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(Basic Chemistry)

S. N. Narkhede

NIRALI PRAKASHAN
ADVANCEMENT OF KNOWLEDGE

A Text Book of

ENGINEERING CHEMISTRY - I

(BASIC CHEMISTRY)

SEMESTER – I

FIRST YEAR DIPLOMA COURSES IN ENGINEERING

[ACCORDING TO SBTE'S NEW REVISED SYLLABUS FOR JHARKHAND, JULY 2017]

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NIRALI PRAKASHAN
ADVANCEMENT OF KNOWLEDGE

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DEDICATED TO

MY BELONGED STUDENTS

PREFACE

It gives me a great pleasure to bring this book of **"Engineering Chemistry - I"** for students of First Semester Diploma in Engineering and Technology. The book is written according to the new revised syllabus of Board of Technical Examinations.

This book also covers the curriculum of Autonomous institutions.

I honestly feel that this edition will be well appreciated by the students as well as the teachers of polytechnics all over the Maharashtra State.

I would like to express my gratitude to the publishers Shri. D. K. Furia, Mr. Jignesh Furia, Shri. M. P. Munde and the staff of Nirali Prakashan, Pune for bringing out this book within a very short time. I would still welcome the constructive suggestions from our colleagues and students for further improvements in the book.

Prof. S. N. Narkhede

SYLLABUS

ENGINEERING CHEMISTRY - I

1. Atomic Structure [Hours 06, Marks - 12]

Definition of Atom, Fundamental Particles of Atom – their Mass, Charge, Location, Definition of Atomic Number, Atomic Mass number, Isotopes and Isobars and their distinction with suitable examples, Bohr's theory, Definition, Shape of orbitals and distinction between Orbits and Orbitals, Hund's Rule, Aufbau's Principle (till Atomic Number 30), Definition and Types of Valency (Electrovalency and Covalency), Octet Rule, Duplet Rule, Formation of Electrovalent and Covalent Compounds e.g. NaCl, $CaCl_2$, MgO, $AlCl_3$, CO_2, H_2O, Cl_2, NH_3, C_2H_4, N_2, C_2H_2. Distinction between electrovalent and covalent compounds.

2. Electrochemistry [Hours - 08, Marks 16]

Electrolytic Dissociation, Arrhenius Theory of Ionisation, Degree of Ionisation and Factors affecting Degree of Ionization. Significance of the terms involved in Electrolysis - such as Conductors, Insulators, Dielectrics, Electrolyte, Non-Electrolyte, Electrolysis, Electrolytic Cell, Electrodes. Mechanism of Electrolysis. Concept of Electrode Potential such as Reduction potential and Oxidation potential. Electrochemical Series, Electrolysis of $CuSO_4$ solution by using Copper electrode and Platinum electrode, Electrolysis of NaCl solution and fused NaCl by using carbon electrode, Faraday's First and Second law of Electrolysis and Numericals, Electrochemical Cells and Batteries, Definition, Types such as Primary and Secondary cells and their examples. Construction, Working and Applications of Dry Cell and Lead - Acid Storage Cell, Applications of Electrolysis such as Electroplating and Electrorefining, Electrometallurgy and Electrotyping.

3. Metals and Alloys [Hours - 10, Marks 18]

3.1 Metals (Marks - 10) : Occurrence of Metals, Definition of Metallurgy, Mineral, Ore, Gangue, Flux and Slag, Mechanical Properties of Metals such as Hardness, Toughness, Ductility, Malleability, Tensile Strength, Machinability, Weldability, Forging, Soldering, Castability. Stages of Extraction of Metals from its Ores in detail i.e. Crushing, Concentration, Reduction, Refining. Physical Properties and Applications of some commonly used metals such as Fe, Cu, Al, Cr, Ni, Sn, Pb, Zn, Co, Ag, W.

3.2 Alloys (Marks - 08) : Definition of Alloy, Purposes of Making Alloy. Preparation Methods, Classification of Alloys such as Ferrous and Non-Ferrous and their examples. Composition, Properties and Applications of Alnico, Duralumin, Dutch Metal, German Silver / Nickel Silver, Gun Metal, Monel Metal, Wood's Metal, Babbit Metal.

4. Non-Metallic Materials [Hours - 06, Marks 12]

4.1 Plastics (Marks - 04) : Definition of Plastic, Formation of Plastic by Addition and Condensation Polymerisation by giving example of Polyethylene and Bakelite Plastic respectively, Types of Plastic, Thermosoftening and Thermosetting Plastic, with Definition, Distinction and Compounding of Plastics - Resins, Fillers, Plasticizers, Accelerators, Pigments and their examples, Engineering Applications of Plastics based on their properties.

4.2 Rubber (Marks - 04) : Natural Rubber : Its Processing, Drawbacks of Natural Rubber, Vulcanisation of Rubber with chemical reaction.

Synthetic Rubber : Definition, Distinction between Natural and Synthetic Rubber. Properties of Rubber such as Elasticity, Abrasion resistant, Stress and Strain and related engineering applications.

4.3 Thermal Insulating Materials (Marks - 04) : Definition and Types. Characteristics of Insulators. Thermal Insulators, Properties and Applications of Glasswool, Asbestos, Cork.

5. Environmental Effects (Awareness Level) [Hours - 12, Marks 22]

5.1 Pollution and Air Pollution (Marks 10) : Definition of Pollution and Pollutant, Causes of Pollution. Types of Pollution - Air and Water Pollution.

Air Pollution : Definition, Types of Air Pollutants - their Sources and Effects, such as Gases, Particulates, Radioactive Gases, Control of Air Pollution, Air Pollution due to Internal Combustion Engine and its Control Methods, Deforestation - their Effects and Control measures. Causes, Effects and Control measures of Ozone Depletion and Green House Effects.

5.2 Water Pollution and Wastes (Marks 12) : Definition, Causes and Methods of Preventing Water Pollution, Types of Wastes such as Domestic Waste, Industrial Waste, their Physical and Biological Characteristics, Concept and Significance of BOD, COD, Biomedical Waste and E - Waste, their Origin, Effects and Control Measures. Preventive Environmental Management (PEM) Activities.

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Chapter **1**

ATOMIC STRUCTURE

1.1 Introduction
1.2 Particles of matter
1.3 Dalton's Atomic Theory
1.4 Size of an Atom
1.5 Thomson's Atomic Model
1.6 Rutherford's Scattering experiment
1.7 Drawbacks of Rutherford's Atomic Model
1.8 Bohr's Atomic Model
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1.25 Formation of electrovalent compounds
1.26 Covalency
1.27 Formation of covalent compounds
1.28 Distinction between electrovalent and covalent compounds

1.1 INTRODUCTION

Ancient Greek and Indian philosophers considered matter to be discontinuous and composed of extremely small and invisible particles. *Decartes in Greece* and *Maharshi Kanad* in *India* were among the *earliest philosophers* who *put forth this view*. The smallest particle of an element was called by them as an atom. *John Dalton, an English school master,* was the first to *give his famous atomic theory in 1808.* However, he *did not distinguish between* the *smallest particle* of an element and that of a *compound.* He only stated that *the last particle* of a compound be called as a *'compound atom'* which is now known as a *molecule*.

1.2 PARTICLES OF MATTER

If we examine very closely any given substance like sugar, either with the naked eye or under a microscope, we find that it is composed of exceedingly small particles. If a crystal of sugar is crushed into a fine powder, each fine particle will show the same properties of sugar crystal, namely white colour, sweet taste, solubility in water etc. Thus, each tiny particle is still a particle of sugar. If these fine particles are dissolved in water, they will be invisible and cannot be seen even with a powerful microscope but still their presence is felt by our sense of taste. These particles have a free existence and possess the same properties as those of the original substance. Such infinitely small particles of the substance are called *'molecules'*.

Molecule

"It is the smallest particle of an element or a compound that can exist in the free state and retain all of its properties."

Atom

Molecules of a substance are found to be capable of splitting up into still smaller and simpler particles by chemical means. A molecule of sugar gives particles of carbon, hydrogen and oxygen. These elementary and very very tiny particles which build up a molecule are known as atoms. Atoms are not further divisible even by chemical means. Atoms are therefore the structural units of molecules. Just as there are rooms in a house, so there are atoms in a molecule. A molecule of an element contains atoms of the same kind. Thus, an element consists of molecules and these molecules further consist of atoms.

1.3 DALTON'S ATOMIC THEORY

Fig. 1.1 : John Dalton (1776 - 1844)

Teacher, New College, Manchester, is regarded as one of the founders of modern Chemistry. He enunciated the Atomic Theory, the law of Partial pressures, the law of Multiple proportion and also devised a method of symbolising the elements and compounds.

John Dalton (in 1808) was the first to give the simplest atomic theory regarding the structure of matter to explain the laws of chemical combination. The main assumptions of his theory are :

1. *Matter is* composed of *extremely small particles called atoms. These atoms cannot be sub-divided by chemical means.*
2. Atoms *neither be created nor destroyed.*
3. Atoms *of the same element are identical in all respects,* viz. shape, size, weight *and properties.*
4. Atoms of *different elements are dissimilar in weights and properties.*
5. Atoms of *different elements combine* in *simple whole numbers* (1 : 1, 1 : 2, 2 : 3 etc.) to form *compound atoms* (now, known as molecules).
6. *Combining weights of elements* represent the *combining weights of atoms.*

Some *modifications* were suggested by *Avogadro in 1811*, to *Dalton's Atomic Theory.* Atom is thus defined as : *"Atom is the smallest particle of an element, which cannot be further sub-divided and which can take part in all chemical changes. It may or may not be capable of free existence."*

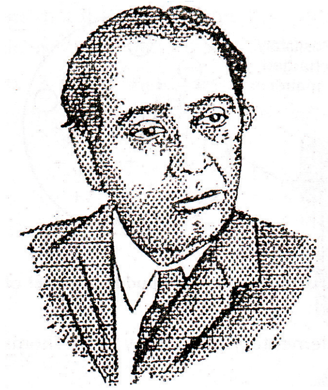


Fig. 1.2 : Homi Jehangir Bhabha (1909 - 1966)

Size of Atoms :

Atoms vary in size. The diameter of the smallest, the hydrogen atom, is about 0.000,000,005 cm. It is so small that 200,000,000 atoms in a row would form a line only 1 cm long. The diameter of the largest known atom is about 10 times the diameter of the hydrogen atom.

Angstrom unit (A°)

Such tiny sizes as those of atoms are often expressed in Angstrom unit (A°). One Angstrom unit is = 0.000,000,01 cm. Thus, a hydrogen atom is about 0.5 A° in diameter.

1.4 SIZE OF AN ATOM

An *atom* of an element *is extremely small* with a *spherical shape* having approximately *1×10^{-8} cm as its radius* (or diameter of 10^{-10} cm or 1 A°). A smallest particle that can be seen under a very *powerful microscope* has *radius* equal to *1×10^{-5} cm.* This means that an atom of element is *10^{-3} or 1000 times smaller* than the *particle* that could be seen under a microscope. *Atoms* of *different elements* vary in *radius* from about *1×10^{-8} cm to 5×10^{-8} cm.*

Atomicity of an Element :

Just as a house may have only one hall or it may have many rooms, similar to this a molecule of an element may have only one atom or many atoms in it.

Molecules of *inert gas elements* like helium (He), neon (Ne), argon (Ar), krypton (Kr) and xenon (Xe) consist of only one atom. Hence, these elements are *'monoatomic.'* Most of the metals and some non-metals (like C, S, P, B, etc.) contain only one atom in their molecule and hence, these elements are also monoatomic. The elementary gases like H_2, O_2, N_2 and Cl_2 contain two atoms in their molecule and hence these are *'diatomic.'* Ozone (O_3) contains three atoms of oxygen and therefore, it is *'triatomic.'* Thus,

The atomicity of an element is defined as the number of atoms present in the molecule of an element.

On the basis of fundamental cause of chemical combination, an element has a tendency to achieve stability by completing its octet or duplet by the lose or gain or sharing of electrons.

Inert gas elements like Ne, Ar, Kr and Xe (except He) having completely filled outermost shell i.e. octet state is already present. Such elements does not involve in chemical combination and therefore they are 'monoatomic'. In non-metallic elements like chlorine the outermost shell contains 7 electrons. Thus 'Cl' atom will achieve octet by sharing of electrons (*covalency*) with other atoms of 'Cl' resulting into their complete octet. *Therefore Cl_2 exhibits diatomic character.*

1.5 THOMSON'S ATOMIC MODEL

The *first model of an atom* was suggested by *J. J. Thomson in 1898.* He suggested that *atoms are uniform spheres* of *positively charged matter* in which *negatively charged electrons* are embedded or fixed like plums in a cake or pudding. Hence, it is called *"Thomson's plum-pudding model"* of an atom. An atom, therefore, contains two types of particles, one positively charged and the other as negatively charged.

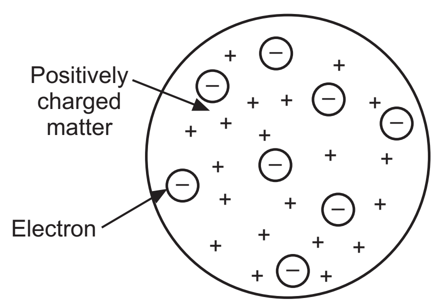


Fig. 1.3 : Thomson's plum-pudding model of an atom

Thus, the electron was first clearly identified as an elementary particle by J. J. Thomson.

1.6 RUTHERFORD'S SCATTERING EXPERIMENT

In 1911, Rutherford performed classic *experiments* and he tested the Thomson's model of an atom. He bombarded thin gold foil with high speed *α-particles* obtained from radioactive element. For detection of α-particles, he used a movable screen coated with zinc sulphide. When α-particles struck the screen, a flash of light was seen *(Fig. 1.4)*.

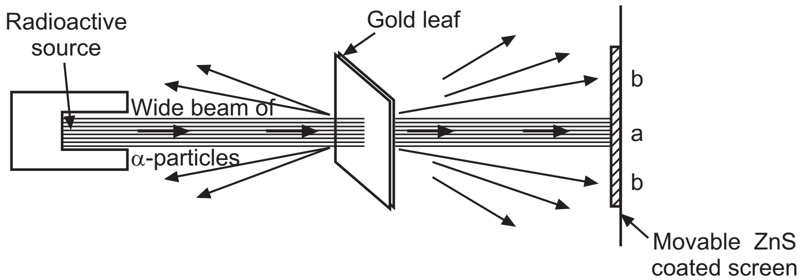


Fig. 1.4 : Rutherford's Scattering Experiment

His observations were as follows :

(i) Most of the α-particles passed straight way through the gold foil without deflection (a).

(ii) Some α-particles suffered little deflection (b).

(iii) Quite a few α-particles suffered a violent deflection through an angle of 90^o or greater (c).

(iv) One α-particle out of 20,000 particles suffered a complete deflection through 180^o.

Rutherford interpreted these observations as follows :

(i) As most of the α-particles passed almost straight through the foil, indicating that an atom is extra-ordinarily hollow with a lot of empty space inside it.

(ii) A few of them were deflected from their original path through large angles. This suggested that the centre of an atom must be positively charged to repel the positively charged α-particles. *He named the positively charged central part of an atom as a 'nucleus.'*

(iii) A few of the α-particles were even turned back on their path, which indicates that the *nucleus is rigid from which α-particles could recoil.*

Fig. 1.5 : E. Rutherford (1911)

Rutherford's Model of an Atom

From the above results, Rutherford suggested model for an atom. The main features of his atomic model are :

(i) An atom contains *protons and* each proton *carries a unit mass* and *unit positive charge.*

(ii) An atom contains *electrons* and each electron *carries a unit negative charge,* but a negligible mass, i.e. $\frac{1}{1850}^{\text{th}}$ of the mass of a proton.

(iii) In an atom, the number of *protons is equal to* the number of *electrons*. Hence, an *atom* is electrically *neutral*.

(iv) In an atom, *all the positive charges and mass* are concentrated in the central part of an atom known as nucleus.

(v) The *electrons* are *revolving* round the nucleus *in a definite path called 'orbit'.* Thus, these electrons are known as *'orbital'* electrons or *'planetary'* electrons.

(vi) The *volume of an atom is* determined by *its last orbit.*

Rutherford's atomic model is just *similar* to the *solar system*, in which the *lighter planets revolve* round the *massive sun.* However, he noticed that atomic masses of different atoms could not be explained, if only protons and electrons are present in them. *In 1920, he predicted* that a kind of neutral particle with mass equal to that of proton must be present in the nucleus of the atom. In 1932, *'Chadwick' discovered* the *neutral particles* and he named these particles as *'neutrons'* on account of their *neutral nature.* Hence, the nucleus of an atom contains protons and neutrons, the only exception being hydrogen ($_1H^1$) in which the nucleus is made up of only one proton.

1.7 DRAWBACKS OF RUTHERFORD'S ATOMIC MODEL

According to Rutherford's atomic model (1911), the electrons moving round the nucleus and the direction of their velocity is constantly changing i.e., the *electrons are accelerating towards the nucleus.* Due to this acceleration, the electron emits or radiates energy and consequently the moving electron will have lesser and lesser energy. Thus, the *electron will get* closer to the nucleus until at last it *will fall into the nucleus* and the atom would *collapse (Fig. 1.6).* But actually atoms are stable. Hence, there must be some basic defect in Rutherford's atomic model.

