shell) m_1 can have only one value, $m_1 = 0$. It means that **sub-shell** has only **one orbital.**

For l = 1 (*i.e., p*-sub-shell) m_1 can have only three value, +1, 0 and -1. This implies that **p-sub-shell** has **three orbitals.**

For 1 = 2 (*i.e., p*-sub-shell), m_1 can have five values, +2, + 1, 0, -1, -2. It means that **d-sub-shell** has **five orbitals.**

For 1 = 3 (i.e., sub-shell), m_1 can have seven values, +3, +2, +1, 0,-1,-2, -3. It means that **f-sub-shell** has **seven orbitals.**

The number of orbitals in various types of subshells are given below in tabular form

Sub shell	*s*	*p*	*d*	*f*	G
Value of 1	0	1	2	3	4
No. of orbitals $(2l + 1$I	1	3	5	7	9

The relationship between the principal quantum number (*n*), angular momentum quantum number (*l*) and magnetic quantum number (m_1) is summed up in Table 2.4.

Table 2.4. Relationship among Value of n, l and m_1

Energy Level	Principal Quantum Numbers (*n*)	Possible value of (*l*)	Designation of sub-shell	Possible values of (m_1)	Number of orbitals	
					In a Given Sub-shell	In a given Energy Level
K	1	0	1*s*	0	1	1
L	2	0	2*s*	0	1	4
		1	2*p*	+1, 0, -1	3	
		0	3*s*	0	1	
M	3	1	3*p*	+1, 0, -1	3	5
		2	3*d*	+2, +1, 0, -1, -2	5	

4. The Spin Quantum Number (m)

This quantum number which is denoted by m, does not follow from the wave mechanical treatment but arises from the spectral evidence that electron in its motion about the nucleus also rotates ar spins about its own axis.

This quantum number determines the orientation of spin angular momentum. Spin angular momentum is quantized and can have two orientations relative to a chosen axis. The spin quantum number can have only two values which are $+\frac{1}{2}$ and $-\frac{1}{2}$. The $+\frac{1}{2}$ value indicates clockwise spin (generally represented by an arrow pointing upwards, i.e.,↑) and the other indicates anti-clockwise spin (generally represented by an arrow painting downwards i.e.,↑).

Due to its spin, the electron behaves as a tiny magnet. The spin of the electron is responsible for most of the magnetic properties of atoms, molecules or ions. If all the electrons in an atom or molecule are paired, it behaves as a **diamagnetic substance** i.e., it is weakly repelled by the magnetic field. On the otherhand, if atoms or molecules of a substance have one or more unpaired or odd electrons, it behaves as an **paramagnetic substance**, i.e., it is weakly attracted by magnetic field.

2.15. SHAPES OF ORBITALS

Boundary Surface Diagrams

The shapes of the orbitals can be represented quite accurately with the help of boundary surface diagrams. In this representation, a boundary surface (also known as contour surface) is drawn in space for an orbital on which the value of probability density (ψ^2) is constant.

A boundary surface which encloses the regions of maximum probability (say 90%) best describes the shape of the orbital. It is not possible to draw a boundary surface diagram which encloses the region of 100% probability because probability density has always some value, howsoever small it may be, at any finite distance from the nucleus. The boundary surface diagrams for *s*-orbitals are spherical in shape. The size of the *s*-orbital, however, increases with increase in value of *n*. If we observe the probability density curve for 2*s* orbital we find that the probability density function for 2*s* orbital decreases to zero, increases to maximum value and finally approaches zero with increase in distance from the nucleus, The region where the probability density function reduces to zero is called nodal surface or node. In any *ns* orbital there are (*n* - 1) nodes. Thus, 2*s* orbital has only one node.

The boundary surface diagrams of the three 2*p* orbitals are not spherical. Each *p*-orbital consists of two lobes which are separated by a region of zero probability called node. The three 2*p* orbitals lie along *x*-, *y*- and *z*-axis respectively and are designated $2p_x$, $2p_y$, and $2p_z$.

The boundary surface diagrams of 1*s*, $2p_x$, $2p_y$, and $2p_z$ orbitals are shown in Fig. 2.17.

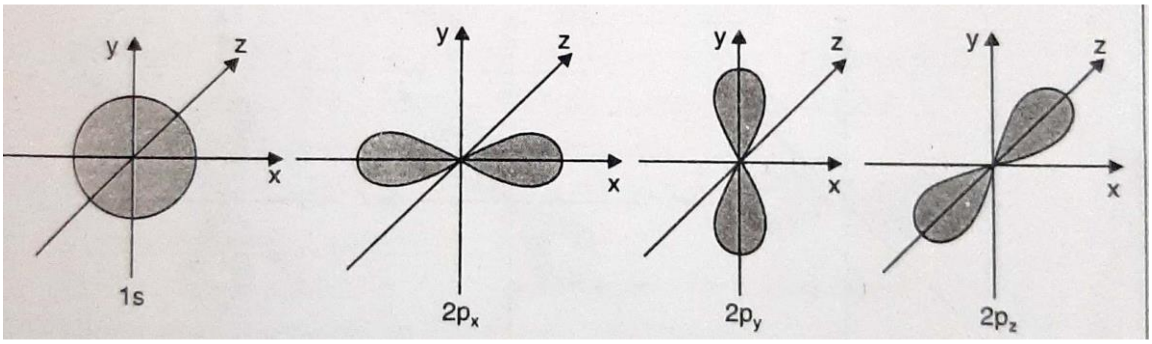


Fig. 2.17. The boundary surface diagrams of 1*s* and 2*p* orbitals

Like s-orbitals *p*-orbitals also increase in size with the increase in value of *n*. Moreover higher *p*-orbitals have nodal surfaces in addition to the nodal plane. The number of nodal surfaces in any *np* orbital is (*n* - 2). Thus, a 2*p*-orbital has no nodal surface whereas a 3*p*-orbital has one nodal surface.

In any orbital, the total number of nodes is equal to (*n* - 1), angular nodes or nodal planes in equal to the angular momentum quantum number, *l* and the radial nodes is equal to *n* - *l* - 1.

Charge Cloud Picture of Orbitals

An alternative way to describe the probability is in terms of negative charge cloud, the density of charge cloud being proportional to ψ^2 probability. In this method, the charge cloud is represented in term of small dots. To understand this method of representation, let us imagine the electron as a very small dot. Let us further suppose that we take a very large number of photographs of the electron in a hydrogen atom at very short intervals of time on the same film. If the film were developed, the picture obtained would be similar to that shown in Fig. 2.18 (*a*). In terms of electron cloud representation the probability of finding the electron in a particular region of space is directly proportional to the density of such dots in that region.

The charge cloud pictures of 1*s*, 2*s* and 3*s* orbitals have been given in Fig.2.18.

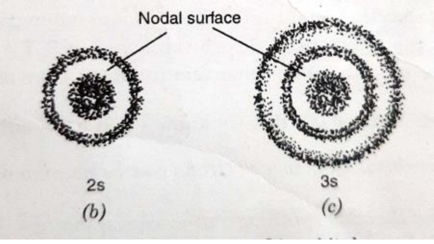


Fig. 2.12. (a) Charges cloud pictures of 1*s* orbitals

(b) Charges cloud pictures of 2*s* orbitals

(c) Charges cloud picture of 3*s* orbitals

For ***p*-orbitals** there are three possible orientations of electron cloud. These three orientation or orbitals of a pub-shell are designated as p_x, p_y and p_z or p_{+1}, p_{-1} and p_0, respectively p_x, p_y and p_z orbitals are oriented along *x*-axis, *y*-axis and *z*-axis respectively Each *p*-orbital has two lobes which are separated by a plane af zero probability called **nodal plane**. Each orbital is, thus, **dumb-bell shaped,** The spatial distribution of 2*p* orbitals are shown in Fig. 2.19.

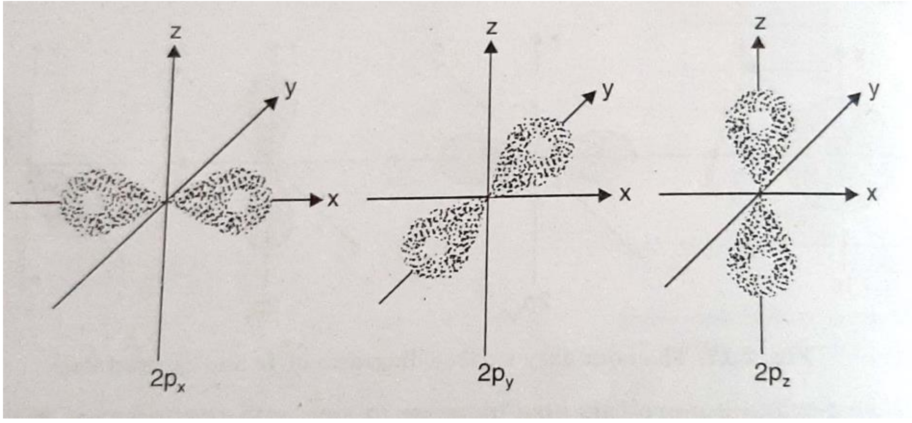


Fig. 2.19. 2*p* orbitals.

In the absence of an external electric or magnetic field, the three p-orbitals of particular energy level have energy. Such orbitals which have equal energy are called **degenerate orbitals.** In the presence of external magnetic or electric field this degeneracy is lust because the three *p*-orbitals are oriented differently with respect to applied field.

2.16. PAULI'S EXCLUSION PRINCIPLE

This principle was discovered by Wolfgang Pauli in 1925. This principle states that:

No two electrons in an atom can hate some values for all the four quantum number

A direct implication of this principle is that it is not possible to accommodate more than two electrons in an orbital. This can be easily understood as follows:

All the electrons in a particular orbital have same values of principal quantum numbers (*n*), azimuthal quantum number (*l*) and magnetic quantum number (m_1). For example, all the electrons in as orbital have n = 3, l = 0 and m_1 = 0. Therefore, in order to have unique suit of quantum numbers they must have different values of spin quantum number (*s*). But we know u can have only two values + $\frac{1}{2}$ and - $\frac{1}{2}$.

Hence, in an orbital only two electrons can be accommodated on spinning clockwise $\left(m_s = +\frac{1}{2}\right)$and the other spinning anti-clockwise $\left(m_s = -\frac{1}{2}\right)$. From the above discussion it follows that

s-sub-shell (containing only **one orbital)** can have a maximum of **2 electrons**

p-sub-shell (containing **three orbital)** can have a maximum of **6 electrons**

d-sub-shell (containing **five orbital)** can have a maximum of **10 electrons**

f-sub-shell (containing **seven orbital)** can have a maximum of **14 electrons**

SOLVED EXAMPLES

Example 2.10. *(a) What sub-shell are possible in n = 3 energy level?*

(b) How many orbitals (of all kinds) are possible in this level?

Solution. *(a) Sub-shell in n = 3 energy level.*

For $n = 3$ the possible values of l are 0, 1 and 2.

The corresponding sub-shell are

$l = 0$, *s* sub-shell; $l = 1$, *p* sub shell ; $l = 2$, *d* sub-shell

(b) Number of orbitals

For $n = 3$ there are one *s*, three *p* and five *d* orbitals.

This makes a total of **nine orbitals** in $n = 3$ level.

Example 2.11. *What are the possible values of l for an electron in*

(a) third energy level (b) 3d sub-shell?

Solution. *(a)* For third energy level $n = 3$. Since l may have values from 0 to $n - 1$, the possible values of l are **0, 1 and 2.**

(b) For *d*-sub-shell $l = 2$, hence, in 3*d*-sub-shell the only possible value of l is **2.**

Example 2.12. *How many sub-shells are there in N shell? How many orbitals are there in d sub-shell?*

Solution. For N shell principal quantum number, $n = 4$.

Number of sub-shells in an energy level = n

∴ Number of sub-shells in N shell = 4

For *d* sub-shell $l = 2$

Number of orbitals in a sub-shell = $2l + 1$

Number of orbitals in a d-sub-shell = 2 × 2 + 1 = 5.

2.17. RULES FOR FILLING OF ORBITALS IN AN ATOM

An atom in its lowest energy state in said to be in the normal state or the ground state. The ground state is the most stable state for the atom. The filling or orbitals in the ground state is determined by the following rules:

1. Aulbau Rule

According to this rule,

the electrons are added progressively to the various orbitals in their order of increasing energies, starting with the orbital of lowest energy.

Increasing order of energies of various orbitals is:

$1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s,$……

Fig. 2.20 shows a simple memory aid or remembering the increasing order of energies of various orbitals.

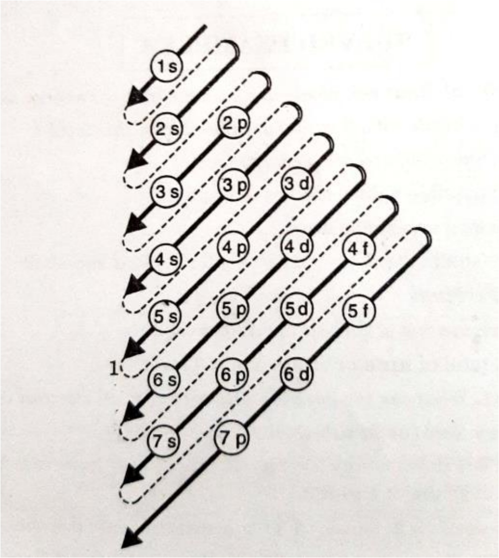


Fig. 2.20. Memory aid for remembering order of energies of various orbitals.

The relative order of energies of various sub-shell in multi-electron atom can be predicted with the help (**n + 1**) rule or **Bohr-Bury's rule.** According to this rule:

(i) In neutral atoms a sub-shell with loser value of (n + 1) has lower energy.

For example, $4s$ orbital has lower energy than $3d$ orbital.

For 4s orbital $n = 4$ and $l = 0$. Hence, $n + 1 = 4 + 0 = 4$.

For 3d orbital $n = 3$ and $l = 2$. Hence, $n + 1 = 3 + 1 = 4$.

(ii) If two sub-shell have equal value ($n + 1$), the sub-shell with lower value of n has lower energy.

For example, consider 3p and 4s orbitals.

For 4s orbital $n = 4$ and $l = 0$. Hence, $n + l = 4 + 0 = 4$.

For 3p orbital $n = 3$ and $l = 1$. Hence $n + l = 3 + 1 = 4$

Here 3p orbital has lower energy then 4s because it has lower value of n.

2. Pauli's Exclusion Principle

This principle states that **no two electron in an atom can have some set of all the four quantum numbers.** From this it follows that an orbital cannot have more than two electrons. Moreover, if an orbital has two electrons then **they must have** opposite spins.

3. Hund's Rule of Maximum Multiplicity

This rule states that

the pairing of electrons in the orbitals of a particular sub-shell (*p*, *d* or *f*) does not take place until all the orbital of the sub-shell are singly occupied. Moreover, the singly occupied orbitals must have the electrons with parallel spins.

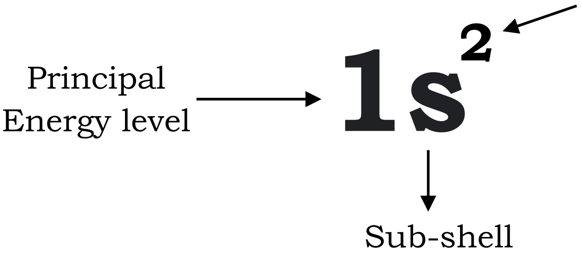
The basis of the rule is that two electrons in a particular orbital feel greater repulsion and hence while filling orbitals of equal energy pairing of electrons is avoided as long as it is possible. Moreover, the singly occupied orbitals should have electrons with parallel spin because this corresponds to state of lower energy. This can be explained in terms of magnetic effects of electron spin. This rule helps us in writing this ground state configurations of those atoms which have partially filled p, d or f sub-shells in them. The application of these rules has been illustrated in the following electronic configurations.

2.18 ELECTRONIC CONFIGURATIONS OF ATOMS

In order to represent electron population of an orbitals, the principal quantum number (n) is written before the orbital symbol while the number of electrons in the orbitals is written superscript near the right hand top of the orbital symbol. For example, if we have two electrons in the s-orbital of first energy level then it is written as $1s^2$. Sometimes, electronic configurations are represented in a different manner by presenting each

Number of Electrons

orbital by a square or a circle and the electrons are represented by patting arrows in it as illustrated below:



Electronic Configuration of Atoms

On the basis of above rules and the sequence of energy levels, let us write electronic configurations of some elements.

Hydrogen (At. No. = 1). Since hydrogen has only electron, it must go to 1*s* orbital. The electronic configuration for hydrogen is

$_{1}\text{H} : 1s^1$ OR $\overset{1s}{\boxed{\uparrow}}$

Helium (At. No = 2). In helium atom, the second electron can also go into 1*s* orbital. The electrons must have opposite spins.

$_{2}\text{He} : 1s^2$ OR $\overset{1s}{\boxed{\uparrow\downarrow}}$

Lithium (At. No. = 3). Since 1*s* orbital is filled with two electrons, it cannot have any more. Therefore, third electron goes to the next lowest energy orbital, 2*s*.

$_{3}\text{Li} : 1s^2, 2s^1$ OR $\overset{1s}{\boxed{\uparrow\downarrow}}\ \overset{2s}{\boxed{\uparrow}}$

Beryllium (At. No. = 4). The fourth electrons in beryllium fiils 2*s* orbital.

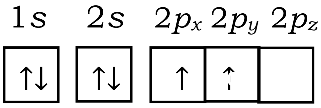
$_{4}\text{Be} : 1s^2, 2s^2$ OR $\overset{1s}{\boxed{\uparrow\downarrow}}\ \overset{2s}{\boxed{\uparrow\downarrow}}$

Boron (At. No. = 5). In this case, the four electrons completely fill 1*s* and 2*s* orbitals. The fifth electron into one of the 2*p* orbitals.

$_{5}\text{B} : 1s^2, 2s^2\ 2p_x^1$ OR $\overset{1s}{\boxed{\uparrow\downarrow}}\ \overset{2s}{\boxed{\uparrow\downarrow}}\ \overset{2p_x}{\boxed{\uparrow}}\overset{2p_y}{\boxed{}}\overset{2p_z}{\boxed{}}$

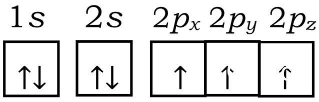
Carbon (At. No = 6). In case of carbon the sixth electron also goes into $2p$ sub-shell, but the two electrons in $2p$ sub-shell are present in different orbitals because according to Hund's rule planning of electrons cannot take place in orbitals of a particular sub-shell unit all the orbitals get one electron each. Hence, configuration of carbon is

$_6$C : $1s^2$, $2s^2$ $2p_x^1$, $2p_y^1$ OR



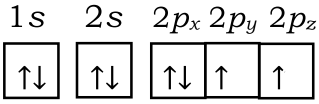
Nitrogen (At. No = 7). Applying Hund's rule, N atom has three unpaired electrons in $2p$ orbitals.

$_7$N : $1s^2$, $2s^2$ $2p_x^1$, $2p_y^1$, $2p_z^1$ OR

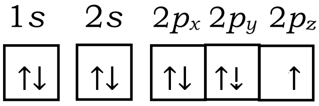


Oxygen, Fluorine and Neon. Beginning with oxygen, the $2p$ orbitals start filling by second electron till neon in which it is completely filled.

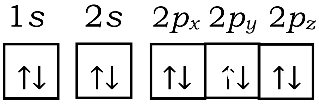
$_8$O : $1s^2$, $2s^2$ $2p_x^1$, $2p_y^1$, $2p_z^1$ OR



$_9$O : $1s^2$, $2s^2$ $2p_x^1$, $2p_y^1$, $2p_z^1$ OR



$_{10}$Ne : $1s^2$, $2s^2$ $2p_x^1$,$2p_y^1$, $2p_z^1$ OR



From sodium (At. No. 11) to argon (At. No. 18) $3s$ and $3p$ orbitals are successively filled. After $3p$, the 19th electron in potassium (At. No. 19) enters the $4s$ orbitals instead of $3d$ because energy of $4s$ orbital is less than that of $3d$. Electronic configuration of first twenty elements haven been given in Table 2.5.

Table 2.5. Electronic Configurations of the First 20 Elements

Atomic Number	elements	Orbital Electronic Configuration			
1	Hydrogen	$1s^1$			
2	Helium	$1s^2$			
3	Lithium	$1s^2$	$2s^1$		
4	Beryllium	$1s^2$	$2s^2$		
5	Boron	$1s^2$	$2s^2$ $2p_x^1$		
6	Carbon	$1s^2$	$2s^2$ $2p_x^1$ $2p_y^1$		
7	Nitrogen	$1s^2$	$2s^2$ $2p_x^1$ $2p_y^1$ $2p_z^1$		
8	Oxygen	$1s^2$	$2s^2$ $2p_x^2$ $2p_y^1$ $2p_z^1$		
9	Fluorine	$1s^2$	$2s^2$ $2p_x^2$ $2p_y^2$ $2p_z^1$		
10	Neon	$1s^2$	$2s^2$ $2p_x^2$ $2p_y^2$ $2p_z^2$		

11	Sodium	$1s^2$	$2s^2\,2p_x^2\,2p_y^2\,2p_z^2$	$3s^1$	
12	Magnesium	$1s^2$	$2s^2\,2p_x^2\,2p_y^2\,2p_z^2$	$3s^2$	
13	Aluminum	$1s^2$	$2s^2\,2p_x^2\,2p_y^2\,2p_z^2$	$3s^2\,2p_x^1$	
14	Silicon	$1s^2$	$2s^2\,2p_x^2\,2p_y^2\,2p_z^2$	$3s^2\,3p_x^1\,3p_y^1$	
15	Phosphorus	$1s^2$	$2s^2\,2p_x^2\,2p_y^2\,2p_z^2$	$3s^2\,3p_x^1\,3p_y^1\,3p_z^1$	
16	Sulphur	$1s^2$	$2s^2\,2p_x^2\,2p_y^2\,2p_z^2$	$3s^2\,3p_x^2\,3p_y^1\,3p_z^1$	
17	Chlorine	$1s^2$	$2s^2\,2p_x^2\,2p_y^2\,2p_z^2$	$3s^2\,3p_x^2\,3p_y^2\,3p_z^1$	
18	Argon	$1s^2$	$2s^2\,2p_x^2\,2p_y^2\,2p_z^2$	$3s^2\,3p_x^2\,3p_y^2\,3p_z^2$	
19	Potassium	$1s^2$	$2s^2\,2p_x^2\,2p_y^2\,2p_z^2$	$3s^2\,3p_x^2\,3p_y^2\,3p_z^2$	$4s^1$
20	Calcium	$1s^2$	$2s^2\,2p_x^2\,2p_y^2\,2p_z^2$	$3s^2\,3p_x^2\,3p_y^2\,3p_z^2$	$4s^2$

2.19 VALENCE BOND THEORY (VBT)

This approach of chemical bonding was developed by Hietler and London (1927) and further improved by Pauling. It is also called orbital concept of bonding.

It is a well-established fact that all the mechanical systems in this universe tend to lower their potential energy. Lower the energy of the system is, greater is its stability to the similar way, the formation of bonds between the atoms occurs only if it is accompanied by decrease of energy. For the sake of illustration let us study the formation of hydrogen molecule.

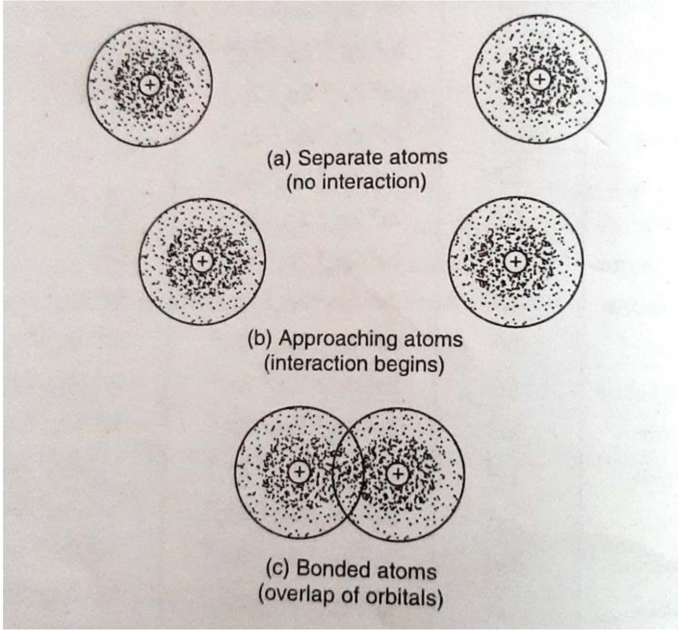
Hydrogen Molecule

It has been shown by the experiments that when hydrogen is heated to a sufficiently high temperature the molecules break up to form atoms of hydrogen.

$$H_2(g) + 433 \text{ kJ} \rightarrow H(g) + H(g)$$

The above equation tells us that one mole of hydrogen molecules (H_2) need 433 kJ of energy to dissociate into hydrogen atoms. Conversely, the formation of one mole of hydrogen molecules from gaseous hydrogen atoms releases 433 kJ of energy. In other words, a molecule of hydrogen (H_2) has lower energy than the hydrogen atoms. Let us study as to how this lowering of energy occurs when hydrogen atoms constitute hydrogen molecule.

We know that hydrogen atom has one electron which is present in its l*s* orbital. Let us assume two hydrogen atoms, Hand He with their corresponding electrons e_A and respectively. The separate hydrogen atoms have been shown in Fig. 2.21 (*a*). When the two atoms start approaching, the electron of each atom starts coming under the influence of the nucleus of the other. In other words, their orbitals begin to interact. This has been shown in Pit 221 (*b*). The following new electrostatic interactions are set up:



(a) Separate atoms (no interaction)

(b) Approaching atoms (interaction begins)

(c) Bonded atoms (overlap of orbitals)

Fig. 2.21. Formation of hydrogen molecule when two hydrogen atoms approach each other.

(a) Attractive forces between: (i) electron e_A and nucleus H_B

(ii) electron e_B and nucleus H_A

(b) Repulsive forces between (i) electron e_A and nucleus e_B

(ii) electron H_A and nucleus H_B

The attractive and repulsive forces have been shown in Fig. 2.22.

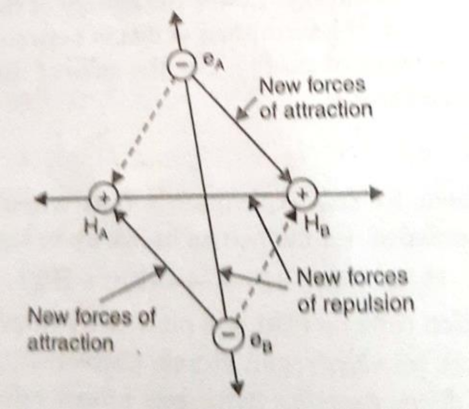


Fig. 2.22. Attractive and repulsive forces between two H atoms approaching each other.

The attractive forces tend to bring the two atoms close to each other whereas repulsive forces tend to put them apart. It has been found that in the beginning the magnitude of attractive forces is greater than the repulsive forces. Therefore, the atoms go on approaching each other and the potential energy of the system continues decreasing.

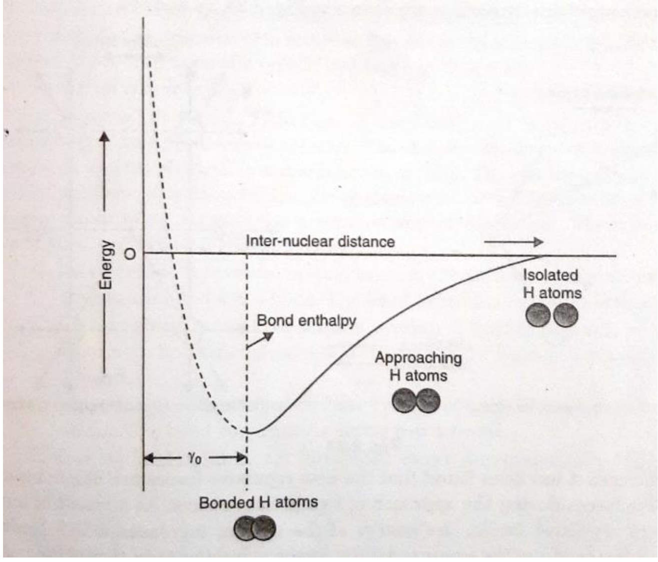


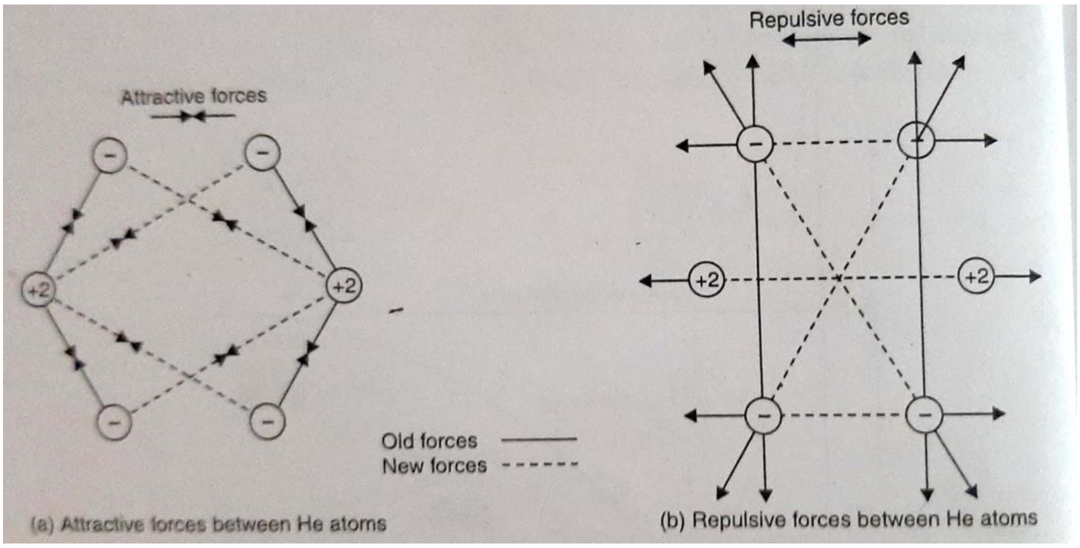
Fig. 2.23. Potential energy curve for hydrogen molecule.

Ultimately, a state is reached where attractive forces, just balance the repulsive forces. This state is reached when the atoms are at critical distance r_0. At a distance greater than the attractive forces are dominant whereas at a distance smaller than r_0, the repulsive forces are dominant. Maximum lowering of energy taken place at critical distance r_0. The lowering of P.E. as a function of internuclear distance has been shown in Fig. 2.23.

It in evident from the curve that the energy of two H atoms when they are held at distance r_0 is smaller than the energy of individual H atoms. Therefore, the H atoms constitute a stable grouping called hydrogen molecule. The critical distance r_0 corresponding to minimum energy is called **bond length.** Experiments have shown that the value of r_0 is 74 pm (0.74×10^{10}m). The energy corresponding to the minimum in the curve is called **bond energy.** If this much energy is supplied from outside, the bond will break and the molecule will dissociate into atoms.

Overlap of orbitals. If we refer to the minimum energy state in the formation of hydrogen molecule the two H-atoms are enough near Ho as to allow their atomic orbitals to undergo partial interpenetration. This partial interpenetration of atomic orbitals is called overlapping of atomic orbital. The electrons belonging to these orbitals are said to be shared. This leads us to the conclusion that orbital overlap is necessary for the electrons to be shared or for the bond to be formed. According to Paul's principle the two electrons occupying same region of space must have different spin quantum numbers. Therefore, the two electrons forming a bond must have opposite spins. The overlapping of atomic orbitals in case of hydrogen molecule has been shown in Fig. 2.21. (*c*).

Why He_2 molecule is not formed? Helium atom ($1s^2$) has 2 electrons in its 1*s*, orbitals. The new attractive and repulsive forces which come into existence when two helium atoms approach each other are shown in Fig.2.24 (*a*) and (*b*).



(a) Attractive forces between He atoms

(b) Repulsive forces between He atoms

Fig. 2.24

In this case it has been found that the new repulsive forces are dominant over the attractive forces during the approach of two helium atoms. As a result of larger magnitude of repulsive forces, the energy of the system increases which leads to instability. Since energy of the separate helium atoms is smaller than that of the system when they are close to each other, they prayer to stay separate and do not form He_2 molecule.

The answer to the above question can also be given on the basis of orbital overlap. 1*s*-orbital of each helium atom has 2 electrons. These orbitals cannot overlap because it would go against Pauli's exclusion principle. Hence, helium atoms do not form bonds to constitute He_2 molecule.

Orbital Concept and Formation of Simple Molecules

We have studied that formation of hydrogen molecule takes place as a result of overlapping of half-filled atomic orbitals of hydrogen atoms. Before we apply the concept of overlapping to study the formation of some simple covalent molecules let us summarise the various postulates of orbital concept regarding the formation of covalent bonds.

(i) Covalent bonds are formed by the overlapping of half-filled atomic orbitals present in the valence shell of the atoms participating in bonding.

(ii) The orbitals undergoing overlapping must have electrons with opposite spins.

(iii) Overlapping of atomic orbitals results in the decrease of energy and formation of covalent bond.

(iv) The strength of a covalent bond depends upon the extent of overlapping. The greater the overlapping more is the energy released and consequently, stronger will be the covalent bond.

The above treatment of formation of covalent bond involving the overlap of half failed atomic orbitals is based upon wave mechanical model and is called **Valence Blond Approach** and the number of half-filled orbitals present in the valence shell of the atoms represents **covalency** of the element.

Types of Overlapping and Nature of Covalent Bond

As pointed out earlier the formation of a covalent bond involves the overlapping of ball filled atomic orbitals. The covalent bands can be classified into two different categories depending upon the type of overlapping. There are:

(a) Sigma covalent bond (b) Pl covalent bond.

(*a*) **Sigma** (σ) **bond.** This type of covalent bond is formed by the **axial overlapping** of half-filled atomic orbitals. The atomic orbitals overlap along the inter-nuclear axis and involve end to end or head on overlap. The electron cloud formed as a result of axial overlap is cylindrically symmetrical about inter-nuclear axis. The electrons constituting sigma bond are called **sigma electrons**. There can be three types of axial overlap as discussed below:

(i) **s-s overlap.** It involves mutual overlap of half-filled r-orbitals of the atom approaching to form a bond. The bond formed is called ***s-s* σ bond.**

(ii) **s-p overlap.** It involves mutual overlap of half-filled *s*-orbital of the one atom with half-filled *p*-orbital of the other. The bond so formed is called **s-p σ bond.**

(iii) **p-p overlap**. It involves mutual overlap of half-filled *p*-orbitals of the two atoms. The bond so formed in called **p-p σ bond.**

The *s-s*, *s-p* and *p-p* overlaps have been shown diagrammatically in Fig. 2.25.

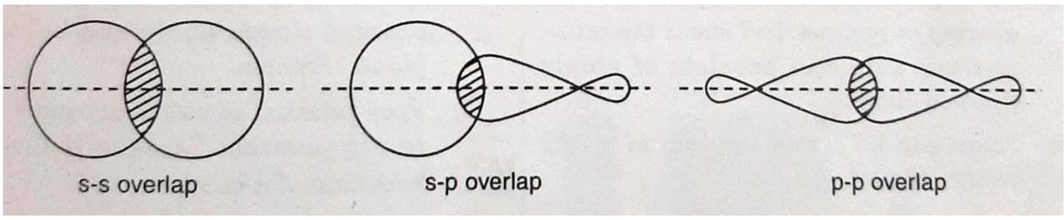


Fig. 2.25. *s-s*, *s-p* and *p-p* overlap of atomic orbitals.

Strength of three types of sigma bonds. The strength of three types of sigma bonds varies as follows:

p-p > ***p-s*** > ***s-s***

It is because of the fact, that p-orbitals allow overlap to a greater extent as compared to *p-s* which is larger as compared to *s-s* overlap.

(*b*) **Pi** (π) **Bond.** This type of covalent bond is formed by the **lateral** or **sidewise overlap** of the atomic orbitals. The orbital overlap takes place in such a way that their axes are parallel to each other but perpendicular to the internuclear axis. The *pi* bond consists of two charge clouds above and below the plane of the atoms involved in the bond formation. The electrons involved in the re-bond formation are called **π-electrons.**

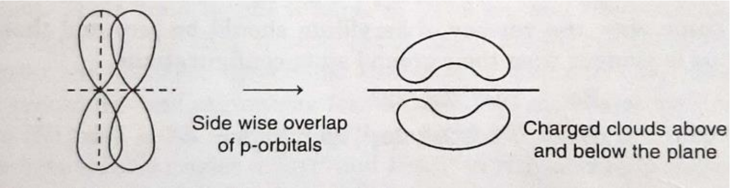


Fig. 2.26. Sidewise overlap of *p*-orbitals

It may be noted that

(i) **Sigma bond is stronger than pi band.** It is because of the fact that over lapping of atomic orbitals can take place to a greater extent during the formation of sigma bond whereas overlapping of orbitals occurs to a smaller extent during the formation of pi bond.

(ii) **Pi bond between the two atoms is formed only in addition to a sigma bond.** It is because of the fact that the atoms constituting a single bond prefer to form a strong siya bond rather than a weak pi bond. Thus, pi bond is always present in molecules having multiple bonds i.e., double or triple bond. In other words, a single bond cannot be a pi bond.

Comparison between sigma and pi bonds. The various points of distinction between sigma and pi bonds are given in Table 2.6.

Table 2.6. Comparison of Sigma and Pi Bonds

Sigma Bond	Pi Bond
1. This bond is formed by the axial overlap of atomic orbitals.	1. The bond is formed by the sidewise overlap of atomic orbitals.
2. This bond can be formed by overlap by *s*-*s*, *s*-*p* or *p*-*p* orbitals.	2. It involves of overlap of *p*-orbitals only.
3. The bond is stronger because overlapping can take place to a larger extent.	3. The bond is weaker because the overlapping occurs to a smaller extent.
4. The electron cloud formed by axial overlap is symmetrical about the inter-nuclear axis and consists of single charged cloud.	4. The electron cloud of pi bond is discontinuous and consists of two charged clouds above and below the plane of atoms.
5. There can be a free rotation of atoms around the σ bond.	5. Free rotation of atoms around π bond is not possible because it involves breaking of π bond.
6. The bond may be present between the two atoms either alone or alongwith π bond.	6. The bond is always present between the two atoms along with the sigma bond i.e., is always superimposed on sigma bond.

2.20 CONCEPT OF HYBRIDIZATION

We have learnt in VBT that covalency of an element is equal to the number of half-filled orbitals present in the valence shell of its atoms. On applying this concept to carbon, we find that the valency of carbon should be equal to 2 because it has only two half-filled orbitals in the valence shell.

$$_6C \quad : 1s^2, 2s^2\ 2p_x^1, 2p_y^1, 2p_z^0$$

In the same way, the valency of beryllium should be zero and that of boron should be one as is evident from their ground state configurations.

$$_4Be \quad : 1s^2, 2s^2\ 2p^0$$

$$_5B \quad : 1s^2, 2s^2\ 2p_x^1, 2p_y^0, 2p_z^0$$

Contrary to this, carbon atom always exhibits a valency of four while beryllium and baron exhibit valency of two and three respectively.

In order to explain the observed valencies of Be, B and C, it is assumed that these atoms acquire excited states before participating in bonding. In the excited state the electron pair present in 2s-orbital gets unpaired and one of the electrons in promoted to vacant 2*p*-orbital.

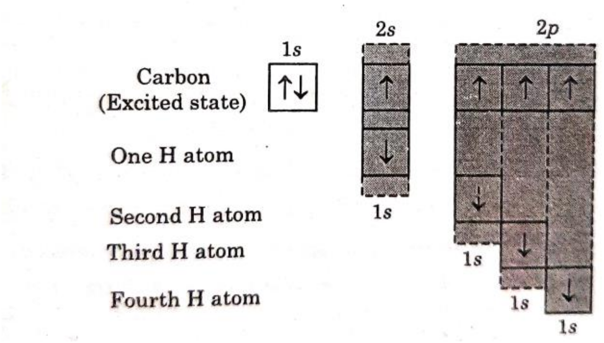
For example, the simple excited state configurations of Be, B and C are shown below:

	1*s*	2*s*	2*p*			
$_4$Be	↑↓	↑	↑			Two half filled orbitals
$_5$B	↑↓	↑	↑	↑		Three half filled orbitals
$_6$C	↑↓	↑	↑	↑	↑	Four half filled orbitals

Thus, concept of excitation or promotion of electrons could very well explain the valency of beryllium, boron and carbon as 2, 3 and 4 respectively. The energy required for excitation is compensated by the energy released during bond formation.

Let us now study the formation of methane from the excited state configuration of carbon.

Carbon uses its four half-filled orbitals for the axial overlap with 1*s* orbitals of four different H atoms as shown below:



It is quite evident that the four C-H bonds in CH_4 (methane) should not be equivalent. Three C-H bonds should be sigma *p-s* bonds and one C-H bond should be sigma *s-s* bond. Moreover, HCH bond angle should be 90° because p-orbitals of carbon are at 90° to one another. Thus, the C-H bonds in CH_4 should be different so far as their (i) strength, (ii) bond length and (iii) bond angle are concerned. The experimental facts about methane reveal that all the C-H bonds in the molecule are equivalent. Their bond length is some i.e., 109 pm and the bond angle H-C-H is 109°28'. Thus, we find that, the concept of simple atomic orbital overlap is not able to account for the observed directional character of bonds in CH_4 molecule. If we use similar procedure and arguments for NH_3 and H_2O molecules we find that the HNH angle in NH_3 and HOH angle in H_2O should be 90° which is again in disagreement with the actual bond angles of 107° and 104.5° in NH_3 and H_2O respectively. In order to explain these experimental facts and characteristic shapes of polyatomic molecules such a CH_4, NH_3, H_2O, etc, a concept called hybridization was introduced Linus Pauling.

According to this concept, Valence orbitals of the atom intermix to give rise to another set of equivalent orbitals before the formation of bonds. These orbitals are called **hybrid orbitals** or **hybridized orbitals** and the phenomenon is referred to as **hybridization.** Thus, **hybridization** may be defined as the **phenomenon of intermixing of atomic orbitals of slightly different energies of the atom (by redistributing their energies) to form new set of orbitals of equivalent energies and identical shape.**

In case of carbon atoms, one orbital of 2*s*-level and three orbitals of 2p-leve) intermix at the time of participation in bonding to produce four equivalent sp^3 hybridized orbitals. There hybrid orbitals overlap axially with 1*s* orbitals of four H atoms to form four equivalent C-H bonds in methane.

Salient Features of Hybridization

Hybridization is a theoretical concept which has been introduced to explain some structural properties such a shapes of molecules or equivalency of bonds, etc., which cannot be explained by simple theories of valency. Some salient features of hybridization are:

- The orbitals taking part in hybridization must have only a small difference of their energies.
- The hybridized orbitals have equivalent energies and identical shapes.
- The number of hybrid orbitals is equal to the number of orbitals taking part in hybridization.
- Both half-filled as well as completely filled orbitals of valence shell can take part in hybridization.
- The hybrid orbital has electron density concentrated on one side of the nucleus. i.e., it has one lobe relatively larger than the other.
- The hybrid orbitals can form stronger bonds as compared to the unhybridised or pure atomic orbitals because they can undergo more effective overlap.
- The hybrid orbitals are directed in space in some preferred directions so as to have minimum repulsive interactions and attain maximum stability.

Types of Hybridization

There are many different types of hybridization such as sp^3, sp^2, sp, etc, depending upon the type of orbitals involved in mixing. Let us now discuss various types of hybridization along with some examples.

(i) **sp^3 hybridization**. The type of hybridization involves the mixing of one orbital of *s*-sub-shell and three orbitals of *p*-sub-shell of the valence shell to form four sp^3 hybrid orbitals of equivalent energies and shape. Each sp^3 hybrid orbital has 25% *s*-character and 75% *p*-character. These hybridized orbitals tend to lie as far apart in space as possible that the repulsive interactions between them are minimum. The four sp^3 hybrid orbitals are directed towards the four corners of a tetrahedron. The angle between the sp^3 hybrid orbitals is 109.5° (Fig. 2.27).

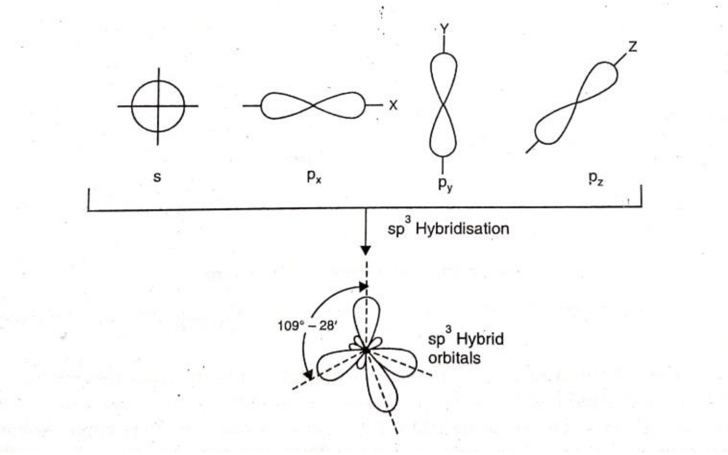


Fig. 2.27. Orientations of sp^3 hybrid orbitals.

sp^3 hybridization is also known as **tetrahedral hybridization.** The molecules in which central atom is sp^3 hybridized and is linked to four other atoms directly, have **tetrahedral shape.**

Let us study some example of molecules where the atoms assume sp^3 hybrid state.

1. Formation of methane (CH_4). In methane carbon atom acquires sp^3 hybrid states as described below:

Here, one orbital of 2*s*-sub-shell and three orbitals of 2*p*-sub-shell of excited carbon atom undergo hybridization to form four sp^3 hybrid orbitals. The process involving promotion of 2*s*-electron followed by hybridization is shown Fig. 2.28.

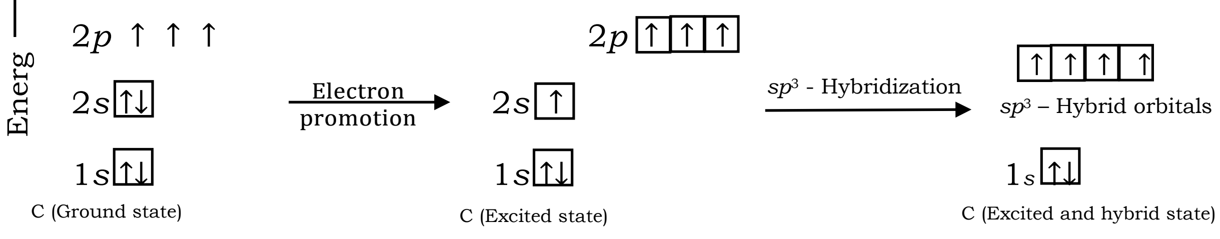


Fig. 2.28. sp^3 hybridisation of carbon.

As pointed out earlier the sp^3 hybrid orbitals of carbon atom are directed towards the corners of regular tetrahedron. Each of the sp^3 hybrid orbitals overlaps axially with half-filled 1*s*-orbital of hydrogen atom constituting a sigma bond (Fig. 2.29.)

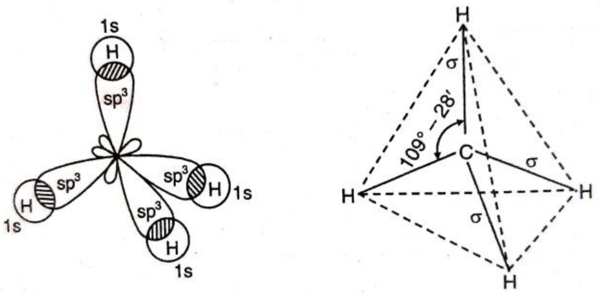


Fig. 2.29. Orbitals picture of methane.

Because of *sp*^{3} hybridization of carbon atom, **CH_4** molecule has **tetrahedral shape.**

(ii) **sp^2 hybridization**. This type of hybridization involves the mixing of one orbital of s-sub-shell and two orbitals of p-sub-shell of the valence shell to form three *sp*^{2} hybrid orbitals. These *sp*^{2} hybrid orbitals lie in a plane and are directed towards the corners of equilateral triangle (Fig. 2.30). Each *sp*^{2} hybrid orbital has one-third s-character and two-third *p*-character, *sp*^{2} hybridization is also called **trigonal hybridization.** The molecules in which central atom is *sp*^{2} hybridized and is linked to three other atoms directly have triangular planar shape.

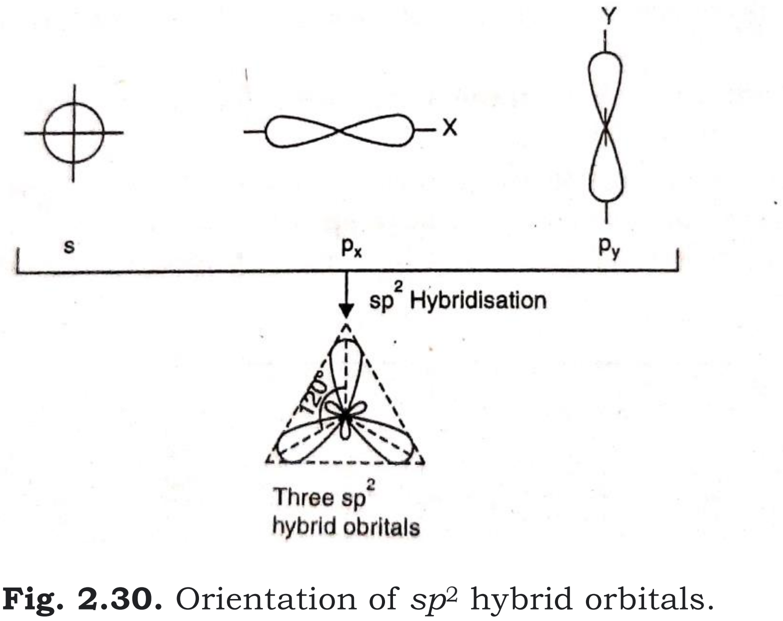


Fig. 2.30. Orientation of *sp*^{2} hybrid orbitals.

Let us study some examples of the molecules which involve *sp*^{2} hybridization.

1. Formation of boron trifluoride (BF_3). Boron ($_5B$) atom has ground state configuration as $1s^2$, $2s^2$, $2p^2$. But in the excited state its configuration is $1s^2$, $2s^2$, $2p_x^1$, $2p_y^1$. One 2*s*-orbital of boron intermixes with two 2*p*-orbitals of excited boron atom to form three $2s^2$ hybrid orbitals as shown in Fig 2.31.

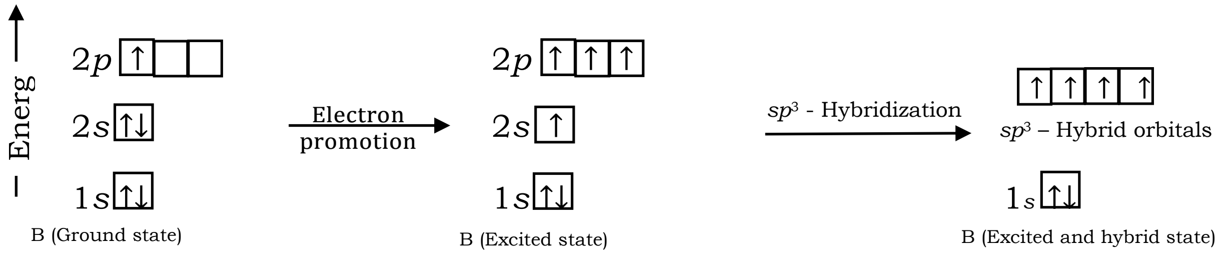


Fig. 2.31. *sp*^{2} hybrid state of brown.

The *sp*^{2} hybrid orbitals of boron are directed towards the corners of equilateral triangle and lie in a plane. Each of the *sp*^{2} hybrid orbitals of boron overlaps axially with half-filled orbital of fluorine atom to form three B-F sigma bonds as shown in Fig. 2.32.

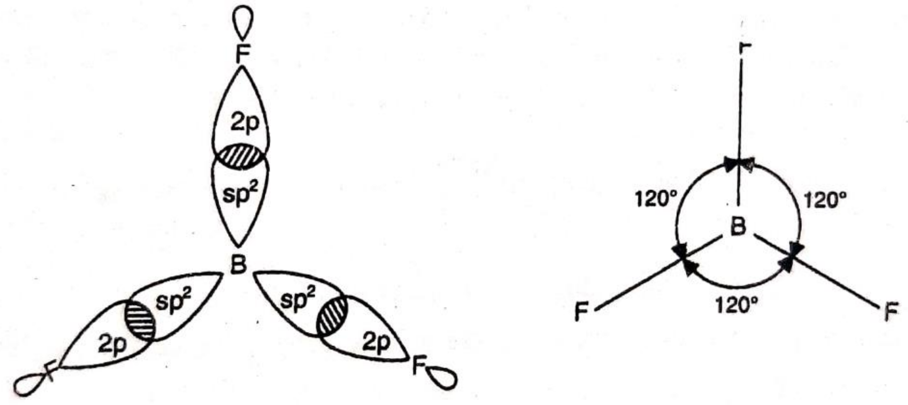


Fig. 2.32. Orbital diagram of BF_3

Because of *sp*^{2} hybridization of boron, BF_3 molecule has triangular planar shape.

(iii) **sp-hybridization.** This type of hybridization involves the mixing of one orbital of *s*-sub-shell and one orbital of *p*-sub-shell of the valence shell of the atom to form two *sp*- hybridized orbitals of equivalent shapes and energies. These *sp*- hybridized orbitals are oriented in space at an angle of 180° (Fig. 2.33). This hybridization is also called **diagonal hybridization.** Each *sp* hybrid orbital has equals *s* and *p* character, *i.e.,* 50% *s*-character and 50% *p*-character. The molecules in which the central atom is *sp*-hybridized and is linked to two other atoms directly have linear shape.

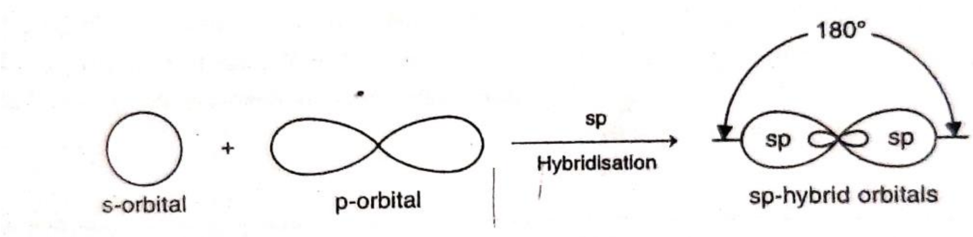


Fig. 2.33. Formation of *sp* hybrid orbitals

Let us study some examples of molecules involving ep hybridisation

1. Formation of beryllium fluoride (BeF_2). Beryllium ($_4$Be) atom has a ground state configuration as $1s^2$, $2s^2$. In the excited state one of the 2*s*-electron is promoted to 2*p*-orbitals. One 2*s*-orbital and one 2*p*-orbital of excited beryllium atom undergo hybridization to form two *sp*- hybridized orbitals as described in Fig. 2.34.

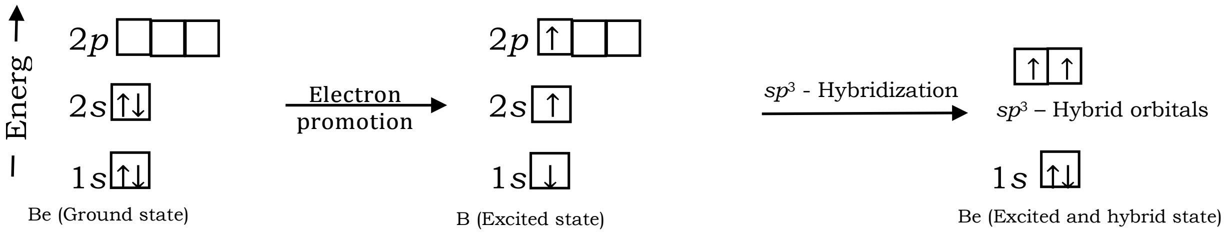


Fig. 2.34. *sp*-hybrid state of Be.

The two *sp* hybrid orbitals are linear and oriented in opposite directions at an angle of 180°. Each of the sp-hybridised orbital overlaps axially with half-filled orbital of fluorine atom to form two Be - F sigma bonds (Fig. 2.35).

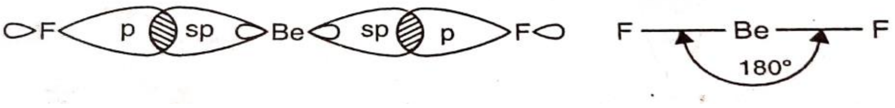


Fig. 2.35. Orbitals diagram of BeF_2.

Due to the *sp*- hybridized state of beryllium, BeF_2 molecule has **linear shape.**

2.21 MODERN PERIODIC LAW

The modern periodic law was proposed by English Physicist Henry Moseley in 1913. The **modern periodic law** states that:

The physical and chemical properties of the elements are the periodic function of their atomic numbers.

It means that if the elements are arranged in order of increasing atomic numbers, the elements with similar properties recur after regular intervals. **The periodical repetition of elements with similar properties after certain regular intervals when the elements are arranged in order of increasing atomic number is called periodicity.** Many new forms of periodic table have been proposed in recent times with modern periodic lawns guiding principle, but the general plan of the table remained the same as proposed by Mendeleev. **The most commonly known periodic table is the long form of the periodic table.**

2.22 LONG FORM OF PERIODIC TABLE

The long form of the periodic table is an improved form of the periodic table which is based upon modern periodic law.

Structural Features of Long Form of Periodic Table

Description of Periods

A horizontal row of a periodic table is called a **period.** A period consists of a series of elements having same valence shell. There are **seven periods** in all, which are numbered as 1, 2, 3, 4, 5, 6 and 7.

There is a close connection between the electronic configurations of the elements and the long form of the periodic table. As pointed out earlier in Unit 2 that the principal quantum number n defines the main energy level of the electron also called main energy shell. Each period of the periodic table begins with the filling of new energy shell. In fact, the number of the period also represents the highest principal quantum number of the elements present in it. The number of elements in each period is equal to the number of electrons which can be accommodated in the orbitals belonging to that electron shell.

The **first period** corresponds to the filling of electrons in first energy shell (*i.e.,* $n = 1$). Now this energy level has only one orbital (*i.e.,* $1s$) and, therefore, it can accommodate two electrons. This means that there can be only **two elements** in the first period.

The **second period** starts with the electrons beginning to enter the second energy shell ($n = 2$). There are only four orbitals (one $2s$ and three

2*p* orbital) to be filled which can accommodate eight electrons. Thus, second period has **eight elements** in it.

The **third period** begins with the electrons entering the third energy shell (n = 3). It may be recalled that out of nine orbitals of this energy level (one *s*, three *p* and five *d*), the five 3*d* orbitals have higher energy than 4*s* orbitals. As such only four orbitals (one 3*s* and three 3*p*) corresponding to n = 3 are filled before the fourth energy level begins to be formed. Hence, there are only **eight elements** in the third period,

The **fourth period** corresponds to n = 4. It starts with the filling of 4*s*-orbitals. However, after the 4*s* but before the 4*p* orbitals, there are five 3*d* orbitals also to be filled. Thus, in all, nine orbitals (one 4*s*, five 3*d* and three 4*p*) have to be filled and as such there are **eighteen** elements in fourth period. It may be noted that the filling of 3*d*-orbitals starts from Sc (Z = 21). The elements from Sc (Z = 21 to Zn (Z = 30) are called 3*d*-transition series.

The **fifth period** beginning with 5*s* orbital (n = 5) is similar to fourth period. There are nine orbitals (one 5*s*, five 4*d* and three 5*p*) to be filled and, therefore, there are **eighteen elements** in fifth period as well.

The **sixth period** starts with the filling of 6*s* orbital (n = 6). There are sixteen orbitals (one 6*s*, seven 4*f*, five 5*d* and three 6*p*) in which filling of electrons takes place before the next energy level starts. As such there are **thirty two elements** in sixth period. The filling up of 4*f* orbitals begins with cerium (Z = 58) and ends at lutetium (Z = 71). It constitutes the first *f*-transition series which is called lanthanoid series.

The seventh period begins with 7*s*-orbit in (n = 7). It would also have contained 32 elements corresponding to the filling of 7*s*, 5*f*, 6*d* and 7*p* orbitals. But it is still incomplete. The filling up of 5*f* orbitals begins with thorium (Z = 90) and ends up at Incomplete (Z = 103). It constitutes second *f*-transition series which is called **actinoid series.** It mostly includes man-made radioactive elements. In order to avoid undue expansion of the periodic table the 4*f* and 5*f*-transition elements have been placed separately.

It may be noted that period 2 and 3 contains 8 elements each and are called **short periods.** There are 18 elements each in 4th and 5th periods and they are called **long periods.** Sixth period containing 32 elements is called the **longest period.**

Description of Groups

A vertical column of the periodic table is called **a group.** A group consists of a series of elements having similar configuration of the outer energy shell. For example, all the group 1 elements have ns^1 valence shell electronic configuration. There are eighteen vertical columns in the long form of the periodic table. According to the recommendation of the International Union of Pure and Applied Chemistry (IUPAC), these groups

Long Form of Periodic Table

Representative Elements
s-Block

Transition Elements
d-Block

Representative Elements
p-Block

Noble gases

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1.								1 **H** $1s^1$										2 **He** $1s^2$
2.	3 **Li** $2s^1$	4 **Be** $2s^2$											5 **B** $2s^2 2p^1$	6 **C** $2s^2 2p^2$	7 **N** $2s^2 2p^3$	8 **O** $2s^2 2p^4$	9 **F** $2s^2 2p^5$	10 **Ne** $2s^2 2p^6$
3.	11 **Na** $3s^1$	12 **Mg** $3s^2$											13 **Al** $3s^2 3p^1$	14 **Si** $3s^2 3p^2$	15 **P** $3s^2 3p^3$	16 **S** $3s^2 3p^4$	17 **Cl** $3s^2 3p^5$	18 **Ar** $3s^2 3p^6$
4.	19 **K** $4s^1$	20 **Ca** $4s^2$	21 **Sc** $3d^1 4s^2$	22 **Ti** $3d^2 4s^2$	23 **V** $3d^3 4s^2$	24 **Cr** $3d^5 4s^1$	25 **Mn** $3d^5 4s^2$	26 **Fe** $3d^6 4s^2$	27 **Co** $3d^7 4s^2$	28 **Ni** $3d^8 4s^2$	29 **Cu** $3d^{10} 4s^1$	30 **Zn** $3d^{10} 4s^2$	31 **Ga** $4s^2 4p^1$	32 **Ge** $4s^2 4p^2$	33 **As** $4s^2 4p^3$	34 **Se** $4s^2 4p^4$	35 **Br** $4s^2 4p^5$	36 **Kr** $4s^2 4p^6$
5.	37 **Rb** $5s^1$	38 **Sr** $5s^2$	39 **Y** $4d^1 5s^2$	40 **Zr** $4d^2 5s^2$	41 **Nb** $4d^4 5s^1$	42 **Mo** $4d^5 5s^1$	43 **Tc** $4d^5 5s^2$	44 **Ru** $4d^7 5s^1$	45 **Rh** $4d^8 5s^1$	46 **Pd** $4d^{10}$	47 **Ag** $4d^{10} 5s^1$	48 **Cd** $4d^{10} 5s^2$	49 **In** $5s^2 5p^1$	50 **Sn** $5s^2 5p^2$	51 **Sb** $5s^2 5p^3$	52 **Te** $5s^2 5p^4$	53 **I** $5s^2 5p^5$	54 **Xe** $5s^2 5p^6$
6.	55 **Cs** $6s^1$	56 **Ba** $6s^2$	57 **La*** $5d^1 6s^2$	72 **Hf** $4f^{14} 5d^2 6s^2$	73 **Ta** $5d^3 6s^2$	74 **W** $5d^4 6s^2$	75 **Re** $5d^5 6s^2$	76 **Os** $5d^6 6s^2$	77 **Ir** $5d^7 6s^2$	78 **Pt** $5d^9 6s^1$	79 **Au** $5d^{10} 6s^1$	80 **Hg** $5d^{10} 6s^2$	81 **Tl** $6s^2 6p^1$	82 **Pb** $6s^2 6p^2$	83 **Bi** $6s^2 6p^3$	84 **Po** $6s^2 6p^4$	85 **At** $6s^2 6p^5$	86 **Rn** $6s^2 6p^6$
7.	87 **Fr** $7s^1$	88 **Ra** $7s^2$	89 **Ac**** $6d^1 7s^2$	104 **Rf** $5f^{14} 6d^2 7s^2$	105 **Db** $5f^{14} 6d^3 7s^2$	106 **Sg** $5f^{14} 6d^4 7s^2$	107 **Bh** $5f^{14} 6d^5 7s^2$	108 **Hs** $5f^{14} 6d^6 7s^2$	109 **Mt** $5f^{14} 6d^7 7s^2$	110 **Ds** $5f^{14} 6d^8 7s^2$	111 **Rg** $5f^{14} 6d^9 7s^2$	112 **Uub** $5f^{14} 6d^{10} 7s^2$	—	114 **Uuq**	—	116 **Uuh**	—	—

Inner Transition Elements
f-Block

*Lanthanoides $4f^n 5d^{0-1} 6s^2$	58 **Ce** $4f^1 5d^1 6s^2$	59 **Pr** $4f^3 5d^0 6s^2$	60 **Nd** $4f^4 5d^0 6s^2$	61 **Pm** $4f^5 5d^0 6s^2$	62 **Sm** $4f^6 5d^0 6s^2$	63 **Eu** $4f^7 5d^0 6s^2$	64 **Cd** $4f^7 5d^1 6s^2$	65 **Tb** $4f^9 5d^0 6s^2$	66 **Dy** $4f^{10} 5d^0 6s^2$	67 **Ho** $4f^{11} 5d^0 6s^2$	68 **Er** $4f^{12} 5d^0 6s^2$	69 **Tm** $4f^{13} 5d^0 6s^2$	70 **Yb** $4f^{14} 5d^0 6s^2$	71 **Lu** $4f^{14} 5d^1 6s^2$
**Actinoides $5f^n 6d^{0-1} 7s^2$	90 **Th** $5f^0 6d^2 7s^2$	91 **Pa** $5f^2 6d^1 7s^2$	92 **U** $5f^3 6d^1 7s^2$	93 **Np** $5f^4 6d^1 7s^2$	94 **Pu** $5f^6 6d^0 7s^2$	95 **Am** $5f^7 6d^0 7s^2$	96 **Cm** $5f^7 6d^1 7s^2$	97 **Bk** $5f^9 6d^0 7s^2$	98 **Cr** $5f^{10} 6d^0 7s^2$	99 **Es** $5f^{11} 6d^0 7s^2$	100 **Fm** $5f^{12} 6d^0 7s^2$	101 **Md** $5f^{13} 6d^0 7s^2$	102 **No** $5f^{14} 6d^0 7s^2$	103 **Lr** $5f^{14} 6d^1 7s^2$

are numbered from **1** to **18.** Earlier, the designation of these groups was the same as in the Mendeleev's periodic table. The relationship between the two ways al numbering the groups is given below:

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	0

It may be noted that the elements belonging to same group are said to constitute a family. For example, elements of group 17 constitute halogen family. Similarly, elements of group 16 constitute chalcogen family or oxygen family.

2.23 IUPAC NOMENCLATURE FOR ELEMENTS WITH ATOMIC NUMBERS, Z > 100

The elements beyond uranium (Z =92) are all synthetic elements and are known as trans-uranium elements. The elements beyond fermium (Z = 100) are known as **trans-fermium elements.** These elements have atomic numbers 101 onwards.

The elements fermium (Z = 100), mendelevium (Z = 101), nobelium (Z = 102) and lawrencium (Z = 103) are named after the names of famous scientists. When elements with Z > 103 were synthesized, the syntheses of some of these elements were reported almost simultaneously in 1970) by scientists in United States and in erstwhile Soviet Union and each group proposed different names. For example, the element with atomic number 104 was named Rutherfordium by American scientists while Soviet scientists named it Kurchatovium. In order to avoid such controversies, it was decided by IUPAC that until a new element's discovery is proved and its name is officially recognized, a systematic nomenclature be derived directly from the atomic number of the element using the Latin words for their numbers: nil for zero, un for one and so on.

The Latin words for various digits of the atomic number are written together in the order of which makes the atomic number and *'ium'* is added at the end. For example, the element with atomic number 104 was named unnilquadium and was assigned symbol Unq. The latin words for various digits are given in Table 2.7.

Table 2.7. Latin Words Roots for Various Digits

Digit	Latin word	Abbreviation
0	nil	*n*
1	un	*u*

2	bi	*b*
3	tri	*t*
4	quad	*q*
5	pent	*p*
6	hex	*h*
7	sept	*s*
8	oct	*o*
9	enn	*e*

Similarly, the elements with atomic number 105-112 were named and given in Table 2.8.

Table 2.8. Name and Symbol in Current Use (or proposed) for Trans-fermium Elements (Z = 101-102)

Atomic number	Systematic name	Symbol	IUPAC Office Name	IUPAC symbol
101	Unnilunium	Unu	Mendelevium	Md
102	Unnilbium	Unb	Nobelium	No
103	Unniltrium	Unt	Lawrencium	Lr
104	Unnilquadium	Unq	Ruthrefordium	Rf
105	Unnilpentium	Unp	Dubnium	Db
106	Unnilhexium	Unh	Seaborgium	Sg
107	Unnilseptium	Uns	Bohrium	Bh
108	Unniloctium	Uno	Hassium	Hs
109	Unnilennium	Une	Meitnerium	Mt
110	Ununnilium	Uun	Darmstadtium	Ds
111	Unununium	Uuu	Roentgenium	Rg
112	Ununbium	Unb	-	
113	Ununtrium	Uut	-	
114	Ununquadium	Uuq	-	
115	Ununpentium	Uup	-	
116	Ununhexium	Uuh	-	
117	Ununseptium	Uus	-	
118	Ununoctium	Uuo	-	
119	Ununennium	Uue	-	
120	Unbinilium	Ubn	-	

Thus, when a new element is dissolved, it first gets a temporary, name, with symbol consisting of three latters. Later, a permanentc mane and sybol are given by a vote by IUPAC representatives from member countries. The permanent name might reflect the country (or state of the country) in which the element was discovered, or pay tribute to a famous scientist. As of now, elements with atomic number up to 112, 114 and 116 have been discovered. Elements with atomic number 113, 115, 117 and 118 are not yet known. For the elements with atomic number 112 and 114 official IUPAC names are yet to be announced.

2.24 DIVISION OF PERIODIC TABLE INTO s-, p-, d- AND f- BLOCKS ON THE BASIS OF ELECTRONIC CONFIGURATIONS

The long form of periodic table can be divided into four main block. These are ***s*-, *p*-, *d*- and *f*-blocks.** The division of elements into blocks is primarily based upon their electronic configuration as shown in Fig. 2,37.

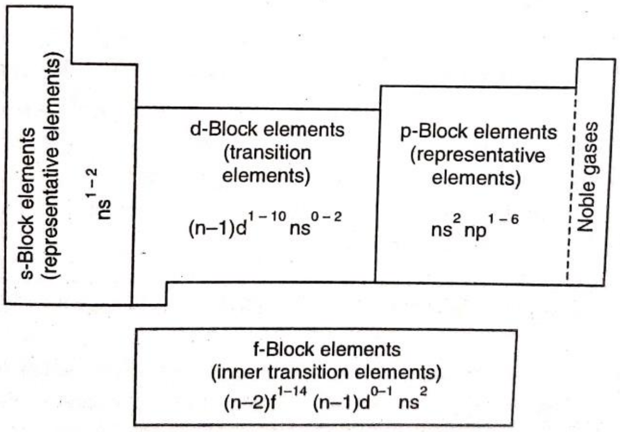


Fig. 2.37. Division of periodic table into various blocks.

1. *s*-Block Elements

The elements in which the last electron enters the s-sub-shell of their outermost energy level are called ***s*-block elements**. This block is situated at extreme left of the periodic table. It contains elements of groups **1 and 2.** Their general configuration is $\mathbf{ns^{1-2}}$, where *n* represents the outermost shell. The elements of group **1** are called **alkali metals** whereas the elements of group 2 are called **alkaline earth metals.**

2. *p*-Block Elements

The elements in which the last electron enters the p-sub-shell of their outermost energy level are called **p-block elements.** The general configuration of their outermost shell is ns^2 $\mathbf{np^{1-6}}$. The only exception is helium ($1s^2$). Strictly, helium belongs to the *s*- block but its positioning in the *p*-block along with other group 18 elements is justified because it has a completely filled valence shell ($1s^2$) and as a result, exhibits properties characteristic of other noble gases. This block is situated at the extreme right of the periodic table and contains elements of groups **13, 14, 15, 16, 17** and **18** of the periodic table. Most of these elements are non-metals, some are metalloids and a few others are heavy elements which exhibit metallic character. The non-metallic character increaser as we move from left to right across a period and metallic character increases as we go down the group.

3. *d*-Block Elements

The elements in which the last electron enters the *d*-sub-shell of the penultimate energy level are called **d-block elements.** Their general valence shell configuration is **$(n - 1)d^{1-10}$, ns^{0-2}**, where a represents the outer most energy level d-Block contain three complete rows often elements in each. The fourth row is incomplete. The three rows are called first, second and third transition series. They involve the filling of $3d$, $4d$ and $5d$ orbital respectively. The *d*-block contains elements of groups **3** to **12** of the periodic table.

On one side of the d-block metal there are reactive elements of groups 1 and 2 and on the right hand side there are less reactive elements of groups 13 and 14. Thus, transition elements form a bridge between reactive metals of groups 1 and 2, and less reactive elements of groups 13 and 14. That is why *d*-block elements are called **transition elements.**

4. *f*-Block Elements

The elements in which the last electron enters the *f*-sub-level of the antepenultimate third to the outer most shell) shell are called f-block elements.

Their general configuration is **$(n - 2)f^{1-14}$ $(n - 1)d^{0-1}$**, **ns^2**, where n represents the outer most shell. They consist of two series of elements placed at the bottom of the periodic table. The elements of first series follow lanthanum ($_{57}$La) and are called lanthanoids. The elements of second series follow actinium ($_{89}$Ac) and are called actinoids. Actinoid elements are radioactive.

METHOD TO PREDICT THE PERIOD, GROUP AND BLOCK OF A GIVEN ELEMENT

Following step are followed to predict the group, period and block of the elements:

1. Electronic configuration of the element is written following various rules.
2. Period of the element is represented by the principal quantum number of the valence shell.
3. Block of the element is predicted on the basis of nub-shell which receives the last electron.
4. Group is predicted from the number of electrons in the outermost or penultimate shell as follows:
   (a) In case the element belongs to ***s*-block,** then the group
   = (number of valence electrons)
   (b) In case the element belongs to **p-block**, then the group
   = (10 + total number of valence electrons)
   (c) In case the element belongs to **d-block,** then the group
   = number of electrons in (n-1) d-sub-shell and n-sub-shell.

Solved examples based on long from of periodic table

Example 2.12. Write the electronic configuration of the elements given below and also predict their period, group and block.

A (At. No. 16), E (At. No. 37) and G (At. No. 30).

Solution. The electronic configurations of the elements are:

$_{16}A$: $1s^2, 2s^2, 2p^6, 3s^2, 3p^4$

$_{37}E$: $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 5s^1$

$_{30}G$: $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2$

As is evident from the electronic configurations:

(i) $_{16}A$ receives last electrons in $3p$ sub-shell, therefore, its:

period = 3

block = p

group = 10 + Number of valence electrons

= 10 + 6 = **16.**

(ii) $_{37}E$ receives last electrons in $5s$-orbitals. Hence its:

period = 5

block = ***s***

group = Number of Valence electrons

= **1.**

(iii) $_{30}$G receives last electrons in 3*d*-orbitals. Hence, its:

block = d

Since its valence shell is 4th. Therefore,

period = 4

group = Number of *n s*-electrons

+ Number of (*n* – 1) *d*-electrons

= 2 + 10 = **12..**

Example 2.13. Elements A, B, C, D and E have the following electronic configurations:

$A : 1s^2 2s^2 2p^1$ $B : 1s^2 2s^2 2p^6 3s^2 3p^1$

$C : 1s^2 2s^2 2p^6 3s^2 3p^3$ $D : 1s^2 2s^2 2p^6 3s^2 3p^5$

$E : 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

Which among these will belong to the same group in the periodic table?

Solution. The elements A and B have similar valence shell electronic configuration ($ns^2 np^1$). Therefore, they belong to same group in the periodic table.

Example 2.14. Predict the position of the element in the Periodic Table satisfying the electron configuration $(n-1)d^1\ ns^2$ for $n = 4$.

Solution. The electronic configuration of the element is $3d^1\ 4s^2$. Thus, the element belongs to *d*-block, fourth period and group 3.

Example 2.15. How would you justify that there are only 18 elements in the fifth period of the periodic table.

Solution. The fifth period begins with the filling of 5*s* orbital and continues till the filling of sixth energy level (6*s*) starts. The sub-shell which follow 5*s* are, 4*d*, 5*p*, 6*s*..... Thus, the elements which involves filling 5*s*, 4*d* and 5*p*, sub-shell are accommodated in the fifth period. These sub-shell have nine orbitals that can accept 18 electrons in all. Hence, there are 18 elements in the fifth period.

SUMMARY

- **Cathode Rays**. Consist of negatively charted material particles called electrons.
- **Electrons.** Fundamental sub-atomic particles carrying negative charge (1.602 × 10^{-19} coulombs) and having mas 9.1 × 10^{-31} kg. Discovered by J.J. Thomson.
- Charge to mass (e/m) ratio for electrons is 1.76 × 10^8 C/g.
- **Anode Rays.** Consist of positively charged ions. e/m ratio for the ions in the anode rays depends on the nature of the gas taken in the discharge tube Discovered by Goldstein.
- $\lambda = \frac{h}{mv} = \frac{h}{p}$ (de Broglie relationship)
- $\boldsymbol{\Delta x \times \Delta p \geq \frac{h}{4\pi}}$ **or** $\boldsymbol{\Delta x \times m\Delta v \geq \frac{h}{4\pi}}$ (Heisenberg's uncertainty principle)
- **Orbital**. Region of space around the nucleus where probability of finding the electrons is maximum.
- **Quantum Mechanics** is a theoretical science that takes into account the dual nature of matter.
- **Ground State.** The lowest energy state of the atom.
- **Excited State.** An atom is said to be in excited state if some lower energy orbital is vacant and the electron is present in higher energy orbital.
- **Electronic Configuration.** Distribution of electrons among various orbitals in an atom.
- **Modern Periodic Law.** It states that the properties of elements are periodic function of their atomic numbers.
- **Group.** A vertical column of elements in the periodic table.
- **Period.** A horizontal row of elements in the periodic table.

REVIEW QUESTIONS

1. What is the value of e/m for the particles in cathode rays?
2. How many quantum numbers are required to specify an orbital?
3. What are the quantum numbers of the valence electron in potassium atom (Z = 19) in ground state?
4. What are the possible values of m for an electron in $3d$ sub-shell?
5. What experimental evidence indicates that
   (i) electrons are negatively charged
   (ii) electrons are universal constituent of matter
   (iii) electrons are material particles
6. Compare the mass and charge of the three fundamental sub-atomic particles.
7. From what observations do you derive the following inferences?

(i) The most of the space inside the atom is empty.
(ii) The volume of the nucleus is very small.

8. How would you obtain the atomic spectrum of hydrogen?
9. Give various postulates of Bohr's atomic model. How does it explain emission spectrum of hydrogen?
10. Why are there so many lines in hydrogen spectrum although there is only one electron in its atom?
11. How does Bohr's model account for only certain specific lines in the emission spectrum of hydrogen?
12. What is the wavelength of a photon (in nm) emitted during a transition from the $n_1 = 5$ state to then, $n_1 = 2$ state in the hydrogen atom?
13. Why is de-Broglie's relationship meaningful for submicroscopic particles such as electrons, protons and atoms and not for macroscopic objects?
14. Derive the relationship between the wavelength of the de-Broglie wave and the kinetic energy of the particle.
15. From the following sets of quantum numbers, state which are possible. Explain why the others are not permitted.
    (i) $n = 1$ $l = 0$ $m_1 = +1$ $m_s = +\frac{1}{2}$
    (ii) $n = 1$ $l = -1$ $m_1 = 0$ $m_s = -\frac{1}{2}$
    (iii) $n = 0$ $l = +1$ $m_1 = 0$ $m_s = +\frac{1}{2}$
    (iv) $n = 0$ $l = 0$ $m_1 = +1$ $m_s = -\frac{1}{2}$
    (v) $n = 2$ $l = 1$ $m_1 = 0$ $m_s = +\frac{1}{2}$
    (vi) $n = 2$ $l = 2$ $m_1 = 0$ $m_s = -\frac{1}{2}$
16. (a) Using the *s, p, d* notation, designate the orbitals with the following quantum numbers:
    (i) $n = 4$; $l = 2$ (ii) $n = 4$; $l = 3$
    (iii) $n = 2$; $l = 0$ (iv) $n = 3$; $l = 1$.
17. What is periodicity? Discuss its cause.
18. On the basis of quantum numbers, justify that the third period of the periodic table should have 8 elements.
19. Predict the period and block to which each of the following elements belongs:
    (i) $_{12}A$ (ii) $_{19}B$
    (iii) $_{30}C$ (iv) $_{37}D$.
20. An element belongs to third period of *p*-block elements. It has 4 electrons in its outer most shell. Predict its group. How many unpaired electrons does it have?
21. In terms of period and group where would you locate the element with Z = 14?

SECTION - B

3

OXIDATION AND REDUCTION

LEARNING OBJECTIVES

- Classical Concept of Oxidation and Reduction
- Electronic Concept of Oxidation an Reduction
- Oxidation Number or Oxidation State
- Oxidation and Reduction in terms of Oxidation Number
- Balancing of Redox Equations
- Direct and Indirect Redox Reactions
- Electrode Potential
- Electrochemical Series
- Dependence of Electrode Potential on Concentration and Temperature

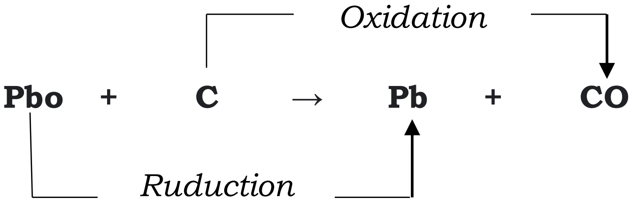
3.1 CLASSICAL CONCEPT OF OXIDATION AND REDUCTION

In our daily life we come across processes like rusting of iron articles, fading of the colour of the clothes, burning of the combustible substances such as cooking gas wood, coal, etc. All such processes fall in the category of specific type of chemical reactions called **reduction-oxidation** or **redox reactions.** A large number of industrial processes like, electroplating, extraction of metals like aluminium and sodium, bleaching of wood pulp, manufacture of caustic soda, etc., are also based upon the redox reactions. Redox reactions also form the basis of electrochemical and electrolytic cells. In order to have proper understanding of redox reactions let us define oxidation and reduction. According to the classical concept, oxidation and reduction, in general, may be defined as follows:

Oxidation is a process of addition of oxygen or any electronegative radical or removal of hydrogen or any electropositive radical.

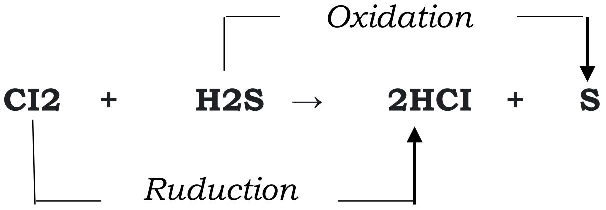
Reduction is a process of addition of hydrogen or any electropositive radical or removal of oxygen or any electronegative radical.

Some examples of oxidation and reduction reactions are :



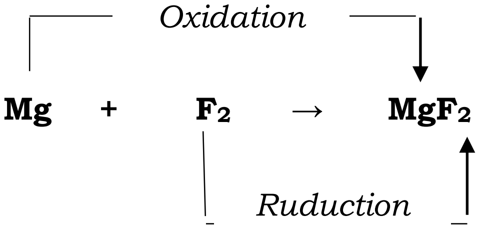
$$\mathbf{Pbo} + \mathbf{C} \rightarrow \mathbf{Pb} + \mathbf{CO}$$

Here, oxygen is being removed from lead oxide (PbO) and is being added to cabon (C). Thus PbO is reduced while C is oxidized.



$$\mathbf{CI2} + \mathbf{H2S} \rightarrow \mathbf{2HCI} + \mathbf{S}$$

Here, hydrogen is being removed from hydrogen sulphide (H_2S) and is being added to chlorine (CL_2). Thus, H2S is oxidized and CL2 is reduced.



$$\mathbf{Mg} + \mathbf{F_2} \rightarrow \mathbf{MgF_2}$$

Here, electronegative radicals fluoride ions are added to magnesium while electropositive radical Mg^{2+} is added to fluorine. Hence Mg is oxidized and F_2 is reduced.

3.2 ELECTRONIC CONCEPT OF OXIDATION AND REDUCTION

Electrochemical reactions occur as a result of transference of electrons from one species to the other. For example, if magnesium is burnt is oxygen it gets oxidized to magnesium oxide (MgO). In the formation of magnesium oxide, two electrons from magnesium atom are transferred to oxygen atom.

$$\mathbf{\overset{..}{Mg} + O : \rightarrow Mg^{2+} [: \underset{..}{\overset{..}{O}} :]^{2-}}$$

The process of transferred of electrons is described as redox process. Let us define oxidation an reduction in terms of electrons.

Oxidation is a process which as atom or a group of atoms taking part in chemical reaction loses one or more electrons. The loss of electrons results in the increase of positive charge or decrease of negative charge of the species. For example,

$MnO_4{}^{2-} \rightarrow MnO_4{}^{-} + e^-$ (Decrease of negative charge)
Manganate Permanganate

$Fe^{2+} \rightarrow Fe^{3+} + e^-$ (Increase of positive charge)
Ferrous Ferric

$Cu \rightarrow Cu^{2+} + 2e^-$ (Increase of positive charge)
Copper Cupric

The species which undergo the loss of electrons during the reations are called **reducing agents or reductants.** $MnO_4{}^{2-}$, Fe^{2+} and Cu are reducing agents in the above examples.

Reduction is a process in which an atom or a group of atoms taking part in chemical reaction gains one or more electrons. The gain of electrons result in the decrease of positive charge or increase of negative charge of the species. For example,

$Ag^+ + e^- \rightarrow Ag$ (Decrease of positive charge)

$Fe^{3+} + e^- \rightarrow Fe^{2+}$ (Decrease of positive charge)

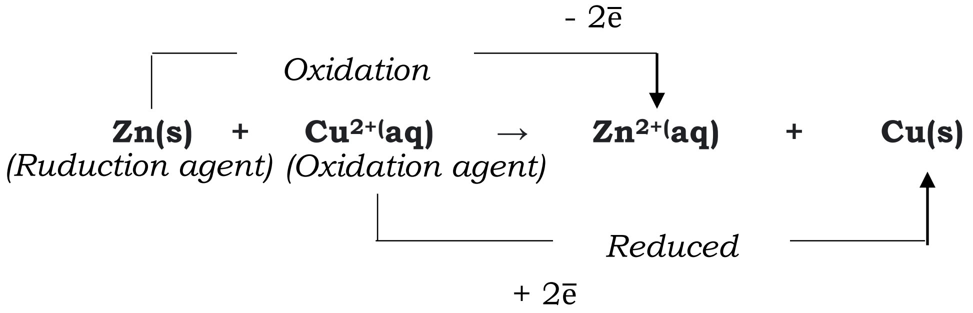
$[Fe(CN)_6]^{3-} + e- \rightarrow [Fe(CN)_6]^{4-}$ (Increase of negative charge)
Ferricyanide Ferrocyanide

The species which undergo gain of electrons during the reactions are called oxdiising agents or oxidants. In the above examples, Ag^+, Fe^{3+}, $[Fe(CN)_6]^{3-}$ ions are oxidizing agents.