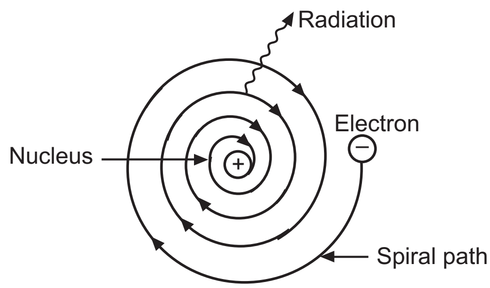


Fig. 1.6 : An electron radiating energy and taking a spiral path

Rutherford's model of an atom was based on the analogy that the *'electrons'* are revolving around the *'nucleus'* in the same manner as the planets in *'Solar system'* revolve around the *'sun.'*

In 1913, 'Bohr' pointed out that this Rutherford's picture of an atom is defective and cannot be stable as both the *'electrons'* and *'nucleus'* are charged bodies. *According to the electromagnetic theory,* such *rotating electrons* would *radiate energy continuously* in the form of electromagnetic *waves*. The energy would be derived from the rotating electron itself. This reduces its speed gradually, until at last it falls into the nucleus and the atom would collapse. In other words, the revolving electron would describe a spiral path along the curvature of decreasing radius. To overcome this difficulty, *'Bohr' discarded the electromagnetic theory and applied the principle of quantum theory to this problem.*

1.8 BOHR'S ATOMIC MODEL

Neils Bohr, a Danish physicist, in 1913 proposed *his revolutionary atomic model* to overcome the drawbacks of Rutherford's nuclear atomic model. Bohr's atomic model is *based* on the following *fundamental principles,* in the light *of quantum theory,* which are known as Bohr's postulates or assumptions.

Fig. 1.7 : Neils Bohr (1885 - 1913 proposed his revolutionary atomic model)

Danish Physicist : was awarded Nobel Prize for Physics in 1922 : greatly extended the theory of atomic structure by devising an atomic model in 1913 and evolving the theory of nuclear structure. Assisted America in Atom Bomb research.

1. An atom consists of a *dense positively charged central part* called as *'nucleus'* and it is at *rest*.
2. *"The electrons revolving around the nucleus in fixed circular paths are called orbits or shells"*. Thus, the electrostatic *force of attraction between the 'nucleus'* and *electron is balanced* by the *centrifugal force.* Hence, the *electron does not fall into the nucleus* and therefore, the atom *remains stable.*
3. Out of the number of possible circular orbits around the nucleus, an *electron* can *rotate only in certain permitted orbits* which are *known* as *'stationary states.'*
4. Each of the *stationary state* is associated *with a definite amount of energy,* hence these are also called as *'energy levels.'*
5. Electrons in the energy level *nearest* to the nucleus have *lower energy*, while those at a greater distance from the nucleus have *higher energy*.
6. As long as the *electron stays in the same energy level,* the energy remains constant. The energy of an electron can change only when it moves from one level to another. It changes *abruptly and not continuously* just as a ball rolls down a stair-case from one step to another.
7. The *angular momentum of electron* (mvr) must be an *integral multiple* of h/2π or *simple whole number multiples* of h/2π such as 2h/2π, 3h/2π, ……… *nh/2π*. This means that the angular momentum of an electron is quantized in units of h/2π. The *change* of electronic energy *by jumping* and *not by flowing* from *one energy level to another is known* as *quantization of electronic energy*. The *number of Bohr's possible orbits* (or energy levels) can be *determined by* using the *relation*,

$$mvr = \frac{nh}{2\pi}$$

where m = *mass* of the electron,
v = tangential *velocity* of the electron in its orbit,
r = radius of orbit,
h = *Planck's* constant 6.62×10^{-34} joules-sec.
n = principal quantum number which can take only *integral values* 1, 2, 3, 4, 5, 6 etc.

Thus, 'n' represents *orbit* or *shell* number.

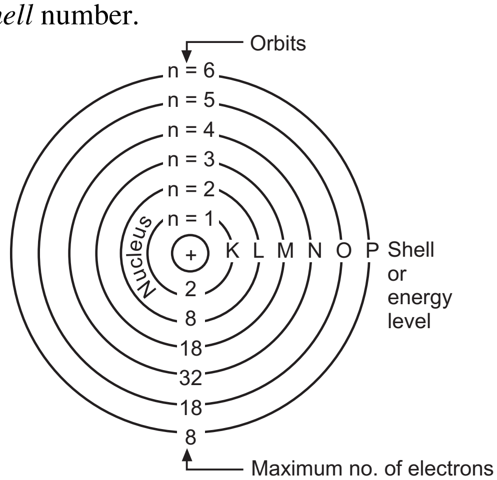


Fig. 1.8 : Representation of Bohr's stationary or energy levels in an atom

8. An *'excited' electron* (when the energy is supplied to the electron, it is said to be in the excited or unstable state) *can jump* from a *lower to higher* energy *level* by *absorbing* discrete packets or *bundles or quanta* = hν, where 'ν' is the frequency of radiation of energy. *On the other hand,* the *'excited' electron jumps from higher to lower energy level by emitting* or *losing* of the *energy* (equal to $h\nu = E_2 - E_1$), the *difference in energy* between two energy levels in the form of *line spectra* or *light* of suitable *wavelength*. The *transition of* electron energy from one *energy* level to another *is not gradual but takes place at once.*

According to Bohr, the various *orbits or shells* or *energy levels* are designated by the letters K, L, M, N, O, P etc. for n = 1, 2, 3, 4, 5, 6 orbits starting from the nucleus respectively *(Fig. 1.8)*. *'Farther the orbit'* or *shell or energy level* from the nucleus, the *greater is the energy associated with it*. *When the electron* is in the *lowest energy level*, it is said to be in the *'ground state.'* Thus, the energy associated with K level is *less* than the energy associated *with L level*. In other words, *the energy levels* are in the *following order* :

$$K < L < M < N < O < P$$

1.9 MODERN ATOM

Modern researches have shown that an atom is not the ultimate particle of a substance, but it is itself composed of some *fundamental particles,* which are *also known as sub-atomic particles*-electrons, protons and neutrons. *An atom has* therefore, *its own structure.*

Electron : It carries a *unit negative* electrical *charge*. Its *mass* is extremely *small* which is $\frac{1}{1850}$ th of the *mass* of hydrogen atom. For practical purposes, its mass is regarded as *negligible*. Its mass though negligible, is equal to 0.000555 amu.* It is represented as $\bar{e}$. It *moves around* the *nucleus* of an atom.

Proton : It carries a *unit positive* electrical *charge*. The *mass* of a proton is practically *equal to* the mass of one *hydrogen atom*. But its exact mass is equal to 1.007825 amu. Its mass is taken to be 1 amu for practical purposes. It is represented as $_1H^1$ *or P*. It is present *in* the *nucleus* of an atom.

Neutron : It is electrically *neutral*. Its *mass* is taken to be *nearly equal* (≈) to that of proton. But its exact mass is equal to 1.008665 amu. It is represented as $_0^1n$ *or (n)*. It is also present *in* the *nucleus* of an atom.

The characteristics of sub-atomic particles are summarised in *Table 1.1*.

Table 1.1 : Characteristics of sub-atomic particles

Sr. No.	Characteristics	Electron	Proton	Neutron
1.	Discovered by (with Year)	J. J. Thomson (1898)	Rutherford (1911)	Chadwick (1932)
2.	Symbol	$\bar{e}$	P	n
3.	Nature	Negatively charged	Positively charged	Neutral
4.	Location in atom	Extra-nuclear part	Inside the Nucleus	Inside the Nucleus
5.	Relative charge	– 1	+ 1	0
6.	Relative mass in amu	0.000555	1.007825	1.008665

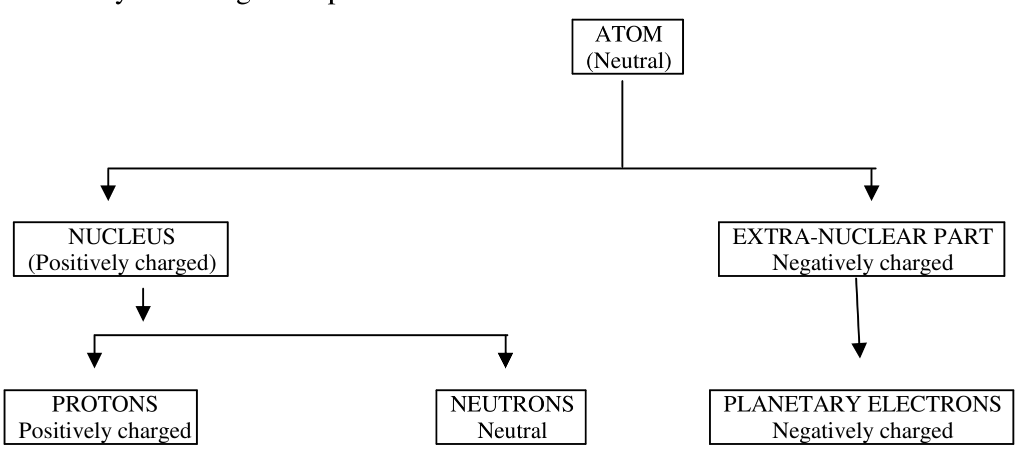
1.10 COMPOSITION OF AN ATOM

The *atom* as a whole is *electrically neutral* and consists of two parts (a) Central part and (b) Extra-nuclear part.

(a) Central Part : (i) The *central part* of an atom where practically the whole mass and the positive charge of an atom is present is known as *'nucleus'*, (ii) it is nearly *spherical in shape.* (iii) The nucleus is *positively charged* as it contains positively charged protons and neutrons of zero charge (or neutral). (iv) The *particles* making up the nucleus (*protons and neutrons*) are called *'nucleons'*. (v) The *total mass of nucleons* is called *mass number.* (vi) The *radius* of atomic *nucleus* is of the order of 10^{-12} *to* 10^{-13} *cm.*

(b) Extra-nuclear part : The extra-nuclear part *consists* of negatively charged *planetary electrons*. These electrons are known as *'planetary or orbital electrons'*, because they revolve round the nucleus in the same manner as the planets in *'solar system'* revolve around the sun.

The number of *protons* present *in* the *nucleus* must *exactly balance* the number of *planetary electrons*, which are continuously revolving in elliptical or circular orbits around the nucleus.



* amu (atomic mass unit) : Since atom is very small it is rather difficult to express its weight in usual units of gram. Hence, smaller unit is considered. 1 amu = 1.66×10^{-24} g.

Atomic Number (Z) :

Atomic number (Z) of an element is defined as *the number of protons (or unit positive charges) in the nucleus, which exactly balances the number of planetary electrons present in the extra-nuclear part of an atom.* It is also known as the nuclear charge.

∴ Atomic number = Nuclear charge

= No. of protons (or positive charges) in the nucleus

As the atom as a whole is electrically neutral, the number of protons (or +ve charges) in the nucleus must be equal to the number of electrons (or –ve charges) in the extra-nuclear part of the atom.

∴ Atomic Number (Z) = No. of electrons in the extra-nuclear part

∴ Atomic Number (Z) = No. of protons = No. of electrons

Or $Z = P = e$

Atomic number is the most fundamental characteristic of an element and it is a whole number. Different elements have different atomic numbers. The elements are arranged in the modern periodic table according to their atomic numbers.

Atomic Mass Number (A) :

It is defined as *"the sum of the number of protons and neutrons present in the nucleus of an atom (or isotope) of the element."*

∴ Atomic mass number (A) = No. of protons + No. of neutrons

$A = P + n$

But, No. of protons = Atomic number = Z

∴ Atomic mass number (A) = Atomic No. + No. of neutrons

∴ $A = Z + n$

or $\boxed{A - Z = n}$

The terms atomic mass number and atomic mass should not be confused with each other. As the mass of electron is negligibly small and each proton and neutron has a mass approximately equal to 1 unit on the atomic scale, the atomic mass of an element is therefore, approximately equal to its atomic mass number. The mass number is always an integer, while atomic masses are fractional.

Atomic mass (atomic weight) of an element is defined as *'the average relative weight of its atom as compared with $\frac{1}{12}^{th}$ weight of an atom of carbon C^{12} isotope."*

Calculation of Average atomic weight of chlorine :

Atomic masses are in fractional parts and not as whole numbers e.g., atomic weight of hydrogen is 1.008 and that of chlorine is 35.5. This is because these elements exist in two or more isotopic forms and the actual atomic mass (atomic weight) depends upon the relative abundance (percentage) of these isotopes. For example, chlorine has two major isotopes of atomic masses 35 (75.4 %) and 37 (24.6 %) and they are present in the ratio 3 : 1. Hence,

$$\text{Average atomic weight of chlorine} = \frac{(35 \times 3) + (37 \times 1)}{(3 + 1)} = \frac{105 + 37}{4} = \frac{142}{4} = \mathbf{35.5\ amu.}$$

Distinction between Atomic number and Atomic mass number :

	Atomic Number (Z)		Atomic Mass Number (A)
1.	The number of protons in the nucleus is equal to the number of electrons in extra-nuclear part of the atom is called atomic number of an element i.e. Z = P = e	1.	The sum of the protons and neutrons present in the nucleus of an atom of element is known as atomic mass number of an element. i.e. A = P + n.
2.	Atomic number fixes the position of an element in the periodic table. Thus, it is a fundamental characteristic of an element.	2.	It does not fix the position of an element in the periodic table. Because atoms of the same element may have different mass numbers (i.e. isotopes).
3.	Different elements have different atomic numbers.	3.	Atoms of the same or different elements may or may not have the same atomic mass number.
4.	Atomic number does not indicate the mass of the nucleus of atom of element.	4.	Atomic mass number indicates the mass of the nucleus of the atom of element.

1.11 RULES OF DISTRIBUTION OF ELECTRONS IN SHELLS (OR BOHR-BURY SCHEME OF DISTRIBUTION OF ELECTRONS)

In *1921, Bury* put forward a *modification of Langmuir scheme,* which is in *better agreement with the physical* and *chemical properties of certain elements.* At about the same time as *Bury developed his scheme on chemical grounds, Bohr (1921) published* an almost *identical scheme* of arrangement of extra-nuclear electrons *on the basis of emission spectra of elements.* Hence, it may be called as Bohr-Bury scheme of distribution of electrons.

The distribution of electrons in an extra-nuclear part of an atom is governed by certain rules framed by Bohr–Bury (1921), which are known as *'Bohr–Bury rules of distribution of electrons.'* These are given below :

1. *"The maximum number of electrons that can be present in an orbit or shell 'n' is $2n^2$"*, where 'n' is the principal quantum number or *the number of orbit* or shell starting *from the nucleus onwards.* Thus,

Maximum number of electrons in different orbits

Shell	Orbit (n)	Maximum number of electrons ($2n^2$)
K	1	$2 \times 1^2 = 2$
L	2	$2 \times 2^2 = 8$
M	3	$2 \times 3^2 = 18$
N	4	$2 \times 4^2 = 32$ and so on.

2. The outermost orbit or shell (or last orbit) *cannot have more than 8 electrons and* the last but one shell (or penultimate orbit or shell) cannot have more than 18 electrons.
3. It is not necessary that the next shell is formed, after completion of the electrons in a shell according to rule (1). Actually, when outer shell has 8 electrons, the next higher shell starts.
4. The outermost shell and its inner one (penultimate) shell cannot have more than 2 and 9 electrons respectively till all the shells inner to them are completed according to $2n^2$ rule.

The arrangement of electrons in the atoms upto the number 38 is governed by first two rules.

1.12 ENERGY LEVELS AND SUB-ENERGY LEVELS

"Bohr's stationary orbits associated with a definite amount of energy are called energy levels or energy states or shells." These energy levels are numbered as 1, 2, 3, 4, 5, 6 etc. starting with the lowest energy level i.e. nearest to the nucleus as 1, the next higher as 2 etc. These energy levels are also denoted by K, L, M, N, O, P etc. letters on the basis of X-ray spectra. The order of energy level is given by 'n' (principal quantum number). i.e. K < L < M < N < O < P etc.

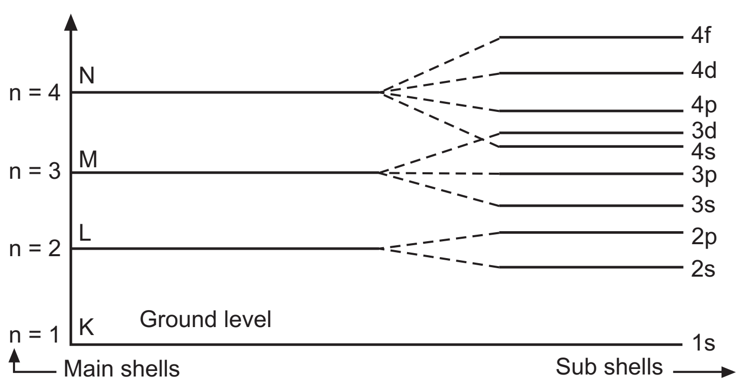


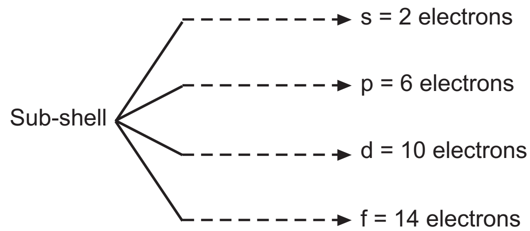
Fig. 1.9 : Energy level scheme for shells and sub-shells

By the study of spectra, the fine structure of individual spectral line indicates the presence of close grouping of several adjacent lines. Similarly, the electron energy in the main energy level can be divided into several levels i.e., the main energy level contains sub-energy levels or sub-shells. The number of sub-energy levels in the main energy level is equal to the order of the main energy level from the nucleus.

The sub-energy levels are designated by the letters s, p, d, f, etc. from the old spectral terms *sharp, principal, diffuse and fundamental*. The number of sub-energy levels (or sub-shells) can be found by its principal quantum number (n).