Simultaneous Occurrence of Oxidation and Reduction

Since oxidation involves loss of electrons and reduction involves gain of electrons, it is evident that if one substance loses electrons, another substance at the same time must gain electrons because electrons cannot be the products in any chemical change. This means that in any process, oxidation can occur only if reduction is also taking place side by side and vice versa. Thus, neither oxidation, nor reduction can occur alone. Both the processes are complementary like give and take and proceed simultaneously. That is why chemical reactions involving reduction oxidation are called **redox reactions.** In fact, during the redox reaction there is a **transference of electrons from the reducing agent to the oxidising agent.**

For example, consider a reaction between zinc and copper ions



In this reaction zinc atoms lose electrons and are oxidised to zinc ions (Zn^{2+}) whereas cupric ions (Cu^{2+}) gain electrons and are reduced to copper atoms. Thus, cupric ions act as oxidising agent and zinc atoms act as reducing agent. In fact, the oxidizing agent gets reduced while reducing agent gets oxidised during the redox reactions.

Oxidation Hall and Reduction Holf Reactions

Every redox reaction can be split up into two **half reactions,** one representing loss of electrons ice, oxidation half reaction while the other representing gain of electrons, i.e., reduction half reaction. Some examples are given below:

(i) The reaction ; **$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$,** can be split up into two ball reactions as

$Zn \rightarrow Zn^{2+} + 2e^-$ (Oxidation half reaction)
$Cu^{2+} + 2e^- \rightarrow Cu$ (Reduction half reaction)

(ii) The reaction $Sn^{2+} + 2Hg^{2+} \rightarrow Su^{4+} + Hg_2{}^{2+,}$ can be split up into hall reaction is

$Sn2+ \rightarrow Sn4+ + 2e-$ (Oxidation half reaction)
$2Hg^{2+} + 2e^- \rightarrow Hg_2{}^{2+}$ (Reduction half reaction)

3.3 OXIDATION NUMBER OR OXIDATION STATE

We have learnt that redox reactions involve the transference of electrons from one species to another. The transference of electrons can be easily understood in case of ionic species because the charge on them also changes during redox reactions. However, the redox changes in case of covalent compounds cannot be easily explained in terms of transference of electrons. For example, in a chemical reaction between zinc and copper ions,

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

It is quite evident that Zn atoms lose electrons and Cu^{2+}ions gain electrons. But in a chemical reactions between H_2 and Cl_2;

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$$

The loss and gain of electrons could not be easily explained. Thus, in order to explain transference of electrons in either of the species in a more convenient way, the concept of oxidation number has been introduced.

Oxidation number (O.N.) of the element is defined as the residual charge which its atom has or appears to have when all other atoms from the molecule are assumed to be removed as ions by counting the shared electrons with more electronegative atom.

For example, in hydrogen chloride molecule, chlorine is more electronegative than hydrogen. Therefore, the shared pair is counted towards chlorine atom as shown below:

$$\mathrm{H}\ \big|\ :\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}:$$

As a result of this, chlorine gets one extra electron and acquires a unit negative charge. Hence, oxidation number of chlorine is **- 1.** On the other hand, hydrogen atom without electron has a unit positive charge. Hence, oxidation number of hydrogen in hydrogen chloride is + 1.

It may be noted that electrons shared between two similar atoms are divided equally between the sharing atoms. For example, in chlorine molecule (Cl_2), the electron pair is equally shared between the two chlorine atoms. Therefore, one electron is counted with each chlorine atom as shown below:

$$:\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}\cdot\ \big|\ \cdot\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}:$$

Now, there is no net charge on each atom of chlorine. In other words, oxidation number of chlorine in Cl_2 molecule is zero.

Thus, atoms can have positive, zero or negative values of oxidation numbers depending upon their state of combination. In fact, oxidation number is the charge assigned to the atom in a species according to some arbitrary rules as described below:

General Rules for Assigning Oxidation Number to an Atom

The oxidation number of various elements in their compounds can be calculated by applying following rules. These rules have been formulated on the basis of the assumption that electron in a covalent bond belong entirely to the more electronegative atom.

1. The oxidation number of the element in the free or elementary state is always zero irrespective of its allotropic form. For example,

Oxidation number of helium in	He=0
Oxidation number of chlorine in	Cl_2 = 0
Oxidation number of sulphur in	S_8 =0

2. The oxidation number of the element in monoatomic ion is equal to the charge on the ion. For example, in K^+CI^-, the oxidation number of K is **+ 1** while that of Cl is **- 1.** In the similar way, oxidation number of all alkali metals is **+ 1** while those of alkaline earth metals is **+ 2** in their compounds.
3. The oxidation number of fluorine is always **- 1** in all its compounds.
4. Hydrogen is assigned oxidation number **+ 1** in all its compounds except in metal hydrides. In metal hydrides like *NaH, MgH_2, CaH_2, LiH, etc.,* the oxidation number of hydrogen is **-1.**
5. Oxygen is assigned oxidation number **-2** in most of its compounds, however, in peroxides (which contain 0-0 linkage) like H_20_2, BaO_2, Na_2O_2 etc., its oxidation number is **- 1.** Similarly, the exception also occurs in compounds of fluorine and oxygen like OF_2 (F-O-F) and O2F2 (F-0-0-F) in which the oxidation number of oxygen is **+ 2** and **+ 1** respectively.
6. In accordance with principle of conservation of charge, the algebraic sum of the oxidation numbers of all the atoms in molecule is **zero.** But in case of polyatomic ion the sum of oridation numbers of all its atoms is equal to the **charge on the ion.**
7. In binary compounds of metal and non-metal, the metal atom has positive oxidation number while the non-metal atom has negative oxidation number. For example, O.N. of K in KI is + 1 but O.N. of I is -1.
8. In binary compounds of non-metals, the more electronegative atom has negative oxidation number, but less electronegative atom has positive oxidation number. For example, O.N. of CI in CIF_3, is positive (+3) while that in ICI negative (-1)

SOLVED EXAMPLES BASED ON CALCULATION OF OXIDATION NUMBERS

Example 3.1. Calculate the oxidation number of underlined elements in the following species:

$$\underline{C}O_2,\ \underline{CO}_2\ O_7^{2-},\ \underline{Pb_3}\ O_4,\ Pb_4^{3-},\ S_2\ 0_3^{-2}$$

Solution. (1) C in CO_2:
Let oxidation number of C be x

O.N. of each O atom = -2
Sum of O.N. of all atoms = $x + 2(-2) = x - 4$
As it is neutral molecule, the sum must be equal to zero.

$$x - 4 = 0 \quad \text{or} \quad x = +4.$$

(ii) Cr in $Cr_2O_7^{2-}$:
Let oxidation number of Cr = x
O.N. of each O atom = -2
Sum of O.N. of all atoms = $2x + 7(-2) = 2x - 14$
Sum of O.N. must be equal to the charge on the ion.
Thus, $2x - 14 = -2$

$$x = \frac{2+14}{2} = +16$$

(iii) Pb in Pb_3O_4:
Let O.N. of Pb be x
O.N. of each O atom = -2
Sum of O.N. of all atoms = $3x + 4(-2) = 3x - 8$
The sum of O.N. must be equal to zero

$$3x - 8 = 0 \quad \text{or} \quad x = \frac{8}{3} = +2\frac{2}{3}.$$

(iv) S in $S_2O_3^{2-}$:
Let O.N. of S be x
O.N. of each O atom = -2
Sum of O.N. of each atoms = $2x + 3(-2) = 2x - 6$
Sum must be equal to the charge, i.e., -2
$2x - 6 = -2$

$$x = \frac{-2+6}{2} = \mathbf{+2.}$$

3.4 OXIDATION AND REDUCTION IN TERMS OF OXIDATION NUMBER

After having discussed the concept of oxidation number, let us now define oxidation and reduction in terms of oxidation number. **Oxidation** is defined as a **chemical process in which oxidation number of the element increases.** On the other hand, **reduction** is defined **as the chemical process in which oxidation number of the elements decreases.** For example, let us consider the reaction between hydrogen sulphide an bromine to give hydrogen bromine and sulphur.

$$H_2S + Br_2 \rightarrow 2HBr + S$$

Increases of O.N.

In the above example, the oxidation number of bromine decreases from 0 to -1 thus, it is reduced. The oxidation number of S increases from -2 to 0. Hence, H_2S is oxidized.

Let us now define oxidizing and reducing agents in the light of the concept of oxidation number:

Oxidation number is a substance which undergoes **decrease in the oxidation number** of one or more of its elements.

Reducing agent is a substance which undergoes **increase in the oxidation number** of one or more of its elements.

In the above example, H_2S is reducing agent while Br_2 is oxidizing agent.

SOLVED EXAMPLES

Example 3.2. Identify the oxidizing agent, reducing agent, substance oxidized and substance reduced in the following reactions:

(i) $MnO_2 + 4HCI \rightarrow MnCI_2 + CI_2 + 2H_2O$

(ii) $2MnO_4^- + 10CI^- + 16H^+ \rightarrow 2Mn^{2+} + 5CI_2 + 8H_2O$.

Solution. (i) Let us write the number of various atoms of reactants and products

Increases of O.N.

$$\overset{+4}{Mn}\ \overset{-2}{O_2} + 4\overset{+1}{H}\ \overset{-1}{CI} \rightarrow \overset{+2}{Mn}\ \overset{-1}{CI_2} + \overset{0}{CI_2} + 2\overset{+1}{H_2}\ \overset{-2}{O}$$

Decreases of O.N.

As a clear, manganese decrease its O.N. from +4 to +2. Hence, **MnO_2** gets **reduced** and is **oxidizing agent.** Chlorine atom in HCI increase it oxidation number from -1 to 0. Thus, **HCI** gets **oxidized** and is **reducing agent.**

Decreases of O.N.

$$+7\ -2 \qquad -1 \qquad\qquad 2+ \qquad 0 \qquad +1\ -2$$

$$(MnO_4)^- + 10CI + 16H^+ \rightarrow 2Mn + 5CI_2 + 8H_2O$$

Increases of O.N.

In the above reaction, chlorine in chlorides ion increases its oxidation number from -1 to 0. Thus, **chloride ion** gets **oxidized** and is **reducing agent.** Manganese in **MnO_4^-** decreases its oxidation number from +7 to -2. Therefore, **MnO_4^-** ion gets **reduced** and its **oxidizing agent.**

3.5 BALANCING OF REDOX EQUATIONS

We know that during redox reactions there is a change in oxidation number of the elements due to the transference of electrons. The number of electrons lost during oxidation is equal to the number of electrons gained during reduction. This forms the basic principle of balancing the redox equations.

The two methods which are frequently employed are: ion electron method and oxidation number method.

(a) Balancing by Ion Electron or Half Reaction Method

The various steps involved in the balancing of redox equations according to this method are:

1. Indicate the oxidation number of each atom involved in the reaction. Identity the elements which undergo a change in the oxidation number.
2. Divide the skeleton redox equations into two half reactions; oxidation half and reduction half. In each half reaction balance the atoms which undergo the change in oxidation number.
3. Add electrons to whichever side is necessary in order to make up for the difference in O.N. in each half reaction.
4. Balance **oxygen** atoms by addition of proper number of H_2O molecules to the side which is failing short of O atoms in each half reaction.
5. This step in meant for **ionic equations** only. It involves the balancing of H atoms in each half reaction.
    (i) For acidic medium. Add proper number of H^+ ions to the side failing short of H atoms.

    (ii) For basic medium. Add proper number of H2O molecules to the side falling short of H atoms and equal number of OH^- ions to the other side.

6. Equalise the number of electrons lost and gained by multiplying the half reactions with suitable integer an add them to get the final equations.

The application of various steps described above has been illustrated as follows by balancing the redox equation representing the reaction between iodine and nitric acid.

$$HNO_3 + I_2 \rightarrow HIO_3 + NO_2 + H_2O.$$

Step 1. Indication of oxidation numbers of each atom.

$$\overset{+1}{H}\,\overset{+5}{N}\,\overset{-2}{O_3} + \overset{0}{I_2} \rightarrow \overset{+1}{H}\,\overset{+5}{I}\,\overset{-2}{O_3} + \overset{+4}{N}\overset{-2}{O_2} + \overset{+1}{H_2}\overset{-2}{O}.$$

Thus, only nitrogen and iodine undergo change in oxidation number.

Step 2. Division into two half reactions and balancing the atoms undergoing change in O.N.

$$\overset{0}{I_2} \rightarrow 2H\overset{+5}{I}\,O_3 \qquad \text{(Oxidation half reaction)}$$

$$H\overset{+5}{N}\,O_3 \rightarrow \overset{+4}{N}\,O_2 \qquad \text{(Reduction half reaction)}$$

Step 3. Addition of electrons to make up the difference in O.N.

$$\overset{0}{I_2} \rightarrow 2H\overset{+5}{I}\,O_3 + 10e^-$$

(Each I atom loses $5e^-$ therefore, two iodine atoms would lose $10e^-$)

$$M\overset{+5}{N}\,O_3 + e^- \rightarrow \overset{+4}{N}\,O_2$$

(Each N atoms gains 1 electrons)

Step 4. Balancing of O by adding proper number of H_2O molecules to the side falling short of O atoms.

$$\begin{array}{lcl} I_2 + 6H_2O & \rightarrow & 2HIO_3 + 10e^- \\ HNO_3 + e^- & \rightarrow & NO_2 + H_2O \end{array}$$

Step 5. Not required because the equation is not ionic.

Step 6. To equalize the electrons multiply reduction half reaction by 10 and add the two.

$$\begin{array}{lcl} I_2 + 6H_2O & \rightarrow & 2HIO_3 + 10e^- \\ [HNO_3 + e^- & \rightarrow & NO_2 + H_2O] \times 10 \\ \hline I_2 + 10HNO_3 & \rightarrow & 2HIO_3 + 10NO_2 + 4H_2O \\ \hline \end{array}$$

SOLVED EXAMPLES BASED ON BALANCING OF EQUATIONS BY ION ELECTRON METHOD

Example 3.3. Balancing the following redox equations by half reaction method.

(i) $Cr_2O_7^{2-} + Fe^{2+} \rightarrow Cr^{3+} + Fe^{3+} + H_2O$ in acidic medium

(ii) $Cr(OH)_3 + IO_3^{-} \rightarrow I^{-} + CrO_4^{2-}$ in basic medium

Solution. (i) $(Cr_2\,O_7)^{2-} + Fe^{2+} \rightarrow Cr^{3+} + Fe^{3+} + H_2O$

Step 1. Indication of O.N. of each atom

$$(\overset{+6}{Cr_2}\,\overset{-2}{O_7})^{2-} + Fe^{2+} \rightarrow Cr^{3+} + Fe^{3+} + \overset{+1}{H_2}\,\overset{-2}{O}$$

Thus, Cr in $Cr_2O_7^{2-}$ and Fe change their oxidation numbers.

Step 2. Writing the Oxidation and reduction half reactions.

$(\overset{+6}{Cr_2}\,\overset{-2}{O_7})^{2-} \rightarrow 2Cr^{3+}$ (Reduction half)

$Fe^{+2} \rightarrow Fe^{3+}$ (Oxidation half)

Step 3. Addition of e- to make up the difference in O.N.

(Cr2 O7)2- + 6e- → 2Cr3+

(Each Cr atom gains 3e-. thus, 2Cr atom will gain $6e^{-}$)

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

Step 4. Balance 'O' by adding equal number of H_2O molecules to the side which is deficient in O atoms.

$Cr_2O_7^{2-} + 6e^{-} \rightarrow 2Cr^{3+} + 7H_2O$

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

Step 5. Balance H by adding H+ ions to the side which is deficient in H atoms.

$Cr_2O_7^{2-} + 6e^{-} + 14H^{+} \rightarrow 2Cr^{3+} + 7H_2O$

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

Step 6. Multiplying oxidation half reaction by 6 of equalize the electrons lost and gained and add the two.

$Cr_2O_7^{2-} + 6e^{-} + 14H^{+} \rightarrow 2Cr^{3+} + 7H_2O$

$Fe^{2+} \rightarrow Fe^{3+} + e^{-} \times 6$

$$\underline{6Fe^{2+} + Cr_2O_7^{2-} + 14H^{+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O}$$

It may be remembered the in balanced equation the number of atoms and also the electrical charges must be **equal** on both the sides of arrow.

(ii) $Cr(OH)_3 + IO_3^- \rightarrow I^- + CrO_4^{2-}$ in basic medium

Step 1. Indication of oxidation number of each elements

$$\overset{+3}{Cr}(\overset{-2}{O}\overset{+1}{H})_3 + (\overset{+5}{I}\overset{-2}{O_3})^- \rightarrow I^- + (\overset{+6}{Cr}\overset{-2}{O_4})^{2-}$$

Thus, we find that Cr in Cr $(OH)_3$ and iodine in IO3 undergo change in oxidation number.

Step 2. Writing oxidation and reduction half reaction.

$$\overset{+3}{Cr}(OH)_3 \rightarrow \overset{+6}{(CrO_4)^{2-}} \quad \text{(Oxidation half)}$$
$$(\overset{+5}{I}O_3)^- \rightarrow I^- \quad \text{(Reduction half)}$$

Step 3. Addition of e- to make up the difference in O.N

$$\overset{+3}{Cr}(OH)_3 \rightarrow (CrO_4)^{2-}$$
$$(\overset{+5}{I}O_3)^- + 6e^- \rightarrow I^-$$

Step 4. Balance O atoms by adding H2O molecules to the side deficient in 'O' atoms.

$$Cr(OH)_3\ H_2O \rightarrow (CrO_4)^{2-} + 3e^-$$
$$IO_3^- + 6e^- \rightarrow I^- + 3H_2O$$

Step 5. Balancing H atoms. Since the medium is basic, therefore add proper number of H_2O molecules to the side following short of H atoms and equal number of OH^- ions to the other side.

$$Cr(OH)_3\ H_2O + 50H^- \rightarrow CrO_4^{2-} + 3e^- + 5H_2O$$
$$IO_3^- + 6e^- + 6H_2O \rightarrow I^- + 3H_2O + 60H^-$$

Step 6. Equalize the electrons lost and gained by multiplying the oxidation half reaction with 2.

$$[Cr(OH)_3\ H_2O + 50H^- \rightarrow CrO_4^{-2} + 3e^- + 5H_2O] \times 2$$
$$IO_3^- + 6e^- + 6H_2O \rightarrow I^- + 3H_2O + 60H^-$$

$$2Cr(OH)_3 + 40H^- + IO_3- \rightarrow 2CrO_4^{2-} + 5H_2O + I^-$$

(b) Balancing Redox Equations by Oxidation Number Method

Various steps involved are:

1. Write skeleton equation and indicate oxidation number of each element and thus, identify the elements undergoing change in oxidation number.
2. Determine the increase and decrease of oxidation number per atom. Multiply the increase of decrease of oxidation number with number of atoms undergoing the change.
3. Equalize the increase in oxidation number and decrease in oxidation number on the reactant side by multiplying the respective formulae with suitable integers.

4. Balance the equation w.r.t. atoms other than O and H atoms.
5. Balance O by adding equal number of water molecules to the side failing short of O atoms.
6. H atoms are balanced (in case of ionic equations) depending upon the medium in same way as followed in ion electron method.

SOLVED EXAMPLES BASED ON BALANCING OF EQUATIONS BY OXIDATION NUMBER METHOD

Example 3.4. Write the skeleton equations for the following chemical reaction and balance them by oxidation number method.

- (i) Chloride ions reduce manganese dioxide to manganese (II) ions in acidic medium and get itself oxidized to chlorine gas.
- (ii) Nitrate ions in acidic medium oxidise magnesium to Mg^{2+} ions but itself gets reduced to nitrogen (I) oxide.
- (iii) Zinc reacts with conc. nitric acid to produce zinc nitrate, nitrogen dioxide and water.

Solution. (i) The skeleton equation for the given process is:

Step 1. $\overset{+4}{Mn}\,\overset{-2}{O_2} + Cl^- \rightarrow Mn^{2+} + \overset{0}{Cl_2} + \overset{+1}{H_2}\,\overset{-2}{O}$

O.N. decrease by 2 per Mn

Step 2. $\overset{+4}{Mn}O_2 + Cl^- \rightarrow Mn^{2+} + Cl_2 + H_2O$

O.N. increase by 1 per Cl

Step 3. Equalize the increase/decrease in O.N. by multiply MnO_2 by 1 and Cl^- by 2

$$MnO_2 + 2Cl^- \rightarrow Mn^{2+} + Cl_2 + H_2O$$

Step 4. Balance other atoms except H and O. Here they are all balanced.

Step 5. Balance O atoms by adding H2O molecules to the side failing short of O atoms.

$$MnO_2 + 2Cl^- \rightarrow Mn^{2+} + Cl_2 + H_2O + H_2O$$

Step 6. Balance H atoms by adding H+ ions to the side falling short of H atoms.

$$\mathbf{MnO_2 + 2Cl^- + 4H^+ \rightarrow Mn^{2+} + Cl_2 + 2H_2O}$$

(ii) The skeleton equation for the given process is

$$Mg\ NO_3^- \rightarrow Mg^{2+} + N_2O + H_2O$$

Step 1. $$\overset{0}{Mg} + \overset{+5}{N}\overset{-2}{O_3} \rightarrow \overset{2+}{Mg} + \overset{+1}{N_2}\overset{-2}{O} + \overset{+1}{H_2}\overset{-2}{O}$$

Multiply NO_3^- by 2 to equalize N atoms

O.N. increase by 2 per Mg

Step 2. $$\overset{0}{Mg} + 2\overset{+5}{N}O_3^- \rightarrow Mg^{2+} + \overset{+1}{N_2}O + H_2O$$

O.N. increase by 4 per N
Total decrease : 4 × 2 =8

Step 3. Equalize increase/decrease of O.N. by multiplying Mg by 4 and ($2NO_3^-$) by 1

$$4Mg + 2NO_3^- \rightarrow Mg^{2+} + N_2O + H_2O$$

Step 4. Balance atoms than O and H

$$4Mg + 2NO_3^- \rightarrow 4Mg^{2+} + N_2O + H_2O$$

Step 5. Balance O atoms

$$4Mg + 2NO_3^- \rightarrow 4Mg^{2+} + N_2O + H_2O + 4H_2O$$

Step 6. Balance H atoms as is done in acidic medium

$$\mathbf{4Mg + 2NO_3^- + 10H^+ \rightarrow 4Mg^{2+} + N_2O + 5H_2O}$$

(iii) The skeleton equation for the given process is:

$$Zn + HNO_3 \rightarrow Zn^{2+} + NO_2 + H_2O$$

Step 1. $$\overset{0}{Zn} + \overset{+1}{H}\overset{+5}{N}\overset{-}{O_3} \rightarrow \overset{2+}{Zn}(\overset{+5}{N}\overset{-2}{O_3})_2 + \overset{+4}{N}\overset{-2}{O_2} + \overset{+1}{H_2}\overset{-2}{O}$$

Here, N retains its oxidation state in $Zn(NO_3)_2$ but change its oxidation number in NO_2. This implies that some nitric acid molecules act as acid while some of them act as oxidizing agents. It is better to reduce this equation to ionic form.

Decrease of O.N. by 1

Step 2. $$Zn + H^+ + \overset{+5-}{NO_3} \rightarrow \overset{2+}{Zn} + \overset{+4}{N}O_2 + H_2O$$

Increase of O.N. by 2

Step 3. Equalize decrease/increase of O.N. by multiplying Zn by 1 and NO_3^- by 2.

$$Zn + 2NO_3^- + H^+ \rightarrow Zn^{2+} + NO_2 + H_2O$$

Step 4. Balance atoms other than O and H

$$Zn + 2NO_3^- + H^+ \rightarrow Zn^{2+} + 2NO_2 + H_2O$$

Step 5. Balance O atoms

$$Zn + 2NO_3^- + H^+ \rightarrow Zn^{2+} + 2NO_2 + 2H_2O$$

Step 6. Balance H atoms

$$Zn + 2NO_3^- + 4H^+ \rightarrow Zn^{2+} + 2NO_2 + 2H_2O$$

Step 7. Changing the equation to molecular form

$$Zn + 2HNO_3 + 2H^+ + 2NO_3^- \rightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O$$

$$\mathbf{Zn + 4HNO_3 \rightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O}$$

3.6 DIRECT AND INDIRECT REDOX REACTIONS

In aqueous solutions, the spontaneous redox reactions can be carried out directly as well as indirectly. The energy liberated during the direct and indirect redox reactions appear in different forms. Let us discuss briefly, the direct and indirect redox reactions.

1. Direct Redox Reactions

A redox reaction in which oxidation and reduction takes place in the some vessel is called direct redox reaction. In such reactions, the transference of electrons from reducing agent to oxidizing agent occurs over a very short distance (generally within the molecular diameters). For example, if a zinc rod is immersed in copper sulphate solution taken in a beaker, (Fig. 3.1) a spontaneous reaction takes place and the following observations are made:

(i) Zinc rod starts dissolving and loses its mass gradually.
(ii) The blue colour of $CuSO_4$ solution slowly fades.
(iii) A reddish brown precipitate of copper sattles down at the bottom of the breaker.
(iv) The reaction is exothermic, i.e., it takes place with the evolution of heat.
(v) The solution remains electrically neutral.
(vi) The reaction does not continue indefinitely but stops after some time.

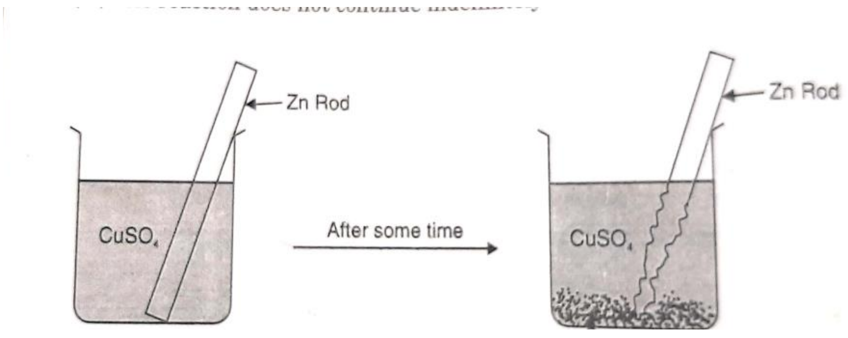


Fig. 3.1. Zn-$CuSO_4$ reaction in breaker.

The overall reaction taking place in the breaker may be represented as:

$$Zn(s) + \underbrace{Cu^{2+}(aq) + SO_4^{2-}(aq)}_{\text{From copper sulphate}} \rightarrow Zn^{2+}(aq) + SO_4^{-2}(aq) + Cu(s)$$

Discarding the common SO_4^{2-} ions.

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

Zinc loses electrons and changes into Zn^{2+} ions. As a result the mass of zinc rod decreases. The electrons lost by zinc rod are gained by $Cu^{2+}(aq)$ ions and they change into Cu(s) atoms which settle down at the bottom of beaker in the form of precipitate. It may be noted that in the **direct redox reaction, the chemical energy appears as heal.**

If a copper rod is placed in $ZnSO_4$ solution, no reaction takes place. But if the copper rod is dipped in the aqueous of silver nitrate, the silver ions oxidise copper to copper ions according to the following reaction:

$$Cu(s) + 2Ag^{+}(aq) \rightarrow 2Ag(s) + Cu^{2+}(aq)$$

2. Indirect Redox Reactions and Electrochemical Cells

The redox reactions in which oxidation and reduction take place in different vessels are called indirect redox reactions. In such reactions, the transference of electrons between reducing agent and oxidizing agent takes place indirectly through the conducting wires. The decrease of energy during the indirect redox reactions appears as electrical energy. In other words, these reactions involve the conversion of the chemical energy into electrical energy. The arrangement for carrying out the indirect redox reaction is referred to as electrochemical cell.

Thus, an electrochemical cell is a device in which chemical energy is converted into electrical energy. These are also called galvanic cells or voltaic cells after the names of Luigi Galvani and Alessandro volta respectively who were among the first few to conduct experiments on conversion of chemical energy into electrical energy.

In order to understand as to how the indirect redox reaction is used to produce electrical energy let us consider the redox reaction between zinc and $CuSO_4$ solution For carrying out the reaction in indirect manner Zn and $CuSO_4$ solution have to be taken in separate vessels. The arrangement consist of two beabers containing solutions of $ZuSO_4$ and $CuSO_4$ respectively. Zinc rod is dipped in $ZuSO_4$ solution so that Zn and Zn^{2+} come in contact at the interface. Copper rod is dipped in $CuSO_4$ solution so as to make the contact between Cu and its oxidised form Cu^{2+} ions.

The two metal rods act as electrodes and are connected by a conducting wire through a galvanometer. The two solutions are joined by the inverted U-tube known as **salt bridge.** The U-tube is filled with aqueous solution of some electrolyte such as KCI, KNO_3 or NH_4Cl to which gelatin or agar-agar has been added to convert it into semi-solid paste. A schematic diagram of this cell has been shown in Fig. 3.2.

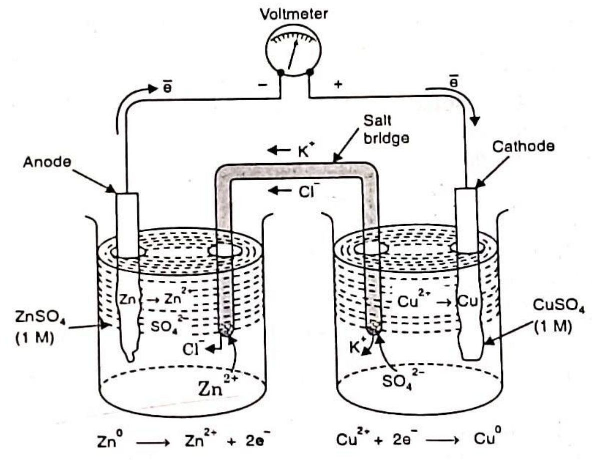


Fig. 3.2. Electrochemical cell.

The following observations are niade when the key is inserted:

1. There is a deflection in the galvanometer which indicates the flow of electrons through the connecting wires.
2. The direction of deflection indicates the flow of conventional current from copper to zinc indicating that copper is +ve terminal and zinc is -ve terminal. In other words, electron flow occurs from zinc to copper.
3. The zinc rod loses mass whereas the copper rod gains mass.
4. The concentration of zinc sulphate solution increases and that of copper sulphate solution decreases.
5. No evolution of heat is observed during the reaction.
6. The solution in the two breakers remain electrically neutral throughout.
7. The reaction as well as the flow of electrons stops after some time.

Now let us explain the above observations in terms of working of cell. Zinc atom undergo oxidation and are oxidised to Zn^{2+} ions, by losing electrons.

(Oxidation)

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

The electrons liberated during oxidation are pushed through the connecting wire to copper rod where these are picked up by Cu^{2+} ions, which get reduced to copper atoms. The copper atoms as formed get deposited on the copper rod. That is why copper rod gains weight.

$$Cu^{2+}(ag) + 2e^- \rightarrow Cu(s) \qquad \text{(Reduction)}$$

The overall reaction taking place in the cell is :

$$Zn(s) + Cu^{2+}(ag) \rightarrow Zn^{2+}(aq) + Cu(s)$$

The electrode at which oxidation takes place is called anode and that at which reduction takes place is called cathode. In the above electrochemical cell oxidation occurs at the zinc rod, therefore, zinc is anode and reduction occurs at the copper rod, hence, copper is cathode. It may be noted that anode electrode constitutes **-ve terminal** and the cathode electrode constitutes **+ ve terminal** of the cell.

By convention, the direction of flow of current is from + ve terminal to - ve terminal which is opposite to the flow of electrons.

Function of salts bridge. In the electrochemical cell a salt bridge serves two very important functions:

1. It allows the flow of current by completing the circuit.
2. It maintains electrical neutrality.

It may be explained as follows:

The transference of electrons from zinc anode to copper cathode leads to development of a net positive charge around the anode due to formation of Zn^{2+} ions and net negative charge around the cathode due to deposition of Cu^{2+} ions as Cu(s) on the cathode. The positive charge accumulated around the anode will prevent electrons to flow from it and the negative charge (due to excess of SO_4^{2-}ions) collected around the cathode will prevent the acceptance of electrons from the anode. As the transference of electrons stops, no current will flow. The salt bridge comes to the aid and restores electroneutrality of the solutions in the two compartments. It contains a concentrated solution of an **inert electrolyte,** the ions of which are not involved in electrochemical reactions. The anions of the electrolyte (e.g., Cl^- in case the salt bridge contains KCI, Fig. 3.2) migrate to the anode compartment and cations (i.e., K^+ ions) migrate to the cathode compartment so that the solutions in these compartments become neutral and the flow of electron continues. Thus, the salt bridge helps to prevent the accumulation of charges and maintains the flow of current.

3. Hall Cells and Half Cell Reactions

It has been pointed out that oxidation and reduction in the electrochemical cell take place in different vessels. These two parts of the electrochemical cell are called **half cells** and reactions taking place in them are called **half cell reactions.** The half cell in which oxidation takes place is called oxidation half cell and the reaction taking place in it is oxidation hall cell reaction. Similarly, the half-cell in which reduction takes place is called reduction half-cell and the reaction taking place in it is called reduction half-cell reaction. For example, the half-cell reactions in zinc-copper sulphate cell are:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

(Oxidation half-cell reaction)

Similarly, copper electrode and copper sulphate solution constitute reduction half-cell.

$$Cu^{2+}(ag) + 2e^- \rightarrow Cu(s)$$

(Reduction half-cell reaction)

Representation of Galvanic Cell

The electrochemical cell can be represented briefly according to certain universally accepted conventions as described:

1. The half-cell is constituted by a redox couple which is represented M/M^{n+} or $M^{n+}+/M$ where M represent the symbol of the element M^{n+} represents its cation in electrolyte. The slash (/) represents the interface between the two phases (may be solid/liquid or liquid/gas). The concentration of electrolyte may also be mentioned in brockets. For example, let us consider copper electrode in contact with cupric ions with concentration equal to 1.0 M.
    (a) It can be represented as Cu^{2+} (1.0 M)/Cu, if it constitutes reduction half-cell.
    (b) It can be represented as Cu/Cu^{2+} (1.0 M), if it constitutes oxidation half-cell.
2. Anodio half-cell (oxidation half) is written on the left hand side whereas cathodic half cell (reduction half) is written on the right hand side.
3. The two half cells are separated by the two vertical lines which indicate salt bridge.

    For example, Zn-$CuSO_4$ cell may be represented as

$$Zn/Zn^{2+}\ (1.0\ M)\ \|\ Cu^{2+}\ (1.0\ M)/Cu$$

4. The electrolyte used in U tube can be represented between the two vertical lines.

$$\mathbf{Zn/Zn^{2+}\ (1M)}\ |\ \text{Saturated KCI}\ |\ \mathbf{Cu^{2+}(1\ M)/Cu}$$

5. In cases where porous pot is used in separating the electrodes, a single vertical line is drawn between the two electrodes as shown below:

$$Zn/Zn^{2+}\ (1.0\ M)\ |\ Cu^{2+}\ (1.0\ M)/CU$$

Sometimes negative and positive signs are also put on the electrodes to show the release or gain of electrons taking place on them. Anode is a negative terminal while cathode is a positive terminal. The flow of electrons through the external circuit takes place from anode to cathode.

3.7 ELECTRODE POTENTIAL

When a strip of a etal M is brought in contact with the solution of its own ions M^{n+}, it has either of the two tendencies.

(a) Tendency of oxidation. Metal atoms may lose electrons to form M^{n+} in solution. In doing so, the metal strip develops a negative charge due to accumulation of electrons released. The solution at the same time develops a positive change due to formation of positive ions. The oxidation process does not continue long and a state of equilibrium is established very quickly.

$$M \rightleftharpoons M^{n+} + ne^-$$

(b) Tendency of reduction. The metal ions in solution may gain electrons from the strip, get reduced and are deposited on the strip as atoms. In doing so, the strip acquires positive charge and the solution develops negative charge due to decrease in concentration of positive ion Ultimately, a state of equilibrium is established:

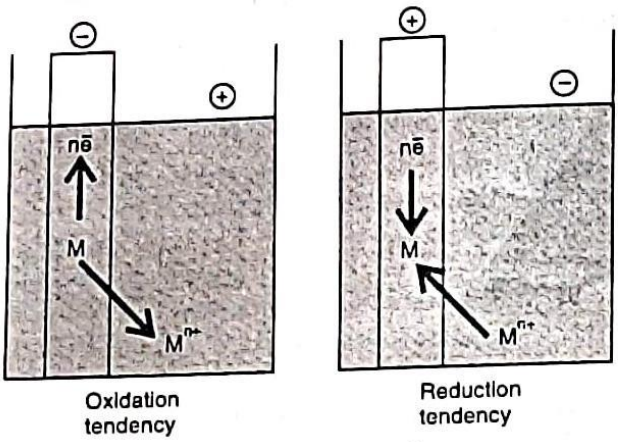


Fig. 3.3

In either case, the equilibrium leads to the separation of charges and results into a potential difference being developed between the metal strip and its solution. The net charge separation and hence, the potential difference at equilibrium depends upon:

1. The nature of metal and its ion
2. Concentration of ions in the solution
3. Temperature

The electrical potential difference set up between the metal and its solution is known as **half-cell electrode potential**. It is, in fact, the measure of the tendency of electrode in the half cell to lose or gain electrons. According to the present conventions, the hall reactions are always written as reduction hall reactions and their potentials are represented by reduction potentials. It may be noted that:

(i) **Reduction potential ($E_{Red.}$)** (tendency to gain electrons) and **oxidation** potential ($E_{Oxi.}$)tendency to lose electrons) of an electrode are numerically equal but have opposite signs.
(ii) Reduction potential of an electrode generally increases with the increase in concentration of its ions and decreases with the decrease in the concentration of the ions in the electrolyte.
(iii) The reduction potential of electrode when the concentration of the ions in the solution is 1 mol L^{-1} and temperature is 298 K is called **standard reduction potential** and represented by $E^{\circ}_{Red.}$

Emf of the Cell

As pointed out earlier thnt the electrochemical cell consists of two half cells, namely, oxidation half and reduction half cells. The electrodes in these half cells have different electrode potentials. When the circuit in completed the loss of electrons occurs at the electrode having lower reduction potential whereas the gain of electrons occurs at the electrode with higher reduction potential. The difference in the electrode potential of the two electrodes of the cell is termed as **electromotive force** (abbreviated as **EMF** or **cell voltage**). Mathematically, it can be expressed as:

$$\mathbf{EMF = E_{Cathode} - E_{Anode}}$$

Since in the representation of a cell cathode in written on right hand side and anode on left hand side, therefore, EMF of a cell is also sometimes written as:

$$EMF = E_{Right} - E_{Left} - E_R - E_L$$

EMF of the cell may be defined as the potential difference between the two terminals of the cell when no current is drawn from it. It is measured with the help of potentiometer of vacuum tube voltmeter,

Standard Electrode Potentials

Absolute value of electrode potential of an electrode cannot be determined because a half cell by itself cannot cause movement of charges (flow of electrons). It is due to the fact that once equilibrium is reached between the electrode and the solution in a half cell, no further displacement of charges can occur unless and until it is connected to another half-cell with different electrode potential. This difficulty is overcome by finding the electrode potentials of various electrodes relative to a reference electrode whose electrode potentials of arbitrarily fixed. The common reference electrode used for this purpose is **standard hydrogen electrode (SHE)** or whose electrode potential is arbitrarily taken to be zero.

Standard hydrogen electrode (SHE). Standard hydrogen electrode (Fig. 3.4) consists of a platinum wire sealed into a glass tube and carrying a platinum foil at one end. The platinum foil is coated with finely divided platinum. This electrode is placed in beaker containing an aqueous solution of some acid having activity of H^+ ions in solutions as unity (nearly one molar HCl solution). Hydrogen gas at one bar pressure is continuously bubbled through the solution at n temperature of 298 K The oxidation or reduction in the SHE takes place at platinum foil.

When SHE acts as anode, oxidation will take place at it as

$$H_2(g) \rightarrow 2H^+(aq) + 2e^-$$

In such a case it is represented as **Pt,** $\mathbf{\frac{1}{2} H_2/H^+ (IM)}$

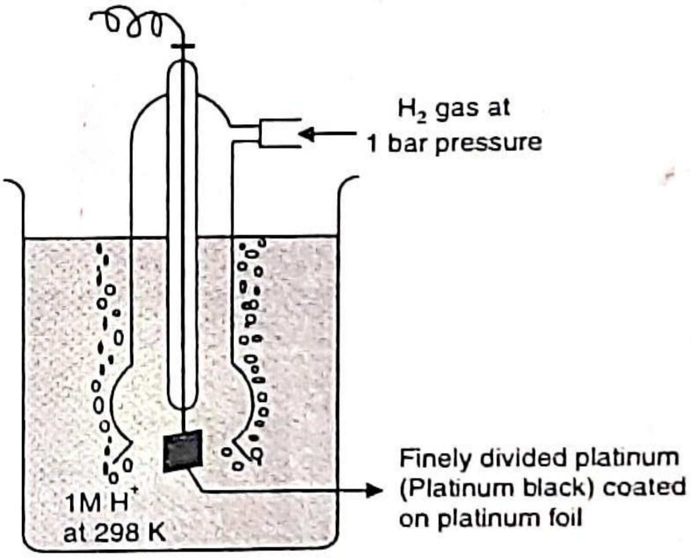


Fig. 3.4. Standard hydrogen electrode (SHE)

The activities of pure solids and liquids are taken as unity.

- In dilute aqueous solution, the activity of a species is nearly equal to its molarity.
- For gaseous species, is nearly equal to its partial pressures expressed in bar. For example at 1 bar the activity of gaseous species is nearly equal to one.

When SHE acts as cathode, reduction will take place of it as

$$2H^+(aq) + 2e^- \rightarrow H_2(g)$$

In this case it is represented as $\mathbf{H^+ (1M)/\frac{1}{2} H_2}$, **Pt.** here is an inert electrode.

The electrode potentials of other electrodes are determined by coupling them with SHE. The electrode potential of an electrode determined relative to the standard hydrogen electrode under standard conditions is called standard electrode potential. It is represented as E°. The standard conditions are 1 M concentration of iops in the solution, 298 K temperature and 1 bar pressure.

Measurement of Standard Electrode Potentials

In order to determine the standard electrode potential of an electrode, the electrode in standard conditions is connected to normal hydrogen electrode to constitute a cell. If the electrode forms the negative terminal of the cell, it is allotted negative electrode potential and if it forms the positive terminal of the cell, it is allotted a positive value of electrode potential. The potential difference between the electrodes is determined with the help of voltmeter (or more correctly by potentiometer). At the same time, direction of flow of current is also observed which gives the idea of direction of flow of electrons Electron flow occurs from anode to cathode whereas current flows from cathode to anode.

$$E^\circ_{Cell} = E^\circ_{Cathode} - E^\circ_{Anode}$$

Knowing the E°_{cell} and electrode potential of one of the electrodes (SHE), the electrode potential of the other electrode can be calculated.

For example, in order to find out standard electrode potential of zinc electrode, zinc electrode containing 1 M concentration of Zn^{2+} ions is the connected to SHE as shown in Fig. 3.5.

The voltmeter reading shows the potential difference (E°_{cell}) of 0.76 volt and direction of conventional current is observed to be from SHE to zinc. This implies that zinc electrode acts as anode and SHE acts as cathode.

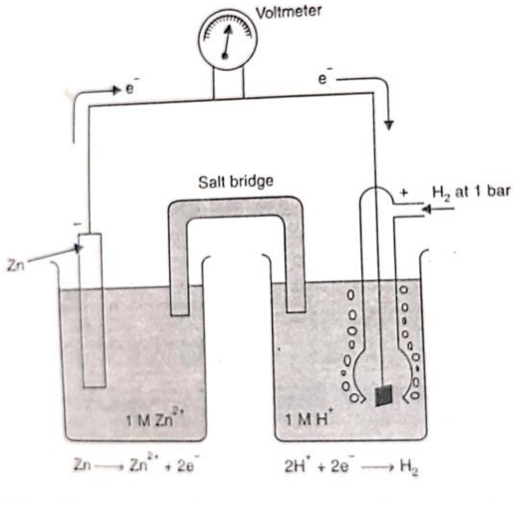


Fig. 3.5. Zinc electrode acts as the anode (-ve side) when it is connected to SHE.

$$E^\circ_{Cell} = E^\circ_{Cathode} - E^\circ_{Anode}$$

$$= E^{\circ}_{2H^{*}/H2} - E^{\circ}_{Zn^{2+}/Zn}$$

$$0.76 = 0 - E^{\circ}_{Zn^{2+}/Zn}$$

$$E^{\circ}_{Zn^{2+}/Zn} = -\ 0.76 \text{ volts.}$$

Similarly, when standard copper electrode is coupled with SHE (Fig. 3.6.), the voltmeter reading shows a potential difference (E°_{cell}) of 0.34 volt. The direction of flow of conventional current is from copper to SHE. This means that, in this cell copper acts as cathode and SHE acts as anode.

$$E^{\circ}_{Cell} = E^{\circ}_{Cathode} - E^{\circ}_{Anode}$$

$$= E^{\circ}_{Cu^{2+}/Cu} - E^{\circ}_{2H^{*}/H2}$$

$$0.34 = E^{\circ}_{Cu^{2+}/Cu} - 0$$

$$E^{\circ}_{Cu^{2+}/Cu} = 0.34 \text{ volts.}$$

In the similar way, the standard reduction potentials of other electrodes including metal as well as non-metals can be determined. For example, the standard electrode potential of chlorine can be determined by using electrode consisting of CI2 gas at one atmospheric pressure and 298 K in equilibrium with 1 M solution.