Energy level (or shell)		Sub-energy level (or sub-shell)
K (n = 1)	……	1s
L (n = 2)	……	2s, 2p
M (n = 3)	……	3s, 3p, 3d
N (n = 4)	……	4s, 4p, 4d, 4f

The maximum number of electrons in a sub-shell is as follows



The *sub-energy levels* are *in the order of* $s < p < d < f$

Distinction between Energy levels and Sub-energy levels

	Energy levels		Sub-energy levels
1.	Bohr's stationary orbits with definite amount of energy are called energy levels.	1.	The close grouping of a number of energy levels in the main energy level are called sub-energy levels.
2.	These are *denoted by* the letters *K, L, M, N* etc.	2.	These are *denoted by* the letters *s, p, d, f* etc.
3.	The *maximum number* of *electrons* in the energy level 'n' is given by $2n^2$.	3.	The maximum number of electrons *in sub-energy levels are s = 2, p = 6, d = 10, f = 14.*
4.	Energy levels are *circular or elliptical in shape* around the nucleus.	4.	Sub-energy levels *consist of orbitals* having *different* geometrical *shapes* i.e. *s = spherical, p = dumb-bell shaped* etc.

1.13 ATOMIC ORBITALS

According to Bohr's theory, an electron is a particle moving around the nucleus in an orbit. According to De Broglie (1923), an electron can also behave as a wave. Therefore, electron behaves as a particle as well as a wave i.e. it shows dual nature, similar to that of light.

According to Heisenberg's uncertainty principle (1927), it is impossible to know the exact position and velocity of the electron relative to the nucleus. The electron moves in somewhat random manner, sometimes being close to the nucleus and sometimes away from it.

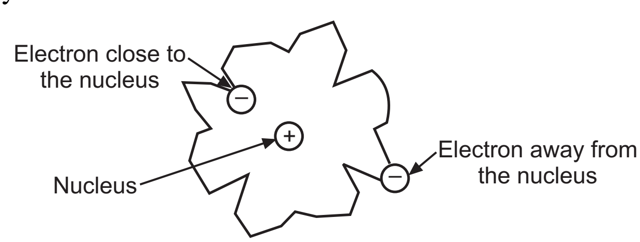


Fig. 1.10 : De Broglie's wave accommodated in Bohr's orbits (Random motion of electron)

Thus, it is meaningless to think of well defined Bohr's orbit for moving electron in an atom. However, to give an idea of the location of electron in an atom, we can only think of the probability of finding the electron at different positions around the nucleus. Here the concept of orbit is changed to an orbital. It is defined as *"The three-dimensional region of space around the nucleus, where the probability of finding the electron is maximum (90 - 95%) i.e., where the electron spends most of the time."* It is also called as *'electron cloud'* of negative charge or *'electron density.'*

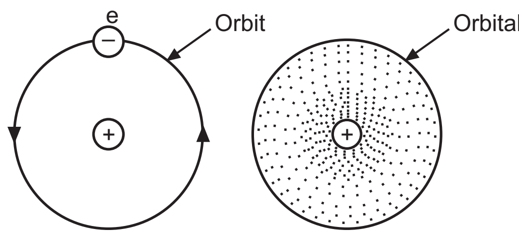


Fig. 1.11 : Orbit and Orbital

The fixed orbits of Bohr's atom are now replaced by orbitals and each orbital can contain a maximum of two electrons with opposite spins.

From the above discussion about sub-energy levels (sub-shells) s, p, d, f contain 2, 6, 10, 14 as the maximum number of electrons. Hence, there is 1s-orbital, 3p orbitals, 5d orbitals and 7f orbitals. If the principal quantum number is 'n', there are $2n^2$ electrons and 'n^2' orbitals in the main energy level.

s - Orbitals

For each main energy level, there is an s-orbital. For n = 1, there is only ($n^2 = 1^2$) = 1s orbital. Electrons moving in 's' orbital are known as 's' electrons and are represented as $1s^2$ or $2s^2$ or $3s^2$ etc. The s-orbitals are spherically symmetrical around the nucleus and hence they are non-directional in character. For each value of 'n' there is one s-orbital and there will be 'ns' orbitals, which are concentric spherical regions increasing progressively away from the nucleus. In between the two spheres, the space is empty and capacity of each s-orbital is of two electrons.

p - Orbitals

For n = 2, there are in all four orbitals ($n^2 = 2^2 = 4$) in second (L) energy level. Out of them, one is 2s and three are p-orbitals. All the p-orbitals are of equal energy except that in magnetic field. Each p-orbital is dumb-bell shaped. It consists of two lobes with an atomic nucleus in between the two lobes, where there is practically zero probability of finding the electron (nodal plane). The three p–orbitals are designated as p_x, p_y and p_z. Each 'p' orbital contains maximum of two electrons present in two lobes. They are oriented along the three mutually perpendicular axes x, y, z respectively. Such orbitals which differ in orientation but having equal energy are called '*degenerate orbitals'*. Therefore, p orbitals have directional character.

The shapes of 's' and 'p' orbitals are shown in Fig. 1.12 (a) and (b).

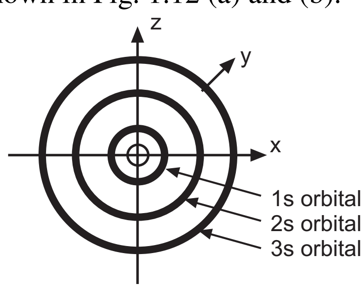


Fig. 1.12 (a) : s - orbital

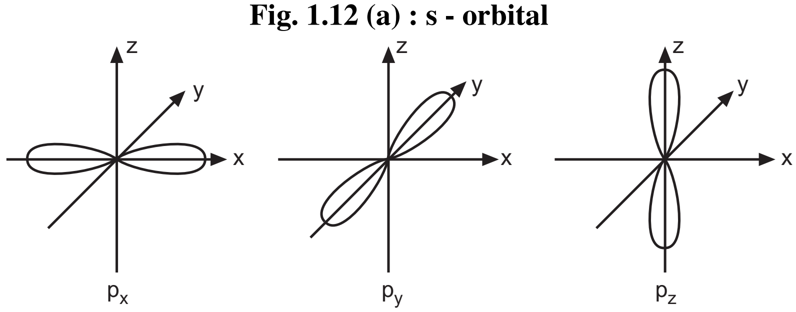


Fig. 1.12 (b) : p-orbitals (Relative orientations of p_x, p_y, p_z orbitals)

d and f orbitals

For n = 3, the total number of orbitals ($n^2 = 3^3 = 9$). Out of these 1 → 3s; 3 → 3p; remaining 5 → 3d orbitals.

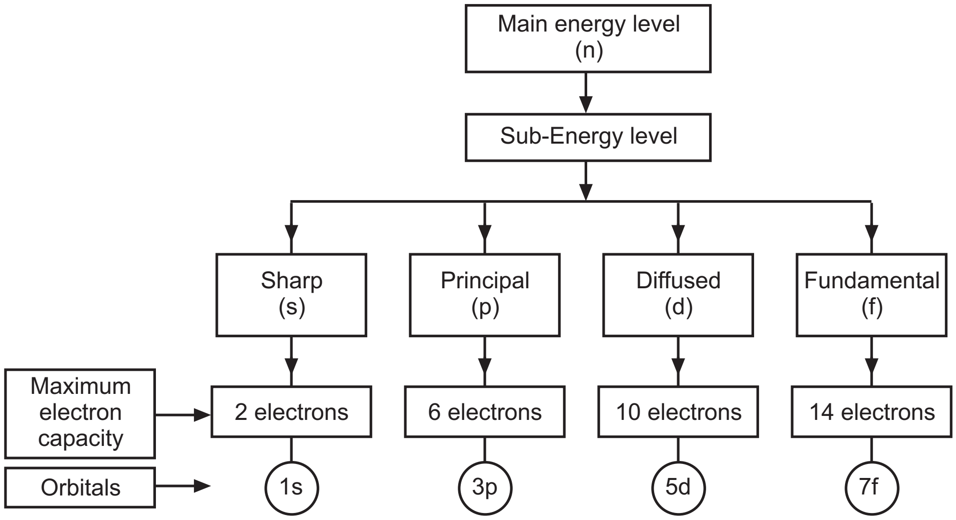
For n = 4, the total number of orbitals is $n^2 = 4^2 = 16$. Out of these 1 → 4s, 3 → 4p; 5 → 4d and remaining 7 → 4f orbitals, the geometrical shapes of d and f orbitals are somewhat complicated.

Table 1.2 : Electronic distribution or configuration of the elements upto At. No. 30

No.	Element	1	2	3	4	5	6
		s	s p	s p d	s p d f	s p d f	s p d f
1	H	1					
2	He	2					
3	Li	2	1				
4	Be	2	2				
5	B	2	2 1				
6	C	2	2 2				
7	N	2	2 3				
8	O	2	2 4				
9	F	2	2 5				
10	Ne	2	2 6				
11	Na	2	2 6	1			
12	Mg	2	2 6	2			
13	Al	2	2 6	2 1			
14	Si	2	2 6	2 2			
15	P	2	2 6	2 3			
16	S	2	2 6	2 4			
17	Cl	2	2 6	2 5			
18	Ar	2	2 6	2 6			
19	K	2	2 6	2 6	1		
20	Ca	2	2 6	2 6	2		
21	Sc	2	2 6	2 6 1	2		
22	Ti	2	2 6	2 6 2	2		
23	V	2	2 6	2 6 3	2		
24	Cr	2	2 6	2 6 4	1		
25	Mn	2	2 6	2 6 5	2		
26	Fe	2	2 6	2 6 6	2		
27	Co	2	2 6	2 6 7	2		
28	Ni	2	2 6	2 6 8	2		
29	Cu	2	2 6	2 6 9	1		
30	Zn	2	2 6	2 6 10	2		

Distinction between Orbit and Orbital

	Orbit		Orbital
1.	Orbit is a fixed circular path described by a moving electron around the nucleus.	1.	Orbital is a three dimensional region around the nucleus, in which the possibility of finding the electron is maximum (90 - 95%).
2.	The orbits are designated by the letters K, L, M, N etc.	2.	Orbitals are designated by the letters s, p, d, f etc.
3.	Orbits are circular paths or elliptical in shape.	3.	Orbitals have different geometrical shapes i.e. spherical, dumb-bell shaped.
4.	The number of orbits (or energy levels) from the nucleus are n = 1, 2, 3, 4, 5, 6 etc.	4.	The number of orbitals relative to energy levels are n^2 = 1, 4, 9, 16 etc.
5.	The maximum number of electrons in an orbit is given by $2n^2$ rule.	5.	Orbital can contain maximum of 2 electrons probability etc.



1.14 QUANTUM NUMBERS

Quantum numbers are like the labels used to describe completely the state of electron in an atom. They specify the energy, position, shape, size and orientation of the orbital to which an electron belongs. *"Quantum numbers may be defined as a set of four numbers (n, l, m, s) with the help of which we can get complete information about all the electrons in an atom. i.e. the location, energy, the type of orbital occupied, shape and orientation of that orbital etc."*

In other words :

These properties taken together describe the state of electron in an atom. The various states available to an electron are governed by the laws of quantum mechanics. Therefore, the numbers used to identify these states are called 'quantum numbers'.

These numbers are like the postal address of a person. To know about a particular person, Mr. X, we should know about his country, town, lane and his house number.

Four quantum numbers and their significance are given below.

(i) Principal quantum number (n) : determines the *'size'* of the orbital.

(ii) Azimuthal quantum number (*l*) : determines the *'shape'* of the orbital

(iii) Magnetic quantum number (m) : describes the *'orientation'* of orbital in space around the nucleus.

(iv) Spin quantum number (s) : describes the *'direction of spin'* of electron about its own axis.

All the four quantum numbers are discussed briefly as follows :

1. Principal quantum number (n) :

This is the most important quantum number as it was used to describe Bohr's stationary states in the atom.

Significance :

(i) It determines the average distance of an electron orbital from the nucleus.

(ii) It represents the size of the electron orbital. Higher the value of '*n*', larger is the size of orbital, so also the energy of the orbit increases.

(iii) 'n' can have positive integral values 1, 2, 3, 4 etc. corresponding to K, L, M, N etc. shells.

(iv) The maximum number of electrons in a shell is given by $2n^2$.

Thus,	Main energy level (n) =	1	2	3	4
	Letter designation =	K	L	M	N
	Maximum number of electrons ($2n^2$) =	2	8	18	32

2. Azimuthal quantum number (*l*) :

This quantum number is also known as subsidiary or orbital quantum number. It is used to describe the sub-shells (sub-energy levels) within a given main shell.

Significance :

(i) This quantum number determines the angular momentum of orbital.

(ii) It indicates the shape of the orbital i.e. whether the orbital is spherical, dumb-bell shaped or of some more complicated shape.

(iii) The value of '*l*' depends upon the values of 'n', hence *l* can have the values from 0 to (n – 1).

∴ $l = 0, 1, 2, 3, \ldots\ldots\ldots\ldots (n-1)$

Thus, when $n = 1, \quad l = 0$

$n = 2, \quad l = 0$ and 1

$n = 3, \quad l = 0$ 1, and 2

$n = 4, \quad l = 0$, 1, 2 and 3

= s, p, d and f orbitals

The orbitals with *l* = 0, 1, 2 and 3 are called s-orbital, p-orbital, d-orbital and f-orbital respectively.

(iv) *In* a *particular energy level, the energies of its orbitals are in the order s < p < d < f.*

3. Magnetic quantum number (m) :

Electron is a negatively charged particle. *Its movement around the nucleus is like that of flow of current. Such a movement of electron creates a magnetic field. Hence, it is known as magnetic quantum number (m).*

Significance :

(i) It determines the 'orientation of the orbital' relative to the magnetic field in which it is placed.

(ii) The values of 'm' depend on the value of '*l*'. For each value of '*l*', the 'm' may have 2*l* + 1 values. These values range from – *l* through 0 to + *l*. Thus, when

i.e. $m = -l \cdot (l-1) \cdot (l-2) \ldots 0 \ldots (l-1) \cdot (l-1) \ldots +1$

1 value 1 value 1 value

Azimuthal quantum number '*l*'	**Magnetic quantum number m = 2*l* + 1**	**Number of orbitals**
l = 0 (s–sub-shell)	m = 0	1s
l = 1 (p–sub-shell)	m = –1, 0, + 1	3p
l = 2 (d–sub-shell)	m = –2, – 1, 0, +1, +2	5d
l = 3 (f–sub-shell)	m = –3, – 2, –1, 0, +1, +2, +3	7f

Each value of 'm' represents one orbital having specific orientation in space around the nucleus.

4. Spin quantum number (s) :

An electron in its motion around the nucleus spins about its own axis. *A spinning electron behaves like a small magnet.*

Significance :

(i) It indicates the *direction in which the electron is spinning about its own axis.*

(ii) The electron can spin clockwise (↑) or anticlockwise (↓). Spin quantum number can have two possible values $+\frac{1}{2}$ and $-\frac{1}{2}$ depending on the direction of spin. Thus, only two electrons can be accommodated in the orbital with opposite spins (↑↓).

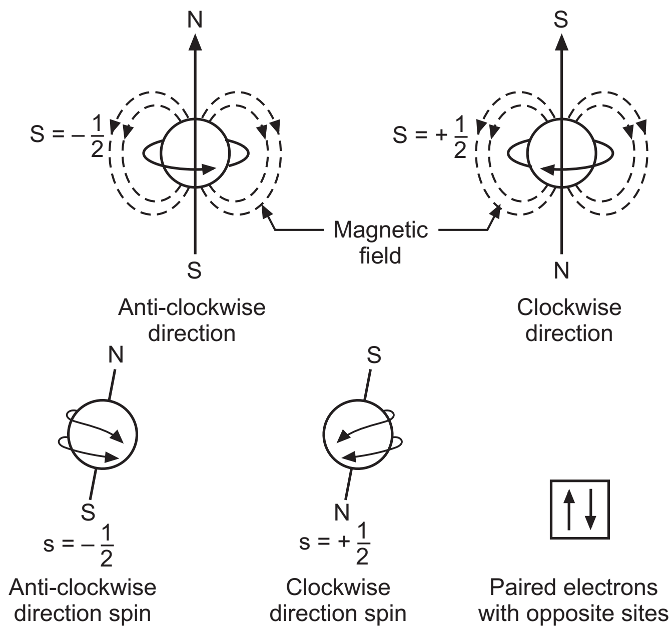


Fig. 1.13 : Anticlockwise spins of electrons about their own axis produce opposite magnetic fields

By *knowing the four quantum numbers (n, l, m, s), the location of electron energy in main energy level, sub-energy level, orbital and spin of the electron in an atom, all are indicated.*

Table 1.3 : Permitted values of total quantum numbers

1		2	3	4	5	6	7	8
Principal quantum No. (n)		Azimuthal quantum No. (*l*)	Magnetic quantum No. (m)	Spin quantum No. (s)	Total No. of orbitals in shell	Designation of orbital in (s, p, d, f)	Maximum no. of electrons in sub shell	Maximum no. of electrons in shell
	Shell	**(0 to n–1)**	**m = 2*l* + 1**		**n^2**		**2 (2*l* +1)**	**$2n^2$**
1	K	0 (1s)	0	$\pm\frac{1}{2}$	1	1s	2	2
2	L	0 (2s)	0	$\pm\frac{1}{2}$	1	2s	2	
		1 (2p)	–1, 0, +1	$\pm\frac{1}{2}$	3 } = 4	2p		8
3	M	0 (3s)	0	$\pm\frac{1}{2}$	1	3s	2	
		1 (3p)	–1, 0, + 1	$\pm\frac{1}{2}$	3 } = 9	3p	6	18
		2 (3d)	– 2, – 1, 0, + 1, + 2	$\pm\frac{1}{2}$	5	3d	10	
4	N	0 (4s)	0	$\pm\frac{1}{2}$	1	4s	2	
		1 (4p)	– 1, 0, + 1	$\pm\frac{1}{2}$	3	4p	6	32
		2 (4d)	– 2, – 1, 0, + 1, + 2	$\pm\frac{1}{2}$	3 } = 16	4d	10	
		3 (4f)	– 3, – 2, – 1, 0, + 1, + 2, + 3	$\pm\frac{1}{2}$	7	4f	14	

Each value of 'm' represents one orbital and each orbital can accommodate only two electrons.