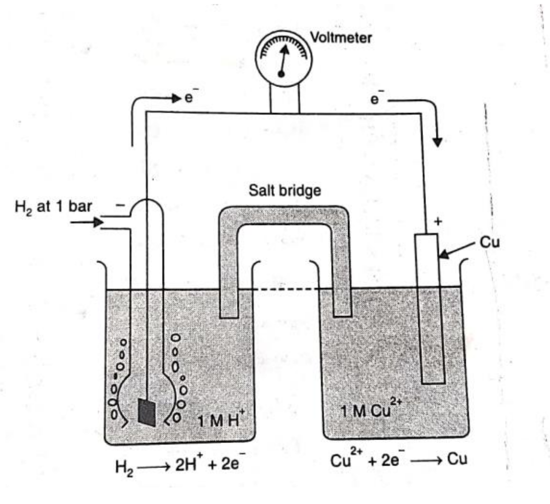


Fig. 3.6. Copper electrode acts as cathode (a positive terminal) when it is connected to SHE.

3.8 ELECTROCHEMICAL SERIES

We have seen that different metal/metal ion combinations have different values of electrode potentials. The various elements can be arranged in order of increasing or decreasing value of their reduction potentials. **The arrangement of various elements in order of increasing values of standard reduction potentials is called electrochemical series or activity series.** The electrochemical series, consisting of some electrodes along with their respective reduction half reactions has been given in table 3.1.

Table 3.1. Standard Electrode (Reduction) Potentials at 298 K (Electro-chemical Series)

Electrode	Half-cell Reaction (Reduction)	E°(volts)
Li^+/Li	Weakest oxidant $Li^+ + e^- \rightarrow Li$ Strongest reluctant	- 3.05
M^+/M (M = K, Rb or Cs)	$M^+ + e^- \rightarrow M$	- 2.93
Ba^{2+}/Ba	$Ba^{2+} + 2e^- \rightarrow Ba$	- 2.90
Ca^{2+}/Ca	$Ca^{2+} + 2e^- \rightarrow Ca$	- 2.87
Na^+/Na	$Na^+ + e^- \rightarrow Na$	- 2.71
Mg^{2+}/Mg	$Mg^{2+} + 2e^- \rightarrow Mg$	- 2.38
Be^{2+}/Be	$Be^{2+} + 2e^- \rightarrow Be$	- 1.70
Al^{3+}/Al	$Al^{3+} + 3e^- \rightarrow Al$	- 1.66
Zn^{2+}/Zn	$Zn^{2+} + 2e^- \rightarrow Zn$	- 0.76
Cr^{3+}/Cr	$Cr^{2+} + 3e^- \rightarrow Cr$	- 0.74
Fe^{2+}/Fe	$Fe^{2+} + 2e^- \rightarrow Fe$	- 0.44
Cd^{2+}/Cd	$Cd^{2+} + 2e^- \rightarrow Cd$	- 0.40
Co^{2+}/Co	$Co^{2+} + 2e^- \rightarrow Co$	- 0.28
Ni^{2+}/Ni	$Ni^{2+} + 2e^- \rightarrow Ni$	- 0.25
Sn^{2+}/Sn	$Sn^{2+} + 2e^- \rightarrow Sn$	- 0.14
Pb^{2+}/Pb	$Pb^{2+} + 2e^- \rightarrow Pb$	- 0.13
$H^+/\frac{1}{2}H_2$ (SHE)	**$H^+ + e^- \rightarrow \frac{1}{2}H_2$**	**-0.00**
Sn^{4+}/Sn^{2+}	$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	+ 0.15
Cu^{2+}/Cu	$Cu^{2+} + 2e^- \rightarrow Cu$	+ 0.34
$\frac{1}{2}I_2/I^-$	$\frac{1}{2}I_2 + e^- \rightarrow I^-$	+ 0.54
Fe^{3+}/Fe^{2+}	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+ 0.77
Ag^+/Ag	$Ag^+ + e^- \rightarrow Ag$	+ 0.80
$\frac{1}{2}Br_2/Br^-$	$\frac{1}{2}Br_2 + e^- \rightarrow Br$	+ 1.07
$\frac{1}{2}Cl_2/Cl^-$	$\frac{1}{2}Cl_2 + e^- \rightarrow Cl^-$	+ 1.36
Au^{3+}/Au	$Au^{3+} + 3e^- \rightarrow Au$	+ 1.50
$\frac{1}{2}F_2/F^-$	Strongest oxidant $\frac{1}{2}F_2 + e^- \rightarrow F^-$ Weakest reluctant	+ 2.87

Applications of the Electrochemical Series

Some of the important applications of the electrochemical series have been discussed as follows:

1. **Calculation of the standard EMF of the cell.** From the electrochemical series, the standard reduction potentials of electrodes are found out. The electrode with higher reduction potential is taken as cathode and other as anode. From this EMF of the cell is calculated as:

$$EMF^\circ = E^\circ_{cathode} - E^\circ_{anode}$$

However, if the reaction taking place in the cell is also to be determined, the following steps are followed:

(a) Write reduction equations for both electrodes along with their reduction potentials, separately.
(b) Balance each reaction with respect to the number of atoms of each kind and the electrical charges.
(c) Multiply the reactions by a suitable number so that the number of electrons involved in both the half reaction are equal.

While multiplying the half-cell reaction is calculations do not multiply the E° values with any such integer because it simply reflects the tendency of reduction.

(d) Subtract the equation for reaction having the lower reduction potential from the other reaction having higher reduction potential. The difference gives the EMF of cell.

The electrode having higher reduction potential acts as cathode and the other electrode acts as anode. Now let us solve some numerical problems to understand the application of this method in calculating EMF.

SOLVED EXAMPLES BASED ON CALCULATION OF STANDARD EMF

Example 3.5. Calculate the EMF of the given cell, also write the overall cell reaction.

$$Zn \mid Zn^{2+}\ (1\ M) \parallel Ag^{+}\ (1\ M) \mid Ag$$

Standard reduction potential for Zn2+/Zn is – 0.76 volts and for Ag^+/Ag is 0.80 volts.

Solution. It is clear from the cell, that silver electrode acts as a cathode and zinc electrode acts as anode:

(a)

$$Ag^+ + e^- \rightarrow Ag \qquad E^\circ = 0.80 \text{ volts}$$
$$Zn^{2+} + 2e^- \rightarrow Zn \qquad E^\circ = 0.76 \text{ volts}$$

Multiply the first equation by 2 so as to equalize the number of electrons

(b) $2Ag^+ + 2e^- \rightarrow 2Ag \quad E^\circ = 0.80$ volts ...(i)

$Zn^{2+} + 2e^- \rightarrow Zn \quad E^\circ = 0.76$ volts ...(ii)

(c)
$$EMF^\circ = E^\circ_{cathode} - E^\circ_{anode}$$
$$= 0.80 - (-0.76)$$
$$= \mathbf{1.56\ volts.}$$

The overall cell reaction can be obtained by subtracting equation (ii) from equation (i). i.e.,

$$2Ag^+(aq) + Zn(s) \rightarrow 2Ag(s) + Zn^{2+}(aq)$$

2. **Comparison of the reactivities of metals.** The metals which occupy higher position in electrochemical series have lower reduction potentials. This indicates that ions of such metals will not be reduced to metals easily. On the contrary, such metals would be easily oxidized to their ions by losing electrons. Therefore, from the position of the metal in the electrochemical series, it is possible to predict the relative reactivities of metals. The metal having smaller reduction potential can displace metals having larger reduction potential from the solution of their salts. In other words, the metal occupying higher position in the series can displace the metal lying below it from the solution of their salts.
   Thus, we may conclude that the metals occupying higher positions in the electrochemical series are more reactive in displacing the other metals from the solutions of their salts. For example, zinc lies above copper in the series and hence, it can displace copper from copper sulphate solution. Copper cannot displace zinc from zinc sulphate solution because it lies below zinc in the series and hence, it is less reactive.
3. **Predicting the feasibility of a redox reaction.** With the help of electromotive series we can predict whether a given redox reaction will take place or not. From the given equation the substances undergoing oxidation and reduction are identified. The substance undergoing oxidation will act as anode and the substance undergoing reduction will act as a cathode. The EMF of this hypothetical cell is calculated as under:

   $$EMF^\circ = E^\circ_{cathode} - E^\circ_{anode}$$

   If EMF comes out to be positive the given redox reaction will take place and if EMF comes out to be negative the given redox reaction will not take place.
4. **To predict the reaction of a metal with dilute acids to liberate hydrogen gas.** Some details like Fe, Zn react with dil. acid like HCl, H_2SO_4 to liberate H_2 gas while some metals like Cu, Ag do not liberate H_2 gas with dil. HCl, dil. H_2SO_4. A prediction about capacity of a given metal to product H_2 gas by its reaction with dilute acids can be easily made from the knowledge of electromotive series. Chemical reaction between metal and acid can be represented, in general as

   $$\underset{\textbf{Metal}}{\mathbf{M}} + \underset{\textbf{From acid}}{\mathbf{nH^+}} \rightarrow \mathbf{M^{n+} + n/2H_2}$$

   For the above reaction to occur, the E°_{red} of metal (M^{n+}/M) must be lower than that of hydrogen. Hence, it can be concluded that **metals which lie**

above hydrogen in the electromotive series can reduce H^+ ions to hydrogen and hence, liberate hydrogen as on reaction with acids. In other words, metals having negative values of reduction potentials can displace hydrogen from acids. For example, zinc ($E^\circ_{Zn^{2+}/Zn}$ = - 0.76 volt) lies above hydrogen in the series and hence, it can displace hydrogen from dilute acids, whereas copper ($E^\circ_{Cu^{2+}/Cu}$ = - 0.34 volts) which is lying below hydrogen in the series cannot displace hydrogen from acids.

3.9. DEPENDENCE OF ELECTRODE POTENTIAL ON CONCENTRATION AND TEMPERATURE

We know that in the electrochemical series, the electrode potentials of various electrodes are given in standard state. However, the galvanic cells are generally operated under conditions different from the standard state conditions. The relationship between electrode potentials and concentrations of the substances involved in the half cell reaction is given by **Nernst equation**. The general reduction half reaction for an electrode may be written as

$$M^{n+} + ne^- \quad \rightarrow \quad M$$

The Nernst equation for the above half reaction can be written as:

$$E = E^\circ - \frac{2.303RT}{nF}\log\frac{[M]}{[M^{n+}]} \qquad \ldots(3.\ 1)$$

or

$$= E^\circ - \frac{2.303RT}{nF}\log\frac{[M^{n+}]}{[M]}$$

where, R = 8.314 JK-1 mol-1
T = Temperature in kelvin scale
F = 96500 coulombs
n = Number of electrons gained by the metal ions

[M] and $[M^{n+}]$ refer to the molar concentrations of element and its cations respectively.

Substituting the value of R, F and T (298) in equation (3. 1), we get,

$$E = E^\circ - \frac{0.059}{n}\log\frac{[M^{n+}]}{[M]} \qquad \ldots(3.\ 2)$$

It may be noted that while using equation (3,2) the molar concentrations of solids and liquids in pure state are taken as **unity.** But the concentrations of gases are expressed in terms of their partial pressure in atmosphere.

Thus, [M] = 1.

SOLVED EXAMPLES BASED ON CALCULATION OF ELECTRODE POTENTIAL

Example 3.6. Calculate the half-cell potential at 298 K for the reaction

$$Zn^{2+}(aq) + 2e^{-} \quad \rightarrow \quad Zn(s) \text{ if } [Zn^{2+}] = 2M$$

and $E^{\circ}_{Zn^{2+}/Zn} = -0.76$ volts.

Solution. $$E = E^{\circ} + \frac{0.059}{n}\log\frac{[Zn^{2+}]}{[Zn]}$$

By convention, $[Zn] = 1$

$$E = -0.76 + \frac{0.059}{2}\log\frac{2}{1}$$

$$= -0.76 + \frac{0.059}{2}\log 2$$

$$= -0.76 + \frac{0.059}{2} \times 0.3010$$

$= -0.76 + 0.0088 =$ **-0.7512 volts.**

SUMMARY

- **Oxidation.** A process involving increase in oxidation number by the loss of electrons.
- **Reduction.** A process involving decrease in oxidation number by gain of electrons.
- **Oxidizing Agents.** A substance which involves decrease in oxidation number of one or more of its elements.
- **Reducing Agents.** A substance which involves increase in oxidation number of one or more of its elements.
- **Oxidation Number.** A residual charge which an atom of the element appears to have when other atoms from the molecule are removed as ions by counting the electrons with more electronegative element.
- **EMF of the Cell or Cell Voltage (E_{cell}).** It is difference in the electrode potential, of the two terminals of the cell when no current is withdraws. Mathematically.

$$E_{cell} = E_{cathode} - E_{anode}$$

- **Electrochemical Series.** The arrangement of various elements in order of their increasing standard electrode potentials.

REVIEW QUESTIONS

1. Explain the terms: Oxidation, reduction, oxidizing agent and reducing agent in terms of electrons. Give suitable example in each case.
2. Justify statement that oxidation and reduction go hand in hand.
3. Find out the oxidation number of **underlined** atoms in the following species:
   $PPb\underline{S}O_4$, $\underline{Br}F_3$, $\underline{Cr}O_4^{2-}$, $\underline{Mn}O_4^{2-}$, CH_4, $\underline{Sb_2}O_5$, $(\underline{NH_4})_2$, SO_4, $\underline{C_6}\ H_{12}O_6$
4. Balance the following redox equations:
   (i) $Zn + HNO3 \rightarrow Zn(NO_3)_2 + N_2O + H_2O$
   (ii) $Cl_2 + IO_3^- \rightarrow Cl + IO_4^-$ in basic medium
   (iii) $AsO_3^{3-} + IO_3^- \rightarrow AsO_4^{3-} + I^-$ in acidic medium
   (iv) $S2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + I^-$
5. Distinguish between the Zn/CuSO4 redox reaction taking place in a breaker and that in a cell.
6. What is salt bridge? What is its function? What is its function? What alternative arrangement do you suggest in place of salt bridge?
7. What cell notations are used to illustrate electrochemical cell?
8. Copper does not react with dilute HCl whereas zinc immediately produce H_2 gas.
9. A student constituted a cell by the two electrodes Zn/Zn^{2+} (1 M) and Mg/Mg^{2+} (1 M) and represented it as
   Zn/Zn2+ (1 M) ‖ Mg2+ (1 M)/Mg. Is he correct or not?

   $E^\circ_{Mg^{2+}/Mg} = -2.37\ V$; $E^\circ_{Zn^{2+}/Zn} = -0.76\ V$)

   Justify.
10. A layer of CuO on copper vessel can be easily cleaned by dilute HCl but oxide layer of aluminium on the aluminium vessel cannot be cleaned by HCl. Give reason.

SECTION - C

4

IONIC EQUILIBRIUM AND ACIDS AND BASES

LEARNING OBJECTIVES

- Introduction
- Ionization of Weak Electrolytes
- Common Ion Effect
- Solubility Product Constant
- Common Ion Effect on Solubility of Ionic Salts
- Applications of Solubility Product
- Arrhenius Concept of Acids and Bases
- Bronsted-Lowry Concept of Acids and Bases
- Ionization of Acids and Bases
- Self-Ionisation of Water
- Expressing Hydronium Ion Concentration-Ph Scale
- Hydrolysis of Salts
- Acid-Base Indicators
- Acid-Base Titrations
- Buffer Solution

4.1 INTRODUCTION

We know that aqueous solutions of certain substances such as sodium chloride sulphuric acid, etc, conduct electricity whereas aqueous solutions of certain substance such as sugar, urea, ete do not conduct electricity. Michael Faraday, in 1824, classified substance into electrolytes and non-electrolytes on the basis of conductivity behavior of their aqueous solutions. The substances which conduct electricity in their aqueous solutions were termed electrolytes while those which do not conduct electricity were termed non electrolyte Svante Arrhenius (1880) explained that electrolytes, when dissolved in water split into charged particles, called ions This process is called ionisation or dissociation Certain electrolytes, such as NaCl, KCL, HCl are almost completely ionised in solutions whereas electrolytes such as NH_4OH, CH_3COOH are weakly ionised. The electrolytes which are almost completely ionised in solutions are called **strong electrolytes.** On the other hand, the electrolytes weakly ionised in their solutions are called **weak electrolytes.** In case of solutions of weak electrolytes the ions produced by dissociation of electrolyte are in equilibrium with undissociated molecules of the electrolyte. The equations for the dissociation of strong electrolytes written with only a single arrow directed to the right.

$$KCl(aq) \rightarrow K^+(aq) + Cl^-(aq)$$
$$NH4Cl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$$

On the other hand, equations for the dissociation of weak electrolytes are written with double arrows (⇌)

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$
$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Electrolytes may be acids, bases or salts. Acids are sour in taste. Vinegar contains acetic acid whereas citrous fruits such as orange, kinoo, lemon, etc. contain citric acid. Tamarind contains tartaric acid. All these substances you know, are sour in taste. Acids turn litmus paper red. Bases are bitter in taste. They turn litmus paper blue. Caustic soda (NaOH), washing soda (Na_2Co_3. $10H_20$) and aqueous ammonia are commonly used bases. Salts are made up of oppositely charged ions. In solid state these ions are held by strong electrostatic forces of attraction. When a salt is dissolved in water the attractive forces between the ions are highly weakened. This is due to the reason that electrostatic forces are inversely proportional to the dielectric constant of the medium and water has a very high dielectric constant (equal to 80). The ions, in solution, are further stabilized by their solvation with water molecules. Water molecules being polar molecules can have ion-dipole interactions with ions of the salt. Thus, ionic compounds get dissociated when dissolved in water.

Now let us consider the case of substances containing polar molecules, such as HCI, CH_3COOH, HCN, etc. These substances when dissolved in water ionize due to dipole-dipole interaction between molecules of water and the polar molecules of the substance.

It may be mentioned here that the term dissociation refers to the process of separation of ions in water in case of ionic solids whereas the term ionization is used in cases where a molecule splits into ions when dissolved in water.

4.2 IONISATION OF WEAK ELECTROLYTES

It has been mentioned earlier that weak electrolytes are ionised only partially. The ions produced as a result of dissociation of weak electrolytes are present in dynamic equilibrium with the undissociated molecules.

The fraction of total number of molecules of electrolyte dissolved, that ionises at equilibrium is called degree of ionisation or degree of dissociation.

Let us consider the ionisation of some weak electrolyte AB in water. Let C be the concentration of the electrolyte in the solution and a be its degree of ionisation. The concentrations of various species at equilibrium would be as follows:

	$AB(aq)$	$\rightleftharpoons$	$A^+(aq)$ +	$B^-(aq)$
Initial conc.	C	—	—	
Equilibrium conc.	C – Ca		Ca	Ca

Applying law of chemical equilibrium

$$K = \frac{[A^+]\,[B^-]}{[AB]} = \frac{(Ca)(Ca)}{C(1-a)}$$

$$= \frac{C^2\,a^2}{C(1-a)} = \frac{Ca^2}{C(1-a)}$$

For weak electrolytes, under normal concentrations, a is very small as compared with unity and hence $(1 - a)$ can be taken as 1 in the denominator.

∴ $$K = Ca^2$$

or $$a^2 = \frac{K}{C}$$

$$a = \sqrt{\frac{K}{C}}$$

$$a \propto \sqrt{\frac{1}{C}}$$

So the degree of ionisation is inversely proportional to concentration.

Thus, as the concentration decreases, the degree of ionisation increases. It can also be followed from the above relationship that as C approaches zero or dilution approaches infinity, **the degree of dissociation approaches unity,** i.e., its maximum value.

In other words, in very dilute solution, the whole of electrolyte is present in dissociated form as ions. This important generalization is known as **Ostwald dilution law.**

4.3 COMMON ION EFFECT

Weak acids and weak bases are ionised only to small extent in their aqueous solutions. In their solutions, unionised molecules are in dynamic equilibrium with ions. The degree of ionisation of a weak electrolyte (weak acid or weak base) is further suppressed if some strong electrolyte which can furnish some ion common with the ions furnished by weak electrolyte, is added to its solution. This effect is called common ion effect. For example, degree of ionisation of NH_4OH (a weak base) is suppressed by the addition of NH_4CI (a strong electrolyte). The ionisation of NH_4OH and NH_4Cl in solution is represented as follows:

$$\begin{array}{lllll} \text{(i)} & NH_4OH(aq) & \rightleftharpoons & \boxed{NH_4^+(aq)} & + OH\text{-}(aq) \quad \text{...weakly ionized} \\ \text{(ii)} & NH_4Cl & \rightleftharpoons & \boxed{NH_4^+(aq)} & + Cl\text{-}(aq) \quad \text{...strongly ionized} \end{array}$$

Common ion

Due to the addition of NH4Cl, which is strongly ionized in the solution, concentration of NH_4^+ ions increases in the solution. Therefore, according to Le-Chatelier's principle, equilibrium in equation *(i)* shifts in the backward direction in the favour of unionised NH_4OH. In this way, addition of NH_4CI suppresses the degree of ionisation of NH_4OH. Thus, the concentration of OH^- ions in the solution is considerably reduced and the weak base NH_4OH becomes still weaker base.

The suppression of the degree of ionisation of a weak electrolyte (weak acid or weak base) by the addition of some strong electrolyte having a common ion, is called common ion effect.

From the above discussion we can arrive at the various **factors on which degree of ionisation depends.** These are:

(i) **Nature of electrolyte.** Weaker the electrolyte smaller is the degree of ionisation

(ii) **Concentration of the electrolyte.** Smaller the concentration of the electrolyte greater the degree of ionisation.

(iii) **Presence of other electrolytes.** The degree of ionisation is suppressed if some strong electrolyte having some ion common with the ions of the weak electrolyte is present in the solution.

SOLUBILITY EQUILIBRIA

Some ionic solids are highly soluble in water whereas others are almost insoluble. The solubility of an ionic solid in water depends mainly on the lattice energy of the salt and the hydration energy of the ions in solution. The energy required to overcome the attractive forces between ions is referred to as lattice energy whereas the energy released during interaction between ions and the solvent molecules is referred to as solvation energy. Thus, lattice energy is always positive while solvation energy is always negative. For a salt to be able to dissolve, its salvation energy must be greater than its lattice energy. Each salt has its characteristic solubility which depends on temperature.

On the basis of their solubility in water, ionic solids can be broadly classified into three categories. *The solids having solubility greater than 0.1*

M are classified as **soluble solids** *whereas the one having solubility between 0.01 M and 0.1 M are classified as* **slightly soluble.** *The ionic solids having solubility less than 0.01 M are termed as* **sparingly soluble solids.** The salts such as barium sulphate, silver chloride, silver chromate, etc. belong to this category of salts.

4.4 SOLUBILITY PRODUCT CONSTANT

When a sparingly soluble salt is dissolved in water then even in the saturated solution, the concentration of the salt is very low. So, whatever little of electrolyte goes into solution, undergoes complete dissociation (due to low concentration). Therefore, in saturated solutions of such electrolytes, the solid electrolyte is in equilibrium with the ions as represented below:

Undissolved electrolyte ⇌ Ions in Solution.

For example, in aqueous solution of silver chloride, following equilibrium exits:

$$AgCl(s) \overset{\text{Water}}{\leftrightharpoons} mAg^{+}(aq) + Cl^{-(}aq)$$

$$K = \frac{[Ag^{+}]\,[Cl^{-}]}{[AgCl]}$$

The concentration of the undissolved salt is constant (say k) at a particular temperature regardless of the amount of solid silver chloride present. (This is true for any solid that its concentration is independent of the amount of solid), We, therefore, have

$$K = \frac{[Ag^{+}]\,[Cl^{-}]}{k}$$

$$K.k = K_{sp} = [Ag^{+}]\,[Cl^{-}]$$

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

In general, for any sparingly soluble salt $A_x\,B_y$ which dissociates to set up the equilibrium

$$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-} \qquad \ldots(4.1)$$

the solubility product constant may be expressed as:

$$K_{sp} = [A^{y+}]^{x}\,[B^{x-}]^{y} \qquad \ldots(4.2)$$

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 of the electrolyte. Thus, The solubility product of a sparingly soluble salt at a given temperature may be defined as the product of the concentrations of its ions in the saturated solution, with each concentration term raised to the power equal to the number of times the ion occurs in the equation representing the dissociation of the electrolyte.

The equation 4.2 is applicable for a saturated solution i.e., under equilibrium situation.

The term K_{sp} in equation 4.2 is replaced by Q_{sp} when concentration of one or more species is not the concentration under equilibrium. The value of Q_{sp} gives the direction of the process in equation 4.1. If Q_{sp} is less than K_{sp} it indicates that the forward process (dissolution) is taking place. On the other hand if Q_{sp} is greater that K_{sp} it indicates that the backward process (precipitation) would take place.

The expressions of solubility products of some sparingly soluble salts are given below:

Zns : $Zns \rightleftharpoons Zn^{2+} + S^{2-}$: $K_{sp} = [Zn^{2+}][S^{2-}]$
$PbCl_2$: $PbCl_2 \rightleftharpoons Pb2+ + 2Cl-$: $K_{sp} = [Pb^{2+}][Cl^-]^2$
$Ca_3(PO_4)_2$: $Ca_3(PO_4)_2 \rightleftharpoons 3Ca^{2+} + 2PO_4^{3-}$: $K_{sp} = [Ca^{2+]3}[PO_4^{3-]2}$
$Zr_3(PO_4)_4$: $Zr_3(PO4)_4 \rightleftharpoons 3Zr^{4+} + 4PO_4^{3-}$: $K_{sp} = [Zr^{4+}]^3[PO_4^{3-}]^4$

Calculation of Solubility Product

Knowing the solubility of the salt, its solubility product (K_{sp}) can be calculated for example, consider the salt AB. Suppose at a particular temperature its solubility is S mol L^{-1}. S moles of salts on ionization will give S moles of A^+ and S moles of B^-.

$$AB(s) \rightleftharpoons A+(aq) + B-(aq)$$

$$K_{sp} = [A^+](B^-] = [S][S] = S^2$$

Knowing the solubility S, K can be calculated. Solubility product of some sparingly soluble salts are given in Table 4.1.

Table 4.1. Solubility Products the Some Sparingly Soluble Salts at 298 K

Name	Formula	K_{sp}	Name	Formula	K_{sp}
Barium hydroxide	$Ba(OH)_2$	5×10^{-3}	Lead chloride	$PbCl_2$	1.6×10^{-5}
Barium oxalate	BaC_2H_4	1.6×10^{-7}	Lead chromate	$PbCrO_4$	2.8×10^{-13}
Barium phosphate	$Ba_3(PO_4)_2$	3.4×10^{-23}	Lead fluoride	PbF_2	
Barium sulphate	$BaSO_4$		Lead hydroxide	$Pb(OH)_2$	2.7×10^{-8}
Barium carbonate	$BaCO_3$	1.1×10^{-10}	Lead sulphate	$PbSO_4$	1.2×10^{-15}
Barium chromate	$BaCrO_4$		Lead sulphide	PbS	
Cadmium carbonate	$CdCO_3$	5.1×10^{-9}	Magnesium hydroxide	$Mg(OH)_2$	1.6×10^{-6}
Cadmium hydroxide	$Cd(OH)_2$	1.2×10^{-10}	Magnesium oxalate	$MgC2O_4$	3×10^{-28}
Cadmium sulphide	CdS		Magnesium carbonate	$MnCO_3$	1.8×10^{-11}
Cadmium carbonate	$CaCO_3$		Magnesium hydroxide	$Mn(OH)_2$	

Cadmium chromate Cadmium fluoride Cadmium hydroxide Cadmium phosphate Cadmium sulphate Chromium(III) hydroxide Cobalt (II) carbonate Cobalt (II) hydroxide Cobalt(III) hydroxide Cobalt (II) sulphide Copper (I) bromide Copper (I) chloride Copper (II) carbonate Copper (II) chromate Copper (II) hydroxide Copper (II) phosphate Copper(II) sulphide Gold (I) chloride] Gold (III) chloride Iron (II) carbonate Iron (II) hydroxide Iron (II) sulphide Iron (III) hydroxide Lead carbonate	$CaCrO_4$ CaF_2 $Ca(OH)_2$ $Ca_3(PO_4)_2$ $CaSO_4$ $Cr(OH)_3$ $CoCO_3$ $Co(OH)_2$ $Co(OH)_3$ CoS $CuBr$ $CuCl$ $CuCo_3$ $CuCrO_4$ $Cu(OH)_2$ $Cu_3(PO_4)_2$ CuS $AuCl$ $AuCl_3$ $FeCO_3$ $Fe(OH)_2$ FeS $Fe(OH)_3$ $PbCO_3$	5.2×10^{-12} 2.5×10^{-14} 8×10^{-28} 2.8×10^{-9} 7.1×10^{-4} 3.9×10^{-11} 5.5×10^{-6} 2.0×10^{-29} 9.1×10^{-6} 6.3×10^{-31} 1.4×10^{-13} 1.6×10^{-15} 1.6×10^{-44} 5×10^{-22} 5.3×10^{-9} 1.2×10^{-6} 1.4×10^{-10} 3.6×10^{-6} 2.2×10^{-20} 1.3×10^{-37} 6×10^{-37} 2.0×10^{-13} 3.2×10^{-25} 3.2×10^{-11} 8.0×10^{-16} 6×10^{-19} 4×10^{-38} 7.4×10^{-14}	Manganese (II) sulphide Mercury (I) chloride Mercury (II) hydroxide Mercury (II) sulphide Nickel carbonate Nickel hydroxide Nickel oxalate Nickel sulphide Silver bromide Silver carbonate Silver chloride Silver chromate Silver cyanide Silver iodide Silver sulphate Silver sulphide Strontium carbonate Tin (II) hydroxide Tin (II) sulphide Zinc carbonate Zinc hydroxide Zinc oxalate Zinc sulphate	MnS Hg_2Cl_2 $Hg(OH)_2$ Hgs $NiCO_3$ $Ni(OH)_2$ NiC_2O_4 NiS $AgBr$ Ag_2CO_3 $AgCl$ Ag_2CrO_4 $AgCN$ Agl Ag_2SO_4 Ag_2S $SrCO_3$ $Sn(OH)_2$ SnS $ZnCO_3$ $Zn(OH)_2$ ZnC_2O_4 ZnS	8.6×10^{-5} 1.8×10^{-11} 1.9×10^{-13} 3×10^{-14} 1.3×10^{-18} 3.0×10^{-26} 2×10^{-53} 6.6×10^{-9} 1.6×10^{-14} 4×10^{-10} 3×10^{-20} 5.0×10^{-13} 8.1×10^{-12} 1.8×10^{-10} 1.1×10^{-12} 1.2×10^{-16} 8.3×10^{-17} 1.4×10^{-5} 6×10^{-51} 1.1×10^{-10} 1.4×10^{-28} 1×10^{-26} 1.4×10^{-11} 1.2×10^{-17} 2.7×10^{-8} 2×10^{-25}

SOLVED EXAMPLES BASED ON SOLUBILITY PRODUCT, K_{sp}

Example 4.1. *The solubility of AgCl is 1.06 × 10-5 mol L-1 at 298 K. Find out its* K_{sp} *at this temperature.*

Solution. The solubility equilibrium of AgCl may be represented as:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

The solubility of AgCl = 1.06×10^{-5} mol L^{-1} Since AgCl is a sparingly soluble salt it is completely ionized in solution. One mole of AgCl on dissociation produces one mole of Ag+ and one mole of Cl^- ions. Therefore,

$$[Ag^+] = [AgCl] = 1.06 \times 10^{-5} \text{ mol } L^{-1}$$

$$[Cl^-] = [AgCl] = 1.06 \times 10^{-5} \text{ mol } L^{-1}$$

$$K_{sp} = [Ag+][Cl-]$$

$$= (1.06 \times 10^{-5})(1.06 \times 10^{-5})$$

$$= \mathbf{1.12 \times 10^{-10}}.$$

4.5 COMMON ION EFFECT ON SOLUBILITY OF IONIC SALTS

In accordance with Le Chatelier's principle if we increase the concentration of one of the ions, in equilibrium with the solid salt, it should combine with the ion of its. opposite charge and some of the salt will be precipitated. Precipitation will continue till Q_{sp} becomes equal to K_{sp}. Similarly, if the concentration of one of the ions is decreased, Q_{sp} becomes less than K_{sp}. Some of the salt dissolves to increase the concentrations of both the ions so that again Q_{sp} becomes equal to K_{sp}. The common ion effect finds application in the purification of sodium chloride and in the precipitation of soap. Pure sodium chloride is precipitated by passing HCl gas through a saturated solution of impure sodium chloride

$$NaCl(s) \rightleftharpoons Na^+(aq) + Cl^-(aq) \qquad \ldots(4.3)$$

$$HCl + H_2O \rightleftharpoons H_3O+(aq) + Cl-(aq)$$

Due to increase in concentration of Cl^- ions the equilibrium in equation (4.3). Shifts in backward direction resulting in the precipitation of pure sodium chloride. Impurities present in the sodium chloride remain in the solution.

Similarly, soup is precipitated from its solution by adding sodium chloride.

$$C_{17}H_{35}COONa(s) \rightleftharpoons C_{17}H_{35}COO\text{-}(aq) + Na^+(aq)$$

$$NaCl(aq) \longrightarrow Na^+(aq) + Cl\text{-}(aq)$$

Due to increase in concentration of Na^+ ions the equilibrium in equation (4.4)shifts in backward direction.

Now let us consider the solubility equilibrium of silver chloride.

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

The precipitate of silver chloride dissolve in aqueous ammonia. In other ward, the solubility of silver chloride increases in the presence of aqueous solution of ammonia. This can be understood as follows:

On addition of aqueous ammonia to the above equilibrium, Ag^+ ions combine with NH_3 molecules to form complex ion $(Ag(NH_3)_2]^+$.

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq)$$

Due to formation of the complex ion, the concentration of Ag+ ions in the solution decreases and in accordance with Le-Chatelier's principles the equilibrium (4.5). Shifts in forward direction, resulting in increasing in solubility of AgCl.

4.6 APPLICATIONS OF SOLUBILITY PRODUCT

1. **Calculation of Solubility**

   If solubility product of a sparingly soluble salt at a particular temperature is known, its solubility at that temperature can be calculated.

   Expression, correlating K_{sp} and solubility (in mol L^{-1}) of some common types of salts are listed below:

Salt Type	Relation between K_{sp} and S	Example
AB	$Ksp = (s)(s) = s^2$	$AIPO_4$, AgCl, AgBr, $PbSO_4$, $BaSO_4$, ZnS
AB_2	$Ksp = (s)(2s)^2 = 4s^3$	$PbCl_2$, $HgCl_2$
A_2B	$Ksp = (2s)^2(s) = 4s^3$	Ag_2CrO_4, $Ag_2C_2O_4$, Ag_2SO_4
AB_3	$Ksp = (s)(3s)^3 = 27s^4$	$Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$
A_3B_2	$Ksp = (3s)^3(2s)^2 = 108s^5$	$Ca_3(PO_4)_2$, $Zn_3(PO_4)_2$
A_3B_4	$Ksp = (3s)^3(4s)^4 = 6912s^7$	$Zr_3(PO_4)_4$

Example 4.2. The solubility product of AgBr at a certain temperature is 2.5×10^{-13}. Find out solubility of AgBr in grams per litre at this temperature.

Solution. The solubility equilibrium of AgBr is

$$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$$

Suppose solubiliy of AgBr is x mol L-1. This would give x mol L-1 of Ag+ ions and x and L-1 of Br- ions on dissociation.

$$[Ag^+] = x \text{ mol } L^{-1}$$

$$[Br^-] = x \text{ mol } L^{-1}$$

Solubility product expressed for AgBr is

$$K_{sp} = [Ag+][Br-] = (x)[x] = x^2$$

But $K_{sp} = 2.5 \times 10^{-13}$

Hence, $x^2 = 2.5 \times 10^{-13}$

Or $x = \sqrt{2.5 \times 10^{-13}} = 5 \times 10\text{-}7 \text{ mol } L^{-1}$

Molecular mass of AgBr = 108 +80 = 188

Solubility of AgBr in $gL^{-1} = 5 \times 10^{-7} \times 188 =$ **9.4 × 10-5 gL^{-1}**

2. **Predicting the Precipitation of a Salt**
   The concept of solubility product helps us to predict whether a salt will precipitate or not, on mixing the solutions containing its ions under particular conditions. **In the solution, the ionic product i.e., product of concentration of ions of the salt (raised to appropriate powers) cannot exceed the value of its solubility product** because solubility product is the highest limit of ionic product at a particular temperature. Thus, if the ionic exceeds solubility product, excess ions combine with each other to form precipitates of the salt. So in other to predict whether a salt will precipitate or not, ionic product of the salt is calculated. If it exceeds the value of solubility product, the salt will be precipitated, otherwise not. Thus, it can be concluded that

   precipitation occurs ; if calculated ionic product > K_{sp}
   no precipitation ; if calculated ionic product < K_{sp}

   The calculated value of ionic product is sometimes given the symbol Q_{sp}

   Precipitation occurs if $Q_{sp} > K_{sp}$

Example 4.3. 50 ml of 0.01 M solution of Ca(NO3)2 is added to 150 ml of 0.08 M solution of (NH4)2SO4. Predict whether CaSO4 will be precipitated or not. Ksp of $CaSO_4 = 4 \times 10^{-5}$.

Solution.

Volume of $Ca(NO_3)_2$ solution = 50 cm^3

Volume of $(NH_3)_2SO_4$ solution = 150 cm^3

Total volume after mixing = 150 + 50 = 200 cm^3

(a) Calculation of Ca^{2+} ion concentration
Applying the relation

$$M_1V_1 = M_2V_2$$

(Before mixing) (After mixing)

$$0.01 \times 50 = M_2 \times 200$$

$$M_2 = \frac{0.01 \times 150}{200} = 2.5 \times 10^{-3} \text{ M}$$

∴ [Ca(NO3)2] after mixing = 2.5 × 10-3 mol L^{-1}

Since Ca(NO3)2 is completely ionized

∴ $[Ca2+] = [Ca(NO3)2 = 2.5 \times 10\text{-}3 \text{ mol } L^{-1}$

(b) Calculation of SO_4^{2-} ion concentration

Applying the relation,

$$\underset{\text{(Before mixing)}}{M'_1V'_1} = \underset{\text{(After mixing)}}{M'_2V'_2}$$

$$0.08 \times 150 = M'_2 \times 200$$

$$M_2 = \frac{0.08 \times 150}{200} = 6 \times 10^{-2} \text{ M}$$

∴ $[(NH_4)_2SO_4]$ after mixing = $6 \times 10\text{-}2 \text{ mol } L^{-1}$

Since $(NH_4)_2SO_4$ is completely ionized

∴ $[SO_4^{2-}] = [(NH_4)_2SO_4] = 6 \times 10^{-2} \text{ mol } L^{-1}$

(c) Ionic product $= [Ca^{2+}][SO_4^{2-}] = [2.5 \times 10^{-3}] [6 \times 10^{-2}] = 1.5 \times 10^{-4}$

Since ionic product (1.5×10^{-4}) is greater than solubility product (4×10^{-5}) hence **precipitate of $CaSO_4$ will be formed.**

3. **Precipitation of Soluble Salts**

   The principle of solubility product is also applied in the precipitation of soluble salts in pure state, from their saturated solutions. The phenomenon, known as **salting out,** is used in the purification of sodium chloride. This is done by preparing a *saturated solution* of impure sodium chloride in water when the following equilibrium exists:

$$NaCl(s) \rightleftharpoons \underset{\text{(In solution)}}{Na^+(aq) + Cl^-(aq)}$$

$$Ksp = [Na^+][Cl^-]$$

   HCI gas is passed through this solution. The concentration of Cl^- ions, therefore, increase considerably. The ionic product (Q_{sp}) exceeds the solubility product (K_{sp}) of NaCl and, in accordance with Le-Chatelier's principle, some of the sodium chloride precipitates out from the solution in pure state so that again Q_{sp} becomes equal to K_{sp}. The impurities, such as sodium and magnesium sulphates remain in solution.

ACID-BASE EQUILIBRIA

4.7 ARRHENIUS CONCEPT OF ACIDS AND BASES

According to Arrhenius concept,

An acid is a substance which can furnish hydrogen ions in its aqueous solution.

A base is a substance which can furnish hudroxyl ions in its aqueous solution.

For example, sustances such HNO_3, HCl, CH_3COOH are acids whereas substances such as NaOH, KOH, NH_4OH are bases, according to this concept.

$$HNO_3(aq) \rightleftharpoons H^+(aq) + NO_3^-(aq)$$

$$HCl(aq) \rightleftharpoons H^+(aq) + Cl^-(aq)$$

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

$$NaOH(aq) \rightleftharpoons Na^+(aq) + OH^-(aq)$$

$$KOH(aq) \rightleftharpoons K^+(aq) + OH^-(aq)$$

$$NH_4OH(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Acids such as HCl and HNO3, which are almost completely ionized in aqueous solutions are termed **strong acids** whereas acids such as CH3COOH which are weakly ionized are called **weak acids.**

Similarly, bases which are almost completely ionized in aqueous solution are called **strong bases,** for example, NaOH and KOH. The bases such as NH4OH are only slightly ionized and are called **weak bases.**

According to Arrhenius theory, neutralization of acids and bases is basically a reaction between H+ and OH- ions in solution.

$$H^+(aq) + OH^-(aq) \rightleftharpoons H_2(O)(l)$$

Nature of Hydrogen Ion and Hydroxyl Ion in Aqueous Solution

Hydrogen atom contains one proton and one electron. H^+ ion is formed by loss of this electron. Therefore, H^+ ion is simply a proton. Charge density of this unshielded proton is very high. Therefore, it is not likely to exist independently as H^+ ion. In an aqueous solution H^+ ion is considered to be present in hydrated from in combination with a water molecule as H_3O^+.

$$H^+ + H_2O \longrightarrow H_2O^+$$

H3O+ ion is called **hydronium ion.**

In aqueous solution hydronium ion is further hydrated to give speies such as $H_5O_2^+$, $H_7O_3^+$ and $H_9O_4^+$. Similarly, hydroxyl ion is hydrated to give species such as $H_3O_2^-$, $H_5O_3^-$, etc.

4.8 BRONSTED-LOWRY CONCEPT OF ACIDS AND

In 1993, a Danish Chemist J.H. Bronsted and an English Chemist TM. Lowry independently proposed new definitions for acids and bases. They proposed that:

An acid is a substance that can donate a proton.

A base is a substance that can accept a proton.

These definitions are more general because according to these definitions even ions can behave us acids or bases. Moreover, these definitions are not restricted to reactions taking place in aqueous solution only. In order to understand this concept of acids and buses let take some specific examples.

$$\underset{\text{Acid}}{HCl(aq)} + \underset{\text{Base}}{H_2O(l)} \rightleftharpoons H_2O^+(aq) + Cl^-(aq)$$

$$\underset{\text{Acid}}{NH_4^+(aq)} + \underset{\text{Base}}{H_2O(l)} \leftrightharpoons H_3O^+(aq) + NH_3(aq)$$

$$\underset{\text{Acid}}{H_2O(l)} + \underset{\text{Base}}{NH_3(aq)} \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$\underset{\text{Acid}}{H_2O(l)} + \underset{\text{Base}}{CO_3^{2-}(aq)} \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$$

From the above equations, it is obvious that acid base reactions according to Bronsted-Lowry concept involve transfer of proton from the acid to a base. A substance can act as an acid only if another substance capable of accepting a proton, is present.

Conjugate Acid-Base Pairs

An acid after losing a proton becomes a base whereas a base after accepting the proton becomes an acid. For example, let us consider the reaction between water and ammonia as represented by the following equilibrium:

$$\begin{array}{ccc} H_2O(l) + \overset{\downarrow}{NH_3}(aq) & \qquad & \overset{\downarrow}{NH_4^+}(aq) + OH^-(aq) \\ \textbf{Acid}_1 \quad \textbf{Base}_2 & & \textbf{Acid}_1 \quad \textbf{Base}_2 \end{array}$$

In the forward reaction, water donates a proton to ammonia (base) and act as acid. In the reverse reaction, NH_4^+ ions donate a proton to the OH^- ions (base) and act as acid A base formed by the loss of proton by an acid is called **conjugate base** of the acid where an acid formed by gain of a proton by the base is called **conjugate acid** of the base. In the above example, OH^- is the conjugate base of H_2O and NH_4^+ is conjugate acid of NH_3. **Acid-base pairs such as H_2O/OH^- and NH_4^+/NH_3 which are formed by loss or gain of a proton are called conjugate acid-base pairs.**

A strong acid would have large tendency to donate a proton. Thus, **conjugate base of a strong acid would be a weak base**. Similarly, **conjugate base of a weak acid would be a strong base.**

Some more conjugated acid-base pairs have been given in the following equations:

$$\textbf{Acid}_1 + \textbf{Base}_2 \rightleftharpoons \textbf{Acid}_2 + \textbf{Base}_1$$

(1) $CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$

(2) $H_2O(l) + CO_3^{2-}(aq) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$

(3) $HCO_3^-(aq) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + CO_3^{2-}(aq)$

(4) $HCl(aq) + HCO_3^-(aq) \leftrightharpoons H_2CO_3(aq) + Cl^-(aq)$

It may be noticed that in equation (1) H_2O behaving as a buse whereas in equation (2) it is behaving as an neid. Similarly, HCO_3^- ion in equation (3) acts as an acid and in equation (4) it acts as a base. **Such substances which can act as acids a well as bases are called amphoteric substances.**

Example 4.4. Write the conjugate bars for the following Bronsted acids:

HCI, HNO_3, HSO_4^-, H_2SO_4 and H_2S.

Solution. The conjurate base is formed by low of a proton by the acid. Thus, the conjugate bases of the given acids are: Cl^-, NO_3^-, SO_4^{2-},-, HSO_4^- and HS^-respectively.

Example 4.5. Write the conjugate acids for the following Bronsted bases:

H_2O, NH_3, C_2H_5OH, OH^- and CH_3COO^-

Solution. The conjugate acid is formed by gain of a proton by the base. Thus, the conjugate acids of the given bases are:

H_3O^+, NH_4^+, $C_2H_5OH_2^+$, H_2O and CH COOH respectively.

4.9 IONIZATION OF ACIDS AND BASES

Strength of an acid in measured in terms of its tendency to lose proton whereas strength of a base is measured in terms of its tendency to accept proton. An acid is considered to be strong if it has great tendency to lose proton. The conjugate base of a strong acid in a weak base.

$$HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$$

Strong acid Weak base

On the other hand, conjugate base of a wenk acid is a strong bane.

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_30^+(aq) + CH_3COO^-(aq)$$

Weak acid Strong base

A base is considered to be strong if it has great tendency to accept a proton. Therefore, conjugate acid of strong base has little tendency to lose proton and hence is a weak acid.

$$CH_3COOH(aq) + OH^-(aq) \leftrightharpoons H_2O(l) + CH_3COO^-(aq)$$

Strong acid Weak base

On the other hand, conjugate seld of a weak base is a strong acid.

$$HCl(aq) + H_2O(l) \leftrightharpoons H_3O^+(aq) + Cl^-(aq)$$

Weak acid Strong base

The strength of acid or bases in experimentally measured by determining its ionization constants or dissention constants.

Ionization Constants of Acids in Water

Strong acids ionize almost completely into hydrogen ion and the corresponding anion in water and therefore, the molar concentration of hydrogen ions in the solution is same as that of acid itself But weale acids are not completely ionize and the relative strengths of weak acids can be compared in terms of their ionization constants. For example, the ionization equilibrium of an acid HA may be represented as:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

$$K = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

Since concentration of water is very large and remains almost contant is solution it can be combined with K to give another constant K_a.

$$K[H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Here K_a is called **ionization constant of acid.**

The value of ionization constant gives an idea about the relative strength of the acid. **Larger the value of K_a, higher is the concentration of H_3O^+, and stronger is the acid.** If dissociation constants of two acids are known, their relative strengths can be predicted. For example,

$$K_{CH3COOH} = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5} \text{ at } 298\text{ K}$$

$$K_{HF} = \frac{[H_3\,O^+][F]}{[HF]} = 6.7 \times 10^{-4} \text{ at } 298\text{ K}$$

Since $K_{HF} > K_{CH3COOH}$, therefore, HF is stronger acid than CH3COOH.

The value of dissociation constant of some of the monoprotic acids have been in that Table 4.2.

Table 4.2. The Ionization Constant of Some Common Weak Acids at 298 K

Acid	Ionization Constant, K_a
Chloroacetic acid, $ClCH_2COOH$	1.4×10^{-3}
Nitrous acid, HNO_2	4.6×10^{-4}
Hydrofluoric acid, HF	3.5×10^{-4}
Formic acid, HCOOH	1.8×10^{-4}
Benzoic acid, C_6H_6COOH	6.5×10^{-5}
Acetic acid, CH_3COOH	1.8×10^{-5}
Hypochlorous acid, HOCl	3.2×10^{-8}
Ammonium ion, NH_4^+	5.6×10^{-10}
Hydrocyanic acid, HCN	4.9×10^{-10}
Phenol, C_6H_6OH	1.3×10^{-10}
Water, H_2O	2.0×10^{-16}

Calculation of $[H_3O^+]$ and Degree of Dissociation

From the knowledge of K_a it is possible to calculate hydronium ion concentration and degree of ionization of a weak acid. As an example, let us take the case of acetic acid. The following equation represents the ionization of acetic acid in aqueous solution:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

$$K_a = \frac{[H_3\,O^+][CH_3COO^-]}{[CH_3COOH]}$$

Suppose C moles of CH_3COOH are dissolved per litre of solution and let a be the degree of ionization of CH_3COOH, then at equilibrium the concentration of various species would be as follows:

$$[CH_3COOH] = C(1 - a)$$
$$[H_3O^+] = Ca$$
$$[CH_3COO^-] = Ca$$

Therefore,

$$K_a = \frac{(Ca)(Ca)}{C(1-a)} = \frac{Ca^2}{(1-a)}$$

Since for weak acid a is very small as compared to 1, a in the denominator can be neglected. The expression of K_a then becomes

$$K_a = Ca^2$$

Knowing the value of K_a it is possible to calculate the degree of ionization of the acid at any particular concentration C.

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

From the degree of ionization, hydronium ion concentration can be calculated as:

$$[H_3O^+] = Ca$$

Dissociation Constants of Bases in Water

The **relative strengths of bases** are also compared in terms of their dissociation or ionization constants. The ionization constant K_b for a weak base B can be represented as follows:

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

$$K_a = \frac{[BH^+][OH^-]}{[B]}$$

Smaller the value of ionization constant for a base, weaker is the base.

If C is the molar concentration of base and a is its degree of dissociation, then by similar calculation (as in case of acids) we can drive the relations,

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

and $$[OH^-] = Ca$$

The value of ionization constants for some weak bases are given in Table 4.3.

Table 4.3. The ionization Constants of Some Bases at 298 K

Base	Ionization Constant, K_b
Ammonia, NH_3	1.8×10^{-5}
Methylamine, CH_3NH_2	1.4×10^{-4}
Dimethylamine, $(CH_3)_2NH$	5.4×10^{-4}
Trimethylamine, $(CH_3)_3N$	6.5×10^{-5}
Aniline, $C_6H_5NH_2$	4.3×10^{-10}
Pyridine, C_5H_5N	1.8×10^{-9}

Polyprotic Acids and Polyhydroxy Bases

The acids, such as HCl, CH3COOH, HCN, etc., which have only one ionizable hydrogen are known as **monoprotic acids.**

$$HCl(aq) \rightleftharpoons H^+(aq) + Cl^-(aq)$$

$$CH_3COOH(aq) \leftrightharpoons CH_3COO^-(aq) + H^+(aq)$$

On the other hand, there are many acids, such as phosphoric and (H_3PO_4), sulphric acid (H_2SO_4), oxalic acid ($H_2C_2O_4$), which have more than one ionizable hydrogen. Such acids are known as **polyprotic acids.** Thus:

The acids which have mote than one ionizable hydrogen atoms are known as polyprotic acids.

Polyprotic acids are also known as **polybasic acids.** A polybasic acid ionizes stepwise. The stepwise ionization of phosphoric acid, H_3PO_4 is shown below:

$$H_3PO_4(aq) \rightleftharpoons H^+(aq) + H_2PO_4^-(aq)$$

$$Ka_1 = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = 7.5 \times 10^{-3}$$

$$H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq)$$

$$Ka_2 = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} = 8.0 \times 10^{-8}$$

$$HPO_4^{2-}(aq) \rightleftharpoons H+(aq) + PO_4^{3-}(aq)$$

$$Ka_2 = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} = 4.8 \times 10^{-13}$$

Here, Ka_1, Ka_2 and Ka_3 are the first, second and third ionization constant of phosphoric acid respectively. It may be noted that Ka_1 is greater than Ka_2 which in turn is greater then Ka_3. The ionization constants for some common polyprotic acids are listed in Table 4.4.

Table 4.4. Ionization Constants of Some Common Polyprotic Acids at 298 K

Acid	Ka_1	Ka_2	Ka_3
Carbonic acid	4.3×10^{-7}	5.6×10^{-11}	
Oxalic acid	5.9×10^{-2}	6.4×10^{-5}	
Hydrogen sulphide	1.0×10^{-7}	1×10^{-19}	
Adipic acid	3.7×10^{-5}	3.9×10^{-6}	
Sulphurous acid	1.7×10^{-2}	6.4×10^{-8}	
Sulphuric acid	Strong acid (complete ionization)	1.2×10^{-2}	
Ascorbic acid	7.0×10^{-5}	3.0×10^{-12}	
Phosphoric acid	7.1×10^{-3}	8.0×10^{-8}	4.8×10^{-13}

Citric acid	7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}

Similarly, polyhydroxy or polyacidic bases ionize in steps and have the corresponding dissociation constants such as Kb_1, Kb_1, etc. For example, $Ba(OH)_2$ is a diacid base, $Fe(OH)_3$ is a triacid base. However, these polyhydroxy bases have very less solubility.

Example 4.6. The dissociation constant of an acid HA is 1.6×10^{-5}. Calculate H_3O^+ ion concentration in its 0.01 M solution.

Solution. The ionization of HA may be represented as

$$HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$$

If degree of ionization of HA is a under the given conditions, then equilibrium concentration of HA is given as

$$[HA] = C(1 - a) = 0.01\ (1 - a).$$

Since a is very small as compred with one. Hence $1 - a$ may be taken as 1.

$$\therefore \quad [HA] = 0.01 \text{ mol L}^{-1}$$

$$Ka = \frac{[A^-][H_3O^+]}{[HA]}$$

$$\text{Since} \quad [H3O+] = [A-]$$

$$\therefore \quad Ka = \frac{[H_3O^+]^2}{[HA]}$$

$$[H_3O^+]^2 = K_a[HA]$$

$$[H_3O^+] = \sqrt{K_a \times [HA]}$$

$$\sqrt{1.6 \times 10^{-5} \times 0.01} = \mathbf{4 \times 10^{-4} \text{ mol L}^{-1}}.$$

Common Ion Effect in the Ionization of Weak Acids and Bases

The degree of ionization of weak acid or a weak base is suppressed (reduced) by common ion effect.

An acid on ionization gives hydrogen ion and the corresponding anion. A strong acid is completely ionized while a weak acid is only partially ionized. In case of weak acids the ions formed are in equilibrium with the unionized molecules of the acid. The fraction of the total number of molecules of the acid dissolved that ionizes in known as degree of ionization of the acid.

The degree of ionization of the acid decreases if some strong electrolyte that can provide any of the product ions is added to the acid. For example, consider the ionization of acetic acid.

$$\begin{array}{rcll} CH_3COOH(aq) & \rightleftharpoons & CH_3COO^-(aq) & + H^+(aq) \\ CH_3COONa(aq) & \longrightarrow & CH_3COO^-(aq) & + Na^+(aq) \\ & & \text{Common ion} & \end{array}$$

If sodium acetate is added to the above solution, the concentration of acetate ions increases and the above equilibrium shifts in backward direction according to Le-Chatelier's principle. Thus, addition of acetate ions reduces the degree of ionization of acetic acid. Similarly, if H+ ions are provided from some source, such as dilute hydrochloric acid, the degree of ionization of the weak acid is suppressed.

Similarly, the degree of ionization of a weak base is suppressed by common ion effect. A bas on ionization gives hydroxyl ions (OH^-) and the corresponding cation (M^+). Addition of some strong electrolyte which provides either of the ions (OH^- or M^+) reduces the degree of ionization of the weak base in accordance with Le-Chatelier's principle. For example, the degree of ionization of ammonia is suppressed by addition of ammonium chloride or sodium hydroxide.

$$\begin{array}{rc|c|l} \cline{3-3} NH_3(aq) + H_2O(l) & \rightleftharpoons & NH_4^+(aq) & + OH^-(aq) \\ NH_4Cl(aq) & \longrightarrow & NH_4^+(aq) & + Cl^-(aq) \\ \cline{3-3} & & \multicolumn{1}{c}{\text{Common ions}} & \end{array}$$

$$\begin{array}{rcc|l|} \cline{4-4} NH_3(aq) + H_2O(l) & \rightleftharpoons & NH_4^+(aq) & + OH^-(aq) \\ NaOH(aq) & \longrightarrow & Na^+(aq) & + OH^-(aq) \\ \cline{4-4} & & & \multicolumn{1}{c}{\text{Common ion}} \end{array}$$

Example 4.7. Calculate the degree of ionization of 0.02 M acetic acid if its $K_a = 1.8 \times 10^{-5}$. What would be the degree of ionization if the solution also contains 0.01 M sodium acetate?

Solution. $CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$

The degree of ionization of this weak acid can be calculated by the approximate relation:

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

$$= \sqrt{\frac{1.8 \times 10^{-5}}{0.02}} = 0.03 = \mathbf{3 \times 10\text{-}2}$$

Now let us calculate the degree of ionization when the solution also contains 0.01 M sodium acetate. Sodium acetate being a strong electrolyte would be completely ionized in solution. Let x mom L^{-1} of acetic acid be ionized.

$$\begin{array}{cccc} CH_3COOH(aq) & \rightleftharpoons & CH_3COO^-(aq) & + H^+(aq) \\ (0.02 - x)M & & x\,M & x\,M \\ CH_3COONa(aq) & \longrightarrow & CH_3COO^-(aq) & + Na^+(aq) \\ & & 0.01\ M & 0.01\ M \end{array}$$

$[H+] = x$ mol L-1

$[CH_3COO^-] = (x + 0.01)$ mol L^{-1} = 0.01 mol L^{-1}

[∴ x is very small as compared to 0.01]

$[CH_3COOH] = (0.02 - x)$ mol L^{-1} = 0.02 mol L^{-1}

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

$$1.8 \times 10^{-5} = \frac{(x)(0.02)}{(0.01)}$$

$$x = 9 \times 10^{-6}$$

Degree of ionization, $a = \frac{x}{0.02} = \frac{9 \times 10^{-6}}{0.02} = 4.5 \times 10^{-4}$

Thus, it may noted that the degree of ionization of acetic acid has decreased from 3×10^{-2} to 4.5×10^{-4} due to the presence of sodium acetate.

4.10 SELF-IONIZATION OF WATER

The conductivity measurements of water indicate that water is a weak electrolyte. Even in pure state water is weakly ionized to give $H^+(aq)$ and $OH^-(aq)$ ions as shown under:

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

The ionization constant of water may be written as

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

Since concentration of water is very high (= 55.5 mol L-1) and only a very very small fraction of it undergoes ionization, therefore, (H_2O) may be taken as constant and may be combine with $Ka_{(H_2O)}$ to have constant K_w.

$$Ka_{(H_2O)}[H_2O] = [H^+][OH^-]$$

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

The constant K_w is called **ionic product of water.** The concentration of H^+ in pure water is found out experimentally to be 1.0×10^{-7} mol L^{-1} at

298 K. Moreover, in pure water concentration of H^+ is equal to the concentration of OH^- ions because dissociation of water produces equal number of H+ ions. Therefore,

$$[H+] = [OH-] = 1 \times 10-7 \text{ mol } L^{-1}$$

$$K_w = [H_3O^+][OH^-]$$

Or $$K_w = (1 \times 10^{-7} \text{ mol } L^{-1})(1 \times 10^{-7} \text{ mol } ^{L-1})$$

$$= 1 \times 10^{-14} \text{ mol}^2 \text{ L}^{-2}$$

The degree of dissociation of water = $\frac{10^{-7}\ \text{mol L}^{-}}{55.55\ \text{mol L}^{-}}$ = 1.8 × 10-9

Since with increase in temperature dissociation of water increases, therefore, value of K_w increases as the temperature is increased. However, at all temperatures $(H_3O^+]$ remains equal to $[OH^-]$ in pure water. The values of K_w at different temperatures have been given in Table 4.5.

Temperature (K)	Ionic Product (K_w)
273	0.113×10^{-14}
283	0.292×10^{-14}
293	0.687×10^{-14}
298	1.008×10^{-14}
313	2.917×10^{-14}
323	5.474×10^{-14}
373	$(56) \times 10^{-14}$

IONIZATION CONSTANT OF WATER

Water can behave as a weak acid as it ionizes according to the equation:

$$H_2O(l) \leftrightharpoons H^+(aq) + OH^+(aq)$$

The ionization constant of water may be written as

$$K_{a(H_2O)} = \frac{[H^+][OH^-]}{[H_2O]}$$

As already discussed $[H^+]$ and $[OH^-]$ is 10^{-7} M at 298 K and $[H_2O]$ = 55.55M, therefore,

$$K_{a(H_2O)} = \frac{(10^{-7})(10^{-7})}{55.55} = \mathbf{1.8 \times 10^{-16}}$$

It may be noted that ionization constant of water, $K_{a(H_2O)}$ is different from ionic product of water, K_w .

$$K_w = K_{a(H_2O)} \times 55.55$$

Concentration of H3O+ and OH- Ions in Aqueous Solutions of Acids and Bases

We have already see that [H2O+] is equal to [OH+-] in pure water. But, on addition of some acid or base to water these concentration no longer remain equal. However, the value of ionic product of water *(K_w)* at a particular temperature always remains constant irrespective of the fact whether water is pure or some acid or base has been added to it. For example, if an acid (sat HCI) is added to water, the concentration of hydronium ion becomes quite high. Consequently, the dissociation equilibrium of water shifts in the revers direction (according to the Le-Chatelier's principle), i.e., H_3O^+ ions would combine with OH^- ions to form undissociated water molecule, so that the value of K_w in the solution may remain the same as that in pure water. Thus, Addition of an acid in water decreases the $[OH^-]$ the according to the relation,

$$[OH^-] = \frac{K_w}{[H_3O^+]}$$

Similarly, the addition of a base such as NaOH increases the [OH-] and decreases the $[H_3O^+]$ according to the relation,

$$[H_3O^-] = \frac{K_w}{[OH^-]}$$

From the above discussion, it is clear that H3O+ ions and OH- ions are always present in the aqueous solution whether it is acidic or basic. However, the relative concentration of these ions vary in different solution. In general,

in neutral solutions $[H_3O^+] = [OH^-]$

in acidic solutions $[H_3O^+] > [OH^-]$

in basic solutions $[H_3O^+] = [OH^-]$

RELATION BETWEEN IONIZATION CONSTANT OF A BASE AND IONIZATION CONSTANT OF ITS CONJUGATE ACID

Ionization of a base B may be expressed as:

$$B + H_2O \longrightarrow BH^+ + OH^-$$

$$K_b = \frac{[BH^+][OH^-]}{[B]} \qquad \ldots(i)$$

Ionization of BH+, the conjugate acid of B may be expressed as:

$$BH^+ + H_2O \longrightarrow B + H_3O^-$$

$$K_b = \frac{[B][H_3O^+]}{[BH^+]} \qquad \ldots(ii)$$

Multiplying equation (i) by (ii), we get

$$K_b \times K_a = \frac{[BH^+][OH^-]}{[B]} \times \frac{[B][H_3O^+]}{[BH^+]}$$

$$K_b \times K_a = [OH^-]\ [H_3O^+]$$

$$K_b \times K_a = K_w$$

Example 4.8. Calculate the concentration of H_3O^+ ions and OH^- ions in *(a)* 0.01 M solution HCl ***(b)*** 0.01 M solution of NaOH at 298 K, assuming that HCl and NaOH are completely ionized under the given conditions.

Solution. (a) $HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$

Since HCl is completely ionized

∴ $[H_3O^+] = [HCl] =$ **0.01 M** or $\mathbf{1 \times 10^{-2}\ mol\ L^{-1}}$

$$[OH\text{-}] = \frac{K_w}{[H_3O^+]}$$

$$= \frac{1 \times 10^{-14}}{1 \times 10^{-2}} = \mathbf{1 \times 10^{-12}\ mol\ L^{-1}}$$

(b) $NaOH(aq) \longrightarrow Na^+(aq) + OH^-(aq)$

Since NaOH is completely ionized

$[OH\text{-}] = [NaOH] =$ **0.01 M** or $\mathbf{1 \times 10\text{-}_2\ mol\ L^{-1}}$

$$[OH\text{-}] = \frac{K_w}{[OH^-]} = \frac{1 \times 10^{-14}}{1 \times 10^{-2}}$$

$$= \mathbf{1 \times 10^{-12}\ mol\ L^{-1}}$$

4.11 EXPRESSING HYDRONIUM ION CONCENTRATION-pH SCALE

We have seen that concept of ionic product of water enables us to classify solutions as acidic, basic, or neutral by specifying the H_3O^+ ion concentration. For expressing the H_2O^+ ion concentration a logarithmic scale was devised by P.L. Sorensen (1909). This scale is called **pH* scale. The pH of a solution may be defined as negative logarithm of hydronium ion concentration in moles per litre.**

*The symbol pH is derived from Potenz, the Danish word for power, pH refers to potency of hydronium ion in solution. The potency of hydroxyl ions of solution may also expressed in terms of pOH.

Mathematically, it may be expressed as

$$pH = -\log [H_3O^+] = \log \frac{1}{[H_3O^+]}$$

From the above relation, the concentration of $[H_3O^+]$ can be written as

$$[H_3O^+] = 1 \times 10^{-pH}$$

This enables us to give alternative definition of pH as the negative power to which 10 must be raised in order to express the hydronium ion concentration of the solution.

For pure water or neutral solutions, at 298 K, $[H_3O^+]$ is equal to 1×10^{-7} mol L^{-1}. Therefore, pH of such solution is given as:

$$pH = -\log [H_3O^+] = -\log [1 \times 10^{-7}] = 7.$$

For acidic solutions, $[H_3O^+]$ concentration is more than 1×10^{-7} mol L^{-1}. Therefore, pH of acidic solution is less than 7. For basic solutions, the pH value is greater than 7. Correspondingly, range of pH is from 0 to 14. The solutions having pH between 0 and 2 are strongly acidic, those with pH between 2 to 4 are moderately acidic while others having pH between 4 to 7 are weakly acidic Similarly, the solutions having pH value between 7 to 10 are weakly basic, those having pH 10 to 12 are moderately basic whereas others which have pH range between 12 to 14 are strongly basic.

The complete range of 1,0 l and pH has been illustrated in Fig. 4.1.

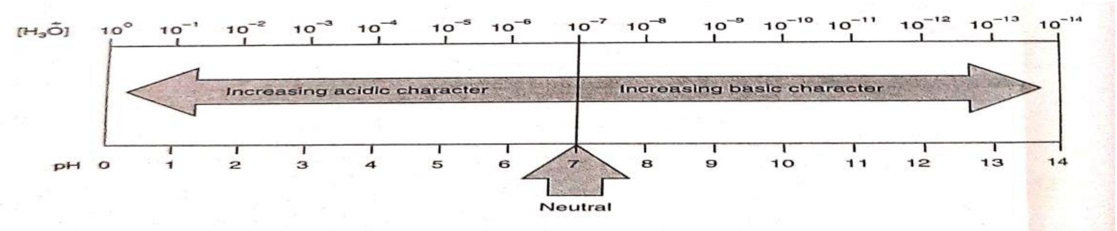


Fig. 4.1. Range of pH and $[H_3O^+]$

The approximate pH of a solution can be determined with the help of **pH papers.** pH papers have different colours in solutions of different pH. A pH paper can determine pH of a solution with an accuracy of about 0.5. However, for accurate measurement of pH (upto accuracy of 0.001 units) pH metres are used.

Example 4.9. Calculate the pH value of

(a) 0.01 M HC1 (b) 0.001 M NaOH (c) 0,001 M $Ba(OH)_2$,
Assuming that HCI, NaOH and $Ba(OH)_2$ are completely ionized.

Solution. (*a*) $HCI(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$

Since HCI in completely lionized,

$$[H_3O^+] = [HCI] = 0.01\ M = 1 \times 10^{-2} \text{ mol } L^{-1}$$

Now $pH = -\log[H_3O^+]$

$pH = -\log[1 \times 10^{-2}]$

$= -(-2)\log 10 = 2.$

(b) $NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$

Because NaOH is completely ionized.

∴ $[OH^-] = [NaOH]$

Or $[OH^-] = 0.001\ M = 1 \times 10^{-3}\ mol\ L^{-1}$

Hence $[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1 \times 10^{-14}}{1 \times 10^{-3}}$

$= 1 \times 10^{-11}\ mol\ L^{-1}$

∴ $pH = -\log[H_3O^+] = -\log 1 \times 10^{-11} =$ **11.**

(c) $Ba(OH)_2(aq) \rightarrow Ba^{2+}(aq) + 2OH^-(aq)$

Since $Ba(OH)_2$ is completely ionized and one mole of $Ba(OH)_2$ furnishes 2 moles of $OH^-(aq)$ ions,

∴ $[OH^-] = 2[Ba(OH)_2] = 2 \times 0.001\ M$

$= 2 \times 10^{-3}\ mol\ L^{-1}$

$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1 \times 10^{-14}}{2 \times 10^{-3}} = 5 \times 10^{-12}\ mol\ L^{-1}$

∴ $pH = -\log(5 \times 10^{-12})$

$= -(\overline{12}.699) = -(-11.301) =$ **11.301.**

Example 4.10. Calculate the $[H_3O^+]$ of a solution having a pH of 10.6

Solution. $pH = -\log[H_3O^+]$

Or $\log[H_3O^+] = -pH = -10.6$

Since mastissas are always positive in logarithmic tables, therefore, add – 1 to the characteristics and + 1 to the mantissa to that mantissa becomes positive.

∴ $\log[H_3O^+] = (-10 - 1) + (-0.6 + 1)$

$= (-11) + (+0.4) = \overline{11}.4$

∴ $[H_3O^+] = \text{Antilog}\ \overline{11}.4 =$ **2.5×10^{-11} mol L^{-1}**

4.12 HYDROLYSIS OF SALTS

Hydrolysis may be defined as the process in which water reacts with salt to form an acid and a base.

$$\text{Salt} + \text{Water} \rightleftharpoons \text{Acid} + \text{Base}$$

$$K = \frac{[\text{Acid}][\text{Base}]}{[\text{Salt}][\text{Water}]}$$

$$K[\text{Water}] = \frac{[\text{Acid}][\text{Base}]}{[\text{Salt}]}$$

Since [Water] remains practically constant during hydrolysis we can write

$$K_h = \frac{[\text{Acid}][\text{Base}]}{[\text{Salt}]}$$

where K_h is the hydrolysis constant of the salt.

The fraction of the total salt that is hydrolysed at equilibrium is called degree or extent of hydrolysis. It is denoted by '*h*'.

1. Hydrolysis of Salt of a Weak Acid and a Strong Base

This type of salts includes salts of sodium and potassium except halides, nitrates and sulphates. For example, sodium carbonate, potassium cyanide, sodium acetate, etc. This type of salts produce **alkaline solutions** on hydrolysis. Let us discuss the hydrolysis of a salt MX of this type.

$$MX + H_2O \rightleftharpoons \underset{\text{Strong base}}{MOH} + \underset{\text{Weak acid}}{HX}$$

In solution MX and the strong base MOH undergo complete dissociation whereas acid HX being weak acid remains almost undissociated. Therefore, we can write,

$$M^+ + X^- + H_2O \rightleftharpoons M^+ + OH^- + HX$$

Or $$X^- + H_2O \rightleftharpoons OH^- + HX$$

Applying laws of mass action,

$$K_h = \frac{[OH^-][HX]}{[X^-]}$$

For the dissociation of weak acid, we can write

$$HX + H_2O \rightleftharpoons H_3O^+ + X^-$$

$$K_a = \frac{[H_3O^+][X^-]}{[HX]}$$

Multiplying with K_h

$$K_a \times K_h = \frac{[H_3O^+][X^-]}{[HX]} . \frac{[H_3O^+][HX]}{[X^-]}$$

$$= [H_3O^+][OH^-]$$

$$= K_w$$

$$\therefore \quad \boxed{K_h = \frac{K_w}{K_a}}$$

Degree of Hydrolysis. $X- + H_2O \rightleftharpoons OH^- + HX$

Suppose initial conc. of salt if C and h is the degree of hydrolysis, then

$$[X^-] = C(1 - h),\ [OH^-] = Ch,\ [HX] = Ch$$

$$K_h = \frac{[OH^-][HX]}{[X^-]} = \frac{(Ch)(Ch)}{C(1-h)}$$

$$= Ch^2 \qquad (\therefore 1 - h = 1)$$

$$h = \frac{K_h}{C}$$

Thus, degree of hydrolysis of salt of this type is inversely proportional to the Square root of conc. of the salt. Substituting the value of K_h from equation (4.6) in equation (4.7)

$$\boxed{h = \sqrt{\frac{K_w}{K_a \times C}}}$$

Hydronium ion conc. and pH

$$[HO^-] = Ch = C\sqrt{\frac{K_w}{K_a \times C}} = \sqrt{\frac{K_w \times C}{K_a}}$$

$$[H_3O^+] = \frac{K_w}{OH^-} = \frac{K_w}{\sqrt{\frac{K_w \times C}{K_a}}} = K_w\sqrt{\frac{K_a}{K_w \times C}} = \sqrt{\frac{K_w \times K_a}{C}}$$

$$pH = \frac{1}{2}(-\log K_w - \log K_a + \log C)$$

$$\boxed{\mathbf{pH = \frac{1}{2}(pK_w + pK_a + \log C)}}$$

2. Hydrolysis of Salt of a strong Acid and a Weak Base

This type of salts includes halides, nitrates and sulphates of all metals except that of sodium and potassium. For example zinc nitrate, copper sulphate, aluminium sulphate, ferric chloride etc. This type of salts produce **acidic solutions** on hydrolysis. Let us discuss the hydrolysis of a salt MX of this type

$$MX + H2O \rightleftharpoons \underset{\text{Weak base}}{MOH} + \underset{\text{Strong base}}{HX}$$

In solution MX and the strong acid HX undergo complete dissociation whereas the weak base MOH remains almost undissociated. Therefore, we can write,

$$M^+ + X^- + 2H_2O \rightleftharpoons MOH + H_3O^+ + X^-$$

Or $$M^+ + 2H_2O \rightleftharpoons MOH + H_3O^+$$

Applying law of mass action

$$K_h = \frac{[MOH]\,[H_3O^+]}{[M^+]}$$

For the dissociation of weak base we can write

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

$$K_b = \frac{[M^+][OH^-]}{[MOH]}$$

Multiplying with Kh

$$K_b \times K_h = \frac{[M^+][OH^-]}{[MOH]} . \frac{[MOH]\,[H_3O^+]}{[M^+]}$$

$$= [H_3O^+][OH^-] = K_w$$

or $$\boxed{K_h = \frac{K_w}{K_b}} \qquad \text{...(4.8)}$$

Degree of Hydrolysis. $M^+ + 2H_2O \rightleftharpoons MOH + H_3O^+$

Suppose initial conc. of salt is C and h is the degree of hydrolysis. Then at equilibrium

$$[M^+] = C(1 - h),\ [H_3O^+] = Ch,\ [MOH] = Ch$$

$$K_h = \frac{[MOH]\,[H_3O^+]}{[M^+]} = \frac{(Ch)(Ch)}{C(1-h)} = Ch^2 \qquad (\because 1\text{-}h = 1)$$

$$h = \sqrt{\frac{K_h}{C}}$$

Thus, degree of hydrolysis of salts of this type increases with dilution (or decrease in conc.). Substituting the value of K_h from equation (4.8) in equation (4.9)

$$\boxed{h = \sqrt{\frac{K_w}{K_b \times C}}}$$

Hydronium ion conc. and pH.

$$[H_3O^+] = Ch = C\sqrt{\frac{K_w}{K_b \times C}}$$

$$= \sqrt{\frac{K_w}{K_b \times C}}$$

$$-\log\ [H_3O^+] = \frac{1}{2}\ [-\log K_w - \log C + \log K_b]$$

$$\boxed{\mathbf{pH = \frac{1}{2}\ [pK_w - \log C - pK_b]}}$$

3. Hydrolysis of Salt of a Weak Acid and a Weak Base

This type of salts includes all salts except halides, nitrates and sulphates of all metals except sodium and potassium. For example, zinc acetate, aluminum phosphate, calcium carbonate, ammonium phosphate, etc. This type of salts produce weak acids and weak bases on hydrolysis. Therefore, aqueous solutions of such salts are **almost neutral** and have pH nearly equal to 7. Let us discuss the hydrolysis of a salt MX of this type

$$MX \quad + \quad H_2O \quad \rightleftharpoons \quad \underset{\text{Weak base}}{MOH} \quad + \quad \underset{\text{Weak acid}}{HX}$$

Or $$M^+ + X^- + H_2O \quad \rightleftharpoons \quad MOH \quad + \quad HX$$

Applying law of mass action

$$K_h = \frac{[MOH]\ [HX]}{[M^+]\ [X^-]}$$

Dissociation of weak base, MOH and weak acid, HX may be expressed as:

$$MOH \quad \rightleftharpoons \quad M^+ + OH^-; \qquad K_b = \frac{[M^+][OH^-]}{[MOH]}$$

$$MX + H_2O \quad \rightleftharpoons \quad H_2O+ + A-; \qquad K_a = \frac{[H_3O^+][X^-]}{[HX]}$$

From equations (4.10), (4.11) and (4.12)

$$K_h \times K_a \times K_b \times = \frac{[MOH]\ [HX]}{[M^+]\ [X^-]} . \frac{[H_3O^+][X^-]}{[HX]} . \frac{[M^+][OH^-]}{[MOH]}$$

$$= [H_3O^+][OH^-] = K_w$$

Or $$K_h = \frac{K_w}{K_a \times K_b} \qquad \ldots(4.13)$$

Degree of Hydrolysis. $M^+ + X^- + H_2O \quad \rightleftharpoons \quad MOH + HX$

Suppose initial conc. of MX is C and h is the degree of hydrolysis. Then at equilibrium

$$[M^+] = C(1-h); \qquad [X^-] = C(1-h)$$

$$[MOH] = Ch; \qquad [HX] = Ch$$

$$K_h = \frac{[MOH]\,[HX]}{[M^+]\,[X^-]} = \frac{(Ch)(Ch)}{C(1-h)C(1-h)}$$

$$= \frac{h^2}{(1-h^2)} = h^2 \qquad (\therefore 1-h=1)$$

$$h = \sqrt{K_h} \qquad \ldots (1.14)$$

Thus, in case of salts of weak acids and weak bases, the degree of hydrolysis does not depend upon the concentration of the salt.

From equation (4.13) and (4.14)

$$h = \sqrt{\frac{K_w}{K_a \times K_b}}$$

Hydronium ion conc. and pH

$$HX + H_2O \rightleftharpoons H_3O^+ + X^-$$

$$K_a = \frac{[H_3O^+][X^-]}{[HX]} = \frac{[H_3O^+]\,C(1-h)}{(Ch)}$$

$$= [H_3O^+]\frac{(1-h)}{h} = \frac{[H_3O^+]}{h} \qquad (\therefore 1-h=1)$$

$$= [H_3O^+] = K_a \times h$$

$$K_a = \sqrt{\frac{K_w}{K_a \times K_b}} = \sqrt{\frac{K_w}{K_a \times K_b}}$$

$$pH = -\log[H_3O^+] = -\log\sqrt{\frac{K_w}{K_a \times K_b}}$$

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

$$\boxed{\mathbf{pH = \frac{1}{2}[pK_w + pK_a - pK_b]}}$$

in case $K_a = K_b$

$$pH = \frac{1}{2}(pK_w) = 7$$

In case $K_a > K_b$ the solution would be slightly acidic and the pH would be less than 7. On the other hand if $K_a < K_b$, the solution would be slightly alkaline and the pH would be greater than 7.

4. Salt of a Strong Acid and n Strong Base

This type of salts includes halides, nitrates and sulphates of sodium and potassium. For example, NaCI, KCI, KNO_3, Na_2SO_4, etc. **Salts of this type are not hydrolyzed** and hence their aqueous solutions are **neutral.**

$$MX + H_2O \rightleftharpoons \underset{\text{Strong base}}{MOH} + \underset{\text{Strong acid}}{HX}$$

MX, MOH and HX are completely dissociated

$$\therefore \quad M^+ + X^- + H_2O \rightleftharpoons M^+ + OH^- + H^+ + X^-$$

Or $$H_2O \rightleftharpoons H^+ + OH^-$$

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

4.13. ACID-BASE INDICATORS

Acid-base indicators are substances which change colour according to hydrogen ion concentration (or pH) of the solution to which they are added. They are usually weak acids or weak beses. A typical indicator is a weak organic acid that has different colour than its conjugate base. Let us consider an indicator which is a weak acid (HIn). The equilibrium between indicator and its conjugate base (In^-) may be represented as:

$$\underset{\substack{\text{Acid} \\ \text{(Colour A)}}}{HIn(aq)} + H_2O(l) \rightleftharpoons H_3O^+(aq) + \underset{\substack{\text{Conjugate band} \\ \text{(Colour B)}}}{In^-(aq)}$$

At low pH, the concentration of H_20^+ is high so the equilibrium is pushed to the left and the equilibrium solution has colour A. At high pH values the concentration of H_3O^+ is low and the equilibrium is pushed to the right and the equilibrium solution has colour B.

We can write equilibrium constant expressions for indicator equilibria. For a weak acid indicator at equilibrium we can write

$$K_{In} = \frac{[H_3O^+][In^-]}{[HIn]}$$

K_{In} is known as **indicator constant.** The colour of the indicator changes from colour A to colour B at a particular point, known as end point of the indicator. At this point

$$[HIn = [In^-]$$

$$K_{In} = [H_3O^+]$$

$$- \text{Log } K_{In} = - \log [H_3O^+]$$

$$pK_{In} = pH$$

The pH of the solution at the end point is equal pK_{In}. When pH of the solution is equal to pK_{In} half the indicator is in the acid form and half in the form of its conjugale base.

The Range of an Indicator

The range of an indicator is the pH range over which it changes colour.

At low pH, a weak acid indicator is mainly present as HIn (in acid form) and the colour of this form predominaten. As the pH increases, the intensity of colour A starts decreasing while that of B starts increasing. The observable change from colour A to colour B takes place over a range of pH and this range of pH is known as the range of in indicator. An indicator is most effective if it undergoes a distinct change in colour over a narrow range of pH. For most of the indicators the range is within ± 1 of the pK_{In} value. Since indicators have quite different values of pK_{In}, the pH ranges of various indicators also vary widely as given in Table 4.6.

Table 4.6. Indicators and their pH Ranges

Indicator	*Colours*		*pK_{In}*	*pH Range*
	Acid	*Base*		
Thymol blue (first change)	Red	Yellow	1.5	12 – 2.8
Methyl orange	Red	Yellow	3.7	3.2 – 4.4
Bromocresol green	Yellow	Blue	4.7	3.8 – 5.4
Methyl red	Yellow	Red	5.1	4.8 – 6.0
Bromothymol blue	Yellow	Blue	7.0	6.0 – 7.6
Phenol red	Yellow	Red	7.9	6.3 – 8.4
Thymol blue (second change)	Yellow	Blue	8.9	8.0 – 9.6
phenolphthalein	colourless	pink	9.4	8.2 – 10.0

It may be noted that end point of each indicator is in the centre of the pH range

Litmus contains several substances and changes colour over a broader range from about pH 5 to pH 8.

A universal indicator is a mixture of indicators which gives a gradual change from one colour to the other over a wide range of pH. The approximate pH of the solution can be determined from the colour obtained when a few drops of universal indictor are added to the solution.

4.14 ACID-BASE TITRATIONS

During titration we determine the volume of one solution which just reacts with a fixed volume of the other solution.

An acid-base titration is a procedure used in quantitative chemical analysis to determine the concentration of either an acid or a base. Generally, an acid solution of known concentration is taken in a burette and is added to an alkaline solution of unknown concentration taken in a conical flask. The solution that is titrated (the solution with fixed volume) is known as **titrate** while the solution with which titration a performed is called **titrant.** The titrate is taken in a conical flask while the titrant is taken in a burette.

The **end point** or the **equivalence point** reaches when the stoichiometric amount of acid has been added to the alkali solution. At this point all the alkali has been neutralized and the solution contains salt and water only.

From the end paint we can find the volume of the base (V_b) having molarity M_b required to neutralize a certain volume of the acid (V_a) of molarity M_a. Now, number moles in V mL of a solution of molarity M is given by $M \times V/1000$. For the titrations involving monobasic acid and monoancid base, one mole of base is required to completely neutralize one mole of the acid.

Therefore, $\frac{M_aV_a}{1000} = \frac{M_bV_b}{1000}$ or $\mathbf{M_aV_a = M_bV_b}$

For titration involving polyacid bases and polyacid acids the above question takes the form

$$n_aM_aV_a = n_bM_bV_b$$

where n_a is the basicity of the acid while n_b is the acidity of the base.

Thus, for the titration of sulpheric acid with sodium hydroxide, the equation applicable is

$$\mathbf{2M_aV_a = M_bV_b}$$

Similarly, for the titration of barium hydroxide (a diacid base) against hydrochloric acid (a monobasic acid) the equation becomes

$$\mathbf{M_aV_a = 2M_bV_b}$$

The end point is indicated by colour chance of the indicator or a sudden rise or fall in pH. The pH of the reaction mixture changes during the course of titration.

A graph of the pH versus the volume (V) of titrating solution is known as titration curve.

With the help of titration curves we can choose proper indicator for a particular titration.

Let us assume that a titration is carried out by adding alkali solution to an acid solution. If the variation of pH is plotted against the volume of alkali solution added four different types of titration curves are obtained depending upon whether the acid and base are strong or weak (Fig. 4,3).

It may be noted that at the equivalence point there is a sharp increase in pH except in case of titration of a weak base with a weak acid. A proper acid-base indicator is the one whose pH range falls on the vertical portion of the titration curve. Such as indicator gives a sharp colour change at the end point.

1. Titration of Strong Acid against Strong Alkali

The graph (A) is Fig. 4.3 shows how pH changes during the titration of 50 cm^2 of 0.1 M HCl with 0.1 M NaOH.

$$NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l)$$

The pH of the 0.1 M solution of HCl in the beginning would be 1. As the alkali is added, the pH changes slowly in the beginning. However, at the equivalence point pH changes rapidly from about 3.5 to 10. It can be shown by simple circulation that pH of the solution is 3.7 when 49.8 cm^3 of the NaOH solution. Thus, any indicator having pH range between 3.5 and 10 will identify the equivalence point. This means that any one of **phenolphthalein, methyl orange or bromothymol blue** could be used as indicator.

II. Titration of Strong Acid against Weak Alkali

The graph (B) in Fig. 4.3 shows how pH changes during titration of 50cm^3 of 0.1 M HCl with 0.1 M NH_3.

$$HCl(aq) + NH_4OH(aq) \longrightarrow NH_4Cl(aq) + H_2O(l)$$

In this case of pH changes rapidly from 3.5 to 7.0 at the equivalence point. **Methyl orange, methyl red and bromocresol green** are suitable indicators for this type of titration. Phenolphthalein is suitable because its pH range lies outside the vertical portion of the curve.