1.15 PAULI'S EXCLUSION PRINCIPLE, HUND'S RULE AND AUFBAU PRINCIPLE

Electronic structures of elements can be build up in terms of filling shells and sub-shells (orbitals) with electrons. It is based on the following important principles :

(a) Pauli's exclusion principle (b) Hund's rule (c) Aufbau principle.

(a) Pauli's Exclusion Principle :

We have discussed that four quantum numbers are necessary to describe an electron completely. The arrangement and distribution of electrons among the atoms of elements are given by W. Pauli (1925). The principle states that, "no two electrons in a single atom or orbital can have the same set of four quantum numbers (n, l, m, s)".

Though two electrons may have the same values of first three numbers, the 4th one must differ in the values of s' $\left(+\frac{1}{2} \text{ and} -\frac{1}{2}\right)$.

The set of four quantum numbers (n, *l*, m, s) of an electron gives its complete address (i.e. shell, sub-shell, orbital and spin) in an atom.

Let us find out the maximum number of electrons that can be accommodated in an orbital in the first two shells.

(i) First (or K) shell : For this shell,

$$n = 1, l = 0, m = 0 ; s = +\frac{1}{2} \text{ and} -\frac{1}{2}$$

According to Pauli's exclusion principle :

Quantum Number	Electron No. in K shell	Letter designation of quantum numbers (Principal) n	(Azimuthal) *l*	(Magnetic) m	(Spin) s	Orbital
n = 1	1st electron	1	0	0	$+\frac{1}{2}$	∴ *l = 0* *i.e. 1s-orbital*
n = 1	2nd electron	1	0	0	$-\frac{1}{2}$	

It follows that a maximum of two electrons can be accommodated in an orbital and they must possess opposite spins [↑↓].

(ii) Second (or L) shell : For this shell,

$$n = 2, l = 0 \text{ and } 1, m = -1, 0, +1, \; s = +\frac{1}{2} \text{ and } -\frac{1}{2}$$

Electron No.	n	*l*	m	s	
1	2	0	0	$+\frac{1}{2}$	
2	2	0	0	$-\frac{1}{2}$	*l = 0 i.e. 2s orbitals*
3	2	1	–1	$+\frac{1}{2}$	
4	2	1	–1	$-\frac{1}{2}$	
5	2	1	0	$+\frac{1}{2}$	*l* = 1 i.e. 2p orbitals
6	2	1	0	$-\frac{1}{2}$	($2p_x$, $2p_y$, $2p_z$) orbitals
7	2	1	+ 1	$+\frac{1}{2}$	
8	2	1	+ 1	$-\frac{1}{2}$	

It is seen that a given sub-shell contains maximum of 2 (2*l* + 1) electrons and given shell contains maximum of $2n^2 = 8$ electrons.

(b) Hund's Rule of Maximum Multiplicity :

It states that *"when several orbitals of the same type (energy) are available, the electrons first fill all the orbitals with parallel spin before pairing in any one orbital."*

There are three p orbitals p_x, p_y and p_z with the same energy (in absence of magnetic field).

Suppose we represent p-orbitals as boxes and electrons by arrows (for $\uparrow +\frac{1}{2}$ and for $\downarrow -\frac{1}{2}$) and two electrons are added to the p sub-shell, then there are two possible arrangements I or II.

p_x	p_y	p_z
↑↓		

I

Not permitted

p_x	p_y	p_z
↑	↑	

II

Permitted

p_x	p_y	p_z
↑↓	↑	↑

III

Hund's rule

'I' is not permitted by Hund's rule and so II takes place. The next electron would enter the third vacant p_z orbital. All these three electrons have parallel spins. Pairing will take place when the fourth electron is introduced as shown in III.

EXAMPLES

Elements with electronic configuration		1s	2s	$2p_x$	$2p_y$	$2p_z$
1. Carbon (At. No. 6)	: $1s^2, 2s^2, 2p^2$	↑↓	↑↓	↑	↑	
2. Nitrogen (At. No. 7)	: $1s^2, 2s^2, 2p^3$	↑↓	↑↓	↑	↑	↑
3. Oxygen (At. No. 8)	: $1s^2, 2s^2, 2p^4$	↑↓	↑↓	↑↓	↑	↑

(Box Diagram)

Thus, in case of carbon (At. No. 6), there are 2 electrons in 1s-orbital, 2 electrons in 2s-orbital and remaining 2 electrons are present in $2p_x$ and $2p_y$ orbitals. There are three p-orbitals (p_x, p_y, p_z) having the same energy and hence before pairing of electrons starts, these orbitals are occupied by unpaired electrons separately. In case of nitrogen (At. No. 7), 2p-orbitals contain three electrons. Hence, according to Hund's rule, each of the three 2p-orbitals must be occupied by single electron. In case of oxygen (At. No. 8), there are two half-filled 2p-orbitals and one 2p orbital contains two paired electrons.

In other words, pairing must begin with the introduction of the 2^{nd} electron in the 's' orbital, 4^{th} electron in the 'p' orbitals, 6^{th} electron in the 'd' orbitals and 8^{th} electron in the 'f' orbital.

(c) Aufbau Principle : (German word aufbau = building up)

In the ground state of an atom, the electrons tend to occupy the available orbitals in the increasing order of energies, the orbitals of lower energy being filled first. This is called building up principle or *Aufbau principle* (*Aufbau* is a German expression meaning *building up or construction; it is pronounced as of bow).*

It states that *'the electrons always enter the various orbitals in the order of increasing energy'*. Lower energy orbitals are therefore, better 'seats for electrons and better seats are occupied first'. Fig. 1.14 shows the energy level scheme of orbitals and this order can conveniently be remembered by the simple way given below.

The order of filling of the orbitals is

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

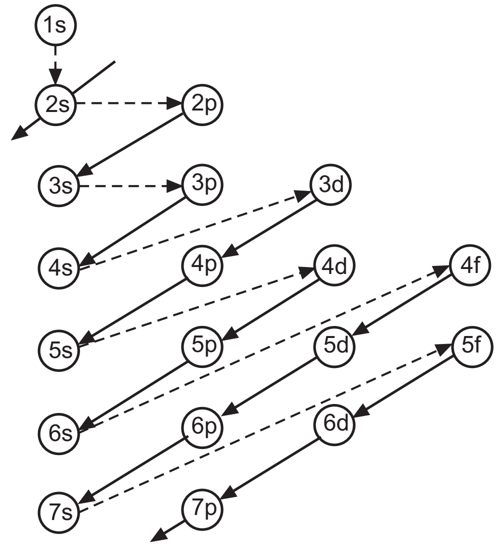


Fig. 1.14 : Aufbau order of orbitals for feeding in electrons

Energy sequence rules

The orbitals may be arranged in the order of their increasing energies using the following rules :

n + *l* Rule :

In a neutral atom, the lower the value of (n + *l*) for an orbital, lower is its energy. However, if the two different types of orbitals have the same value of (n + *l*), the orbital with lower value of n has lower energy.

To illustrate the (n + *l*) rule, different examples are given in Table 1.4.

Table 1.4 : Illustration of (n + *l*) rule

Type of orbital	Value of n	Value of *l*	Value of n + *l*	Relative energy
1s	1	0	1 + 0 = 1	Lowest energy
2s 2p	2 2	0 1	2 + 0 = 2 2 + 1 = 3	Higher energy than 1s orbital. 2p orbitals (n = 2) have lower energy than 3s (n = 3) orbital
3s 3p	3 3	0 1	3 + 0 = 3 3 + 1 = 4	3p orbitals (n = 3) have lower energy than 4s (n = 4) orbital
4s **3d** 4p	4 3 4	0 2 1	4 + 0 = 4 3 + 2 = 5 4 + 1 = 5	3d orbitals (n = 3) have lower energy than 4p (n = 4) orbital.

As a rule, a new electron enters that orbital where (n + *l*) is minimum. When (n + *l*) has same value for two or more orbitals, the new electron enters that orbital where 'n' is minimum.

General order for increasing energies of the orbitals is represented below.

Orbital	1s	2s	2p	3s	3p	4s	3d	4p	5s	4d	5p	6s
(n + *l*)	1	2	3	3	4	4	5	5	5	6	6	6

1.16 ELECTRONIC CONFIGURATION OF ATOMS

From the above discussion about the ‘build-up’ of the electronic configuration of elements has been presented in the form of Table 1.4 in which the distribution of electrons in the main energy levels and sub-energy levels (or orbitals) has been clearly shown. The ‘building-up’ process for the electrons is governed by the following rules :

(i) Each electron shell can hold a maximum of $2n^2$ electrons, where ‘n’ is the shell number.

(ii) Electrons are added one by one as we move from one element to the next in the order of increasing atomic number.

(iii) These electrons are accommodated in s, p, d, f orbitals. The maximum number of electrons in each type of orbital being s = 2, p = 6, d = 10, f = 14.

(iv) Aufbau principle : (Aufbau = building up) : According to Aufbau principle, electrons tend to occupy orbitals of minimum energy. In other words, 'electrons enter various orbitals in the order of increasing energy.' i.e.

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f$$

(v) n + *l* rule (Energy sequence rules)

(vi) Hund's rule [Refer article 1.15 (b)]

"Pairing of electrons does not take place in any p, d, f orbitals until each of such orbitals contain at least 1 electron each."

(vii) Pauli's exclusion principle : "No two electrons in a single atom can have the same set of four quantum numbers." In other words, any orbital can have a maximum of only two electrons.

(Please see Table on page no. 1.16)

Exceptions : We find some exceptions in which the elements exhibit slight variation from the standard pattern e.g. in the case of transition elements like chromium (Cr) and copper (Cu), the electronic configurations are :

Chromium (Cr)	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^4, 4s^2$	… Expected
At. No. 24	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5, 4s^1$	… Observed

i.e. Ar structure and

3d					4s
↑	↑	↑	↑	↑	↑

Copper (Cu)	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^9, 4s^2$	… Expected
At. No. 29	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^1$	… Observed

i.e. Ar structure and

3d					4s
↑↓	↑↓	↑↓	↑↓	↑↓	↑

The reason for such irregularities or disparity occur due to more stability of half filled or completely filled orbitals. A half filled or completely filled orbital has less energy content and hence it is more stable.

Hence, chromium has a more stable structure with $3d^5$, $4s^1$ as both d and s orbitals are half filled. Similarly, copper with $3d^{10}$, $4s^1$ has a stable structure. Here $3d^{10}$ is completely filled and $4s^1$ is half filled.

1.17 ELECTRONIC CONFIGURATION OF INERT GAS ELEMENTS

The six inert gases helium, neon, argon, krypton, xenon and radon forming a family of monoatomic elements constitute a group by themselves in the periodic table known as *'zero group elements'* as these elements have zero valency. On account of their rare occurrence in nature, they were also called as *'rarer gases'* of the atmosphere or *'noble gases'* on account of their analogy (similarity) to gold and platinum. The electronic configuration of inert gases is given in Table 1.5 (on page no. 1.20)

From the electronic configuration of inert gases, it is clear that all these gases have 8 (i.e. s^2 p^6) electrons (except He having 2 electrons) in their outermost shell. *"The electronic arrangement in which 8 electrons are present in the outermost shell of an atom is called stable configuration (Octet rule)."* Such stable elements have no tendency to gain or lose or share electrons, and they do not ordinarily combine chemically with any other element or with each other. Due to their chemical inertness, they are called *inert gases.*

1.18 ISOTOPES

According to **Dalton (1808)**, the atoms of the same element are identical in mass, but it is not so. **Soddy (1913)** first introduced the term *'isotope' (Greek – iso-same; topes - place).* Since the place of an element in the periodic table is determined by its atomic number, isotopes occupy the same place in the table. Atoms of the same element have same atomic number but different masses due to the different number of neutrons in the nucleus.

"Different atoms of the same element having the same atomic number but different mass numbers are called isotopes."

Elements are represented by $^{A}_{Z}E$ *or* $^{A}_{Z}X$*, where A is the mass number and Z the atomic number and E or X an atom of any element.*

Examples : Isotopes and their structure :

Since isotopes of an element have the same atomic number, each of these contains equal number of protons. They have different atomic masses which is accounted for by the different number of neutrons present in the nucleus. Thus *the isotopes of an element are characterised by different number of neutrons in the nucleus.*

Table 1.5 : Orbital Electronic Configuration of Elements upto At. No. 30

At. No.	Element	Symbol	Orbital Electronic Configuration			
			K **n = 1**	**L** **n = 2**	**M** **n = 3**	**N** **n = 4**
1	Hydrogen	H	$1s^1$			
2	Helium	He	$1s^2$			
3	Lithium	Li	$1s^2$	$2s^1$		
4	Beryllium	Be	$1s^2$	$2s^2$		
5	Boron	B	$1s^1$	$2s^2\ 2p^1$		
6	Carbon	C	$1s^2$	$2s^2\ 2p^2$		
7	Nitrogen	N	$1s^2$	$2s^2\ 2p^3$		
8	Oxygen	O	$1s^2$	$2s^2\ 2p^4$		
9	Fluorine	F	$1s^2$	$2s^2\ 2p^5$		
10	Neon	Ne	$1s^2$	$2s^2\ 2p^6$		
11	Sodium	Na	$1s^2$	$2s^2, 2p^6$	$3s^1$	
12	Magnesium	Mg	$1s^2$	$2s^2, 2p^6$	$3s^2$	
13	Aluminium	Al	$1s^2$	$2s^2, 2p^6$	$3s^2\ 3p^1$	
14	Silicon	Si	$1s^2$	$2s^2, 2p^6$	$3s^2\ 3p^2$	
15	Phosphorous	P	$1s^2$	$2s^2, 2p^6$	$3s^2\ 3p^3$	
16	Sulphur	S	$1s^2$	$2s^2, 2p^6$	$3s^2\ 3p^4$	
17	Chlorine	Cl	$1s^2$	$2s^2, 2p^6$	$3s^2\ 3p^5$	
18	Argon	Ar	$1s^2$	$2s^2, 2p^6$	$3s^2\ 3p^6$	
19	Potassium	K	$1s^2$	$2s^2\ 2p^6$	$3s^2\ 3p^6$	$4s^1$
20	Calcium	Ca	$1s^2$	$2s^2\ 2p^6$	$3s^2\ 3p^6$	$4s^2$
21	Scandium	Sc	$1s^2$	$2s^2\ 2p^6$	$3s^2\ 3p^6\ 3d^1$	$4s^2$
22	Titanium	Ti	$1s^2$	$2s^2\ 2p^6$	$3s^2\ 3p^6\ 3d^2$	$4s^2$ Transition elements
23	Vanadium	V	$1s^2$	$2s^2\ 2p^6$	$3s^2\ 3p^6\ 3d^3$	$4s^2$
24	Chromium	Cr	$1s^2$	$2s^2\ 2p^6$	$3s^2\ 3p^6\ 3d^{5*}$	$4s^1$
25	Manganese	Mn	$1s^2$	$2s^2\ 2p^6$	$3s^2\ 3p^6\ 3d^5$	$4s^2$
26	Iron	Fe	$1s^2$	$2s^2\ 2p^6$	$3s^2\ 3p^6\ 3d^6$	$4s^2$
27	Cobalt	Co	$1s^2$	$2s^2\ 2p^6$	$3s^2\ 3p^6\ 3d^7$	$4s^2$
28	Nickel	Ni	$1s^2$	$2s^2\ 2p^6$	$3s^2\ 3p^6\ 3d^8$	$4s^2$
29	Copper	Cu	$1s^2$	$2s^2\ 2p^6$	$3s^2\ 3p^6\ 3d^{10*}$	$4s^1$
30	Zinc	Zn	$1s^2$	$2s^2\ 2p^6$	$3s^2\ 3p^6\ 3d^{10}$	$4s^2$

Table 1.6 : Electronic configuration of inert gases

Element	At. No.	Electronic Configuration						Electrons in last shell ns^2, np^6
		K	L	M	N	O	P	
		1s (2)	2s, 2p (2, 6)	3s, 3p, 3d (2, 6, 10)	4s, 4p, 4d, 4f (2, 6, 10, 14)	5s, 5p, 5d (2, 6, 10)	6s, 6p (2, 6)	
He	2	$1s^2$						$1s^2$
Ne	10	$1s^2$	$2s^2, 2p^6$					$2s^2, 2p^6$
Ar	18	$1s^2$	$2s^2, 2p^6$	$3s^2, 3p^6$				$3s^2, 3p^6$
Kr	36	$1s^2$	$2s^2, 2p^6$	$3s^2, 3p^6, 3d^{10}$	$4s^2, 4p^6$			$4s^2, 4p^6$
Xe	54	$1s^2$	$2s^2, 2p^6$	$3s^2, 3p^6, 3d^{10}$	$4s^2, 4p^6, 4e^{10}$	$5s^2, 5p^6$		$5s^2, 5p^6$
Rn	86	$1s^2$	$2s^2, 2p^6$	$3s^2, 3p^6, 3d^{10}$	$4s^2, 4p^6, 4d^{10}, 4f^{14}$	$5s^2, 5p^6, 5d^{10}$	$6s^2, 6p^6$	$6s^2, 6p^6$

The atomic structure of an isotope with atomic number Z and mass number A (atomic mass in amu) can be given as follows :

(1) The number of extranuclear electron is Z.

(2) The number of protons in the nucleus is Z.

(3) The mass number A is equal to the total number of protons (Z) and neutrons (n) in the nucleus.

i.e. $$A = Z + n$$

$\therefore$ $$n = A - Z$$

1. Isotopes of Hydrogen : There are three isotopes of hydrogen : protium (^1_1H), deuterium (^2_1H or ^2_1D) and tritium (^3_1H or ^3_1T), with atomic number 1 and mass numbers 1, 2, 3. Their names, symbols and relative abundance are given in Table 1.7.