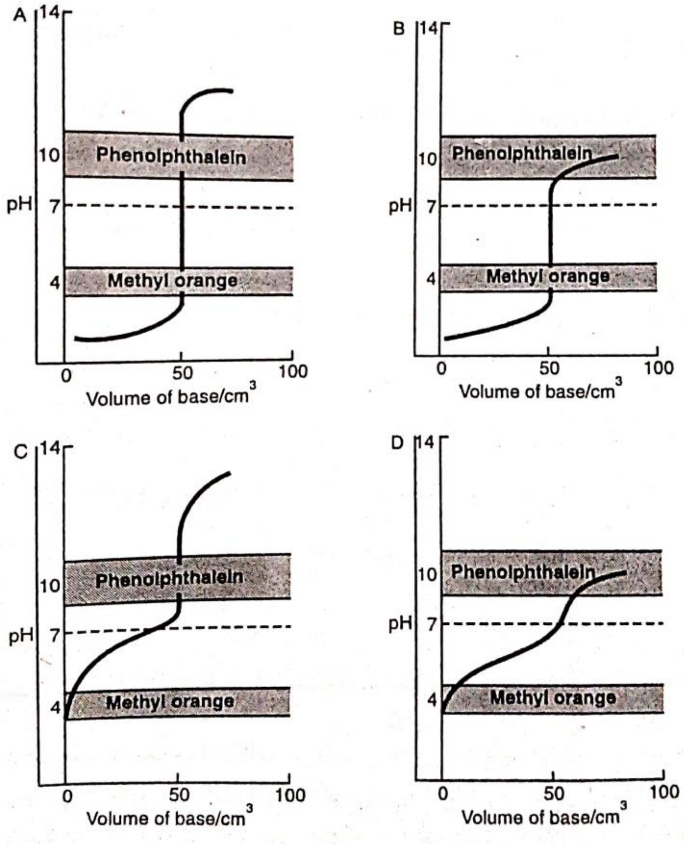


Fig. 4.3.

III. Titration of Weak Acid against Strong Base

The graph (C) in Fig. 4.3. shows how pH changes during titration of 50cm^3 of 0.1 M CH_3COOH with 0.1 M NaOH.

$$CH_3COOH(aq) + NaOH(aq) \longrightarrow CH_3COON(aq) + H_2O(l)$$

The vertical portion of this titration curve lies between pH 7 and pH 10.6. **Phenolphthalein** is suitable indicator for this titration. Methyl orange is not suitable for this titration because its pH range lies on the flat portion of the curve.

IV. Titration of Weak Acid against Weak Base

The graph (D) in Fig. 4.3. represents the titration curve obtained for titration of 50cm^3 of 0.1 M CH_3-COOH with 0.1 M NH_3.

$$CH_3COOH(aq) + NH_4OH(aq) \longrightarrow CH_3COONH_4(aq) + H_2O(l)$$

For this type of titration there is no sharp increase in pH at the equivalence point. No indicator is suitable for this type of titration.

Example 4.11. Suggest suitable indicators for the following acid base titration:

(i) HCl against KOH.

(ii) HBr against aqueous ammonia (NH_4OH).

(iii) HCOOH against KOH.

Solution. (i)HCl is a strong acid and KOH is a strong base. For much titration phenolphthalein, or methyl orange can be used as indicator.

(ii) HBr is a strong acid and NH_4OH is a weak base. For the titration of strong, acid against weak base methyl orange, methyl red, or bromocresol green can be used is indicator.

(iii) HCOOH is a weak acid whereas KOH is a strong base. For such a titration phenolphthalein is suitable indicator.

Example 4.12. Calculate the pH of a solution in which 25.0 ml of 0.10 M NaCH is added to 35.0 ml of 0.10 M HCl.

Solution. Moles of $H_30 = \frac{35.0 \times 0.10}{1000} \times 3.5 \times 10^{-3}$ mol

Moles of OH- $= \frac{25.0 \times 0.10}{1000} \times 2.5 \times 10^{-3}$ mol

All of the OH reacts leaving an excess of H_3O^+ ions

Excess H_3O^+ ion $= (3.5 \times 10^{-3} - 2.5 \times 10^{-3})$ mol $= 1.0 \times 10^{-3}$ mol

$$[H_3O^+] = \frac{1.0 \times 10^{-3}\text{mol}}{60 \times 10^{-3}} = 1.67 \times 10^{-2} \text{ mol L}^{-1}$$

$$\text{pH} = -\log [H_3O^+] = -\log (1.67 \times 10^{-2})$$

$$= \mathbf{1.75.}$$

4.15 BUFFERS SOLUTIONS

Generally, pH of the solution changes on addition of small amounts of acids or buses to it. But if the solution contains a weak acid and its conjugate base, or a weak base and its conjugate acids, such a solution can resist change in pH and is called a buffer solution.

A buffer solution is the solution which can resist the change in pH on addition of small amount of acid or base. The ability of buffer solution to resist change in pH on addition of acid or base is called buffer action.

Depending upon pH values, buffer solutions are divided into two classes. If the pH of the buffer solution in less than 7, it is called **acidic buffer** and if it is more the 7, it is called **basic buffer.**

1. Strong Acid Buffers

A strong acid such a nitric acid or hydrochloric acid can act as a buffer with a low pH Strong acids are completely ionized in aqueous solution and there the concentration of hydrogen ions is high. The addition of a small amount of acid or base to the acid will have negligible effect on the pH of the solution.

For example, if 10 cm^3 of 0.1 M hydrochloric acid is added to 100 cm^3 of 0.01 M nitric acid, the pH of the solution changes from 2.00 to 1.96, which is a negligible chance. On the other hand if cm^3 of 0.1 M hydrochloric acid is added to 100 cm^3 of pure water pH changes from 7.00 to 4.00. Thus, pure water does not act as a buffer.

2. Strong Base Buffers

A strong base such as NaOH, KOH etc. can act us buffer with a high pH. The addition of small amount of acid or base has negligible effect on pH of solution of such based. For example, when 1 cm^3 of 0.1 M HCl is added to 100 cm^3 of 0.01 M NaOH solution, the pH changes from 12.00 to 11.96, which is negligible change.

3. Weal Acid Buffers

Buffer solutions with pH range 4 to 7 can be prepared from weak acids and their salts with strong bases. For example, acetic acid and sodium acetate are commonly used for this purpose.

Now let us understand how an acidic buffer such as solution of acetic acid (weakly dissociated) and sodium acetate (largely dissociated) resists the change in pH. This solution contains a large amount of sodium and acetate ions and a large amount of undissociated acetic acid molecules along with a small amount of hydronium ions.

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

$$CH_3COONa(aq) \longrightarrow CH_3COO^-(aq) + Na^+(aq)$$

Suppose, a few drops of HCl*(aq)* are added to this buffer solution. This would provide H_3O^+ ions. These H_3O^+ ions would combine with CH_3COO^- ions to form weekly ionized acetic acid molecules as shown below:

$$\underset{\text{From buffer}}{CH_3COO^-(aq)} + \underset{\text{From HCl}}{H_3O^+\underline{(aq)}} \rightleftharpoons CH_3COOH(aq) + H_2O(l)$$

Since the additional H_3O^+ ions are neutralized by CH_3COO^- ions in the solution, there will be no change in its pH value. On the other hand, if a few drops of NaOH are added to the buffer solution, it would provide OH^- ions. These OH^- ions will combine with H_3O^+ ions present in the buffer solution to form unionized water molecules. This would result in the greater ionization of acetic acid in order to restore the concentration of H_3O^+ ions to its original value.

$$H_3O^+(aq) + OH^-(aq) \rightleftharpoons 2H_2O(l)$$

From buffer From NaOH

Therefore, pH of the solution remains unchanged.

4. Weak Base Buffers

Buffer solutions with pH values between 7 and 10 can be prepared from weak bases and their salts with strong acids. For example, a solution containing NH_4OH and NH_4Cl acts as a buffer.

Now let us understand how a solution containing ammonium hydroxide and ammonium chloride acts as a buffer and resists change in pH.

In case of a basic buffer solution containing equimolar quantities of ammonium hydroxide and ammonium chloride, there is a large concentration of ammonium ions, chloride ions, undissociated ammonium hydroxide and small amount of OH^- ions.

$$NH_4OH(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$NH_4CI(aq) \longrightarrow NH_4^+(aq) + Cl^-(aq)$$

When a few drops of HCl*(aq)* are added, the additional H_3O^+ ions are neutralized by OH^- ions present in the buffer.

$$OH^-(aq) + H_3O^+(aq) \rightleftharpoons 2H_2O(l)$$

From buffer From acid

As some of OH- ions from NH4OH combine with H3O+ ions from the acid, it would result in the greater ionization of NH_4OH to restore the OH^- ion concentration.

On the other hand, when a few drops of NaOH solution are added to the buffer solution. it would give OH^- ions. The additional OH^- ions will combine with NH_4^+ ions.

$$NH_4^+(aq) + OH^-(aq) \rightleftharpoons NH_4OH(aq)$$

From buffer From acid

If we observe the titration curves (Fig. 4.3) we find that in certain region (flat portions of the titration curve) the pH of the solution is insensitive to small changes in the concentration of acid or base. These portions of the curve are known as buffer **regions.**

Importance of Buffer Solutions

Buffer solutions play an important role in many industrial processes such as electroplating, manufacture of medicines, dyes, photographic materials, etc. Many biological fluids such as blood, urine etc. have a definite pH which is maintained by buffer action of many substances. The pH of human blood is maintained between 7.35 and 7.45 by buffer action of carbonic acid (H_2CO_3), bicarbonate ions (HCO_3^-) and carbon dioxide (CO_2). The pH values of some biological fluids and other systems are given in Table 4.7.

Table 4.7. pH Values of Some Biological Fluids and other Liquids

Liquid	*pH*
Gastric juices	1.0-3.0
Orange juice	2.6-4.4
Tomatoes	4.3
Lemon juice	2.2-2.4
Carbonated drinks such as coke	2.5
Vinergar	3.0
Urine	4.8-7.5
Saliva	6.5-7.5
Milk	6.6-6.9
Human blood	7.4
Tears	7.4
Sea water	8.0

pH of a Buffer Solution

pH of buffer solution is calculated by applying **Henderson-Hasselbalch equation.** In order to derive this equation let us consider an acidic buffer consisting of weak acid HA and its salt NaA

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \quad \text{... Weakly dissociated}$$

$$NaA \longrightarrow Na^+ + A^- \quad \text{... Completely dissociated}$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Since HA is weakly dissociated, the conc. of HA in solution can be taken equal to the initial conc. of the acid. Since NaA is completely dissociated, conc. of A^- can be taken equal to the conc. of NaA (salt)

$$K_a = \frac{[H_3O^+][Salt]}{[Acid]}$$

$$[H_3O^+] = \frac{[K_a][Salt]}{[Acid]}$$

$$-\log [H_3O^+] = -\log K_a - \log \frac{[Salt]}{[Acid]}$$

$$\boxed{\mathbf{pH = pK_a + \log \frac{[Salt]}{[Acid]}}}$$

Similarly, for basic buffers,

$$\boxed{\mathbf{pOH = pK_{\mathit{B}} + log\,\frac{[Salt]}{[Acid]}}}$$

It may be noted that pH of a buffer solution does not change with dilution because the ratio of concentration of salt to concentration of acid or base does not change with dilution.

SOLVED EXAMPLES BASED ON BUFFER SOLUTIONS

Example 4.13. Calculate the pH of a solution which is 0.1 M in HA and 0.5 M in NaA, for HA if 1.8 × 10^{-6}.

Solution.

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

$$NaA \rightleftharpoons Na^+ + A^-$$

Suppose x moles of HA dissociate per litre of solution

$$[H_3O^+] = x$$

$$[A^-] = x + 0.5 = 0.5\text{ M}$$

$$[HA] = 0.1 - x = 0.1\text{ M}$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$1.8 \times 10 \;\; = \frac{(x)\,(0.5)}{0.1}$$

$$x = 3.6 \times 10^{-7}$$

$$[H_3O^+] = 3.6 \times 10^{-7}\text{ M}$$

$$pH = -\log\,[H_3O^+] = -\log\,(3.6 \times 10^{-7})$$

$$= 7 - \log 3.6 = \mathbf{6.44.}$$

Alternatively, pH can be calculated by applying Henderson's equation

$$pH = pK_a + \log\frac{[Salt]}{[Acid]}$$

$$= -\log\,(1.8 \times 10^{-6}) + \log\left(\frac{0.5}{0.1}\right)$$

$$= 5.744 + 0.6990 = \mathbf{6.44.}$$

Example 4.14. What should be the ratio of concentration of formate ion and formic acid in a buffer solution so that its pH should be 4? Around what pH will this buffer have maximum buffer capacity? K_a for formic acid is 1.8×10^{-4}.

Solution. We know, $pH = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$

$$4 = -\log(1.8 \times 10^{-4}) + \log \frac{[\text{Fromate}]}{[\text{Formic acid}]}$$

$$4 = 3.74 + \log \frac{[\text{Fromate}]}{[\text{Formic acid}]}$$

$$\text{Log} \frac{[\text{Fromate}]}{[\text{Formic acid}]} = 4 - 3.74 = 0.26$$

$$\frac{[\text{Fromate}]}{[\text{Formic acid}]} = \mathbf{1.8}$$

The buffer capacity of this solution would be maximum near the pK_a of the acid.

∴ For maximum buffer capacity

$$pH = pK_a = -\log K_a = -\log(1.8 \times 10^{-4}) = \mathbf{3.74.}$$

SUMMARY

- **Common Ion Effect.** It refers to the suppression of the ionization or a weak electrolyte by any of the ion common with those of the electrolyte already present in the solution.
- **Acid.** A substance which furnishes H^+ ions in aqueous solution (Arrhenius concept) proton donor (Bronsted concept) and donor of electron pair (Lewis concept).
- **Base.** A substance which gives OH- ions in aqueous solution, (Arrhenius concept); acceptor of proton (Bronsted concept) and donor of electron pair (Lewis concept).
- **Acid-base indicators** are substance which change color with pH. They are generally weak acids of which either the undissociated molecule or the dissociated anion, or both are coloured.
- The equilibrium of a weak acid indicator may be represented as

$$\underset{\text{(Colour A)}}{HIn(aq) + H_2O(l)} \rightleftharpoons \underset{\text{(Colour B)}}{H_3O^+(aq) + In^-(aq)}$$

- **Hydrolysis.** It is reverse d neutralization. It involves the interaction of the ions of electrolyte with H_2O molecules in solution to give acidic or basic solution.
- Salts of strong acids and strong base do not undergo hydrolysis and the aqueous solutions are neutral.
- **Buffer Solution.** À solution which resist the change in its pH value on addition of small amount of acid or a base.

- A buffer solution is generally a mixture of weak acid and its conjugate base weak base and its conjugate acid.

REVIEW QUESTIONS

1. What are the applications of concept of solubility product?
2. How does degree of ionization of n weak electrolyte depend upon concentration of the solution?
3. Explain why calcium sulphate is less soluble in sodium sulphate solution than in pure water.
4. Write down solubility product expressions for the following salts:
   (i) $Ca_3(PO_4)_2$ (ii) Ag_2CrO_4
   (iii) $Fe(OH)_3$ (iv) $Pb(OH)_2$
5. Derive and state Oswald's dilution law.
6. Calculate the solubility of A_2X_3 in pure water, assuming that neither kind of ion reacts with water. The solubility product of A_2X_3, K_{sp} -1.1×10^{-23}.
7. Calculate the solubility of AgCl at 373 K. The solubility product of AgCl is 3.4×10^{-4}.
8. The K_{sp} of $PbBr_2$ is 4×10^{-6}.at 300 K. Find out the solubility of $PbBr_2$ at this temperature.
9. What is the Arrhenius theory of acids and bases ? Give its two important limitations.
10. What do you understand by dissociation constant of an acid ? How it is related to the strength of the acid ?
11. What are buffer Solutions ? Explain the buffer action by taking an example of acidic buffer.
12. What in pH scale ? How does it tell on whether a solution is acidic or basic ?
13. Calculate the pH of a solution obtained by mixing 20 ml of 0.1 M NaOH and 40 ml of 0.1 M HCl.
14. Explain the following terms:
    (i) Acid-base indicator
    (ii) Range of an acid-base indicator
    (iii) Titration.
15. Can we use phenolphthalein as indicator to detect the equivalence point during titration of 0.1 M HCl against 0.1 M NH_3 ? Explain with the help of titration curve.
16. Calculate the dissociation constant of an acid, 0.1 M solution of which has pH equal to 5.
17. The value of at a certain temperature is 9.55×10^{-14} Calculate the pH of water at this temperature.
18. Find the pH value of 0.1 M acetic acid, its degree of ionization is 0.013 under the given conditions. $K_{CH_3COOH} = 1.8 \times 10^{-5}$

5

ELECTROLYSIS

LEARNING OBJECTIVES

- Introduction
- Electrolysis Cells and Electrolysis
- Criteria of Product Formation in Electrolysis
- Quantitative Aspect of Electrolysis
- Engineering Applications of Electrolysis

5.1 INTRODUCTION

In electrochemical cells chemical energy is converted into electrical energy. On the other hand when direct current is passed through an electrolyte in molten or dissolved state, the electrolyte undergoes decomposition. In this process, called electrolysis, electrical energy is converted into chemical energy. Electrolysis finds many important industrial applications. In this chapter we will study the process of electrolysis and some of its important industrial applications,

5.2 ELECTROLYTIC CELLS AND ELECTROLYSIS

The process of chemical decomposition of the electrolyte by the passage of electricity through its molten or dissolved state is called **electrolysis.**

Electrolytic cell. The device in which the process of electrolysis is carried out is called electrolytic cell. It consists of:

(i) **Electrolytic tank,** which is made of some non-conducting material like glass, wood or bakelite.

(ii) Electrolyte in its dissolved state or molten state.

(iii) Source of electricity, an electrochemical cell or battery.

(iv) Two metallic rods, suspended in the electrolyte and connected to the battery through conducting wires. These rods are called electrodes. The electrode connected to the negative terminal of battery is called cathode while the other one which is connected to the positive terminal is called anode. The apparatus used to constitute electrolytic cell has been shown in Fig. 5.1.

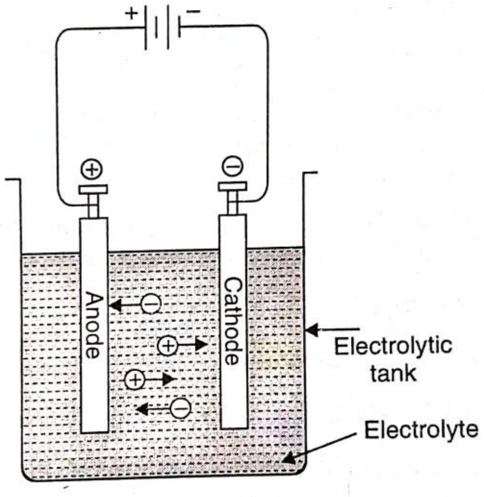


Fig. 5.1 Electrolytic cell

5.3 CRITERIA OF PRODUCT FORMATION IN ELECTROLYSIS

The process of electrolysis can be explained on the basis of the theory of ionization. When an electrolyte is dissolved in water, it splits up into charged particles called ions. The positively charged ions are called **cations** while the negatively charged ions are called **anions.** The ions are free to move about in aqueous solution. When electric current is passed through the solution, the ions respond to the applied potential difference and their movement is directed towards the oppositely charged electrodes. The cations move towards the negatively charged electrode (cathode) while anions move towards the positively charged electrode (anode). The formation of products at the respective electrodes is due to **oxidation** (loss of electrons) at the **anode** and **reduction** (gain of electrons) at the **cathode.**

For example, when electricity is passed through the molten sodium chloride, sodium is deposited at the cathode while Cl_2 gas is liberated at the anode. The process can be represented as:

$$NaCl(I) \longrightarrow Na^+ + Cl^-$$

Cathode: $Na+ + e- \longrightarrow Na$ (Reduction)

Anode: $Cl- \longrightarrow \frac{1}{2} Cl_2 + e^-$ (Oxidation)

Similarly, electrolysis of molten lend bromide produces lead at the cathode and Br_2 at the anode.

In case there is a possibility of formation of more than one products at the electrodes, or there is a competition between the liberation of ions at the electrodes, then the products formed depends upon their respective electrode potentials.

(a) At the Cathode. Cathode involves reduction process at its surface. Therefore, for the different competing reduction processes, the one with **higher reduction potential, will preferably take place.** For example, during the electrolysis of aqueous solution of sodium chloride there is possibility of following reactions at the cathode:

Reduction of Na^+ ions:

$$Na^+(aq) + e- \longrightarrow Na(s); \qquad E^{\ominus}_{red} = -2.17\ V$$

Reduction of H2O molecules:

$$H2O(l) + 2e^- \longrightarrow \frac{1}{2} H_2(g) + OH^-(aq); \quad E^{\ominus}_{red} = -41\ V$$

The reduction of water will preferably take place at the cathode because $E^{\ominus}_{red}$ of water is higher. Hence, the product of electrolysis of aqueous solution of NaCl at the cathode will be H, gas instead of Na(s).

Similarly, during electrolysis of aqueous solution of copper sulphate reduction of Cu^{2+} ions will take place at the cathode in preference to the reduction of H_2O molecules because $E^{\ominus}_{Cu^{2+}/Cu}$is greater than $E^{\ominus}_{H_2O/H_2}$.

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)\ ; \qquad E^{\ominus} = 0.34\ V$$

$$H_2O(l) + 2e^- \longrightarrow \frac{1}{2} H_2(g) + OH^-(aq)\ ; \qquad E^{\ominus} = -0.41\ V$$

(b) At the Anode. Anode involves oxidation process at its surface. Therefore, for different competing oxidation processes, the one with **higher oxidation potential** (or lower reduction potential) will preferably occur. For example, if we carry out electrolysis of aqueous solution of copper sulphate, the competing oxidation processes at the anode are as follows:

Oxidation of SO_4^{2-} ions

$$2SO_4^{2-}\ (aq) \longrightarrow S_2O_8^{2-} + 2e^- \qquad E^{\ominus}_{oxi} = -2.01\ V$$

Oxidation of water molecules

$$H_2O(l) \longrightarrow \frac{1}{2} O_2(g) + 2H^+(aq) + 2e^-\ ; \quad E^{\ominus}_{oxi} = -1.23\ V$$

As oxidation potential of water is higher, the product formed at the anode will be O_2 as instead of $S_20_8^{2-}$ ion.

When the electrolysis of copper sulphate solution is carried out using copper electrodes, then the process occurring at the anode will be oxidation of copper atoms to copper ions instead of oxidation of water because oxidation potential of Cu is higher.

$$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^- ; \quad E^{\ominus}_{oxi} = -0.34\ V$$

$$2H_2O(l) \longrightarrow \frac{1}{2} O_2(g) + 2H^+(aq) + 2e^- \quad E^{\ominus}_{oxi} = -1.23\ V$$

Thus, in such a case copper from anode will go on dissolving into solution as Cu^{2+} ions while Cu^{2+} ions from solution will go on depositing at the cathode as copper atoms.

The above discussion lead us to a general conclusion that for different competing reactions at the electrodes:

Cathodic reaction will be the one with higher $E^{\ominus}_{red}$ value
Anodic reaction will be the one with higher $E^{\ominus}_{oxi}$ value

In the light of the above discussion let us discuss the product formed during the electrolysis of some of the electrolytes.

1. Electrolysis of Aqueous Solution of NaCl

NaCl in aqueous solutions ionizes as

$$NaCl(aq) \longrightarrow Na^+(aq) + Cl^-(aq)$$

At anode : $Cl^-(aq) \longrightarrow \frac{1}{2} Cl_2(g) + e^-$

At cathode: $H_2O(l) + 2e^- \longrightarrow \frac{1}{2} H_2(g) + OH^-(aq)$

Thus, Cl_2 gas is liberated at the anode whereas H_2 gas is liberated at the cathode.

2. Electrolysis of Copper Sulphate Solution Using Platinum Electrodes

Copper sulphate ionises in aqueous solution

$$CuSO_4(aq) \longrightarrow Cu^{2+}(aq) + SO_4^{2-}(aq)$$

At anode : $H_2O(l) \longrightarrow \frac{1}{2} O_2(g) + 2H^+(g) + 2e^-$

At cathode : $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

Thus, copper is deposited at the cathode, and O_2 is liberated at the anode.

3. Electrolysis of Copper Sulphate Solution using Copper Electrodes

Copper sulphate ionises as:

$$CuSO_4(aq) \longrightarrow Cu^{2+}(aq) + SO_4^{2-}(aq)$$

At anode : $Cu(l) \longrightarrow Cu^{2+}(aq) + 2e^-$

At cathode : $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

Thus, copper dissolves at the anode and is deposited at the cathode.

5.4 QUANTITATIVE ASPECT OF ELECTROLYSIS

As pointed out earlier that during electrolysis, anodic reaction involves oxidation and cathodic reaction involves reduction. For example, cathodic reaction in electrolysis of copper (II) sulphate is:

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

This means that for the production of one mole of copper, 2 moles of electrons are needed. In the number of electrons available to copper ions are less than 2 moles. the amount of copper deposited at the cathode will also be less than 2 moles. Thus, the amount of product formed at the electrode depends on the number of electrons, which in turn depends on the quantity of electricity flowing through the electrolytic cell.

Now charge on one electron has been found to be 1.602×10^{-19} coulombs.

Charge on one mole of electrons = $1.602 \times 10^{-19} \times 6.02 \times 10^{23} = 96488 \text{ C mol}^{-1}$

This magnitude of charge (= 96488 C mol^{-1}) is called **Faraday constant** and is denoted by **F.**

$$F = 96488 \text{ C mol}^{-1} \text{ or } = 96500 \text{ C mol}^{-1}$$

Charge on **n moles** of electrons (**Q**) is given by **Q = nF**

Thus, for n moles of electrons, the charge equal to **nF,** i.e., $n \times 96500$ C of electricity has to be passed through the electrolyte. For example, during the electrolysis of aluminum chloride 3 moles of electrons are required for producing 1 mole of aluminum.

$$Al^{3+} + 3e^- \longrightarrow Al$$

Therefore, charge equal to 3 F or 3 × 96500 C has to be passed though the electrolyte.

Now, quantity of charge flowing though the electrolyte can be calculated from the current strength and time for which the current is passed according to following realtion.

$$\mathbf{Q = f \times t}$$

Where **Q** = Quantity of charge (coulombs)

I = Current in amperes

t = Time in second.

Thus, from the above consideration. It is possible to calculate the amount of a substance deposited or evolved from when a definite amount of current is passed for a definite period of time.

Faraday's Lawn of Electrolysis

The relationship between the quantity of electricity passed and the quantity of a substance liberated at the electrode is given in the form of Faraday's laws of electrolysis.

Faraday's First Law of Electrolysis

This law states that **the mass of a substance liberated at the electrode is directly proportional to the quantity of electricity passed.**

$m \propto Q$ Here, $\mathbf{Q}$ = quantity of electricity

$\propto I \times t$ I = current in amperes

$= Z \times I \times t$ t = time in seconds

Z = constant of proportionally called electrochemical equivalent (ECE)

If $I = 1$ ampere and $t = 1$ second, then $m = Z$

Thus, **electrochemical equivalent** of a substance to the amount of substance liberated at the electrode when current of one ampere in passed through the electrolyte for one second.

Faraday's Second Law of Electrolysis

This law states that the amounts of different substance liberated by the same quantity of electricity passing through their electrolytic notation are directly proportional to their chemical equivalent masses (chemical equivalent man of metal can be obtained by dividing its atomic man with number of electrons required to reduce its cation). The law can also be stated an follow ; when same quantity of electricity is passed through different electrolytes then the masses of the substances liberated at the electrodes are in the ratio of their equivalent masses or the ratio of their chemical equivalents.

For example, the two electrolytic cells A (containing ANO_3 solution) and B (containing $CuSO_4$ solution) are connected in series and same quantity of electricity is passed through the call, then the ratio of them of copper deposited at cathode in their chemical equivalent masses.

$$\frac{\text{Mass of Cu}(x)}{\text{Mass of Ag}(y)} = \frac{\text{Eq. mass of Cu}}{\text{Eq. mass of Ag}} = \frac{Z_{\text{Cu}}}{Z_{\text{Ag}}}$$

It may be noted that moalr ratio and mass ratio are related as

$$\frac{\text{Mass of Cu}}{\text{Mass of Ag}} = \frac{\text{Molar mass of Cu}}{2 \times \text{Molar mass of Ag}} \text{ or } \frac{x}{y} = \frac{63.5}{2 \times 108}$$

SOLVED EXAMPLES

Example 5.1. For how long a current of 1.5 ampere has to be passed though the electrolyte in order to deposit 1.0 g of Al when the electrode reaction is

$$Al^{+3} + 3e^- \longrightarrow Al \text{ (At. Mass of Al = 27)}$$

Solution. Step 1. Calculation of number of coulombs required.

From the electrode reaction, it is clear that

For depositing one mole of Al atoms the electrons required = 3 mole

Charge on 3 mole of electrons = 3 × 96500 C

Now 1 mole of Al = 27g

∴ Deposition of 27 g of Al requires charge = 3 × 96500 C

Deposition of 1.0 g of Al requires charge $= \frac{3 \times 96500}{27} \times 1.0 =$ **10722.2C.**

Step 2. Calculation of time

Current strength = 1.5 amp.

Let the time required by t sec

∴ No. of coulombs = 1.5 × t C

Equate (i) and (ii), $1.5\, t = 10722.2$

$$t = \frac{10722.2}{1.5} = 7148 \text{ sec} = \frac{7148}{60 \times 60} \text{ hrs}$$

= **1.98 hrs.**

Difference Between Electrochemical Cell and Electrolytic Cell

We have learnt that there are two types of cells namely: electrochemical cells and electrolytic cells. The former is a device which converts chemical energy into electrical energy. On the other hand, electrolytic cell in a device which converts electrical energy into chemical energy. The main points of difference have been summed up as Follow in Table 5.1

Table 5.1. Differences between Galvanic Cell and Electrolytic Cell

Galvanic Cell	Electrolytic Cell
1. In galvanic cell, electrical energy in produced.	1. In electrolytic cell, electrical energy is consumed.

2. In galvanic cell, reaction taking place is spontaneous. 3. The two half cells are set up in different containers and are connected though salt bridge or porous partition. 4. In galvanic cell, anode is negative and cathode is positive. 5. The electrons move from anode to cathode in external circuit.	2. In electrolytic cell, reaction taking place is non-spontaneous. 3. Bothe the electrodes are placed in the solution or molten electrolyte in the same container. 4. In electrolytic cell, the anode is positive and cathode is negative. 5. The electrons are supplied by the external source. They enter through cathode and come out through anode.

5.5 ENGINEERING APPLICATIONS OR ELECTROLYSIS

Electrolysis has a number of important industrial applications. These include the extraction and purification of metals, electroplating and anodizing and the manufacture of many important chemicals.

1. Extraction of Metals

Metals in groups I and II of the Periodic Table are extracted by electrolysis of fused halide Sodium, for example, is obtained by electrolysis of molten sodium chloride in the Downs cell.

$$NaCl(l) \rightleftharpoons Na^{2+} + Cl^{-}$$

At cathode : $Na^{2+} + e^{-} \longrightarrow Na^{2+}$

At anode : $2Cl^{-} \longrightarrow Cl_2 + 2e^{-}$

Magnesium is obtained by the electrolysis of magnium chloride, which is obtained from dolomite und seawater.

Similarly, aluminium is extracted by electrolysis of $A1_2O_3$ dissolved in molten cryolite ($Na_3\ AIF_6$) using graphite electrodes.

At cathode : $Al^{3+} + 3e^{-} \longrightarrow Al$

At anode : $O^{2-} \longrightarrow O + 2e^{-}$

$$C + 2\,[O] \longrightarrow CO_2$$

2. Purification of Metals

Metals such as copper silver and zinc can be purified by electrolysis. The purification of metal is known as refining. A schematic diagram of the purification of copper is shown in Fig. 5.2. The impure copper is the anode and the cathode is pure copper. Copper (1) suphate solution can be used as an electrolyte.

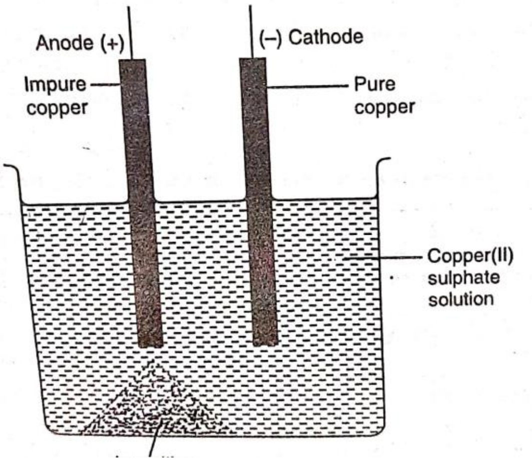


Fig. 5.2. Purification copper.

At the anode the reaction is oxidation of copper:

$$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$$

The impurities drop to the bottom of the vessel an anode sludge. This sludge may contain valuable metals such as gold and silver. Copper ions are discharged and deposited on the pure copper cathode. The reaction at cathode is:

$$Cu^{2+}(aq) \longrightarrow Cu(s) + 2e^-$$

3. Electroplating

In this process the object to be plated is made the cathode. This is immersed in am electrolyte containing the ions of the plating metal. The anode is the pure plating metal. Successful electroplating requires that the electric current, concentration of electrolyte and temperature are exactly right, the cathode must also be clean.

Electroplating may involve a number of stages. For example, chromium plating of iron involves four stages:

1. The iron object, which is the cathode, is cleaned with sulphuric acid and then washed with deionized water.

2. The iron cathode is plated with copper.

3. It is then plated with nickel. This prevents corrosion.

4. Finally, the object is chromium-plated,

4. Anodising

This is the process of coating aluminium objects with aluminium oxide. The object forms the anode. The electrolyte is dilute sulphuric acid. The coating of aluminium oxide protects the metal from corrosion.

5. Manufacture of Other Chemicals

The most important example of this application in the manufacture of sodium hydroxide, hydrogen and chlorine by means of the flowing mercury cathode cell.

SUMMARY

- **Electrolysis.** The process of chemical decomposition of an electrolyte by passage of electricity through its molten or dissolved state.
- During electrolysis oxidation takes place at anode while reduction takes place at cathode.
- $Q = I \times t$ $\quad$ I = current in amps
  t = time in seconds
- **Faraday's Laws of Electrolysis**
  - ✓ The first law states that the mass of substance liberated or deposited at an electrode is directly proportional to the quantity of electricity passed.
  - ✓ The second law states that when came quantity of electricity is passed through different electrolytes then the masses of the substances liberated at different electrodes are in the ratio of their equivalent masses.

$$\frac{M_A}{M_B} = \frac{E_A}{E_B}$$

REVIEW QUESTIONS

1. Give the product of electrolysis in each of the following, writing cathodic and anodic reactions:
   (i) Fused NaCl $\quad$ (ii) aqueous solution of NaCl
   (iii) Fused $PbBr_2$ $\quad$ (iv) acidulated water
2. Give the electrolysis is product of
   (i) $AgNO_3$ solution using Ag electrodes
   (ii) Fused CaH_2 using Pt electrodes.
3. If the aqueous solution of FeSO4 is electrolyzed using platinum electrodes what reaction will take place at the electrodes?
   Hint. Cathode: $Fe^{2+} + 2^{e} \longrightarrow Fe.$

Anode: 2H2O $\longrightarrow$ $4H^+ + O_2 + 4e^-$

4. If a current of 0.5 ampere flows through a metallic wire for 2 hours, then how many electrons flow though the wire? (**Ans.** 2.24×10^{23} electrons)
5. A solution of CuSO4 is electrolyzed with a current of 1.5 amperes. What is the mass of copper deposited at the cathode? (**Ans.** 0.294 g)
6. Calculate the mass of lead produced at a cathode by a current of 2 amps flowing through molten lead (II) bromide for 30 minutes (atomic mass of lead = 207). (**Ans.** 3.86 g)

6

WATER

LEARNING OBJECTIVES

- Introduction
- Sources of Water
- Hard and Soft Water
- Equivalents of CaCO3 Concept
- Units of Water Hardness
- Effects of Water Hardness
- Determination of Alkalinity of Water
- Determination of Degree of Hardness
- Softening of Water
- Boiler Feed Water
- Water for Drinking Purpose

6.1 INTRODUCTION

Water is the most abundantly available and most extensively used chemical. It is essential part of human life. It constitutes 78 per cent of blood and 70 per cent of body weight. Water also forms a life line for most of the industries. In an industry, water requirement may be from 100 m^3 to 10,000 m^3 per ton of finished product. In industry water is used mainly na coolant, solvent, washing agent, steam generator, etc. Among the industries the chemical industry, iron and steel industry, paper and pulp industry, food industry, aluminum and copper industries are the major users of water.

6.2 SOURCE OF WATER

There are two major sources of water for industry - surface water and ground water.

1. Surface Water

This includes water from rivers, reservoirs, sea and rain..

2. Underground Water

This is the water accumulated underground through seepage of rain water forming different table of water depending upon the unpermeable rocks. This water is obtained by tube wells and wells, and occasionally an spring where a water table finds an opening.

Industries for most of their water requirement depend on surface water.

6.3 HARD AND SOFT WATER

Water is classified into two categories depending upon its behaviour towards soap solution. These are: soft water and hard water

1. Soft water. Water which produce lather with soap solution readily is called soft water. Distilled water and rain water are common examples of soft water.

2. Hard water. Water which does not produce lather with soap solution daily a called **hard water.** River water en water, tap water are common examples of hard water.

Cause of Hardness of Water

Hardness of water is due to the dissolved impurities of the salt like bicarbonates, chlorides and sulphate of calcium and magnesium. Water gets the contamination of those salts when it passes through the ground and rock Hard water does not produce Lather with soap solution readily because the cations (Cs^{2+} and Mg^{2+}) present in hard water react with saop (which is a mixture of sodium salts of higher fatty acid like stearic acid, palmitic acid, oleic acid, etc.) to form a precipitate of calcium and magnesium salts of fatty acids.

$$\underset{\text{From hard water}}{CaCl_2} + \underset{\text{Sodium stearate}}{2C_{17}H_{35}COONa} \longrightarrow \underset{\text{Calcium stearate}}{(C_{17}H_{35}COO)_2Ca} \downarrow + 2NaCl$$

Thus, no lather is produced until all the calcium and magnesium ions have been completely precipitated.

Types of Hardness

The hardness of water is of two types: temporary hardness and permanent hardness.

(i) **Temporary hardness.** It is due to the presence of soluble bicarbonates of calcium and magnesium. Such water is also said to possess **carbonate hardness**. The term temporary indicates that the hardness can be removed by simply boiling the water. The bicarbonates of calcium and magnesium are formed in water by dissolution of carbonates of calcium and magnesium in the presence of atmospheric carbon dioxide.

(ii) **Permanent hardness.** It is due to the presence of chloride and sulphates of calcium and magnesium. Such water is also said to possess **non-carbonate hardness.** The term permanent indicates that such type of hardness cannot be removed by simple boiling operation.

6.4 EQUIVALENTS OF CaCO3 CONCEPT

The concentration of hardness constituting impurities are usually expressed in terms of equivalent amount of $CaCO_3$.

All the substances causing hardness should be converted into their respective $CaCO_3$ equivalent, as a matter of convention and convenience.

$CaCO_3$ equivalent of hardness causing impurity

$$= \frac{\text{Weight of the impurity}}{\text{Chemical equivalent weight of the impurity}} \times 50$$

(50 is the chemical equivalent weight of $CaCO_3$).

For instance, 136 parts of weight of $CaSO_4$ would contain the same amount of Ca as that of 100 parts by weight $CaCO_3$. Hence, in order to convert the weight of $CaSO_4$ as its $CaCO_3$ equivalent, the weight of $CaSO_4$ should be multiplied by a factor of $\frac{100}{136}$ or $\frac{50}{68}$

Conversion factors for some of the commonly occurring impurities in water are given in Tables 6.1 and 6.2

Table 6.1. Calculation of Equivalents of $CaCO_3$

Compound	Molar mass	Equivalent mass	For equivalent as $CaCO_3$ multiply by
$Ca(HCO_3)_2$	162	81	100/162
$Mg(HCO_3)_2$	146	73	100/146
$CaSO_4$	136	68	100/136
$CaCl_2$	111	55.5	100/111
$MgSO_4$	120	60	10/120
$MgCl_2$	95	47.5	100/95
$Mg(ON_3)_2$	148	74	100/148
HCl	36.5	36.5	$\frac{100}{36.5 \times 2}$

H_2SO_4	98	49	100/98
CO_2	44	22	100/44
$Al_2(SO_4)_3$	342	57	$\frac{100}{114}$
$FeSO_4.7H_2O$	278	139	100/278
$CaCO_3$	100	50	100/100
$MgCO_3$	84	42	100/84
$NaAlO_2$	82	82	$\frac{100}{82 \times 2}$

Table 6.2. Calculation of Equivalents of $CaCO_3$ for Some Ions

Formula of the Ion	Formula mass	Equivalent mass	For equivalent as $CaCO_3$ multiply by
Al^{3+}	27	9	50/9
Ca^{2+}	40	20	50/20
Mg^{2+}	24	12	50/12
NH_4^+	18	18	50/18
Na^+	23	23	50/23
$H+$	1	1	50/1
Fe^{2+}	56	28	50/28
Fe^{3+}	56	56/3	$\frac{50 \times 3}{56}$
SO_4^{2-}	96	48	50/48
CO_3^{2-}	60	30	50/30
HCO_3^-	61	61	50/61
AlO_2^-	59	59	50/59
Cl^-	35.5	35.5	50/35.5
OH^-	17	17	50/17

6.5 UNITS OF WATER HARDNESS

The hardness of water is expressed in the following units,

1. **Milligram per litre *(mg/l).*** It is number of milligrams of $CaCO_2$ present per litre of water.

   1mg/litre = 1mg $CaCO_3$ equivalent in 1L of water.

2. **Parts per million.** It is the number of parts by weights of calcium carbonate per million parts by weight of water.

   1ppm = 1 part of $CaCO_3$ in 10^6 parts of water

3. **Degree Clark *(◦Cl).*** It is the number of grains of $CaCO_3$ present per gallon of water.

   1° Clark = 1 grains of $CaCO_3$ per gallon of water
   = 1 part of $CaCO_3$ per 70,000 parts of water.
   1ppm = 0.07° Clark.

4. **Degree French *(°Fr).*** It is the $CaCO_3$ equivalent hardness per lac parts of water.

   1° Fr = 1 part of $CaCO_3$ equivalent per 105 parts of water.
   1 ppm = 0.1° Fr.

6.6 EFFECTS OF WATER HARDNESS

The harmful effect of hard water are as follows:

1. Hard water is harmful for potable purposes. It causes deposition of calcium in the bone joints and the possibility of forming calcium oxalate crystals in urinary tracts is increased.
2. It cause many problems in boilers when it is directly fed for steam generation. The problems include, scale and nudge formation, corrosion, priming and foaming and caustic embrittlement.
3. It does not form lather with one or detergents. On the other hand it produces precipitates of calcium and magnesium soaps. The formation of such insoluble, sticky precipitates continues till all calcium and magnesium salt present in water are precipitated. After that, the soap (Sodium stearate) given lather with water.

   This causes wastage a lot of nonp is being used.

4. Due to the presence of dissolved hardness producing salts, the boiling point of water in elevated.

6.7 DETERMINATION OF ALKALINITY OF WATER

The alkalinity in the quantitative ability of water to react with a strong acid. It is primarily n function of carbonate, bicarbonate and hydroxide content. Alkalinity in natural waters is due to free hydroxyl and hydrolysis of salts formed by weak acids and strong bases.

$$A^- + OH \longrightarrow HA + OH^-$$

Most of the alkalinity in natural water is formed due to dissolution of Co_2 in water Carbonates and bicarbonates thus formed, are dissolved to yield hydroxyl ions.

$$C0_3^{2-} + 2H_2O \rightleftharpoons H_2CO_3 + 20H^-$$

$$HC0_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$$

Thus, the alkalinity of water is mainly due to hydroxides, carbonates and bicarbonates. Following possibilities may arise with respect to the constituents causing alkalinity in natural waters.

(a) Hydroxides only
(b) Carbonates only
(c) Bicarbonates only
(d) Hydroxide and carbonates
(e) Carbonates and bicarbonates

Hydroxides and bicarbonates cannot exist together as they combine with each other to form carbonates.

$$OH- + HC0_3^- \longrightarrow C0_3^{2-} + 2H_2O$$

The type and extent of alkalinity present in a water sample can be determined by titrating the sample with a standard solution of acid using phenolphthalein and methyl orange successively as indicators.

$$Ca(OH)_2 + H_2SO_4 \longrightarrow CaSO_4 + 2H_2O \qquad \ldots(i)$$

$$2CaCO_3 + H_2SO_4 \longrightarrow Ca(HCO_3)_2 + CaSO_4 \qquad \ldots(ii)$$

$$Ca(HCO_3)_2 + H_2SO_4 \longrightarrow CaSO_4 + 2CO_2\uparrow + 2H_2O \qquad \ldots(iii)$$

The volume of acid run down for phenolphthalein end point, P ml, corresponds to the completion of equations (i) and (ii) while the volume of acid run-down after P mL. corresponds to the completion of equation (iii).

The total amount of acid red from the beginning of the experiment, i.e., (M) corresponds to the total alkalinity and presents the completion of reaction shown by equations (i) to (ii).

The titration values P and Mare red to calculate the three forms of alkalinity as shown in the table:

Titre value with phenolphthalein end point (P) and methyl orange and point (M)	OH- alkalinity	$C0_3^{2-}$ alkalinity	$HC0_3^-$ alkalinity
P = 0	0	0	M
$P < \frac{1}{2} M$	0	2P	M – 2P
$P = \frac{1}{2} M$	0	2P or M	0
$P > \frac{1}{2} M$	2P – M	2(M – P)	0
P = M	P or M	0	0

6.8 DETERMINATION OF DEGREE OF HARDNESS

One of the important constituents for which water is analysed is hardness of the water. Hardness of the water is represented in the form of $CaCO_3$ ppm equivalent.

With the help of conversion tables (Table 6.1 and 6.2) almost all dissolved chemicals and ions can be expressed in the form of $CaCO_3$.

1. Determination of Degree of hardness by Hehnar's method.

Temporary as well as permanent hardness of a sample can be found out by determining alkalinity of water before boiling and after boiling. The difference between the readings will give temporary hardness.

$$X(HCO_3)_2 \xrightarrow{\text{Boiling}} XCO_3 \downarrow + H_20 + CO_2$$

(X = Ca, Mg)

A known volume (x mL) of sample water is pipetted out and 2-3 drops of methyl orange are added to it. It is then titrated with standard HCl (y normality). The titre value (V) is determined. Then x ml of sample water is boiled and evaporated to dryness avoiding any bumping and bubbling out of the material. 50 ml of warm distilled water is then added in order to dissolve the solids. The solution to obtained is filtered into a 100 ml flask followed by washings by distilled water. Filtrate is titrated again with standard HCl (y normality) using methyl orange as indicator and the titre value (V_2) is recorded.

Now volume of standard HCl used for temporary hardness = (V_1 – V_2) mL

Strength of alkalinity (S) due to temporary hardness will be

$$S = \frac{(V_1 - V_2)}{x}$$

Replacing the strength by grams per litre of $CaCO_3$ equivalent

$$S = \frac{(V_1 - V_2)y}{x} \times 50\text{gm/lit.}$$

or

$$S = \frac{(V_1 - V_2) \times 50 \times 1000y}{x} = \text{mg/l. or ppm.}$$

where x is the volume taken for titration in the normality, and 50 is gram equivalent weight of $CaCO_3$.

Similarly, the volume of standard HCl used for permanent hardness = V_2 mL

From this we can calculate permanent hardness on the same pattern as discussed above for temporary hardness.

2. Determination of Degree of Hardness by Soap Solution Method

This method depends upon the fact that when soluble on (sodium/potassium salts of higher fatty acids) is added to hard water, then, Ca, Mg, and other heavy metals present in hard water react with soap to form insoluble compounds. The lather in produced only when all the constituents causing hardness are precipitated by saop.

When sample for analysis is taken without boiling, Soap analysis given total hardness and when staple is treated after removing temporary hardness by boiling, it gives permanent hardness. However, in both cases end point is accepted by production of lather stable for minimum of 2 minutes.

Preparation of standard hard water. 1.000 gm of $CaCO_3$ dried at 105°C for 3 hours, is suspended into 200 ml of distilled water contained in a one litre beaker. 1:1 hydrochloric acid in then added drop wine through a dropping funnel till all the $CaCO_3$ is dissolved. After the requisite addition of acid, the solution is boiled to remove any CO_2. Solution is cooled and made neutral with 3N ammonium hydroxide to methyl red indicator. The whole solution in transferred to standard one litre volumetric flank with rinsing's and volume in made one litre. This solution represents 1.000 mg of $CaCO_3$ per mL.

Preparation and standardization of soap solution, 10 gm of pure dry soap is dissolved in 800 ml of alcohol mixed with 200 ml of distilled water. For standardization 50 ml of standard hard water is taken in a conical flank of 250 ml capacity, and then the soap solution is added dropwise from a burette with constant stirring. The end point should be noted when lather lasts even after two minutes of continuous shaking The titre value (x_1) is recorded. Lather factor of distilled water is carried out by taking 50 ml of distilled water in 250 ml conical flask and titrating it to end point as above. Say the titre value is x.

Total hardness is determined by repeating the above experiment for 50 ml of water sample to be analysed and say the titre value in x_2.

Permanent hardness is determined as follows:

250 ml of the sample solution is taken in a 500 ml beaker and boiled for quite sometime till the volume is reduced nearly to hall The solution is then cooled and filtered into a 250 ml measuring flask. Precipitate formed of insoluble carbonates is washed with distilled water and the volume of the solution is made up with distilled water. From this solution, 50 ml is taken and titrated against soap solution as earlier.

Say the titre value in

The various hardnesses of water can be calculated as follows:

Total hardness $= \frac{x_2 - x}{x_1 - x} \times 1000$ mg $CaCO_3$/litre

Permanent hardness $= \frac{x_3 - x}{x_1 - x} \times 1000$ mg $CaCO_3$/litre

Temporary hardness = Total hardness – Permanent hardness

$= \frac{1000\,(x_2 - x_3)}{x_1 - x}$ ppm.

SOME SOLVED EXAMPLES

Example 6.1. 20 mL of 0.1 Na_2CO_3 solution was added to 100 mL of a sample of hard water. The filtrate from the solution required 30 mL of 0.05 H_2SO_4 for example neutralization. Calculate the hardness of water sample.

Solution. The filtrate = 30 mL of 0.05N H_2SO_4

$= \frac{30 \times 0.05}{0.1}$ mL of 0.1N H_2SO_4 = 15 mL of 0.1N H_2SO_4

15 mL of 0.1 N H_2SO_4 = 5 mL of 0.1N Na_2CO_3

Thus, volume of 0.1N Na_2CO_3 solution consumed in precipitating hardness in 100 mL of hard water = 20 - 15 = 5 mL.

∴ 100 mL of water sample = 5 mL of 0.1N Na_2CO_3 solution

or, $100 \times N_{Hardness} = 5 \times 0.1$

or, $N_{Hardness} = \frac{5 \times 0.1}{100} = 0.005$

Strength of hardness as $CaCO_3$ equivalents = 0.005 × 50g/litre

$= \frac{0.005 \times 50 \times 10^6}{100}$ mg/litre = **250 ppm.**

Example 6.2. How many grams of $FeSO_4$ dissolved per litre gives 200 ppm of hardness? (Fe = 56, S = 32, O = 16, Ca = 40, C = 12).

Solution. $FeSO_4$ = $CaCO_3$

56 + 32 + 64 = 152 g   100 g

∴ 100 ppm of hardness = 150 ppm of $FeSO_4$

200 ppm of hardness $= \frac{152 \times 200}{100}$ = 304 ppm of $FeSO_4$

= **304 mg/L** or 0.304 g/L of $FeSO_4$.

6.9 SOFTENING OF WATER

The process of removal of metallic ions (Ca^{2+}, Mg^{2+}, etc.) respondible for hardness of water is known as **softening of water.** The main methods of removing hardness of water are discussed as follow:

Removal of Temporary Hardness

Temporary hardness can be removed by following method:

1. Boiling

Temporary hard water is taken in large boilers and boiled for about fifteen munities. Consequently, the bicarbonates of calcium and magnesium present in the water decompose into their insoluble carbonates which settle at the bottom of the tanks as precipitator. The insoluble precipitate are removed by filtration or decantation.

$$\underset{\text{(Soluble)}}{M(HCO_3)_2} \xrightarrow{\text{Heat}} \underset{\text{(Insoluble)}}{MCO_3} + H_2O + CO_2$$

2. Calcium hydroxide (or Clark's) method

Calculated quantity of lime (calcium hydroxide) is added to temporary hard water. The soluble bicarbonates are converted into insoluble carbonates which settle at the bottom of the tank and are removed by filtration.

$$\underset{\text{(Soluble)}}{Ca(HCO_3)_2 + Ca(OH)_2} \longrightarrow \underset{\text{(Insoluble)}}{2CaCO_3 + 2H_2O}$$

$$\underset{\text{(Soluble)}}{Mg(HCO_3)_2 + Ca(OH)_2} \longrightarrow \underset{\text{(Insoluble)}}{MgCO_3 + CaCO_3 + 2H_2O}$$

Removal of Temporary as well as Permanent Hardness

1. Lime-Soda (L-S) Process

In this process generally lime and soda ash (Na_2CO_3) are used for the precipitation process of softening. The lime is required for the precipitation of compounds causing temporary or carbonate hardness and the soda-ash is used for the precipitation of compounds causing permanent hardness. The reactions involved in the process are:

(i) For temporary hardness

$$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3\downarrow + H_2O$$

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + 2H_2O$$

$$Mg(HCO_3)_2 + Ca(OH)_2 \longrightarrow MgCO_3 + CaCO_2\downarrow + 2H_2O$$

MgCO3 formed further further react in following manner

$$MgCO_3 + Ca(OH)_2 \longrightarrow Mg\ (OH)_2\downarrow + CaCO_3\downarrow$$

(ii) For permanent hardness

$$CaSO4 + Na2CO3 \longrightarrow CaCO3\downarrow + Na2SO4$$

$$MgSO4 + Ca(OH)2 + Na2CO3 \longrightarrow Mg(OH)_2\downarrow + CaCO_3\downarrow + Na_2SO_4$$

$$MgCl2 + Ca(OH)2 \longrightarrow Mg(OH)2\downarrow + CaCl2$$

$$CaCl2 + Na2CO3 \longrightarrow CaCO3\downarrow + Na2SO4$$

It is clear from the above equations that in case of temporary hardness, each unit of calcium bicarbonate requires one mole of lime, whereas each unit of $Mg(HCO_3)_2$ requires two moles of lime. In case of permanent hardness, magnesium salts require one mole each of lime and soda ash, whereas calcium salts require one mole of soda- ash only. So, it can be summarized that for the removal of permanent hardness by Na_2CO_3, no lime is necessary to remove permanent hardness caused by calcium salts only, but some lime is necessary to remove such hardness caused due to the presence of magnesium salts. If there is excess of lime in softened water, the water will become hard due to soluble $Ca(OH)_2$. Hence, it in most essential to add calculated amount of $Cu(OH)_2$ and Na_2CO_3 to the hard water for softening.

Disadvantages of Lime-Soda Process

1. It cannot be used for household purposes as requisite amount of chemicals are not own.
2. It is not fit for many Industrial purposes is the water obtained in super saturated with CaCO3.

2. Zeolite or Permutit Process

This process involves softening of water by n natural or artificial zeolite. Zeolite is hydrated sodium aluminosilicate, $Na_2O.A1_2O_3xSiO_2.yH_2O$($x$ = 2 to 10 and y = 2 to 6). Zeolites are the substance insoluble in water and can exchange calcium and magnesium ions present in hard water with sodium ions when hard water it passed through them. Zeolites are commercially known as permutits and are of two main types:

(a) Natural zeolites. Natural zeolites include, e.g.,
  (i) Thomsonite, $(Na_2O.CaO)\ Al_2O_3.2SiO_2.2.5H_2O$;
  (ii) Natralite, $Na_2O.Al_2O_3.3SiO_2.2H_2O$.

These zeolites are derived from green and by washing, heating and treatment with NaOH.

(b) Synthetic zeolite ne prepared from sodium silicate and sodium aluminate.

Process. The zeolite softener consists of a steel tank packed with a thick layer of loosely packed zeolite over a layer of coarse sand and gravel (Fig. 6.1. The water enters at the top and passes through the bed of zeolite, where following reactions take place.

$$Na_2Z + Ca(HCO_3)_2 \longrightarrow CaZ + 2NaHCO_3$$

$$Na_2Z + Mg(HCO_3)_2 \longrightarrow MgZ + 2NaHCO_3$$

$$Na_2Z + CaCl_2 \longrightarrow CaZ + 2NaCl$$

$$Na_2Z + MgCl_2 \longrightarrow MgZ + 2NaCl$$

$$Na_2Z + CaSO_2 \longrightarrow CaZ + Na_2SO_4$$

$$Na_2Z + MgSO_4 \longrightarrow MgZ + Na_2SO_4$$

where Z = $Al_2Si_2O_8.xH_2O$

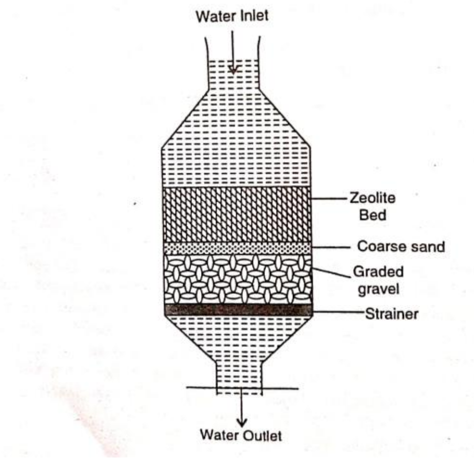


Fig. 6.1. Zeolite Softener.

The process removes both temporary and permanent hardness. The utility of the process lies in the fact that when zeolite bed gets exhausted, it can be regenerated simply by passing 10% solution of sodium chloride through it. The following reaction take place:

$$\underset{\text{Exhausted zeolite}}{CaZ} + 2NaCl \longrightarrow \underset{\text{Regenerated zeolite}}{Na2Z} + CaCl2$$

$$MgZ + 2NaCl \longrightarrow Na_2Z + MgCl_2$$

Advantage

1. The equipment occupies small space and say to operate.
2. The method can even produce zero hardness water.
3. No sludge formation occur during the process.
4. The method in cheap as the permutit can be regenerated.

Disadvantages

1 Treated water contains mere sodium, salt.
2. All acidic ions such as HCO3- and CO32- are left in softened water.
3. Highly turbid water cannot be treated by this method.

Comparison between zeolite process and lime-soda process is summarized in Table 6.3.

Table 6.3. Comparison of Zeolite Process with Lime-soda Process

Zeolite process	Lime-soda process
1. Water of 10-15 ppm residual hardness is obtained.	1. Water of, generally, 15-50 ppm hardness is obtained.
2. Treated water contains larger amount of dissolved salts than in original taw water.	2. Treated water contains lesser amount of dissolved salts.
	3. Capital cost is lower.

3. Cost of plant and material is higher.	
4. Operation expenses are lower.	4. Operation expenses are higher.
5. It cannot be used for treating acidic water, because the permutit material undergoes disintegration.	5. There is no such limitation.
6. The plant occupies less space.	6. Plant occupies more space.
7. The raw water to be softened must be free from suspended matter otherwise the pores of permutit material are blocked and the bed loss its exchange capacity.	7. There is no such limitation.
8. It involves no problem of settling, coagulation, filtration and removal of the sludge and precipitates.	8. In involves difficulty in settling, coagulation, filtration and removal of the precipitates.

3. Organic Ion Exchange Method

Organic ion exchange resins are complex organic molecules having giant hydrocarbon frame work with either acidic group (-SO_3H or –COOH) or basic group (OH^- or NH_2^-) attached to them. The resins with acidic group are capable of exchanging the H^+ ions for the cations and are called **cation exchangers.** They are represented as H^+**-resin.** The resins with basic group are capable of exchanging their OH^- or NH_2^- ions for other anions and are called **anion exchangers.** They are represented as **HO^- -resin.**

Process. The hard eater is passed first through cation exchange column, which removes all the cations like Ca2+. Mg2+, etc. from it, and equivalent amount of H+ ions are released from this column to water. Thus:

$$2RH^+ + Ca^{2+} \longrightarrow R2Ca^{2+} + 2H^+$$
$$2RH^+ + Mg^{2+} \longrightarrow R2Mg^{2+} + 2H^+$$

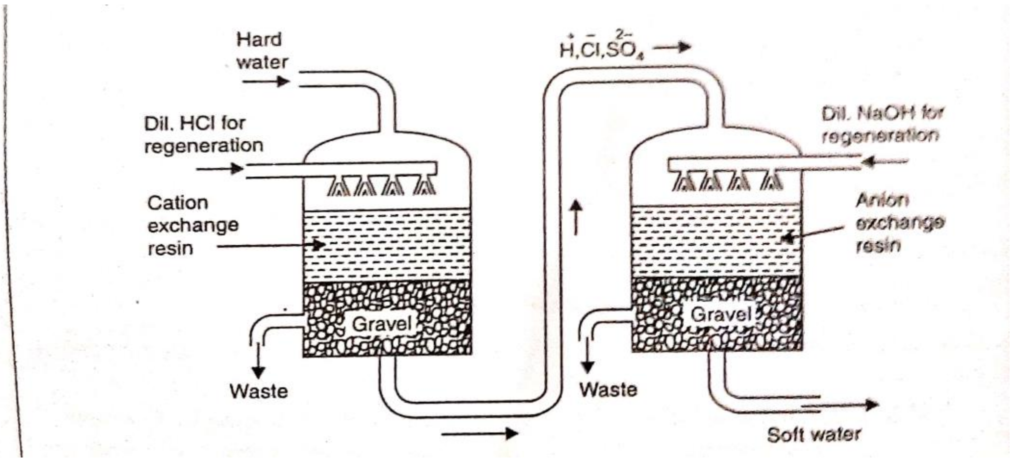


Fig. 6.2. Removal of hardness by the organic ion exchangers.

After cation exchange column, the hard water is passed through anion exchange column, which removes all the anions like SO_4^{2-}, Cl^-, etc. present in the water and equivalent amount of OH^- ions are released from this column to water. Thus:

$$R'OH^- + Cl^- \longrightarrow R'Cl^- + OH^-$$

$$2R'OH^- + SO_4^{2-} \longrightarrow R_2'SO_4^{2-} + 2OH^-$$

$$2R'OH^- + CO_3^{2-} \longrightarrow R_2'CO_3^{2-} + 2OH^-$$

H^+ and OH^- ions (released from cation exchange from anion exchange column respectively) combine to produce water molecules.

$$H^- + OH^+ \longrightarrow H_2O$$

Thus, the water coming out from the exchanger is free from mineral contains as well as anions. Ion-free water, is known as deionized or demineralized water.

Regestration. When capacities of cation and anion exchangers to exchange H^+ and OH^- ions respectively are lost, they are then said to be exhausted.

The exhausted cation exchange column is regenerated by passed a solution of dil. HCI or dil. H_2SO_4. The regeneration can be represented as:

$$R_2Ca^{2+} + 2H^+ \longrightarrow 2RH^+ + Ca^{2+}$$

The column is washed with deionized water and washing (which contains Ca2+, Mg2+, etc. ions) is passed to sink or drain.

The exhausted anion exchange column is regenerated by passed a solution of dil. NaOH. The regeneration can be represented as:

$$R_2'SO_4^{2-} + 20H^- \longrightarrow 2ROH^- + SO_4^{2-}$$

The column is washed with deionised water and washing (which contains Na^+ and SO_4^{2-} or Cl^- ions) is passed to sink or drain.

The rerenernted ion exchange resins are then used again.

Advantages

1. The process can be used to soften highly acidic or alkaline water.
2. It products water of very low hardens (about 2 ppm). So it is very rood for treating water for we in high-pressure boilers.

Disadvantages

1. The equipment is costly and more expensive chemicals are needed.
2. If water contains turbidity, then the output of the process is reduced. The turbidity must be below 10 ppm. If it is more, it has to be removed first by coagulation and filtering.

6.10 BOILER FEED WATER

For steam generation, boilers are almost invariably employed in industries. The boiler feed water requires following conditions to be met before being used as feed water.

(i) Hardness of water should be below 0.2 ppm.
(ii) Caustic alkalinity should be between 0.15-0.45 ppm.
(iii) Soda alkalinity should lid between 0.45-1.00 ppm.
(iv) Excess soda ash should be 0.3-0.5 ppm.

When the natural water without any pretreatment is directly fed into the boiler, various physical as well as chemical reactions in boiler water take place with the action of heat. This results in following defects:

1. Scale or Sludge Formation

In a boiler, water is continuously converted into steam, increasing the concentration of salts. A stage is reached when the change into a loose and slimy precipitate called sludges and if these are hard adhering coatings, these are called scaler. Thus scales are hard deposits, which stick very firmly to the inter surfaces of the boiler. On the basis of chemical composition, scales formed in the boiler units can be divided into following groups:

(a) Alkaline earth metal scales. These consist the compounds such as $CaCO_3$, $CaSO_4$, $CoSiO_3.(PO_4)_2$, $Mg(OH)_2$, $Mg_3(PO_4)_2$, $3MgO.2SiO_2.H_2O$. These substances are precipitated from the solution and get deposited on a hot or cooled surface. These are formed as:

$$Ca(HCO_3)_2 \longrightarrow \underset{\text{Scale}}{CaCO_3}\downarrow + H_2O + CO_2\uparrow$$

$$MgCl_2 + 2H_2O \longrightarrow \underset{\text{Scale}}{Mg(OH)_2}\downarrow + 2HCl\uparrow$$

(b) Iron-oxide scales. These consist of iron oxides, iron silicates and run phosphates. These are farmed due to the presence of iron impurities in feed water.

(c) Silicate scales. Silica present in feed water forms scale with calcium forming calcium silicate and with aluminum forming sodium aluminum silicate.

Effect of Scale or Sludge Formation

(i) These are poor conductors of hunt so they hinder the flow of heat from source to water.
(ii) Scales decrease the efficiency of Boiler by closing the Boiler tubes.
(iii) Due to scales, boiler plates are overheated which reduces the life of the plates.

2. Toiler Corrosion

Boiler corrosion in decay of boiler material by a chemical or electrochemical attack of its environment. Main reason for boiler corrosion are:

1. Dissolved oxygen. Water usually contains about 8 mL of dissolved oxygen point litre at room temperature. Dissolved oxygen in water, in presence of prevailing high temperature, attacks boiler material.

$$2Fe + 2H_2O + O_2 \longrightarrow 2Fe(OH)_2\downarrow$$
$$\underset{\text{Ferrous hydroxide}}{4Fe(OH)_2\downarrow + O_2} \longrightarrow \underset{\text{(Rust)}}{2[Fe_2O_3.2H_2O]\downarrow}$$

Removal of dissolved oxygen. (i) By adding calculated quantity of sodium sulphite or hydrazine sodium sulphide, following reaction occurs.

$$2Na_2SO_3 + O_2 \longrightarrow 2Na_2SO_4$$

$$\underset{\text{Hydrazine}}{N_2H_4} + O_2 \longrightarrow N_2 + 2H_2O$$

$$Na_2S + 2O_2 \longrightarrow Na_2SO_4$$

Hydrazine is an ideal internal treatment chemical for the removal of dissolved oxygen. It reacts with oxygen, forming nitrogen and water. Nitrogen is harmless. Consequently, hydrazine remover oxygen without increasing the concentration of dissolved solids/salts. While with sodium sulphite ar sodium sulphide, the sodium sulphate so formed is liable to decompose giving SO2, particularly in high pressure boilers. The SO_2 enter the term pipes and appears as sulphurous acid (H_2SO_3) in the term condensate.

(i) By mechanical deaeration, i.e., spraying water in a perforated plate-fitted tower, heated from sides and connected to vacuum pump High temperature, low pressure and larger exposed surface provided by perforated plates reduces the dissolved oxygen in water.

2. Dissolved carbon dioxide. CO_2 forms carbonic acid, which has a slow corrosive effect on the boiler material. Carbon dioxide is also released inside the boiler if water used for steam generation contains bicarbonate e.g.,

$$CO_2 + H_2O \longrightarrow H_2CO_3$$
$$Mg(HCO_3)_2 \xrightarrow{\text{heat}} MgCO_3 + H_2O + CO_2$$

Removal of Co_2 (i) By adding calculated quantity of ammonia.

$$2NH_4OH + CO_2 \longrightarrow (NH_4)_2CO_3 + H_2O$$

(ii) By mechanical deaeration process along with oxygen.

3. Acids from dissolved salts. Water containing dissolved magnesium salts liberate acids on hydrolysis For example,

$$MgCl_2 + 2H_2O \longrightarrow Mg(OH)_2\downarrow + 2HCl$$

The liberated acid react with iron (of the boiler) in chin-like reaction producing HCl main and again. Thus:

$$Fe + 2HCl \longrightarrow FeCl_2 + H_2\uparrow$$
$$FeCl_2 + 2H_2O \longrightarrow Fe(OH)_2\downarrow + 2HCl$$

Consequently, presence of even small amount of $MgCl_2$ will cause entre of iron to a large extent.

4. Priming and Foaming

When a boiler is producing team very rapidly, some water parties are carried with the steam. This process of wet steam formation la called priming. It is caused by:

(i) The presence of large quantities of all sulphate and chloride in water
(ii) sudden boiling
(iii) sudden increase in steam production rate
(iv) improper boiler design.

Foaming is the persistent formation of foam or bubbles in the boiler which do not break easily. Foaming is due to the presence of all which generally reduce the surface table of water is boiler. Due to priming and foaming, as steam emerges from the surface of the water, it is associated with tiny droplets of water. Such team is called wet steam. Such carrying over of water by steam along with the suspended and dissolved solids is called carry over.

Effect of Priming and Foaming

(i) A considerable amount of heat is wasted by the removal of hot water.
(ii) Water reduces superheat of team in the super heaters.
(iii) Water takes along with it grit which impinges upon the surface at high Velocity and damage the walls of the cylinders Priming.
(iv) Water contains considerable amount of dissolve solids which gradually get deposited and the deposits restrict the postage in the pipelines, causing, corrosion and insulation.
(v) Foaming of water makes it difficult to know the exact height of water in the guage glass.

Priming and foaming can be prevented by following method:

(i) Addition of antifoaming agents like castor oil.
(ii) Mechanical purifiers easily check priming.
(iii) Addition of compounds like sodium aluminate.
(iv) Avoiding rapid change in steaming rate.

5. Caustic Embrittlement

It is the intercrystalline cracking of the boiler metal from the caustic attack and is caused by using highly alkaline water and high pressure in boiler. During water softening by lime-soda process, free sodium carbonate in generally left in small proportion in softened water which decomposes to NaOH und Co_2.

$$Na_2CO_3 + H_2O \longrightarrow 2NaOH + CO_2$$

The NaOH containing water flown into the small cracks of boiler dissolving the iron of surrounding area inside the boiler. At these areas corrosion takes place in such a manner that intergranular cradles occur in an irregular alia, this is called caustic embrittlement. It can be prevented by following methods:

(i) Tannin or lignin should be added in boiler feed water.
(ii) During softening process sodium phosphate should be used in place of sodium carbonate.
(iii) Sodium sulphate should be added to water. This prevent hair crack in the boiler.

6.11 WATER FOR DRINKING PURPOSES

Water supplied for human consumption should be free of colour, turbidity, taste odour and pathogenic bacteria. It should also be relatively free of hardness, Water being a good solvent dissolves minerals and picks up contaminants as it passes through the earth. The contaminants may include bacteria, algae, viruses, fungi and manmade chemical pollutants. It becomes in this way a natural carrier for a number of human and animal infections particularly of the entire group of intestinal tract diseases. Therefore, it is very important to treat water for removal of these contaminants. The various steps for treatment of water for purifications are discussed below:

Steps For Treatment of Water

1. Screening

The first step in purifying sure water in to remove large debris like sticks, leaves, trash, fish, etc. by passing raw water through screen with small holes. Ground water does not need screening before other purification steps Virtually all modern water supplies for urban communities are drawn from surface sources rather than from underground.

2. Storage

Water from rivers may be stored in reservoirs for periods between a few days and many months to allow natural biological purification to take place. During storage solid impurities also settle down. Many bacteria find water an unnatural habitat and decrease in a storage reservoir through simple devitalization.

3. Coagulation and Sedimentation

Natural storage alone cannot accomplish complete purification of water. Therefore, artificially controlled sedimentation basins are used for further removal of suspended impurities. In these, the conditions of entrance and exit are carefully regulated. In order to facilitate settling, artificial stimulation of the settling is provided through introduction of native chemicals called **coagulants.** The primary purpose of coagulants is to provide a nucleus for agglomeration of suspended particles and increase their specific gravity to cause more rapid settling. The joining of particles so that they form larger settleable particles is called **flocculation** and the larger formed particles are called **floc.** One of the commonest coagulant is ordinary alum or aluminum sulphate. It is one of the best and almost universally applied chemical for purposes of coagulation Some other coagulants are iron (III) sulphate or chloride, lime, etc.

As particles settle to the bottom of the basin, a layer of sludge is formed on the floor of the tank. The amount of sludge that is generated is quite large. It may be upto 3-5% of the total volume of water that is treated. The sludge is removed from the bottom of the tank from time to time.

4. Filtration

After removal of most floe by sedimentation, the water is subjected to filtration to remove remaining suspended particles and unsettled floc. The most common type of filter is a **rapid sand filter.** In this type of filter water moves vertically through sand which often has layer of activated carbon above the sand. The top layer removes compound which impart taste and odour to the water. The space between and particles is larger than the size of the suspended particles. Most particles pass through the surface layer but are trapped in pure spaces or adhere to sand particles So, it is not just the top layer of the filter that cleans the water, but effective filtration extend into the depth of the filter The filter is cleaned by back flushing i.e., by passing water through the filter in the direction opposite to the normal direction.

When sufficient land and space is available, water may treated through **slow sand filters.** Slow sand filters are constructed using graded layers of sand with the coarsest at the base and finest at the top. Slow and filters rely on biological treatment processes for their action rather than physical filtration. When a new slow sand filter is brought into use, raw water is circulated through the filter. Within a few hours, a film of bacteria, fungi and algae builds on the surface of the sand. It is this layer that remove all the impurities. A slow sand filter may remain in service for many weeks or even months.

5. Disinfection

Water after filtration is subjected to disinfection Water is disinfected to destroy pathogens which passed through the filters Possible pathogens include bacteria, protozoans and viruses.

Chlorine gas and **sodium hypochlorite** are the most commonly used disinfectant because they are exceedingly cheap, and their action is rapid. They are effective in killing bacteria but have limited effectiveness against protozoans. Chlorine gas and sodium hypochlorite both have strong disinfectant residuals in the water even when water enters the distribution system. The main drawback in using chlorine on or sodium hypochlorite is that these react with organic compounds in the water to form potentially harmful levels of the chemical by-products trihalomathanes and haloacetic acid, both of which are carcinogenic. Chlorine also imparts some offensive taste and odour to the water. Formerly, it was common practice to chlorinate water at the beginning of the purification process, but this practice has been mostly abandoned to minimize the formation of trihalomethanes.

Ozone, a very strong and wide spectrum disinfectant, is used in many developed countries to disinfect water. It is most effective against prozoans and works well against almost all other pathogens. Other advantages of ozone a disinfectant are that it does not form any dangerous by-products and does not import any taste or dour to the water. One of the main problems with ozone is that it leaves no disinfectant residual in the water.

Ultra-violet (UV) radiation can also be used to disinfect water. It is very effective and can destroy even viruses. The main drawback of UV radiation is that like ozone it also leaves no disinfectant residual in water.

SUMMARY

- The two major sources of water for industry are surface water and ground water.
- **Soft Water.** Water which produces lather with soap solution readily.
- **Hard Water.** Water which does not produce lather with soap solution readily.
- The concentration of hardness constituting impurities is usually expressed in terms of equivalent amount of $CaCO_3$.
  $CaCO_3$ equivalent of a hardness causing impurity

$$= \frac{\text{Weight of impurity}}{\text{Equivalent mass of the impurity}} \times 50$$

- **Priming and Foaming.** The process of wet steam formation is called priming, and the persistent formation of foam or bubbles is called forming.
- **Caustic Embrittlement.** The inter crystalline cracking of the boiler metal from the caustic attack.

REVIEW QUESTIONS

1. What are the units in which degree of hardness is expressed?
2. Why should water be softened before use in boilers?
3. Describe the organic ion exchange process for treating hard water.
4. Describe the method for determination of derree of hardness by soap solution.
5. How is temporary hardness determined by Hehnar's method?
6. How are boiler scales formed? Discuss the four disadvantages of scale formation in boilers.
7. 50 mL of a sample of water required 20 mL of N/50 H_2SO_4 for complete neutralization. Calculate the degree hardness of water.
8. What is the carbonate and non-carbonate hardness of a sample of water containing:

   $Ca(HCO_3)_2$ = 15.2 mg/L ; $Mg(HCO_3)_2$ = 8.4 mg/L

   $MgSO_4$ = 9.5 mg/L ; $CaCl_2$ = 14.8 mg/L

9. 100 mL of water sample has a hardness equivalent to 12.5 mL of 0.02 N $MgSO_4$. Calculate the hardness in ppm.

7 SOLUTIONS AND COLLOIDS

LEARNING OBJECTIVES

- Solution, Solute and Solvent
- Methods of Expressing the Concentration of a Solution
- Colloidal State
- Phases of Colloidal Solution
- Classification of Colloids
- Preparation of Colloidal Solutions
- Purification of Colloidal Solutions
- Properties of Colloidal Solutions
- Coagulation of Colloidal Solutions
- Interaction between Colloids – Gold Number
- Gels
- Applications of Colloids
- Emulsions

7.1 SOLUTION, SOLUTE AND SOLVENT

A solution is a homogeneous mixture of two or more pure substances whose composition may be altered within certain limits. Though the solution is homogeneous in nature, yet it retains the properties of its constituents. The substances which make up the solution are generally called its components. The solution of two components is referred to as binary solution. Similarly, the solutions of three and four components are called ternary and quaternary solutions respectively. The two components of the binary solutions are respectively called a solvent and a solute. **Solvent** is that component in the solution whose physical state is the same as that of the resulting solution while the other component is called **solute.** For solutions in which both the components have the same physical state as that of solution, the component which is in excess is called **solvent** and the other one is called **solute.** For example, in case of solution of sugar and water, sugar is the solute and water is the solvent. Each component of binary solution may be in solid, liquid or gaseous state. Consequently, there can be nine different types of solutions as shown in Table 7.1.

Type of Solution	Solvent	Examples
Gaseous Solutions	Gas	
• Solid in gas		Sublimation of solid in gas; camphor vapours in N_2 gas
• Liquid in gas		Water vapours in air (mist)
• Gas in gas		Mixture of gases, air
Liquid Solutions	Liquid	
• Solid in gas		Salt in water, sucrose in water
• Liquid in gas		Alcohol in water, mixture of miscible liquids
• Gas in gas		Aerated drinks, CO_2 in water
Solid Solutions	Solid	
• Solid in gas		Alloys; homogeneous mixture of two or more metals
• Liquid in gas		Mercury in zinc, mercury in gold
• Gas in gas		Absorption of gases on metals, solution of hydrogen in palladium

7.2 METHODS OF EXPRESSING THE CONCENTRATION OF A SOLUTION

The concentration of a solution refers to the amount of solute present in the given quantity of solution or solvent. The concentration of the solution may be expressed in any of the following ways:

1. Mass Percentage

Mass percentage may be defined as the number of parts by mass of solute per hundred parts by mass of solution. For example, a 5% (aqueous solution of sugar by mass means that 100 g of solution contain 5 g of sugar.

If W_B be the mass of solute (B) and W_A be the mass of solvent (A), then

$$\textbf{Mass percentage of B} = \frac{W_B}{W_A + W_B} \times 100$$

2. Volume Percentage

This mode of concentration is used in case of solutions when solutes and solvents are both liquids.

Volume percentage may be defined as the number of parts by volume of solute per hundred parts by volume of solution. For example, a 25% solution of ethyl alcohol (by volume) means that 100 cm^3 of the solution contain 25 cm^3 of ethyl alcohol and 75 cm^3 of water.

If V_A and V_B be the volumes of component A and B, then

Volume percentage of B = $\frac{V_B}{V_A + V_B} \times 100$

3. Normality (n)

Normality of a solution is defined as the number of gram-equivalent of the solute present in one litre of the solution. It is represented by N.

Mathematically,

$$\text{Normality (N)} = \frac{\text{Gram-equivalents of solute}}{\text{Volume of soution in litre}}$$

$$= \frac{\text{Mass of solute in gram}}{(\text{Gm. Eq. Mass of solute}) \times (\text{Volume of Solution (L)})}$$

A solution having normality equal to one is called a normal solution. Such a solution contains one yram equivalent of solute per litre of solution. A decinormal solution contain 1/10 gram equivalent of solute per litre of solution. Similarly, a semi- normal solution contains $\frac{1}{2}$ tram equivalent and a centinormal solution contains 1/100 from equivalent per litre of the solution.

I

4. Molarity (m)

Molarity of a solution is defined as the number of gram mole of the solute present in one litre of the solution. It is represented by M.

Mathematically,

$$\text{Molartity (M)} = \frac{\text{Gram-moles of solute}}{\text{Volume of soution in litre}}$$

$$= \frac{\text{Mass of solute in gram}}{(\text{GMM of solute}) \times \text{Volume of Solution (L)}}$$

A solution having molarity one is called molar solution. Such a solution contains one mole of solute per litre of solution. Molarity is expressed in units of **mol L^{-1}** or **mol dm^{-3}**. It may be noted that **both normality as well as molarity of a solution change with change in temperature.**

5. Molality (m)

Molality of a solution may be defined as the number of gram mole of the solute present in 1000 g (1 kg) of the solvent It is represented by m.

Mathematically,

$$\text{Molartity } (m) = \frac{\text{Gram-moles of solute}}{\text{Mass of solvent (kg)}}$$

$$= \frac{\text{Mass of solute (g)}}{(\text{GMM of solute}) \times (\text{Mass of solvent (kg)})}$$

A solution containing one mole of solute per 1000 g of solvent has molality equal to one and is called a molal solution Molality is expressed in units of moles per kilogram **(mol k^{-1})**. The **molality of a solution does not change with temperature.**

6. Formality

Formality of a solution may be defined as the number of gram formula masses (moles) of the ionic solute present in one litre of the solution. It is represented by F.

Mathematically,

$$\text{Formality (F)} = \frac{\text{Number of gram formula masses of solute}}{\text{Volume of solution in litres}}$$

$$= \frac{\text{Mass of ionic solute (g)}}{(\text{Gm. formula mass of solute}) \times (\text{Volume of Solution (L)}}$$

Commonly, the term formality is used to express the concentration of the ionic solids which do not exist as molecules but exist as ions. A solution containing one gram formula mass of solute per litre of the solution has formality equal to one and is called formal solution. It may be mentioned here that like normality and molarity, **the formality of a solution changes with change in temperature.**

7. Parts Per Million (ppm)

When a Solute in present in very minute amounts, its concentration is expressed in part per million. It may be defined in the number of parts by means of Solute per million parts by man of the solution. It is abbreviated as ppm.

$$\text{Parts per million (ppm)} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$$

This mode of concentration is generally used to express very low concentration such as hardness of water or concentration of Cl_2 in public supply of potable water.

SOLVED EXAMPLES BASED ON DIFFERENT MODES OF CONCENTRATION

Example 7.1. An aqueous solution of glucose in labelled as 10 percent W/W. If density of solution is 1.2 g mL^{-1} calculate the molarity and molality of solution. Also calculate the mole fraction of each component.

Solution. Molar mass of glucose $C_6H_{12}O_6$ = 180 g mol^{-1}

Mass of solution = 100 g

Mass of solute (W_B) = 10 g

Moles of solute $= \frac{10}{180}$

Mass of solvent (W_A) = 100 – 10 = 90 g

Volume of solution (V) $= \frac{\text{Mass}}{\text{Density}} = \frac{100}{1.2} = 83.33 \text{ mL} = \frac{83.33}{100} \text{ L}$

Molarity of solution $= \frac{\text{Moles of solute}}{\text{Volme of solution in litres}}$

$= \frac{10 \times 100}{180 \times 83.33} = \mathbf{0.66M}$

Molality of solution $= \frac{\text{Moles of solute}}{\text{Mass of solvent in kg}}$

$= \frac{10}{180} \times \frac{1000}{90} = 0.617 \text{ m}$

Mole of solute n_B $= \frac{10}{180} = 0.055$

Mole of solvent nA $= \frac{90}{18} = 5.0$

Mole fraction of glucose $= \frac{0.055}{5+0.055} = \mathbf{0.0108}$

Mole fraction of water $= \frac{5}{5.055} = \mathbf{0.9892.}$

7.3 COLLOIDAL STATE

Thomas Graham (1861) studied the process of diffusion of dissolved substances through a parchment paper or an animal membrane. He divided substances into two classes:

(i) Crystalloids and (ii) Colloids

Substances like sugar, urea, common salt, etc. which readily passed through the membrane while in the dissolved state were called **crystalloids.** Substances like starch, glue, geltin, etc., which in the dissolved state either do not pass at all or pass through very slowly were called **colloids.**

This arbitrary division substances into crystalloids and colloids was soon proved to be wrong since a crystalloid could behave as a colloid under different conditions and vice versa. For example, common salt, a typical crystalloid in an aqueous solution, behaves as a colloid in the benzene medium while soap, a typical colloid in water behaves as a crystalloid in alcohol. A colloidal substance therefore, does not represent a separate class of substances. We now speak of the colloidal state of matter in which every substance can be obtained by a suitable method. The nature of the substance whether colloid or crystalloid depends upon site of the solute particles. **When the site of solute particles lies between 1 to 1000 nm, it behaves as a colloid.** On the other hand, if size of solute particles is greater than 1000 nm, it exists as suspension and if particle site is less than 1 nm, it exists as true solution and behave like a crystalloid. Thus, colloid is not a substance but is a particular state of the substance which depends upon site of its particles. The colloidal state in intermediate state between true solution and suspension. A comparison between suspension, colloidal solution and true solution has been given in Table 72.

Table 7.2. Distinction between True Solutions, Colloidal Solutions and Suspensions

Name of Property	True solutions	Colloidal Solutions	Suspensions
1. Size of particles	The solute particles in true solutions are molecules having size less than 1nm.	The particles size in colloidal solution lies in the range of 1nm to 1000 nm.	The size of the particles in the case of suspension is greater than 1000 nm.
2. Visibility	The solute particles are invisible to the naked eye as well as under the most powerful microscope.	The solute particles are invisible to the naked eye but their scattering effect can be viewed with the help of a microscope	The solute particles are visible even to the naked eye or can be seen with the help of a microscope.
3. Separation	The solute and the solvent cannot be separated from each other by ordinary filtration or ultrafiltration.	The solute and the solvent cannot be seprated from each other by ordinary filtration, but ultra-filtration is possible.	The solute and solvent can be separated by ordinary filtration.
4. Settling	The solute particles in the true solution do not settle.	The solute particles in the colloidal solution can be made to settle by centrifugation.	The solute particles in the suspension settle under gravity.
5. Filterability	The solute particles in the true solution diffuse rapidly, pass through a parchment	The solute particles in the colloidal solution do not pass through a	The solute particles in the suspension cannot pass the through a

	membrane as well as through filter paper.	parchment membrane, but pass through a filter paper.	parchment membrane or a filter paper.
6. Tyndall effect	True solution does not show Tyndall effect.	Colloidal solution shows Tyndall effect.	Suspension may or may not show. Tyndall effect.
7. Brownian movement	True solution does not show Brownian movement.	Colloidal solution shows Brownian movement.	Suspension may show Brownian movement.

7.4 PHASES OF COLLOIDAL SOLUTION

It may be noted that colloidal solution is heterogeneous in nature and always consists of at least two phases: the disperse phase and the dispersion medium.

(a) Disperse Phase: It is the component present in small proportion and consists of particles of colloidal dimensions (1-1000 nm).

(b) Dispersion Medium: The medium in which colloidal parties are disposed is called dispersion medium. In a colloidal solution of sulphur in water sulphur particles constitute disperse phase and water constitutes dispersion medium.

It may be mentioned here that the specific surface area of substance in colloidal state in very large. For example, let us consider a solid lump of the site one centimetre cube. The surince area of this lump will be 6 cm^2. When the same lump is broken into smaller particles of colloidal dimensions (say 1 nm cube size), the total surface area becomes 6×10^7 cm^2.