Table 1.7 : Isotopes of Hydrogen

	Name of Isotope	Symbol	Mass Number	% abundance in nature	Average At. wt.
1.	Protium or hydrogen	$_1H^1$	1	99.984	
2.	Deuterium or heavy hydrogen	$_1H^2$ or $_1D^2$	2	0.015	1.008
3.	Tritium	$_1H^3$ or $_1T^3$	3	10^{-7}	

Protium is the most abundant in natural hydrogen, deuterium about 0.015 % and tritium only one out of 10,000,000 hydrogen atoms.

Structure : The atomic number of the three isotopes of hydrogen is 1, while their mass numbers are : protium 1, deuterium 2, and tritium 3. Therefore, each of the three isotopes has one extranuclear electron and one proton in the nucleus. The nucleus of protium is made of one proton only, while the number of neutrons (A – Z) present in deuterium is 2 – 1 = 1, and in tritium 3 – 1 = 2. The structure of three isotopes of hydrogen can be pictorially represented as **(May 2009)**

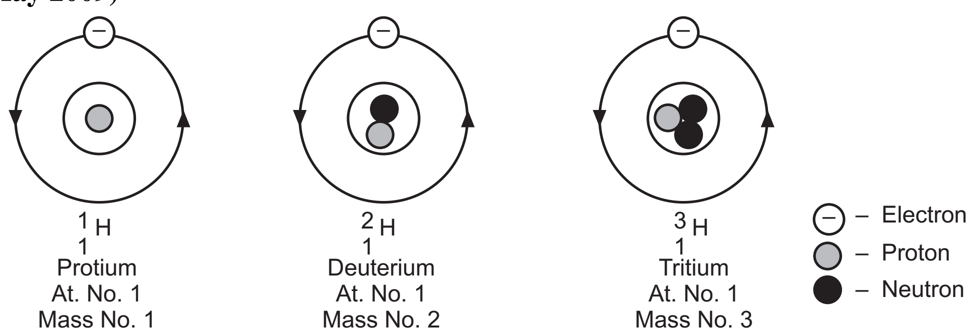


Fig. 1.15 : Atomic diagrams of three isotopes of hydrogen

2. Isotopes of Oxygen : Oxygen has three isotopes $_8O^{16}$, $_8O^{17}$, $_8O^{18}$. Each isotope has the same atomic number 8, but different mass numbers 16, 17, 18 respectively. These are found with the relative abundance of 99.759, 0.037 and 0.204 respectively. Each isotope has 8 extranuclear electrons and 8 protons in the nucleus. The number of neutrons (A – Z) in three isotopes are 8, 9, 10 respectively.

Structure :

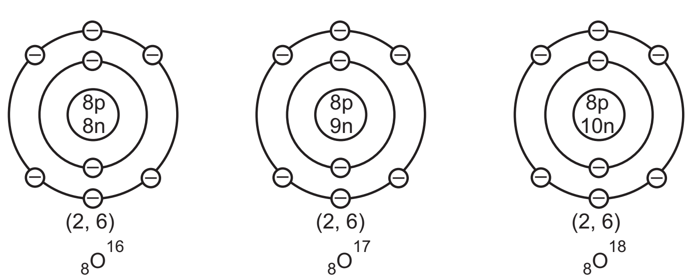


Fig. 1.16 : Atomic structure of three isotopes of oxygen

3. Isotopes of Chlorine : Chlorine is a mixture of two isotopes : $^{35}_{17}Cl$ and $^{37}_{17}Cl$. Their percentage abundance is 75.53 and 24.47 respectively.

Structure : The atomic number of two isotopes of chlorine is 17, while their mass numbers are 35 and 37. Therefore, each isotope has 17 extranuclear electrons and 17 protons in the nucleus. The number of neutrons (A – Z) in these isotopes is :

^{35}Cl 35 – 17 = 18 neutrons

^{37}Cl 37 – 17 = 20 neutrons

The atomic structure of isotopes of chlorine can be pictorially represented as :

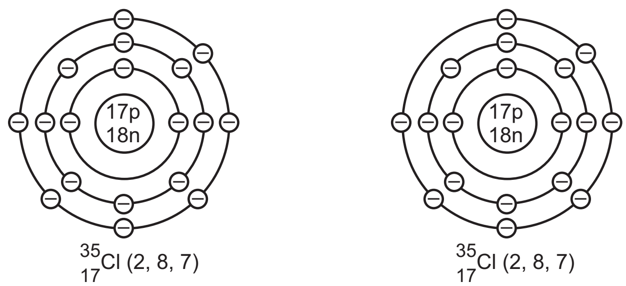


Fig. 1.17 : Atomic structure of two isotopes of chlorine

4. Isotopes of Neon : Neon has been found to consist of three isotopes : $^{20}_{10}Ne$, $^{21}_{10}Ne$ and $^{22}_{10}Ne$. Their percentage abundance is

^{20}Ne	^{21}Ne	^{22}Ne
90.92 %	0.257 %	8.82 %

Structure : The atomic number of three isotopes of neon is 10, while their mass numbers are 20, 21 and 22 respectively. Therefore, each of these isotopes has ten extranuclear electrons and ten protons in the nucleus. The number of neutrons (A – Z) are : ^{20}Ne, 20 – 10 = 10, ^{21}Ne, 21 – 10 = 11; ^{23}Ne, 22 – 10 = 12. The atomic structure of isotopes of neon can, therefore, be represented diagrammatically as shown below.

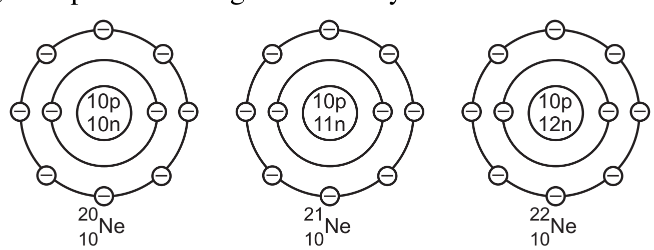


Fig. 1.18 : Atomic structure of three isotopes of Neon

5. Isotopes of Uranium : There are three isotopes of uranium :

$$^{238}_{92}U,\ ^{235}_{92}U,\ \text{and}\ ^{234}_{92}U.$$

Natural uranium consists almost entirely of ^{238}U, with about 0.72 % of ^{235}U and 0.006 % of ^{234}U. These isotopes are particularly important in atomic energy.

Structure : The atomic number of three isotopes of uranium is 92 and their mass numbers are 238, 235 and 234. Thus each isotope has 92 extranuclear electrons and 92 protons. The number of neutrons (A – Z) in these isotopes is :

^{238}U 238 – 92 = 146 neutrons

^{235}U 235 – 92 = 143 neutrons

^{234}U 234 – 92 = 142 neutrons

The atomic structure of three isotopes of uranium may be represented pictorially as :

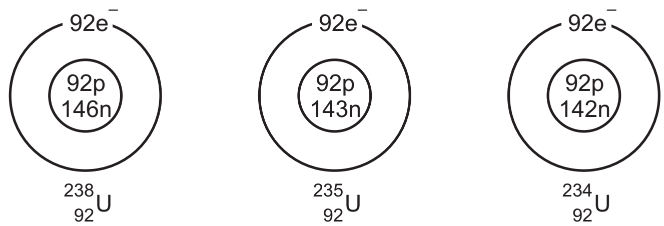


Fig. 1.19 : Atomic structure of three isotopes of uranium

Table 1.8 : The naturally occurring isotopes of elements with atomic numbers 1 to 10 are given in the following table

Isotope	Atomic number (Z)	Atomic mass Mass number (A)	Composition of nucleus		Number of Electrons in K and L shells
			Protons (Z)	Neutrons (A – Z)	
Hydrogen - 1	1	1	1	0	1
Hydrogen - 2	1	2	1	1	1
Hydrogen - 3	1	3	1	2	1
Helium - 3	2	3	2	1	2
Helium - 4	2	4	2	2	2
Lithium - 6	3	6	3	3	2, 1
Lithium - 7	3	7	3	4	2, 1
Boron - 10	5	10	5	5	2, 3
Boron - 11	5	11	5	6	2, 3
Carbon - 12	6	12	6	6	2, 4
Carbon - 13	6	13	6	7	2, 4
Carbon - 14	6	14	6	8	2, 4
Nitrogen - 13	7	13	7	6	2, 5
Nitrogen - 14	7	14	7	7	2, 5
Nitrogen - 16	7	16	7	9	2, 5
Oxygen - 16	8	16	8	8	2, 6
Oxygen - 17	8	17	8	9	2, 6
Oxygen - 18	8	18	8	10	2, 6
Neon - 20	10	20	10	10	2, 8
Neon - 21	10	21	10	11	2, 8
Neon - 22	10	22	10	12	2, 8

The differences in isotopes due to mass differences are termed as *isotopic effects.*

Almost every element in nature exists as a mixture of isotopes. The isotopes of the elements with atomic numbers 1 to 10, and their structure is listed in Table 1.7. It may be noted that some elements e.g. fluorine, are monoisotropic. These are found in nature only as a single isotope. Only about 20 elements are monoisotropic.

Isotopic Effects :

Although in many respects the chemistry of isotopes of an element is the same, there are significant differences between them due to difference in masses. Thus the physical properties of compounds of each isotope of an element are distinctly different from those of others. Similarly, reaction rates of the individual isotopes are also different.

Properties of isotopes : Isotopes of an element have

1. Same atomic number
2. Same position or place in periodic table
3. Identical electronic configuration
4. Identical chemical properties
5. Different number of neutrons in their nucleus
6. Slightly different physical properties as their mass numbers are different.

1.19 ISOBARS

The word *isobar means 'equally heavy' is taken from Greek isos = equal and barys = heavy.*

The *atoms* which have the *same mass number (A)* but *different atomic numbers (Z)* are called *isobars*.

For example, $^{40}_{18}Ar$, $^{40}_{19}K$, and $^{40}_{20}Ca$ are isobaric atoms. Similarly, $^{235}_{92}U$, $^{235}_{93}Np$ and $^{235}_{94}Pu$ are isobars.

Structure : Since isobars have the same mass number, the number of (protons + neutrons) in the nucleus in each of these is equal. The number of protons being given by atomic number (Z), the number of neutrons is, therefore, (A – Z), where A is the mass number. The number of extranuclear electrons is equal to (Z). Thus the atomic structure of the isobars $^{40}_{18}Ar$, $^{40}_{19}K$ and $^{40}_{20}Ca$ is depicted below.

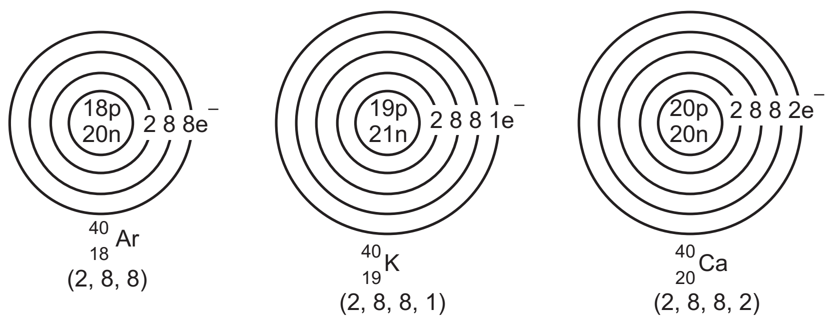


Fig. 1.20 : Isobars of Argon, Potassium and Calcium

Other examples of isobars are :

1. $^{64}_{28}Ni$, $^{64}_{30}Zn$
2. $^{86}_{36}Kr$, $^{86}_{38}Sr$
3. $^{210}_{82}Pb$, $^{210}_{83}Bi$
4. $^{235}_{92}U$, $^{235}_{93}Np$, $^{235}_{94}Pu$

Properties of Isobars :

Thus isobars have

1. different atomic numbers
2. different positions in periodic table
3. different electronic configurations
4. different chemical properties
5. different physical properties
6. identical mass numbers only

Distinction between Isotopes and Isobars

	Isotopes	Isobars
1.	They have the same atomic number but different mass numbers.	They have the same mass number but different atomic numbers.
2.	They have identical electronic configuration.	They have different electronic configurations.
3.	They occupy the same place in the periodic table. e.g. $^{35}_{17}Cl$, $^{37}_{17}Cl$	They occupy different places in the periodic table. e.g. $^{40}_{18}Ar$, $^{40}_{19}K$, $^{40}_{20}Ca$
4.	Their chemical properties are identical.	Their chemical properties are different.
5.	They have the same number of protons and electrons but different number of neutrons.	They have unequal number of protons, electrons and neutrons.

1.20 ELECTRONIC THEORY OF VALENCY

According to classical (or old) concept, valency may be defined as *'the number of atoms of hydrogen that ordinarily combine with one atom of the element.' As per this definition, the elements like chlorine, oxygen, nitrogen and carbon form stable compounds with hydrogen such as HCl, H_2O, NH_3 and CH_4*. So the valency of chlorine, oxygen, nitrogen and carbon is 1, 2, 3, 4 respectively. But the above simple definition of valency cannot explain the valency of carbon in compounds, such as C_2H_2, C_2H_4, C_2H_6 etc. According to this concept, the valency of carbon is 1, 2, 3 respectively, which is absurd (not possible). In order to explain such compounds, the electronic theory of valency was put forward by Lewis, Langmuir and Kossel (1916) from the study of electronic configuration of inert gases and other elements.

Fig. 1.21 : Linus Pauling

"Pauling is best known for his remarkable work in investigating the nature of 'chemical bond,' that is the forces that join atoms together to form molecules. It was for this work that he was awarded Nobel Prize in Chemistry in 1954.

1.21 LEWIS AND LANGMUIR CONCEPT OF STABLE CONFIGURATION

From the study of electronic configuration of inert gases, Lewis and Langmuir put forward the following postulates :

1. The electrons present in the outermost orbit of an atom determine the valency of an atom and are therefore, called *'valency electrons.'* If the last orbit is removed, the rest of the atom is called *'kernel'* or core of the atom.

2. Atoms of the elements containing 8 electrons in the outermost orbit or shell (or 2 electrons as in the case of helium) are stable. The electronic arrangement in which 8 electrons (octet) or 2 electrons (duplet) are present in the outermost shell of atom is known as stable configuration.

3. Only those elements having less than 8 electrons in the outermost shell of their atoms are capable of chemical combination. Such elements having the tendency to take part in chemical combination in such a way so as to acquire the stable configuration of the nearest inert gas element.

   It has been observed that, the atom of an element tends to achieve an octet by the smallest possible change. Thus, the elements having less than four valency electrons will lose (or lend) and the elements having more than four valency electrons will gain (or borrow) the electrons to complete the octet. This is the fundamental cause of chemical combination.

4. The valency of an element may be defined as the *number of electrons its atom can lose or gain or share so as to complete its octet and become stable.*

There are three modes of chemical combination :

(a) By transference of electrons

(b) By mutual sharing of electrons

(c) By one sided sharing of electrons.

In all the cases, a chemical bond is formed between the two combining atoms :

Chemical bond : "In chemical bond formation, atoms interact by losing, gaining or sharing of electrons so as to acquire a inert gas configuration."

Octet Rule (or Rule of Eight) : "The tendency of atoms to acquire eight electrons in the outer shell is also known as the "Octet Rule" or the Rule of Eight. Since helium has two electrons in the outer shell, for hydrogen and lithium having one and three (2, 1) electrons respectively, it is the "Rule of two or Duplet".

1.22 CONCEPT OF VARIABLE VALENCY

Generally, valency of an element is fixed or constant but in certain cases of elements, valency varies according to conditions. The valency of copper compounds is either +1 or +2. The distribution of electrons in Cu atom (At. No. 29) is 2, 8, 18, 1. In the formation of an electrovalent compound, the electron in the last shell is removed and its valency becomes +1. With a little more energy one more electron from the penultimate shell of Cu atom is removed, as this electron is close in energy content to the outermost electron and electrovalency of copper becomes +2.

Similarly iron (Fe) shows +2 and +3 electrovalency in its electrovalent compounds. The distribution of electrons in iron atom (At. No. 26) is 2, 8, 14, 2. When it loses two electrons in the formation of electrovalent compounds like $FeCl_2$, its electrovalency becomes +2. When more energy is used (i.e. using more powerful oxidising agent), it can lose one more electron from the penultimate shell of Fe atom, as this electron is close in energy content to the outermost electron. Same reasoning explains the variable valency of mercury (+1 and +2), tin (+2 and +4), lead (+2 and +4).

In the above cases, the radical with lower valency is designated by '–ous', while the one with higher valency by '–ic'. For example :

$FeCl_2$ (ferrous chloride) ;	$FeCl_3$ (ferric chloride)
Hg_2Cl_2 (mercurous chloride ;	$HgCl_2$ (mercuric chloride)
CuCl (cuprous chloride) ;	$CuCl_2$ (cupric chloride)
$SnCl_2$ (stannous chloride) ;	$SnCl_4$ (stannic chloride)

The variable valency shown by certain elements cannot be satisfactorily explained by the loss of their valency electrons during electrovalent bonding.

1.23 TYPES OF VALENCY

There are three types of valency :

(1) Electrovalency (or Electrovalent bond or Ionic bond)

(2) Co-valency (or Covalent bond or non-ionic bond)

(3) Co-ordinate valency. (Not in syllabus)

1.24 ELECTROVALENCY

"The number of electrons that an atom of an element gains or losses to complete its last orbit is called electrovalency."

In this type of valency, one atom loses certain number of valency electrons and attains a stable configuration (with 8 electrons in the last shell), thus acquiring a positive charge. The other atom gains or accepts the same number of electrons and completes its octet, thus acquiring the same negative charge. This loss and gain of electrons takes place in dissimilar atoms to complete their respective orbits. Since, the two atoms have developed charges due to gaining and losing of electrons, therefore, they are held together by electrostatic forces of attraction.