7.5 CLASSIFICATION OF COLLOIDS

Colloids may be classified into very types on the base of following criteria

1. Physical state of dispersed phase and dispersion medium.
2. Nature of interaction between disperse phase and dispersion medium.
3. Nature of colloidal particles.

Classification Based on Physical States of Disperse Phase and Dispersion Medium

The two phases namely, dispersed and dispersion can be solid, liquid or a gas Thus, different types of colloidal solutions are possible depending upon the physical state of the two phases. Such types of colloidal solutions are shown in Table 7.3. It is shown be borne in mind that gases between themselves cannot form a colloidal solution due to their property of diffusion to give homogeneous mixtures.

Table 7.3. Types of Colloidal Solutions

Dispersed Phase	Dispersion Medium,	Common Name	Examples
Solid	Solid	Solid sol	Coloured gems and glasses, some alloys, rock salt.
Solid	Liquid	Sol	Arsenious sulphide sol, gold sol, starch, paints muddy water.
Solid	Gas	Aerosol	Smoke, dust storm.
Liquid	Solid	Gels	Jellies, cheese, iron, hydroxide, shoe polish
Liquid	Liquid	Emulsion	Milk, cod liver oil.
Liquid	Gas	Liquid aerosol	Mist, fog, cloud, insecticide sprays.
Gas	Solid	Solid foam	Pumicestone, occluded gases, rubber.
Gas	Liquid	Foam	Soap lather, whipped cream, lemonade froth.

The colloidal solutions having fluid like appearance are called **sols.** The dispersion medium in sols is generally liquid. Colloids are sometimes given specific names depending upon the nature of the dispersion medium. Some common examples are given below:

Dispersion Medium	Name of Colloids
Water	Hydrosols or Aquasols
Alcohol	Alcosols
Benzene	Benzosols
Gases	Aerosols

Classification Based on Nature of Interaction between Disperse Phase and Dispersion Medium

Depending upon the interaction between the disperse phase and the dispersion medium, the colloidal sols are classified into two types:

1. Lyophilic sols
2. Lyophobic sol

1. Lyophilic Sols

In the type of colloidal cols, the disperse phase has great affinity for the dispersion medium. In such colloid, the dispersed phase does not get easily precipitated and the sols are quite stable. The solids obtained after evaporation may be reconverted to the sol state by simply agitating them with the dispersion medium. Examples of lyophilic sols include sols of gum, gelatin starch, proteins and certain polymers in organic solvents. Such sols are called **reversible sols**. If water is the dispersion medium, these are called hydrophilic sols.

2. Lyophobic Sols

In this type of sols, disperse phone has little affinity for the dispersion medium. These sols are relatively less stable than lyophilic sols. These sols are early precipitated (or coagulated) on the addition of small amounts of electrolytes, by heating or by shaking These are irreversible as their precipitated mass cannot be brought back into the colloidal state by simply shaking them up with the dispersion media. Hence, these sols are called **irreversible sols.** Examples of lyophobic sols include sols of metals, and their insoluble compounds like sulphides and oxides. They need stabilizing substances for preservation. If water is the dispersion medium, these are known as hydrophobic sols.

The distinction between lyophilic and lyophilic sols is given in Table 7.4.

Table 7.4. Distinction between Lyophilic and Lyophobic Sols

Lyophobic Sols	Lyophilic Sols
1. They are irreversible sols.	1. They are reversible sols.
2. They are less stable and get coagulated by electrolytes, by heating or by agitating.	2. They are quite stable are not easily coagulated by electrolysis.
3. They are prepared by indirect methods which ar not so easy.	3. They are obtained by simple solution method, e.g., starch solution.
4. They are obtained from inorganic materials such as metals, metal sulphides, metal hydroxides etc.	4. They are obtained from organic materials such as starch, gum, gelatin, etc.
5. These are unstable and hence require stabilizers.	5. These are self-stabilized.
6. The particles are not hydrated.	6. The particles are hydrated.

Classification Based on Nature of the Particles of the Dispersed Phase

Depending upon nature of the particles of the dispersed phase, the colloidal solutions are classified as:

1. Multimolecular colloids,

2. Macromolecular colloids and

3. Associated colloids.

1. Multimolecular Colloids

In this type of colloids, colloidal particles are aggregates of atoms or small molecules with molecular size less than I nm. For example, a gold sol consists of particles of various sizes which are clusters of several gold atoms. A sol of sulphur consists of colloidal particles which are aggregates of S_8 molecules. These molecules in the aggregate are held by van der Waal's forces.

2. Macromolecular Colloids

In this type of colloids, colloidal particles are themselves large molecules having colloidal dimensions. They have very high molecular masses varying from thousands to millions. Naturally occurring macromolecules are such as starch, protein and cellulose. Artificial macromolecules consist of polymers such as polyethylene, nylon, plastics, polystyrene, etc. These colloidal solutions resemble true solutions in some respects.

3. Associated Colloids

There are certain substances which behave as normal, strong electrolytes at low concentration but at higher contention they behave as colloidal solutions due to the formation of aggregated particles. Such colloids are called associated colloids and the aggregated particles are called **micelles.** Soaps and detergents are example of associated colloids.

A micelle may be defined as the cluster or aggregated particles formed by associated colloids in solutions. The formation of micelle takes place above certain concentration called **Critical Micellization Concentration (CMC)** and above a particular temperature called **Kraft Temperature (T_k).** Every micelle system has a specific value of CMC.

Mechanism of Micelle Formation

Micelles are generally formed by the specific type of molecules which have hydrophilic as well as hydrophobic ends. Such molecules are known as surface active molecules or surfactant molecules. Sodium oleate, $C_{17}H_{33}COO^- Na^+$ (one of the soaps) is a typical example of such type of molecules. The long hydrocarbon part of oleate radical ($C_{17}H_{33}$ -) is hydrophobic and while COO- part is hydrophilic end. When the concentration of the solution is below its *CMC* (3×10^{-3} mol L^{-1}) sodium oleate behave as normal electrolyte and ionises to give Na^+ and $C_{17}H_{33}COO^-$ ions. As the concentration exceeds *CMC,* the hydrophobic parts starts receding away from the water and are made to approach each other. However, the polar COO^- part tend to interact with the water. This ultimately leads to the formation of the duster having the dimension of the colloidal particles. In each such cluster a large number of (usually 100 or more) oleate groups are clumped together in a spherical manner so that their hydrocarbon parts interact with one another but COO^- parts remain projected in water.

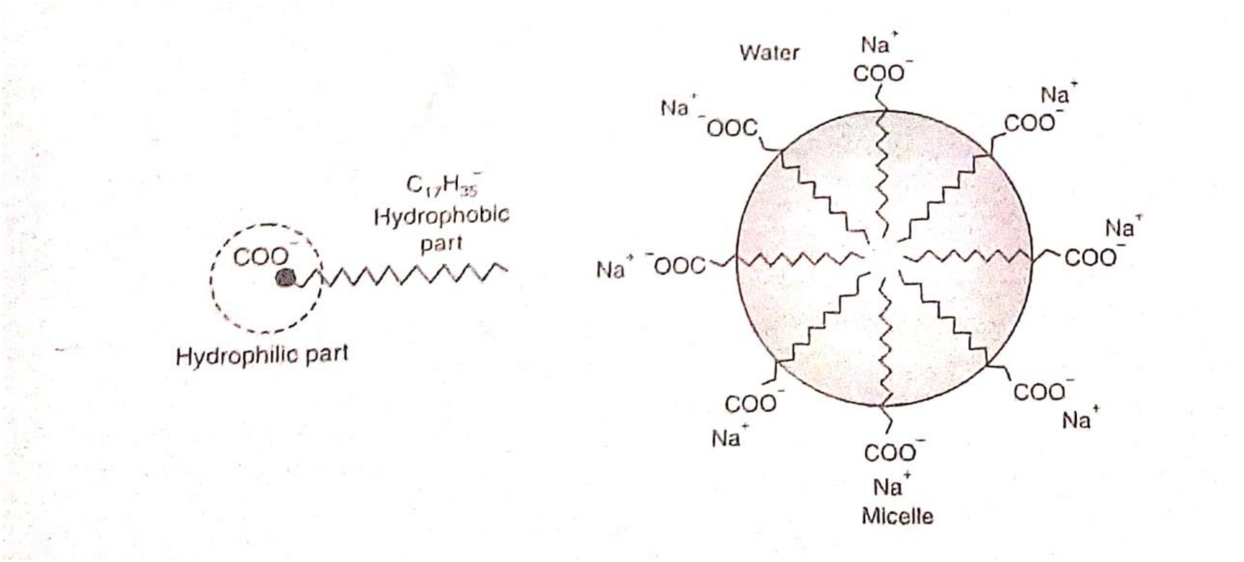


Fig. 7.1. Micelle formation by aggregation of $RCOO^-$ ions.

Some other examples of micelle systems are:
1. Sodium lauryl sulphate; $CH_3\ (CH_2)_{11}\ SO_4^-\ Na^+$
2. Sodium stearate; $CH_3\ (CH_2)_{16}\ COO^-\ Na^+$
3. Cetyl trimethyl ammonium bromide; $CH_3\ (CH_2)_{15}\ (CH_3)_3\ N^+\ Br^-$.

7.6 PREPARATION OF COLLOIDAL

For the preparation lyophobic and lyophilic sols different types of methods are employed.

Preparation of Lyophobic Sols

Lyophobic sols can be prepared by two types of methods

1. **Condensation methods**, and
2. **Dispersion methods.**

1. Condensation Methods

In this type of methods particles of atomic or molecular site are induced to combine to form aggregates having colloidal dimensions. For this purpose chemicals as well as physical methods can be applied.

(a) **By Chemical Methods**

Colloidal solutions can be prepared by chemical reactions involving, double decomposition oxidation, reduction and hydrolysis.

(i) Double decomposition. A colloidal sol of arsenious sulphide is obtained by passing hydrogen sulphide into a solution of arsenious oxide in distilled water.

$$As_2\ O_3 + 3H_2S \longrightarrow As_2S_3 + 3H_20$$

Sols of silver halides are obtained by mixing dilute solutions of silver salts and alkali halides in equivalent amounts. Silica gel sol is prepared by this method between dilute solutions of sodium silicate and HCI.

(ii) Oxidation. A colloidal solution of sulphur can be obtained by passing hydrogen sulphide into a solution of sulphur dioxide in water or through a solution of an oxidizing agent (bromine water, nitric acid, etc.)

$$SO_2 + 2H_2S \longrightarrow 3S + 2H_2O$$

$$H_2S + [O] \longrightarrow H_2O + S$$

(iii) Reduction. A colloidal solution of a metal like silver, gold and platinum can be prepared by reducing its salt solution with a suitable reducing agent, such as stannous chloride, formaldehyde, hydrazine, etc.

$$2AuCl_3 + 3SnCl_2 \longrightarrow 2Au + 3SnCl_4$$

$$2AuCl_3 + 3HCHO + 3H_20 \longrightarrow \underset{\text{Gold sol}}{2Au} + 3HCOOH + 6HCI$$

(iv) Hydrolysis. This method is used to prepare hydroxides and oxides of weakly electro-positive metals like Fe, Al or Sn. A red sol of ferric hydroxide is obtained by the hydrolysis of ferric chloride with boiling water.

$$FeCl_3 + 3H_20 \rightleftharpoons Fe(OH)_3 + 3HCI$$

(b) By Physical Methods

(i) By exchange of solvent. When a true solution is mixed with an excess of the other solvent in which the solute in insoluble but solvent is soluble, a colloidal solution is obtained. For example, when a solution of sulphur in alcohol is poured in excess of water, a colloidal solution of sulphur is obtained.

(ii) By excessive cooling. The colloidal solution of ice in an organic solvent such as $CHCl_3$, or ether can be obtained by free solution of water in the solvent. The molecules of water which can no longer be held in solution separately combine to form particles of colloidal size.

2. Dispersion Methods

In these methods large particles of the substance are broken into particles of colloidal dimensions in the presence of dispersion medium. Since the sols formed are highly unstable. They are stabilized by adding some suitable stabilizer Some of the methods employed for carrying out dispersion are riven an follow:

(i) Mechanical dispersion. In this method, the course suspension of the substance is brought into a colloidal state in the dispersion medium by grinding it in a colloid mill (Fig. 7.2.), ball mill or ultrasonic disintegrator. The colloid mill consists of two metal dines, close together, rotating at high speed (7,000 revolutions per minute) in opposite direction when the suspension particles are torn off to the colloidal size.

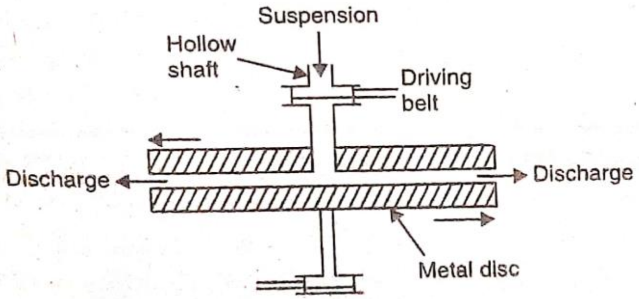


Fig. 7.2. A colloid mill

(ii) Electrical disintegration or Bredig's are method. This process involves dispersion as well as condensation Colloidal solutions of metals such as gold, silver, platinum, etc., can be prepared by thin method. In this method, electric arc is struck between electrodes of the metal immersed in the dispersion medium (Fig. 7.3.). The intense heat produced vaporize some of the [illegible] dal size.

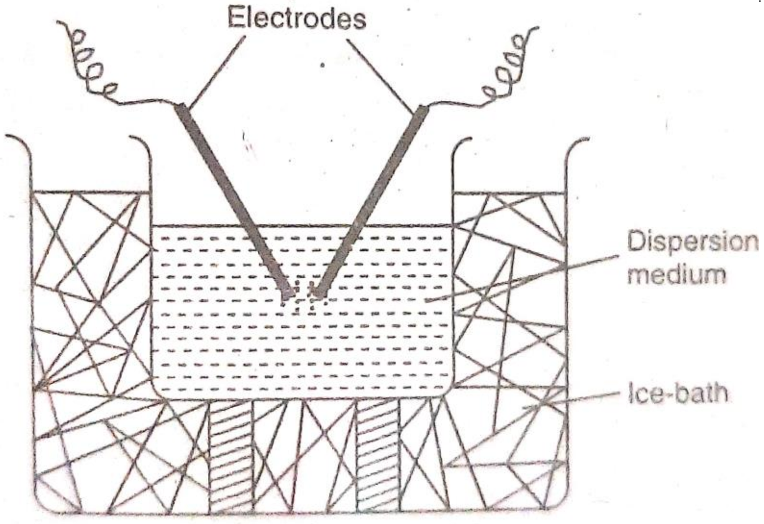


Fig.7.3. Bredig’s method.

(iii) Peptization. Peptization may be defined as the process of converting a precipitate into colloidal form by shaking it with dispersion medium in the presence of small amount of electrolyte. The electrolyte used for this purpose is called peptizing agent. This method is applied, generally, to convert fresh precipitate into colloidal pollution because such precipitates are simply clusters of particles of colloidal size held by weak forces.

Cause of peptization. During peptisation, the precipitate adsorbs one of the ion of the electrolyte on its surface. The adsorbed lon is generally common with those of the precipitate. This causes the development of positive or negative charge on precipitates which ultimately break up into matter particles having the dimensions of colloids. For example, when freshly precipitated Fe(OH)$_3$ is shaken with aqueous solution of FeCl$_3$ (peptizing agent) it absorbs Fe$_{3+}$ ions and thereby break up into small-sized particles of the types [Fe(OH)$_3$]Fe^{3+}. Similarly, a precipitate of AgCl on shaking with dilute solution of AgNO$_3$ absorbs Ag+ ion and get peptized to colloidal particles of the type [AgCl] Ag$^+$. In some cases, peptization can also be achieved by organic solvents. For example, cellulose nitrate is peptized by ethanol. The colloidal solution so obtained is known as collodion.

Preparation of Lyophilic Sols

Lyophilic sols are quite stable and can be easily prepared by shaking the material to be dispersed with dispersion medium. Some examples are: colloidal solutions of gelatin, gum, starch, egg albumin, etc.

7.7 PURIFICATION OF COLLOIDAL SOLUTIONS

The colloidal solutions obtained by various methods are impure and contain impurities of electrolytes and other soluble substances. These impurities may destabilize the sol. Hence, they have to be removed. A very important method of removal of soluble impurities from sols by semi-permeable membrane is known as dialysis.

1. Dialysis

Particles of true solutions can pass through parchment paper or cellophane membrane. On the other hand, sol particles cannot pass through these membranes. A bag made up of such a membrane is filled with the colloidal solution and in then suspended in fresh water. The electrolyte particles pass out leaving behind the colloidal solution.

Movement of ion across the membrane can be expedited by applying electric current through two electrodes (Fig. 7.4). This method is very fast and is known as Electrodialysis.

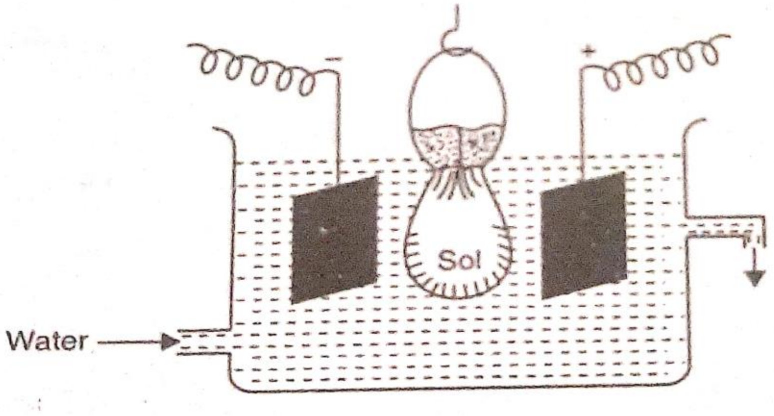


Fig. 7.4. Electrodialysis

2. Ultra Filtration

In this method, colloidal solutions are purified by carrying out filtration through special type of graded filters called ultra-filter. These filter papers allow the electrolytes to pass through them but do not allow colloidal particles. These filter papers are made from ordinary filter papers by impregnating them with colloidal particles. In order to hasten the filtration through such filter papers increased pressure or suction is required.

3. Ultra-Centrifugation

In this method, the colloidal solution is placed in a high speed centrifugal machine. On centrifuging, the colloidal particles settle down. The impurities remain in the centrifugate and are removed. The settled colloidal particles are mixed with water to form the colloidal solution again.

7.8 PROPERTIES OF COLLOIDAL SOLUTIONS

1. Heterogeneous Nature. Colloidal system is of two phases: (a) dispersed phase and (b) dispersion medium. In a colloidal solution, each particle is contained within its own boundary surfaces which separate it from the dispersion medium.

2. Colligative Properties. Due to high average molecular masses of colloidal particles, they give very low mole fractions in colloidal solution. Hence, they possess very low values of colligative properties such as relative lowering of vapour pressure, elevation in boiling point depression in freezing point and osmotic pressure. The molecular man of polymers are determined by osmotic pressure measurements because this is the only colligative property which has significant value and can be conveniently determined experimentally.

3. Filterability. The site of the colloidal particles is less than the pores of the filter paper, and therefore, they easily and through a filter paper. Colloidal particles, however, cannot pass through the parchment paper or an animal membrane or ultra-filter.

4. Optical Properties. Tyndall Effect. Tyndall, in 1869, observed that if a strong beam of light is passed through a colloidal solution placed in dark place, the path of the beam gets illuminated by a bluish light (Fig 76). This phenomenon is called **Tyndall effect**. The phenomena in due to the scattering of light by the colloidal particles.

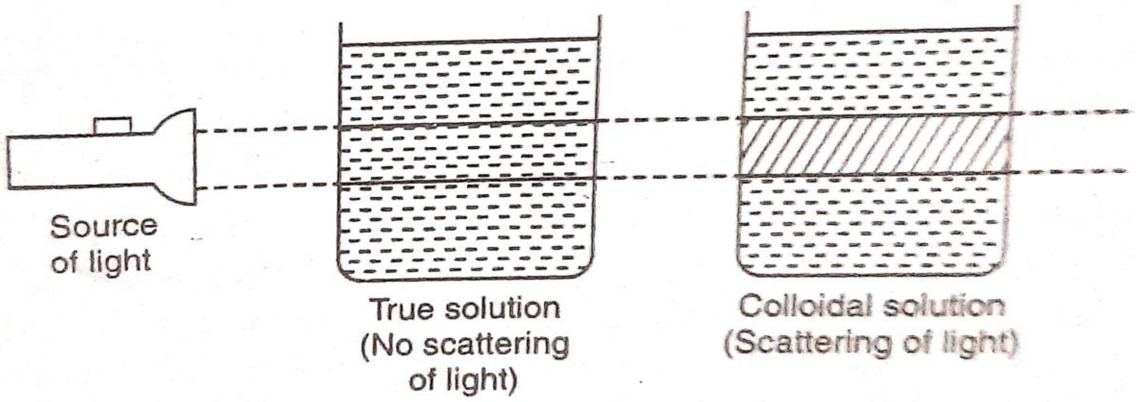


Fig. 7.5. Tyndal effect

The same phenomenon is noticed due to scattering of light by dust particles, when a team of sunlight enter a dark room through a slit.

True solutions do not exhibit Tyndall effect because the particles in them are too small in size and hence do not cause any scattering.

5. Visibility. Colloidal particles are tool small to be seen with naked eye. They however, setter light ad become visible a **bright spots** or **discs of light** against a black background when viewed through an **ultramicroscope**. Zsigmondy (1903) devised this microscope based on the principle of scattering of light by colloidal particles. The arrangement of the instrument is shown in Fig. 7.6. A strong beam of light is focused by a series of lens-combinations on vessel containing the sol. The colloidal solution is seen through a microscope placed at right angle to the beam.

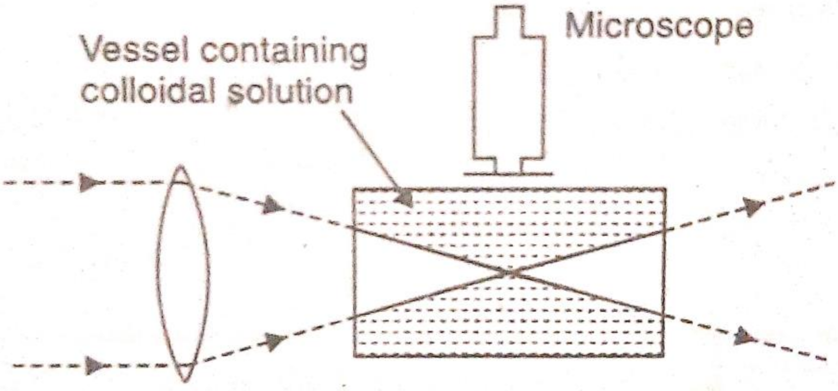


Fig. 7.6. Ultra-microscope

6. Mechanical Properties

(a) Brownian Movement. Robert Brown, a botanist covered in 1827 that pollen grains placed in water do not remain at rest but move about continuously and randomly. Later on, this phenomenon was observed in case of colloidal particles when they were seen under the ultramicroscope. The particles were seen to be in constant motion in zig-zag path in all possible direction (Fig. 7.7). This zig-zag motion of colloidal particles is called **Brownian movement.**

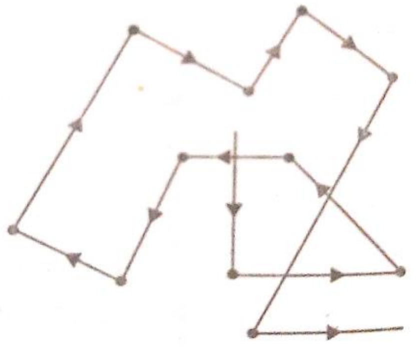


Fig. 7.7. Brownian movement

Cause of Brownian Movement. Brownian movement arises because of the impact of the molecules of the dispersion medium with the colloidal particles. It has been postulated that the impacts of the particles of the dispersion medium on the colloidal particle are unequal which ultimately causes its zig-zag motion. However, as the size of the particle increases, the probability of unequal impacts decreases and the Brownian movement becomes slow. Ultimately, when the dispersed particle becomes bigger enough to acquire the dimensions of suspension, no Brownian movement is observed.

Significance of Brownian Movement

(i) Brownian movement provides a direct demonstration of ceaseless motion of molecules as postulated by kinetic theory.
(ii) It counter the force of gravity acting on colloidal particles and hence helps in providing stability to colloidal sols.

(b) Diffusion. Colloidal particles like solute particles diffuse from a region of higher concentration to that of lower concentration. However, because of their bigger size colloidal particles move slowly and henco diffuse at slower rate.

(c) Sedimentation. Under the influence of gravity, the sol particles tend to settle down very slowly. This rate of setting down or sedimentation can be accelerated by the use of a high speed centrifuge called *ultra-centrifuge.*

7. Electrical Properties

Electrophoresis. The particles of the colloidal solution are electrically charged and carry same type of charge; either positive or negative. The dispersion medium has an equal and opposite charge making the system neutral as a whole. Due to similar nature of the charge carried by the particles, they repel each other and do not combine to form bigger particle. That is why, a sol is stable and particles do not settle down. Arsenious sulphide, gold, skiver and platinum particles in their respective colloidal sols are negatively charged while particles of ferric hydroxide, aluminum hydroxide are positively charged. The existence of the electric charge is shown by the phenomenon of **electrophoresis.** It involves the "movement of colloidal particles either towards the cathode or anode, under the influence of the electrical field". The apparatus used for electrophoresis is shown in Fig. 7.8.

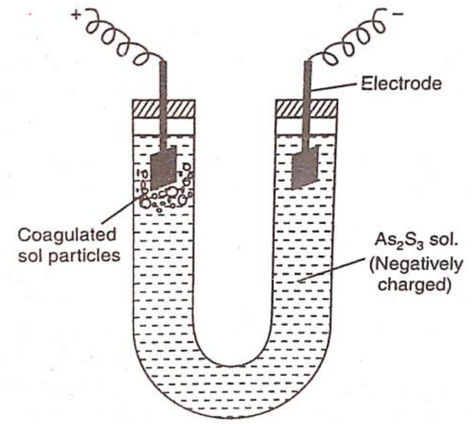


Fig. 7.8. Electrophoresis

The colloidal solution is placed in a U-tube fitted with platinum electrodes. On passing an electric current, the charged colloidal particles move towards the oppositely charged electrode. Thus, if arsenious sulphide sol is taken in the U-tube, its particles move towards the anode.

Origin of charge on colloids. The reasons for the origin of electrical charge on colloidal particles are given below:

(i) Frictional electrification. The rubbing of colloidal particles with molecules of dispersion medium leads to appearance of electrical charges on colloidal particles.

(ii) Electron capture. The colloidal particles may acquire charge by capturing electrons from air or during electro-dispersion in Bredig's are method.

(iii) Preferential adsorption of ions from solutions. An ionic colloid adsorbs ions common to its own lattice structure. Thus, AgCl particles can adsorb Cl^- ions if excess of KCl solution is used for its preparation whereas, if it is prepared by using excess of $AgNO_3$ solution it adsorbs Ag^+ ions from solutions. The sol will be negatively charged if it adsorbs Cl^- ions and positively charged if it adsorbs Ag^+ ions.

Similarly, if $Fe(OH)_3$ sol is prepared by hydrolysis of $FeCl_3$ by hot water, there is adsorption of Fe^{3+} ions and particles acquire positive charge.

On the other hand, if the sol is prepared by adding excess of NaOH solution to $FeCl_3$ solution, then, there is adsorption of OH^- ion and the colloidal particles acquire negative charge.

(iv) Dissociation of surface moleculen. Soaps expel alkali ions to acquire a negative charge Dye particles con dissociate to furnish positive or negative ions in the solution according to their composition.

(v) Dissociation of molecular electrolytes adsorbed on the surface of particles H_2S molecules get adsorbed on sulphides during precipitation. By dissociation of H_2S, hydrogen ions are lost and the colloidal particles become negatively charged due to sulphide (S^{2-}) ions which are left on the colloidal particles.

Some common positively charged and negatively charged colloids are given below:

Positively charged: $Fe(OH)_3$ sol, $Cr(OH)_3$ sol, $Al(OH)_3$ sol, $Ca(OH)_2$ sol, TiO_2, dyes like methylene blue and hemoglobin.

Negatively charged: As_2S_3, Sb_2S_3, CdS, metal sols like Cu, Au, Pt, Ag etc,; and acid dyes, like congo red, starch, clay silicic acid.

7.9 COAGULATION OF COLLOIDAL SOLUTIONS

Presence of small concentrations of appropriate electrolytes is necessary to stabilize the colloidal solutions. However, if the electrolytes are present in higher concentration, then the fun of the electrolyte neutralize the charge on the colloidal particles. Now these colloidal particles may unite together to form biker particles which are then precipitated. **The precipitation of a colloid through induced aggregation by the addition of some suitable electrolyte is called coagulation or flocculation.**

The coagulation of a colloidal solution by an electrolyte does not take place until the added electrolyte has certain minimum concentration in the solution **The minimum amount of the electrolyte in millimoles that must be added to one litre of the sol No as to bring about coagulation is called the coagulation or flocculation value of the electrolyte for the sol.**

Different electrolytes have different coagulation values. Smaller the coagulation value of the electrolyte larger is its **coagulating** or **precipitating power.**

The coagulation behaviour of various electrolytes was studied in details by Hardy and Schulze. They observed that:

(i) The ions carrying charge opposite to that of al particles are effective in causing the coagulation of the sol.

(ii) Coagulating power of an electrolyte is directly proportional to the valency of the active ions, i.e., ions causing coagulation.

Thus, for the coagulation of sols carrying negative charge (like As2S3 sol). Al3+ ions are more effective than Ba^{2+} or Na^+ ions. Similarly, for the coagulation of sols carrying positive charge, such as $Fe(OH)_3$ sol P_4^{3-} ions are more effective than SO_4^{2-} or Cl^- ions. The two observations given above are collectively called **Hardy Schulze rule.**

Coagulation values of few electrolytes are given below in tabular form

For coagulation of – ve charged sol As_2S_3				
Electrolyte	NaCl	$MgCl_2$	$BaCl_2$	$AlCl_3$
Cation	Na^+	Mg^{2+}	Ba^{2+}	Al^{3+}
Coagulation value	52	0.75	0.69	0.093
For coagulating + vely charged sol $Fe(OH)_3$				
Electrolyte	KBr	K2SO4	K2C2O4	
Anion	Br^-	SO_4^{2-}	$C_2O_4^{2-}$	
Coagulation value	138	0.210	0.238	

Coagulation of colloidal solution can also be achieved by the following methods:

(i) By mutual precipitation. When two oppositely charged sols (such as $Fe(OH)_3$ and As_2S_3) are mixed in equi-molar proportions, they neutralize each other and may get coagulated. Sometimes the sols may get coagulated due to the mutual destruction of stabilizing agents.

(ii) By electrophoresis. We know that during electrophoresis the sol particles move towards the oppositely charged electrodes. If the process is carried for a long time, the particles will touch the electrode, lose their charge and get coagulated.

(iii) By repeated dialysis. The stability of colloidal sols is due to the presence of a small amount of electrolyte. If the electrolyte is completely removed by repeated dialysis, the sol will get coagulated.

(iv) By heating. The sol may be coagulated even by simple heating.

7.10 INTERACTION BETWEEN COLLOIDS – GOLD NUMBER

When two lyophobic sols are mixed together, it may result in coagulation because of mutual neutralization of electrical charges or due to destruction of each other's stabilizers. However, when n lyophilic sol in mixed with lyophobic sol, it is observed that in many cases lyophilic solo exert protecting influence on lyophobic sol against their coagulation by electrolytes. This is presumably because the lyophilic particles form a protective layer around the lyophobic particles. For example, a gold sol or a silver sol, protected by gelatin, rum or starch may not be coagulated easily. Different lyophilic sole exert protective influence to different extent. The protecting power of a protective colloid is expressed in terms of **gold number** which may be defined as:

The number of milligrams of the protective colloid which Just prevent coagulation of 10 ml of standard gold so when 1 ml of 10% solution of sodium chloride is added to it.

The coagulation is detected by the chance of colour of the old sol from red to blue, It may be noted that smaller the gold number of the protective colloid is, greater will be its protectite power. The told number of a few protective colloids are given below:

Gum-arabic	:	0.15-0.25	Haemoglobin	:	0.03
Gelatin	:	0.005-0.01	Caseinate	:	0.01
Egg albumin	:	0.15-0.25	Sodium oleate	:	0.4
Potato starch	:	25	Dextrin	:	6-20

7.11 GELS

Certain sols live the property of setting to a semi-solid, Jelly form by enclosing the entire amount of liquid within itself when they are present at high concentration. This process in called relation and colloidal system with jelly-like appearance are known as **gels.** Some common example of gels are: gum arabic, gelatin, agar, processed cheese, silicic acid, ferric hydroxide etc.

Gels possess rigid structures which are formed when the particles of dispersed phase get interlocked and creates a loose network frame. The particles of dispersion medium are trapped within the loose framework. The degree of rigidity of structure varies from substance to substance. Thus, gel represents liquid-solid system i.e., a liquid dispersed in solid.

When the gels are allowed to stand for long time, they give out small quantity of trapped liquid which accumulates on its surface. This action of gels is known as **syneresis** or **weeping.**

Gels are divided into two categories i.e., **elastic gels** and **non-elastic gels.** The characteristic differences between the two re tabulated below:

Elastic gels	Non-elastic gels

1. These gels change to solid mass on dehydration which can be changed back to original form by addition of water followed by warming. 2. They absorb water when placed in it with simultaneous swelling of get body. This phenomenon is called **imbibition.**	1. These gels change to solid mass on dehydration which cannot be changed back to original form by addition of water and warming. 2. These do not imibibe.

Some gels such as silica, gelatin, ferric phosphate, etc., liquify on mechanical shaking and change to sols losing their semi-solid gel character. The sol on standing changes back to the gel. This phenomenon is called **thixotropy.**

7.12 APPLICATIONS OF COLLOIDS

Due to the presence of electrical charge on colloidal particles, colloidal solutions are somewhat good conductors. This fact finds many important applications, some of which are given below:

1. Rubber Plating. The negatively charged rubber particles from the rubber sol are deposited on wares, handles of different tools, rubber gloves, etc., by electroplating.

2. Sewage Disposal. Sewage water contains particles of dirt, rubbish, etc., which are of colloidal size, carry charge and therefore do not nettle down easily. These particles can be removed by electrophoresis. Dirty water is passed through a tunnel fitted with metallic electrode which in maintained at high potential difference. The particles migrate to the oppositely charged electrode, lose their charge and are coagulated. The deposited matter is used as manure and the water left behind is used for irrigation.

3. Cottrell Smoke Precipitator. Smoke is made free of colloidal particles by passing it through cottrell precipitator installed in the chimney of an industrial plant. It consists of two metal discs charged to a high potential. The charge on the colloidal dust and carbon particles of smoke is neutralized and they are precipitated down, while free gases come ant through the chimney.

4. Formation of Delta. River water in a sort of colloidal solution of clay in water Sea water, on other hand, contains a large number of dissolved salts and is a sort of electrolyte. When river water comes in contact with sea water coagulation of colloidal particles occurs. These coagulated clay particles settle down at the point of contact and gradually river bed starts rising. This lands river water to adopt different course and ultimately results in the formation of delta.

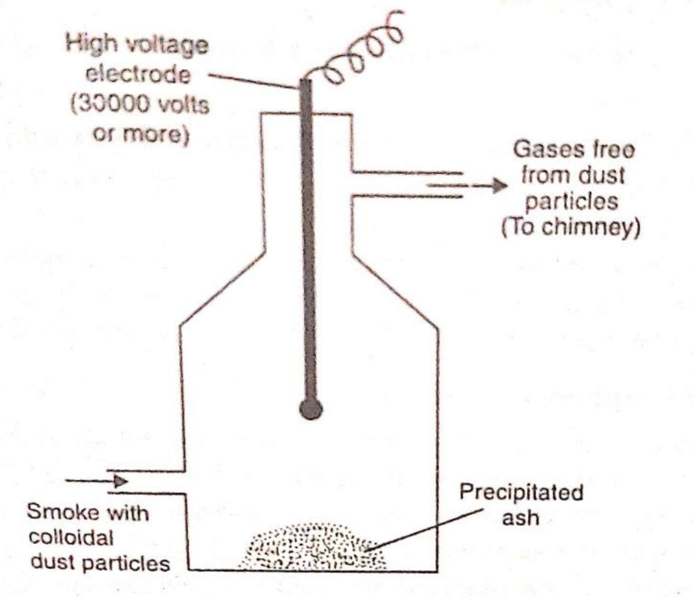


Fig. 7.9. Cottrell smoke precipitator

5. Artificial Rain. Artificial rain is caused by spraying oppositely charged colloidal dust or sand particles over the clouds by aeroplane. The colloidal water particles of the clouds get neutralized and coagulate to biter water drops which cause artificial rain.

6. Purification of Water. The colloidal particles present in water can be precipitated by addition of small amount of alum ($K_2SO_4.Al_2(SO_4)_3.24H_20$). The Al^{3+} ions furnished by alum help in coagulation of impurities which are present in the colloidal form.

7.13 EMULSIONS

Emulsions are colloidal solutions in which disperse phase as well as dispersion medium are liquids. Emulsions can be broadly classified into two types:

(i) Oil in water emulsions. In this type of emulsions, oil acts as disperse phase and water acts as dispersion medium. Some examples of this type of emulsions are milk, vanishing cream, etc.

(ii) Water in oil emulsions. In this type of emulsions, water acts as disperse phase and oil acts as dispersion medium. For example, cold cream, butter, cod liver oil, etc.

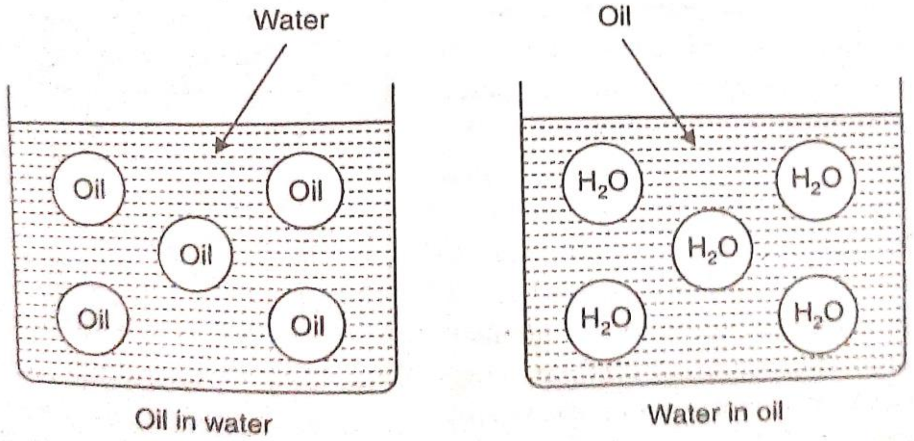


Fig. 7.10. Types of emulsions

Identification of Emulsions

The following texts may be employed to distinguish between the two types of emulsion:

(i) Dye test. To the emulsion some oil soluble dye is added. If the background becomes coloured the emulsion in water-in-cil type and if the droplets become coloured, the emulsion is oil-in-water type.

(ii) Dilution test. If the emulsion can be diluted with water, this indicates that water is the dispersion medium and the emulsion in of oil-in-water type. In case the added water forms a separate layer, the emulsion is water-in-oil type.

Preparation of Emulsions

The process of making an emulsion known as emulsification Emulsions may be obtained by vigorously agitating a mixture of both the liquids. But this gives an unstable emulsion, the dispersed drops at once come together and form a separate layer. To stabilize an emulsion, the addition of a small quantity of the third substance known as **emulsifying agent** or **emulsifier** is essential Soaps and detergents are most frequently used an emulsifiers. They cost the drops of an emulsion and check them from coming together and the emulsion is, thus, stabilized. The other common stabilizing agents are proteins, um and agar.

Demulsification

The decomposition of an emulsion into its constituent liquids is called demulsification. The various techniques applied for demulsification are freezing, boiling filtration, centrifugation, electrostatic precipitation or chemical methods which destroy the emulsifying agents. For example, cream is separated from milk by centrifugation.

Application of Emulsions

Some important applications of emulsions are being discussed as follows:

1. Cleansing Action of Soap. Washing action of soap is due to the emulsification of grease and taking it away in the water along with dirt or dust present on grease.

Explanation. The cleansing action of soap can be explained keeping in mind that a soap molecule contains a non-polar hydrophobic group and n polar hydrophilic group. The dirt is held on the surface of clothes by the all or grease which in present there. Since ail or grease are not soluble in water, therefore, the dirt particles cannot be removed by simply washing the cloth with water. When soap is applied, the non-polar alkyl group dissolves in oil droplets while the polar-C00-Na^+ groups remain dissolved in water (Fig. 7.11) In this way, each oil droplet is surrounded by negative charge These negatively charged oil droplets cannot coalesce and a stable emulsion is formed. These oil droplets (containing dirt particles) can be washed away with water along with dirt particles.

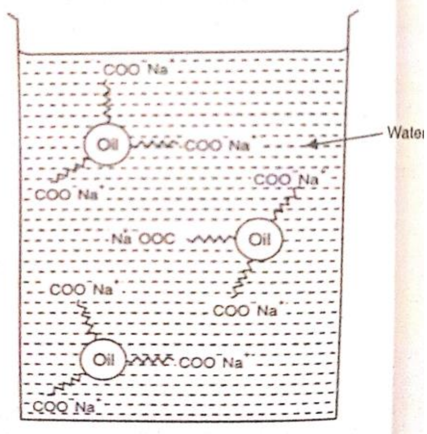


Fig. 7.11. Cleansing action of soaps.

2. in Medicines. A wide variety of pharmaceutical preparations are emulsions. For example, emulsion of cod Liver oil Theme emulsified oils are easily acted upon by the digestive juice in the stomach und hones, are readily digested.

3. Digestion of Fats. Digestion of fats in the intestines is aided by emulsification. A little of the fat forms sodium soap with the alkaline solution in the intestine, and the soap emulsifies the rest of the fat. It is easier for the digestive enzymes to carry.

4. In Disinfectants. The disinfectants such as Dettol and Lysol give emulsion of the oil-in-Water type when mixed with water.

5. In Metallurgical Operations. Emulsions play an important role in industry. The metal ores are concentrated by froth-flotation process which involves the treatment of the pulverized ore in emulsion of pine oil.

SUMMARY

- **Solution.** A homogeneous mixture of two or more substances whose concentration ca be varied with in certain limits.
- **Mass per cent.** Mans of solute per 100 g of solution.
- **Molarity.** Number of males of solute per litre of solution.
- **Normality.** Number of gram-equivalent of solute per litre of solution.
- **Molality.** Number of moles of solute per kilogram of solvent.
- **Lyophilic sol.** A colloidal solution in which there in front affinity between the disperse phase and the dispersion medium.
- **Lyophobic sol.** A colloidal solution in which there is little affinity between the disperse phase and the dispersion medium Lyophobic sols are less stable.
- **Macromolecular colloid.** A colloid in which colloidal particles are macromolecules.
- **Hardy-Shulze rules.** In case of electrolytes, the ion carrying charge opposite to that of colloidal particles is effective in causing coagulation Greater the valency of the ion causing the coagulation greater is the coagulating power.
- **Brownian movement.** The zig-zag movement of colloidal particles.
- **Tyndall effect**. Scattering of light by colloidal particles.
- **Electrophoresis.** The movement of colloidal particles towards one of the electrodes on passage of electricity through colloidal solution.

Reviews Questions

1. Explain the following terms with suitable examples as applied to solutions:
   (i) molality (ii) molarity (iii) mole fraction.
2. Explain the following molality and formality clearly indicating the difference between the two.
3. Explain the terms molality and formality clearly indicating the difference between the two.
   (i) molarity (ii) molality (iii) mole fraction
4. How are the colloidal solutions classified on the basis of dispersed phase and dispersion medium?
5. What do you understand by lyophilic and lyophobic colloids? How will you distinguish between them?
6. Write brief note on:

(i) Coagulation (ii) Gold number (iii) Hardy-Schulze law

7. What is an emulsion? Give an example.
8. What is the role played by an emulsifier?
9. Explain the following in connection with colloids:
   (i) Gold number
   (ii) Hardy-Schulze rule
10. Explain what happens when:
    (a) beam of light is passed through colloidal solution of As_2S_3.
    (b) an electrical current is passed through a colloidal solution.
11. What are emulsion? Give one example each of water-in-oil type and oil-in-water emulsions.