Thus, a bond or linkage is formed between the two dissimilar atoms or ions due to electrostatic forces of attraction, which is called *'electrovalent bond'* or electrovalent linkage or ionic bond.

Types of Electrovalency : Electrovalency is of two types :

(a) Positive electrovalency : The valency obtained by the loss of valency electrons from the atom of metallic element so as to complete its last shell is known as positive electrovalency. For example

(i) Sodium atom losses *'one valency electron'* to complete its octet. Thus, positive electrovalency of sodium atom is +1 (Na^+).

$$\underset{(2,\,8,\,1)}{Na} \longrightarrow \underset{(2,\,8)}{Na^+} + e^-$$

(ii) Magnesium atom losses *'two valency electrons'* to complete its octet. Thus, positive electrovalency of magnesium atom is +2 (Mg^{++}).

$$\underset{(2,\,8,\,2)}{Mg} \longrightarrow \underset{(2,\,8)}{Mg^{++}} + 2\bar{e}$$

(iii) Aluminium atom losses *'three valency electrons'* to complete its octet. Thus, positive electrovalency of aluminium atom is +3 (Al^{+++}).

$$\underset{(2,\,8,\,3)}{Al} \longrightarrow \underset{(2,\,8)}{Al^{+++}} + 3e^-$$

(b) Negative electrovalency : The valency obtained by the *'gain of electrons'* by the atoms of non-metallic elements, so as to complete their octets is known as negative electrovalency.

Examples :

(i) Chlorine atom gains *'one valency electron'* so as to complete its last shell. Hence, the negative electrovalency of chlorine is –1 (Cl^-).

$$\underset{(2,\,8,7)}{Cl + e^-} \longrightarrow \underset{(2,\,8,\,8)}{Cl^-}$$

(ii) Sulphur atom gains *'two valency electrons'* from its neighbouring atom to complete its last shell. Thus, the negative electrovalency of sulphur is – 2 (S^{--}).

$$\underset{(2,\,8,\,6)}{S} + 2e^- \longrightarrow \underset{(2,\,8,\,8)}{S^{--}}$$

(iii) Phosphorus atom gains *'three valency electrons'* to complete its last shell. Thus, the negative electrovalency of phosphorus is – 3 (P^{---}).

$$\underset{(2,\,8,\,5)}{P} + 3e^- \longrightarrow \underset{(2,\,8,\,8)}{P^{---}}$$

1.25 FORMATION OF ELECTROVALENT COMPOUNDS

1. Formation of Sodium Chloride : Sodium chloride is formed by electrovalent linkage. Sodium atom has an electronic configuration of (2, 8, 1), while chlorine atom has the configuration (2, 8, 7).

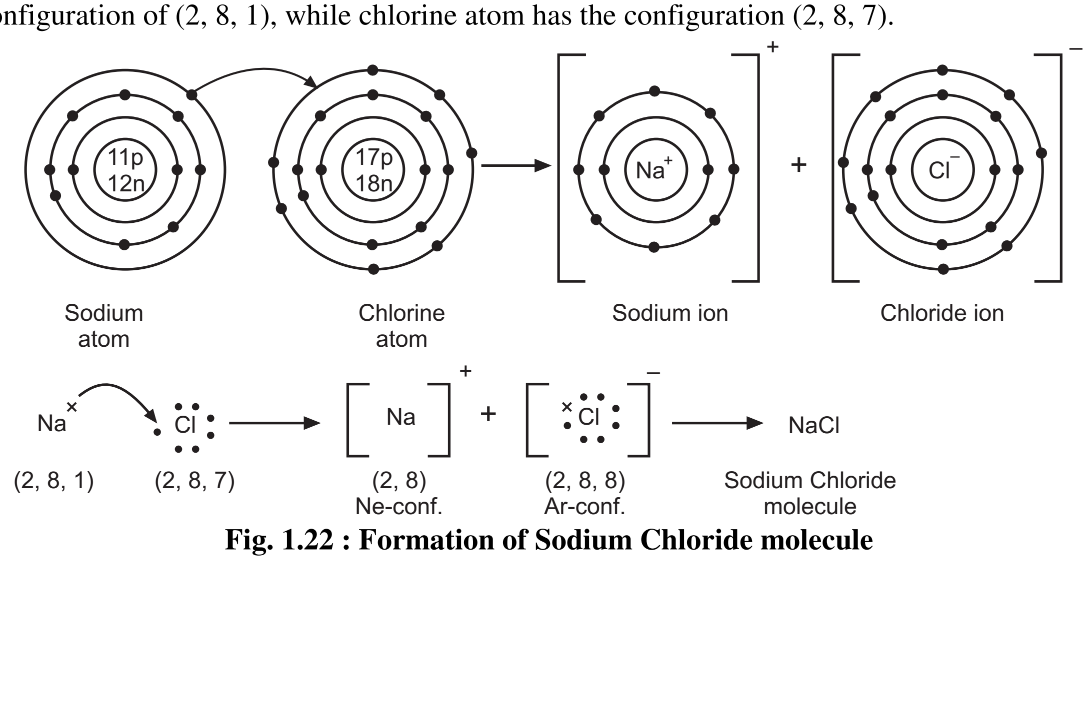
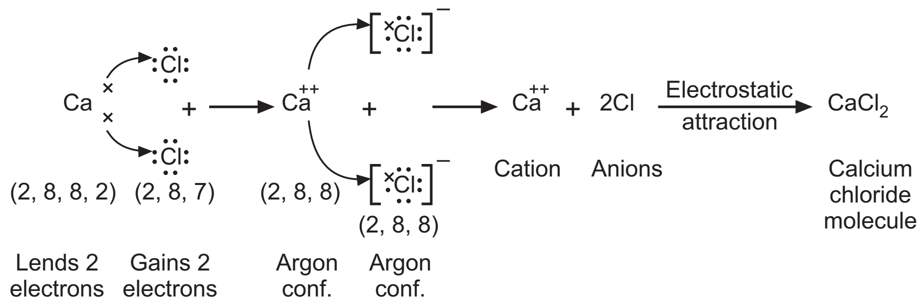


Fig. 1.22 : Formation of Sodium Chloride molecule

During their combination, Na–atom losses its one valency electron and acquires a unit +ve charge and attains a stable configuration (2, 8) as that of neon. The electron lossed by Na–atom is gained by Cl atom, which acquires a unit –ve charge and attains a stable configuration (2, 8, 8) as that of argon. These charged ions (Na^+ and Cl^- ions) thus produced are bound together with electrostatic forces of attraction and produce apparently neutral molecule of sodium chloride (NaCl).

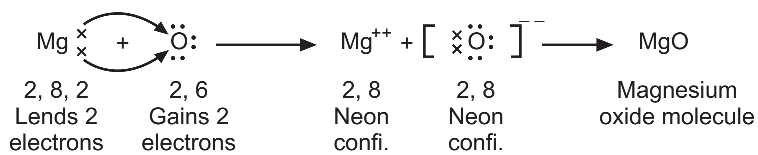
Such a union of atoms which takes place by the loss and gain of electrons is called *'electrovalent linkage'.*

2. Formation of Calcium Chloride Molecule ($CaCl_2$) : A molecule of calcium chloride ($CaCl_2$) consists of one atom of calcium and two atoms of chlorine. Calcium atom (At. No. 20) has the electronic configuration (2, 8, 8, 2), while each chlorine atom (At. No. 17) has the configuration (2, 8, 7).



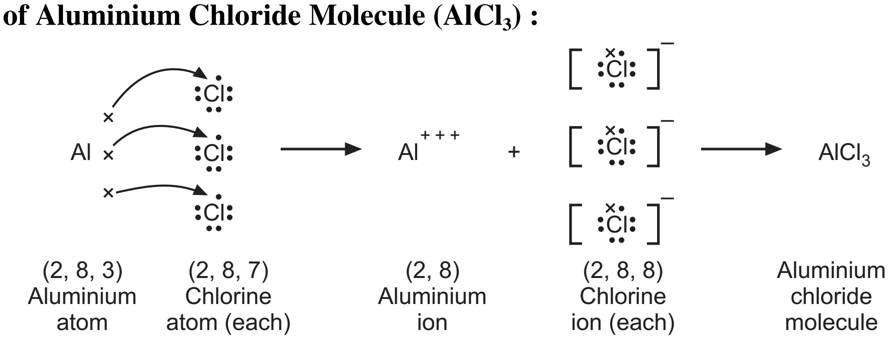
In the formation of calcium chloride molecule, 2 electrons are transferred from calcium atom to two chlorine atoms. By the loss of two electrons, the Ca atom acquires +2 charges and converts into Ca^{++} ion and attains a stable configuration of nearest inert gas element argon. Similarly, two Cl atoms gain one electron each and acquire –1 charge and form 2 Cl^- ions. These oppositely charged ions (Ca^{++} and 2 Cl^-) combine together by the forces of electrostatic attraction to form apparently neutral molecule of $CaCl_2$.

3. Formation of Magnesium Oxide : The formation of magnesium oxide can be diagrammatically represented as follows :



In the formation of magnesium oxide, 2 electrons are transferred from magnesium atom to oxygen atom. By the loss of 2 electrons, the magnesium atom acquires +2 charge and attains the stable configuration of neon gas. On the other hand, oxygen atom acquires –2 charge by the gain of 2 electrons from magnesium atom and attains the stable configuration of neon gas. These two equal and oppositely charged ions (Mg^{++} and O^{--}) unite together by the forces of electrostatic attraction to form apparently neutral molecule of magnesium oxide. Thus, MgO is formed by electrovalency.

4. Formation of Aluminium Chloride Molecule ($AlCl_3$) :



In the formation of aluminium chloride molecule, 3 electrons are transferred from aluminium atom to three chlorine atoms. By the loss of 3 electrons, the aluminium atom acquires +3 charges and attains the stable configuration of the nearest inert gas element neon. On the other hand, each chlorine atom gains one electron from Al atom and acquires –1 charge and attains the stable configuration that of argon. These two equal and oppositely charged ions (Al^{+++} and 3 Cl^-) combine together by the force of electrostatic attraction to form apparently neutral molecule of aluminium chloride ($AlCl_3$).

Properties of Electrovalent Compounds :

1. Electrovalent or ionic compounds are soluble in polar solvents like water, and are insoluble in non-polar solvents like benzene, carbon disulphide and carbon tetra chloride.
2. Electrovalent compounds are ionised in the fused as well as in solution state, hence they conduct electricity.
3. Electrovalent compounds have high melting and boiling points.
4. These are mostly inorganic compounds.

1.26 COVALENCY

"The valency obtained by the mutual sharing of electrons between the similar or dissimilar atoms so as to complete their last orbits is called co-valency or covalent bond." The compounds formed by sharing of electrons between the atoms are called covalent compounds.

It should be noted that in covalent bond (or linkage), no electrical charges are developed as there is no loss and gain of electrons. Here only sharing of electrons takes place. Sharing of electrons occurs in the following ways :

(a) When a covalent compound is formed by mutual sharing of *'one pair'* of electrons between the two atoms, it is called *'single covalent bond'* (–).

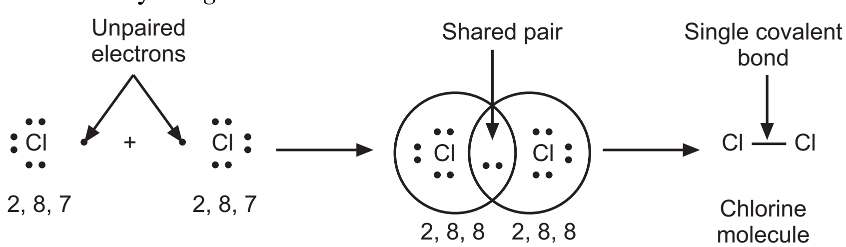
(b) When the covalent compound is formed by mutual sharing of *'two pairs'* of electrons between the two atoms, it is called *'double covalent bond'* (=).

(c) When the covalent compound is formed by mutual sharing of *'three pairs'* of electrons between the two atoms, it is called *'triple covalent bond'* (≡).

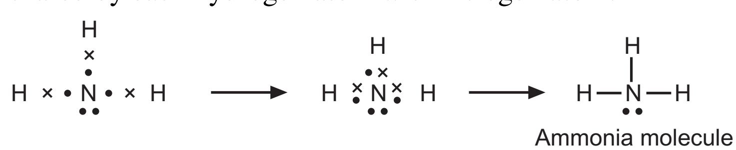
1.27 FORMATION OF COVALENT COMPOUNDS

1. Single Covalent bond (–) :

(a) Formation of chlorine molecule (Cl_2) : In the formation of chlorine molecule, each atom of chlorine contains 7 valency electrons. So each chlorine atom is in short of one electron to complete the octet. Thus, a molecule of chlorine is formed by *'single covalent bond'*.

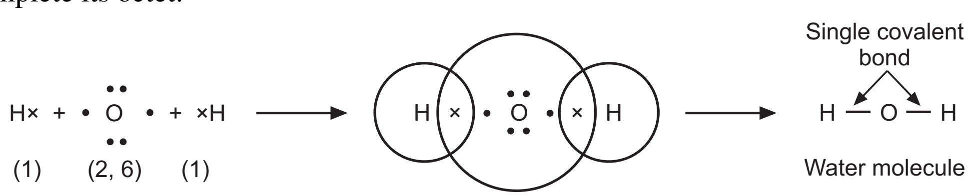


(b) Formation of ammonia molecule (NH_3) : In the formation of ammonia molecule, three atoms of hydrogen (1) combine with one atom of nitrogen (2, 5). Each hydrogen atom contributes one electron with a atom of nitrogen so that a pair of electrons is shared by each hydrogen atom with nitrogen atom.



Thus, nitrogen atom acquires an octet and hydrogen atoms acquire duplets, hence the molecule of ammonia becomes stable.

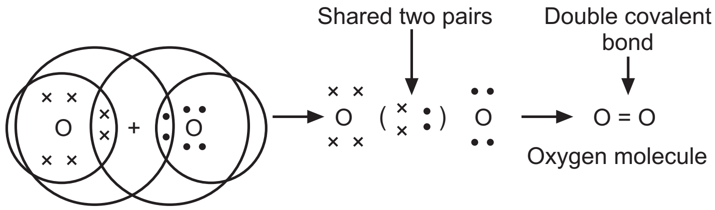
(c) Formation of water molecule (H_2O) : Water molecule (H_2O) contains two atoms of hydrogen and one atom of oxygen. Each hydrogen atom is in short of 1 electron to complete its duplet and oxygen atoms is in short of 2 electrons to complete its octet.



In the formation of water molecule, oxygen atom completes its octet by sharing two electrons with two hydrogen atoms. Similarly, hydrogen atoms complete their duplet by sharing one electron each with oxygen atom. Thus, two separate single covalent bonds are formed between hydrogen and oxygen atoms.

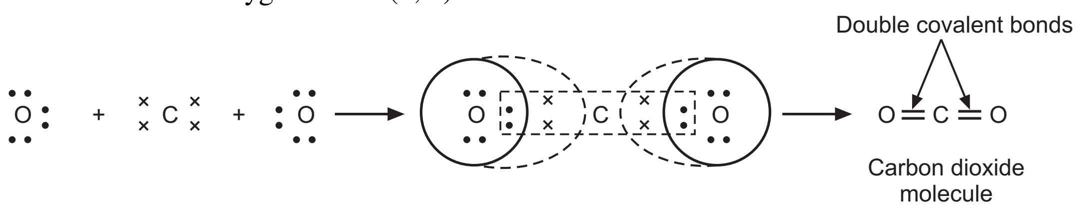
2. Double Covalent bond (=) :

(a) Formation of oxygen molecule (O_2) : Oxygen molecule is diatomic. In the formation of oxygen molecule, each atom of oxygen (2, 6) contains 6 valency electrons. Each oxygen atom is in short of 2 electrons to complete its octet.



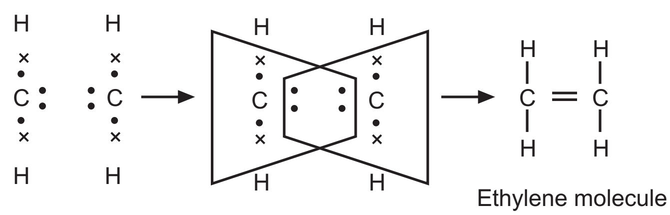
Thus, oxygen molecule is formed by sharing two pairs of electrons between two atoms of oxygen by completing the octet of each. Two shared pairs form a double covalent bond.

(b) Formation of carbon dioxide molecule (CO_2) : In the formation of carbon dioxide molecule, one carbon atom (2, 4) combines with two oxygen atoms (2, 6).



Carbon atom is in short of 4 electrons and each oxygen atom is in short of 2 electrons to complete their octets. Hence, carbon dioxide molecule is formed by two oxygen atoms sharing two pairs of electrons each with a carbon atom. Thus, two double covalent bonds are formed in the formation of CO_2 molecule.

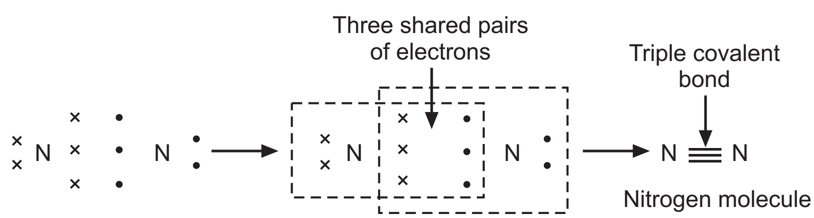
(c) Formation of ethylene molecule (C_2H_4) : The ethylene molecule is formed by the combination of two atoms of carbon (2, 4) and four atoms of hydrogen (1). Each carbon atom is in short of 4 electrons to complete the octet and each hydrogen atom is in short of 1 electron to complete the duplet.



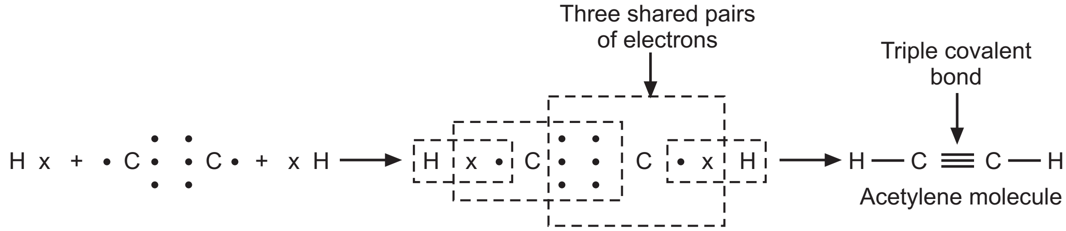
The ethylene molecule is formed by sharing two pairs of electrons between two carbon atoms and by sharing one electron with each of four hydrogen atoms. Thus, the two shared pairs form a double covalent bond between two carbon atoms in ethylene molecule.

3. Triple Covalent bond (≡) :

(a) Formation of nitrogen molecule (N_2) : Nitrogen molecule is diatomic. Each nitrogen atom (2, 5) is in short of 3 electrons to complete the octet. So each nitrogen atom contributes 3 electrons for sharing. Thus, nitrogen molecule is formed by sharing three pairs of electrons between two atoms of nitrogen and hence completing the octet of each. Three shared pairs form a triple covalent bond.



(b) Formation of acetylene molecule (C_2H_2) : Acetylene molecule consists of two atoms of carbon (2, 4) and two atoms of hydrogen (1). Each atom of carbon is in short of 4 electrons to complete the octet, while each hydrogen atom is in short of 1 electron to complete the duplet.



Thus, acetylene molecule is formed by sharing three pairs of electrons i.e. forming triple covalent bond between two carbon atoms and one pair of electrons i.e. single covalent bond with each hydrogen atom.

Properties of covalent compounds :

1. Covalent compounds are generally insoluble in water (polar solvent), but readily soluble in organic solvents such as benzene, carbon tetrachloride (non-polar solvents).
2. Covalent compounds do not ionise when dissolved in water. Thus, they are non-polar in nature. Hence, they do not conduct electricity.
3. Covalent compounds are generally volatile in nature and usually have low melting and boiling points.
4. These are generally organic compounds.

1.28 DISTINCTION BETWEEN ELECTROVALENT AND COVALENT COMPOUNDS

Sr. No.	Electrovalent Compounds	Sr. No.	Covalent Compounds
1.	These are formed by loss and gain of electrons between dissimilar atoms.	1.	These are formed by mutual sharing of electrons between similar or dissimilar atoms.
2.	They are found to exist in the form of ions even in the solid state.	2.	They are not found to exist in the form of ions in the solid or liquid state.
3.	These are polar compounds. Thus, when melted or dissolved in a solvent, they are ionised and hence conduct electric current.	3.	These are non-polar compounds. Thus, when melted or dissolved in a solvent, they are generally not ionised and hence do not conduct electric current.
4.	They possess comparatively high melting and boiling points.	4.	They possess comparatively low melting and boiling points.
5.	They are generally non-volatile and insoluble in organic solvents.	5.	They are generally volatile and usually soluble in organic solvents.

EXERCISE

1. Write short answers of the following : [2 marks]
   (a) Why is an atom electrically neutral ?
   (b) (i) The nucleus consists of 9 protons and 10 neutrons. What should be its atomic weight and electrochemical nature ?
   (ii) For an element having atomic number 9 and mass number 19, write number of protons and neutrons in it.
   (c) State the number of sub-shells in K, L, M, N shells.
   (d) State the relation between atomic number, mass number and neutrons in an atom.
   (e) Define atomic orbital.
   (f) Why is the nucleus of an atom positively charged ?
   (g) Calculate the atomic number and atomic mass number of an atom containing 19 electrons and 20 neutrons.

(h) Explain the term planetary electrons.

(i) Why is the radius of cation always smaller than its parent atom ?

(j) (i) Name the four quantum numbers.

(ii) State the significance of quantum numbers.

(k) What is Pauli's exclusion principle ?

(*l*) Explain (i) Hund's maximum multiplicity rule, (ii) Aufbau principle.

(m) (i) Which are the most stable elements ? What is their unique feature ?

(ii) Why inert gases are inactive ?

(n) Neon molecule is monoatomic and chlorine molecule is diatomic. Why ?

(o) Distinguish with respect to definition of isotopes and isobars.

(p) Distinguish with respect to definition of mass number and atomic number.

(q) Which type of particles are responsible for the presence of isotopes ?

(r) Name different sub-energy levels and give with the maximum number of electrons in each of them.

(s) State Aufbau's principle.

(t) State the maximum number of electrons that can occupy K, L, M and N energy levels if 'n' is the principal quantum number of that element.

2. Give the assumptions of Bohr's theory of atomic structure.

OR

State assumptions of Bohr's model of an atom.

3. Give the comparison of electron, proton and neutron with respect to their symbol, charge, mass and location within the atom.

4. (i) State two rules of distribution of planetary electrons. Explain with suitable examples.

(ii) State the maximum number of electrons that can occupy K, L, M and N energy levels, if 'n' is principal quantum number of that element.

5. Calculate the atomic number and atomic mass of an atom containing 19 electrons and 20 neutrons. Express the isotopes of hydrogen, in terms of atomic weight and atomic number.

6. State two rules of distribution of planetary electrons. Give the electronic configuration of an element having atomic number 11 and atomic mass number 23.

7. The atomic number is 17. Give the electronic configuration (in s, p, d, f orbitals) and explain the electro-chemical nature and activity of this element.

8. What do you understand by sub-energy levels ? How these are denoted ? How many electrons (maximum) can be accommodated in the sub-energy levels ?

9. Distinguish between energy level and sub-energy level.

10. How many atomic orbitals are present in each of s-sub-level, p-sub-level, d-sub-level and f-sub-level ?

11. Explain the difference between orbit and orbital.

12. What is the difference between orbit and orbital ? Name the different orbitals known in elements with the number of electrons present in them.

13. Give the role of four quantum numbers in determining the energy and probability of location of an electron.

14. Name the four quantum numbers. What does each quantum number describe ?

15. Give the names, significance and possible values of quantum numbers.

16. Write down the values of different quantum numbers of electrons in nitrogen atom.

17. Write down the values of different quantum numbers of electrons present in oxygen atom.

18. Write down the values of different quantum numbers of electrons present in carbon atom.

19. Nucleus of an atom has 5 protons and 6 neutrons. What would be the (i) Atomic number, (ii) Mass number, (iii) Number of electrons and (iv) Number of valency electrons ?

20. Compositions of the nuclei of two atomic species A and B are given as under :

	No. of protons	No. of neutrons
A	6	6
B	6	8

(i) Give mass numbers of A and B.

(ii) What is the relation between two species ?

(iii) Which element they represent ?

21. Substances from A to E have in them the distribution of electrons, neutrons and protons as follows :

Substance	Electron	Neutron	Proton
A	4	4	3
B	8	9	9
C	18	22	18
D	17	20	17
E	17	18	17

Making use of these data, find

(i) a cation

(ii) an anion

(iii) pair of isotopes

(iv) an atom of noble gas.

22. For n = 3 energy level, how many orbitals of all kinds are possible ?

23. What do you mean by magnetic quantum number ? What it represent ? How are m and *l* inter-related ?

24. State and explain Hund's rule and its limitation.

25. Draw the diagrams showing s and p orbitals.

26. What is Aufbau principle ? Write the sequence in which the orbitals are filled.

27. State and explain Pauli's exclusion principle.

OR

State Pauli's exclusion principle and its application.

28. Give the electronic configuration of atoms with atomic numbers 11, 14, 21, 24 and 29.

29. Explain the anamolies in electronic configuration of chromium and copper.

30. Arrange the following in the increasing order of energy : 2p, 4p, 3d, 4s, 3p, 3s, 2s

31. Write the electronic configuration of three inert elements.

32. What do you understand by inert elements ? Give the electronic configuration of Helium and Argon.

OR

What are stable elements ? What is their unique feature ?

33. Write short notes on :

(i) Pauli's exclusion principle

(ii) Hund's rule

(iii) Aufbau principle

34. What are isotopes ? Draw the atomic diagram of three isotopes of hydrogen atom.

35. Distinguish between isotopes and isobars. Explain why atomic weight of chlorine is 35.5.

36. Define isotopes and isobars. Give one example of each.

37. What are isotopes ? Explain with two examples, which type of particles are responsible for their presence ?

38. Write the electronic configuration of any four of the following elements :

$$Mg_{12}^{24}\ ,\ K_{19}^{39}\ ,\ N_{7}^{14}\ ,P_{15}^{31}\ ,Ne_{10}^{20}$$

39. Draw the electronic configuration of -

$$Si_{14}^{28},\ Cl_{17}^{35}, S_{16}^{32}, Ca_{20}^{40}, P_{15}^{31}$$

40. Naturally occurring lithium is known to contain two isotopes of mass numbers 6 and 7, the relative abundance of the isotopes being 6% and 94% respectively. What is the atomic weight of natural lithium ?

(**Ans.** 6.94)

41. Define atomic number and mass number. Draw electronic configuration of any two elements :

$$S_{16}^{32},\ Al_{13}^{27},\ Si_{14}^{28},\ Ca_{20}^{40}$$

42. Give any two points of difference between electrovalent and covalent compounds.

43. Draw the electronic configuration of any two elements :

$$O_{8}^{16},\ N_{7}^{14},\ S_{16}^{32}$$

44. Draw the figure of formation of sodium chloride or carbon dioxide molecule.

45. Draw electronic configuration of K_{19}^{39}, Fe_{26}^{56} and write the orbital electronic configuration of Ni_{28}^{59} and Zn_{30}^{65}.

46. Write short answers of the following : (2 marks)

    (a) Differentiate between electrovalent and covalent compounds on the basis of their electrical conductance.

    (b) What is the type of bonding between two chlorine atoms in chlorine molecule ?

    (c) Which elements are most likely to form covalent compounds ?

    (d) Water is a polar covalent compound. Explain.

    (e) Name the type of valency in MgO molecule.

    (f) Write the two points of difference between electrovalent and covalent compounds.

47. An element (X) has atomic number 14. Write electronic configuration of the element (in s, p, d, f, orbitals). If all the valencies are satisfied by combination with hydrogen resulting in compound XH_n, what will be the value of n ?

48. Define electrovalency. Explain the formation of NaCl compound with the help of atomic diagrams.

49. Explain the formation of $CaCl_2$ (electrovalent compound) and predict the electrovalency of calcium and chlorine.

50. How does the electronic theory of valency explain the formation of magnesium chloride ? Show that this compound is an electrovalent compound.

51. Define valency on the basis of electronic theory. Why sodium is electropositive ? Explain.

52. Two elements X and Y have the electronic configuration 2, 8, 2 and 2, 8, 7. What is the formula of ionic compound they form ? With the help of figure, explain the formation of that compound.

53. With the help of figure, explain the formation of magnesium oxide and carbon dioxide molecules.

54. Explain the electropositive and electronegative nature of the element on the basis of electronic theory of valency.

55. Define (i) valency, (ii) valency electrons. What are the electropositive and electronegative elements ?

56. Define covalency. Explain the formation of oxygen molecule.

57. Define electrovalency and covalency. Explain the formation of Cl_2 molecule by covalent bonding.

58. Distinguish between electrovalent and covalent compounds.
59. Explain the formation of MgO and N_2 molecules on the basis of electronic theory of valency.
60. With suitable example, explain electrovalency.
61. What are the types of electrovalency ? Explain.
62. Explain the concept of variable valency.
63. Explain the formation of aluminium chloride molecule.
64. Define electrovalency. During formation of electrovalent compound sodium loses one electron, magnesium loses two electrons and chlorine accepts one electron. Write their type of electrovalency.
65. Define electrovalency and give one example of electrovalent compound.
66. Sulphur atom gains two electrons, phosphorus atom gains three electrons, calcium atom loses two electrons, iron atom loses three electrons. Write the type of valency in all these elements.

❒❒❒

Chapter **2**

ELECTROCHEMISTRY

2.1 Introduction
2.2 Atoms and Ions
2.3 Ionisation and Electrolytic Dissociation
2.4 Arrhenius Theory of Electrolytic Dissociation
2.5 Degree of Ionisation
2.6 Significance of the terms involved in electrolysis
2.7 Mechanism of electrolysis
2.8 Types of cells
2.9 Faraday's laws of electrolysis
2.10 Relation between C.E. and E.C.E.
2.11 Applications of electrolysis
2.12 Conductivity of electrolyte
2.13 Electric cells and Battery
2.14 Dry cell
2.15 Lead-Acid storage cell

2.1 INTRODUCTION

Electrochemistry is a branch of chemistry which deals with the relationship between chemical reaction and electrical energy. The electrochemistry comprises : (1) the study of chemical changes produced by the passage of an electric current, and (2) the generation of electric current from chemical changes. A chemical change produced by the passage of electric current, resulting in the chemical decomposition of a substance is known as *'electrolysis'*.

Electric current is a flow of electrons generated by a battery and taken out from the negative pole of the battery when the circuit is completed. A substance which allows electric current to pass through it is called a conductor e.g. all metals, graphite, fused salts, aqueous solutions of acids, bases and salts. The conductors are of two types :

(i) Metallic conductors : In a metallic wire, electrons can pass from one end to the other without any chemical decomposition, e.g. almost all metals. In metals, there are mobile electrons.

(ii) Electrolytic conductors : For the passage of electric current through solutions, the ions must be present in solution as ions are the carriers of electric current.

Difference between Metallic and Electrolytic Conduction :

Metallic Conduction	Electrolytic Conduction
1. Electricity is conducted by the movement of electrons, which flow from negative end to the positive end.	1. Electricity is conducted by the movement of ions, which move towards the oppositely charged electrodes.
2. There are no chemical reactions and there is no change in the composition of the conductor.	2. The chemical reactions take place at the electrodes with the decomposition of the electrolyte.
3. No transfer of matter takes place.	3. Transfer of matter takes place in the form of ions.
4. If temperature is increased, the resistance to the flow of current also increases. Hence, the conduction decreases.	4. If temperature is increased, the resistance to the flow of current decreases. Hence, the conduction increases.

2.2 ATOMS AND IONS

An atom as a whole is electrically neutral (i.e. it consists of equal number of protons and electrons). Electrons in the outermost shell of an atom are called valency electrons. An atom with less than four valency electrons will lose (or lend) and an atom with more than four valency electrons will gain (or borrow) the electrons to complete its octet. Thus, when atoms lose or gain electrons, they acquire positive or negative charge and they are called as ions. *"Atoms or groups of atoms when they carry electrical charges are known as ions."*

There are two types of ions.

(a) Cations (or positive ions) : These are formed from the metallic atoms by the loss of electrons. Thus,

$$Na \longrightarrow \underset{\text{(Sodium ion)}}{Na^{+}} + e^{-}$$

$$Mg \longrightarrow \underset{\text{(Magnesium ion)}}{Mg^{++}} + 2e^{-}$$

If an atom loses electrons, the valency orbit vanishes, hence it decreases in size and becomes positively charged. It is called positive ion or cation. The cation is therefore, smaller than the corresponding atom.

(b) Anions (or negative ions) : These are formed from the non-metallic atoms by the gain of electrons. Thus,

$$Cl + e^{-} \longrightarrow Cl^{-} \text{ (Chloride ion)}$$

$$O + 2e^{-} \longrightarrow O^{--} \text{ (Oxide ion)}$$

If an atom gains electrons, it increases in size and it becomes negatively charged. It is called negative ion or anion. The anion is therefore bigger in size than the corresponding atom.

Just as there are simple negative ions like (Cl^{-}, Br^{-}, I^{-}, S^{--} etc.) there are groups of atoms acting as positive ions (NH_4^{+}) or negative ions like hydroxide (OH^{-}), sulphate (SO_4^{--}), carbonate (CO_3^{--}), phosphate (PO_4^{---}), etc.

Distinction between Atom and Ion :

An atom of an element differs to a great extent from the ions of the same element. Thus, sodium atom differs in properties from sodium ion.

Sodium atom (Na) : (i) It has incomplete outermost shell (2, 8,1).
(ii) It is electrically neutral.
(iii) It possesses all the properties of sodium metal i.e. it reacts with water at ordinary temperature and liberates H_2 gas.

Sodium ion (Na^{+}) : (i) It has complete outermost shell (2, 8).
(ii) It is positively charged.
(iii) It does not react with water and no H_2 gas is liberated.

Similarly, metallic copper is red in colour while Cu^{++} ions are blue in colour. Chlorine gas ($Cl_2 \uparrow$) is greenish-yellow in colour and has a pungent smell, but chloride ion (Cl^{-}) does not possess these properties. On the other hand, chloride ion (Cl^{-}) gives a white precipitate of $AgCl\downarrow$ with $AgNO_3$ solution, whereas chlorine gas does not give the precipitate.

Atom (Na, Cl)	Ion (Na^+, Cl^-)
1. Atom is electrically neutral. e.g. Na, Cl.	1. Ion carries either positive or negative charge. e.g. Na^+, Cl^-.
2. Atom is of one element only.	2. Ion may be a single charged atom (Na^+ or Cl^-) or a group of charged atoms (CO_3^{--}, SO_4^{--}, NH_4^+ etc.).
3. Atom may or may not have a free existence.	3. Ions exist in pairs i.e., positive and negative together in solids (Na^+ and Cl^-). In solution, they become free.
4. Atom may react with solvent.	4. Ions do not react with solvent.
5. Atom has incomplete outermost shell. e.g. Na = 2, 8, 1; Cl = 2, 8, 7	5. Ion has complete outermost shell. e.g. Na^+ = 2, 8 ; Cl^- = 2, 8, 8
6. An atom takes part in molecular reactions. e.g. $2Na + 2H_2O \rightarrow 2NaOH + H_2\uparrow$	6. An ion takes part in ionic reactions. e.g. $Ag^+ + Cl^- \rightarrow AgCl\downarrow$

2.3 IONISATION AND ELECTROLYTIC DISSOCIATION

Ionisation :

"The process of breaking up of a substance into the charged atoms or radicals is known as ionisation." The charged atoms or radicals are called ions.

Ionisation is a general term indicating the process of formation of ions in solution or in fused state or in gaseous state. For example, heat causes ionisation of a gas and making it a fairly good conductor of electricity. A high tension electric current brings about the ionisation of neon gas and other inert gases, due to which these gases glow with various colours (called neon signs), which are used in advertisements. Similarly, on melting the electrovalent compounds, which are poor conductors of electricity before melting, suddenly become good conductors. This is because, on melting, the ions become free to move.

Electrolytic Dissociation :

"The process of splitting up of an electrovalent compound when dissolved in a solvent like water is called electrolytic dissociation."

2.4 ARRHENIUS THEORY OF ELECTROLYTIC DISSOCIATION

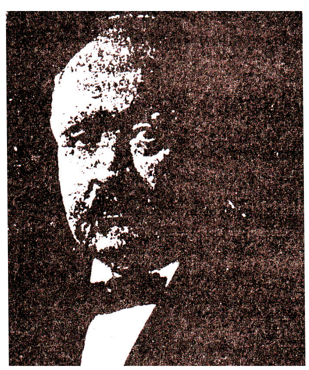


Fig. 2.1 : Svante Arrhenius (1859 - 1927)

Of the different contributions of Arrhenius to Science, his name is chiefly associated with the classical theory of electrolyte dissociation and activation theory for chemical reactions. He received the Nobel Prize for Chemistry in 1903 for theory of electrolytic dissociation.

Arrhenius put forward his ionic theory in 1887 to account for the fact that the products of electrolysis appear only at the surface of electrode. The main postulates of the theory in its modern form (ionic theory) are :

1. The molecules of an electrolyte (e.g., acids, bases and salts) when dissolved in water split up into two kinds of charged particles. One is carrying a positive charge (cation) and the other equal but negative charge (anion).

2. Cations are generally metallic radicals obtained by lose of electrons from metallic atoms. Anions are generally non-metallic radicals obtained by gain of electrons from non-metallic atoms or groups of non-metals.
3. In solution, the total number of cations (positive charges) is equal to the total number of anions (negative charges) and hence the solution as a whole is electrically neutral.
4. The number of positive or negative charges on the cation or anion corresponds to the valency of the element or radical from which the ion is derived.
5. The ions present in solution are constantly reuniting to form undissociated molecules. For example,

$$HCl \rightleftharpoons H^{+} + Cl^{-}$$

$$NaOH \rightleftharpoons Na^{+} + OH^{-}$$

$$CuSO_4 \rightleftharpoons Cu^{++} + SO_4^{--}$$

Thus, all the molecules of an electrolyte present in solution are not dissociated. Hence, the process of electrolytic dissociation is a reversible one.

2.5 DEGREE OF IONISATION

"The fraction of the total number of molecules of an electrolyte that ionises in solution is called the degree of ionisation" or degree of dissociation of the electrolyte.

$$\text{Degree of ionisation} = \frac{\text{Number of molecules ionised}}{\text{Total number of molecules dissolved}}$$

Factors affecting the degree of ionisation :

The degree of ionisation of different electrolytes is different and depends upon the following factors :

1. Nature of Solute : Ionic compounds such as acids, bases and salts are highly ionised in solution. e.g. strong acids like HCl, HNO_3, H_2SO_4 and strong bases like NaOH, KOH and all soluble salts like NaCl, KNO_3 etc. are highly ionised in solution. Partially ionic compounds such as weak acids (like acetic acid, oxalic acid) and a weak base like NH_4OH etc. are weakly ionised in solution.

2. Nature of solvent : The nature of solvent have a marked effect on ionisation. It cuts the forces of binding the two ions and thus separates them. This effect of solvent is due to its dielectric constant. (It is defined as the capacity of solvent to weaken the forces of attraction between the ions immersed in that solvent.) It has been observed that polar solvents such as water and ammonia have a great tendency to separate the ions in solution. Hence, *water ionises electrovalent compounds to a great extent as the dielectric constant of water is very high (about 80) and it acts as a strong ionising solvent.* The non-polar solvents such as benzene, and carbon disulphide have no tendency to separate the ions in the solution.

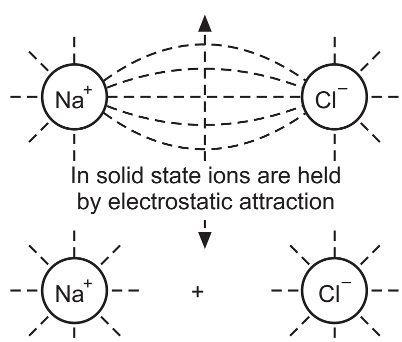


Fig. 2.2 : Separation of ions by solvent like water

3. Concentration of the solution : The degree of ionisation is inversely proportional to the concentration of the solution. The degree of ionisation increases with the dilution and at infinite dilution it approaches unity and dissociation is said to be complete. In dilute solution, the ratio of solute molecules to the solvent molecules is less and greater number of solvent molecules will separate more solute molecules into ions.

4. Temperature : The higher the temperature, the greater is the ionisation. Because, at high temperature, the molecular velocities are increased and they overcome the forces of attraction between the ions and consequently the ionisation is more.

2.6 SIGNIFICANCE OF THE TERMS INVOLVED IN ELECTROLYSIS

To understand the mechanism of electrolysis, we should know the significance of the terms involved in it. The important terms are discussed below.

1. Conductor : It is a substance which allows the electric current to pass through it. e.g. almost all metals, graphite, gas-carbon, fused salts and aqueous solutions of acids, bases and salts are conductors.

2. Non-conductor (or Insulator or Dielectric) : It is a substance which do not allow the electric current to pass through it. e.g. sulphur, glass, wood, paper, rubber, plastics, oils, alcohol, petrol, etc.

3. Electrolyte : *"The substance which is in fused state or in aqueous solution liberates ions and allows the electric current to pass through it, resulting in the chemical decomposition, is known as an electrolyte."*

Strong and Weak electrolytes : On the basis of the degree of ionisation, the electrolytes are called strong and weak electrolytes. Those electrolytes which are highly ionised in solution and hence, have a high degree of ionisation are called *'strong electrolytes'*. Examples are strong acids like HCl, HNO_3, H_2SO_4, strong bases such as NaOH, KOH and almost all soluble salts are strong electrolytes.

Those electrolytes which are only feebly ionised in the solution and hence, have a low degree of ionisation are called *'weak electrolytes.'* Examples are weak acids like H_2CO_3, CH_3COOH, weak bases like NH_4OH and salts like $Al(OH)_3$, $BaSO_4$, etc.

4. Non-electrolyte : It is a substance which is a non-conductor of electricity e.g., alcohol, petrol, oils, starch, sugar (covalent compounds) are non-electrolytes.

5. Electrolysis : *"The process of chemical decomposition of an electrolyte by the passage of electric current through it is called electrolysis."*

6. Voltameter or Electrolytic cell : It is an apparatus of convenient shape, size and material (glass or steel) in which the electrolysis is carried out. For electrolysis, always a D.C. (direct current) must be used.

(a) ***Positive and negative poles :*** An electric battery is one in which the chemical energy is converted into electrical energy. It is a source of electric current which consists of stream of electrons. An electric battery has two poles, one positive and the other as negative, which are generally coloured. The positive pole is generally *'red'* and the negative pole is either *'black'* or *'blue.'*

(b) ***Electrodes :*** These are the metallic or non-metallic rods/plates immersed in an electrolyte. They conduct the electric current into and out of the solution. The electrodes which act as electron carriers and also take part in chemical reaction are called *'active electrodes'* (e.g. copper, silver, etc.). The electrodes which simply act as electron carriers are known as *'inert electrodes'* (e.g. platinum, graphite, etc.).

(i) Cathode : It is an electrode which is connected to the negative pole of battery. When an electric current is passing, there is a flow of electrons from negative pole of battery to the cathode.

(ii) Anode : It is an electrode which is connected to the positive pole of battery. When an electric current is passing, there is a flow of electrons from the anode to the positive pole of battery.

7. Current density : It is the *ratio of current in amperes to the area of cross-section of electrode.* Generally, area is measured in sq.cm. or decimeter and the current in amperes.

$$\therefore \quad \text{Current density} = \frac{\text{Current}}{\text{Area}} = \frac{\text{Amperes}}{\text{Decimeter}} = \text{Amperes/100 sq. cm.}$$

Current density has a great significance in the extraction of metals and electroplating.

8. Temperature : If aqueous salt solutions are used in electrolysis, the temperature of the solution is always slightly above the room temperature. However, when a fused salt is used, the temperature of the electrolyte should be 50-60^{o}C higher than the melting point of the salt.

2.7 ELECTRODE POTENTIAL

A metal (M) consists of metal ions (M^{n+}) with the valency electrons that bind them together. If a metal is in contact with a solution of its own salt, then there are two opposing processes taking place.

1. The metal atoms have a tendency to go into the solution in the form of metal ions leaving behind an equivalent number of electrons on the metal or electrode. Thus, the metal acquires a negative charge. This process is an oxidation process and is called 'de-electronation'. e.g. Zn in $ZnSO_4$ solution.

$$\underset{\text{(Metal atom}}{M} \longrightarrow \underset{\text{(metal ions)}}{M^{n+}} + \underset{\text{(electrons)}}{n\,e^-} \quad \text{(loss of electrons or oxidation)}$$

2. The positive metal ions present in the solution have the tendency to accept the electrons from metal rod and form neutral metal atoms that enter the metallic lattice. Thus, metal acquires positive charge. This process is a reduction process and is called 'electronation'.

$$\underset{\text{(Metal ions)}}{M^{n+}} + \underset{\text{(electrons)}}{n\,e^-} \longrightarrow \underset{\text{(Metal atoms)}}{M} \quad \text{(gain of electrons or reduction)}$$

e.g. Cu metal in $CuSO_4$ solution.

Thus, soon a dynamic equilibrium is established between the two reverse reactions (1) and (2) and electrical double layer is formed between the metal surface and the surrounding salt solution.

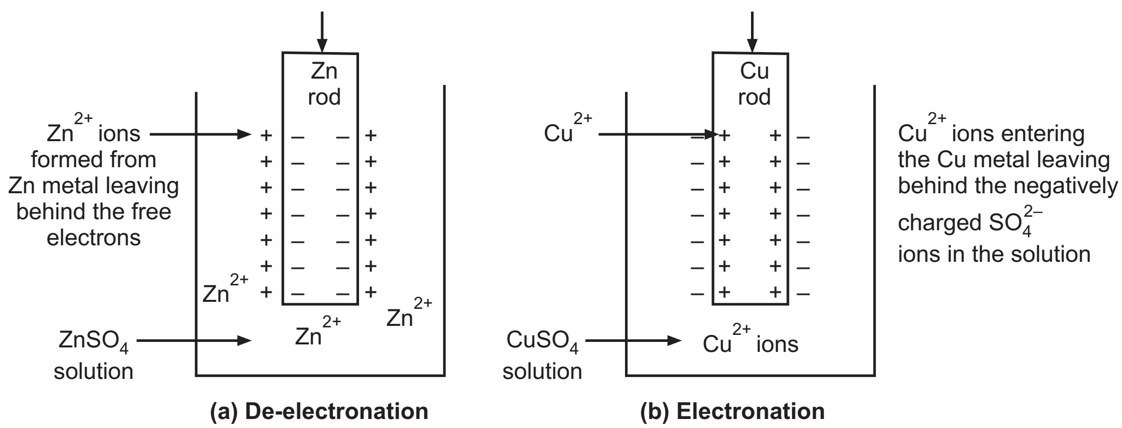


Fig. 2.3 : Electrode potential

The metal rod (electrode) acquires negative or positive charge.

Due to the formation of electrical double layer, the potential developed at the junction of the electrode and the aqueous salt solution is known as **'electrode potential'**.

Depending upon which process is easier than the other (either electronation or de-electronation), the electrode acquires positive or negative charge, that causes the electrode potential.

Electrode potential of a metal is the measure of the tendency of a metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt of unit molar concentration at 25°C.

The tendency of an electrode to lose electrons is a direct measure of its tendency to get oxidised, and this tendency is called **'oxidation potential'**. Similarly, the tendency of an electrode to gain electrons is a direct measure of its tendency to get reduced and this tendency is known as '**reduction potential**'.

It is quite obvious that the value of reduction potential is negative of its oxidation potential and vice-versa. Thus, if the oxidation potential of an electrode is +X volt, then its reduction potential will have the value of –X volt.

2.8 MECHANISM OF ELECTROLYSIS

According to Arrhenius theory, the molecules of electrolyte present in the fused or solution state break up into two types of ions. These ions under the influence of electric current travel towards the oppositely charged electrodes. Those ions travelling towards the cathode are called *'cations'* (or positive ions), while those moving towards the anode are called anions or (negative ions). When the anions reach the anode and cations at the cathode, the electric discharge (or primary reactions) takes place.

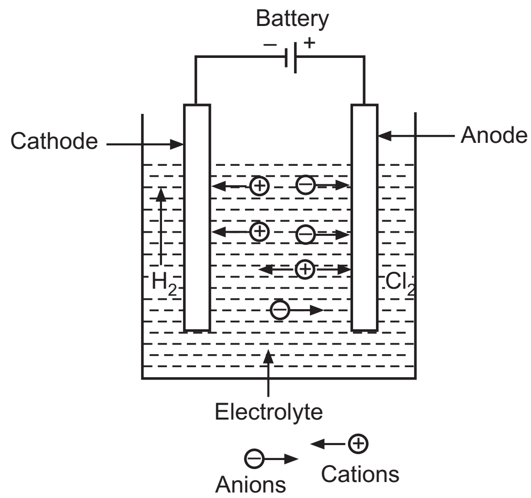


Fig. 2.4 : Mechanism of Electrolysis

At Cathode : When the cation reaches the cathode, it acquires electrons from the cathode, thereby its charge is neutralised.

$$Na^+ + e^- \longrightarrow Na \text{ (Reduction)}$$

At Anode : When the anion reaches the anode, the electrons are given or removed leaving behind the discharged neutral atom or group of atoms.

$$Cl^- \longrightarrow Cl + e^- \text{ (Oxidation)}$$

Thus, an electric current which passes through the electrolyte consists of flow of electrons from cathode to anode.

Primary Reactions at the Cathode (Cathode Process) :

At the cathode, the primary reaction consists of the removal of electrons from the cathode. It takes place by the gain of electrons by the cations (positive ions) with the formation of neutral atoms. Thus, at the cathode, there is a reduction of cation. (Gain of electrons is reduction).

For example,

$Na^+ + e^- \longrightarrow$ Na (Neutral sodium atom)

$Cu^{++} + 2e^- \longrightarrow$ Cu (Neutral copper atom)

$H^+ + e^- \longrightarrow$ H (Neutral hydrogen atom)

If the neutral atoms are those of a gaseous element such as hydrogen then, they combine to form molecules and these are evolved at the electrode as bubbles of the gas.

$$H + H \longrightarrow H_2 \uparrow$$

Thus, at the *'primary stage'*, electrons are accepted by cations at cathode. At the *'secondary stage'*, these neutral atoms like hydrogen combine to form stable products.

The above cathode process takes place, only when one type of the cation (or positive ion) is present in the vicinity of the cathode. If two or more different types of cations are present, then in most cases, the cation which can gain electrons more easily is the one that will be discharged at the cathode and the others remain in the solution.

A more active metal readily forms its ion (cation) by the loss of electrons and such ion has a less tendency to accept electrons. Such cation is difficultly discharged at the cathode.

K^+
Na^+
Ca^{++}
Mg^{++}
Al^{+++}
Zn^{++}
Fe^{++}
Sn^{++}
Pb^{++}
H^+
Cu^{++}
Ag^+
Au^{+++}

Activity series of cations : Given aside indicates the relative ease with which the various cations can gain electrons. The cations at the *'bottom'* of the series can gain electrons more easily than those at the top. Thus, if a solution contains Cu^{++}, K^+ and H^+ ions, then Cu^{++} ions will be selectively discharged and the metallic copper will be deposited on cathode. If the process is continued until all the Cu^{++} ions originally present in the solution have been removed at a particular voltage, then H^+ ions will be discharged at the cathode in the form of gas at a slightly higher voltage. The more active K^+ ions, however, remain in the solution, because they require a very high voltage for their discharge.

Magnus Rule : Thus, *when a solution of salts of different metals are electrolysed, there is a certain definite voltage at which one and only one of the metals is deposited on the cathode. This is known as 'Magnus Rule.'* e.g. When one cation, say Zn^{++} is present in very much higher concentration than other cation say Fe^{++}, then Zn^{++} may be discharged before Fe^{++} even though Zn^{++} is placed above Fe^{++} in the activity series.

In short, when two or more kinds of cations are present in a solution, which of them will be discharged depends :

(i) mainly on their position in the activity series of cations.

(ii) on the concentration of cations in the solution; and

(iii) in some cases on the nature of the electrode.

Primary Reaction at the Anode (Anode Process) : In the anode process, the primary reaction consists of giving up the electrons to the anode. It takes place by the loss of electrons by anions (negative ions) with the formation of neutral atoms or radicals. At the anode, there is oxidation of anion. (Loss of electron is oxidation).

$$Cl^- \longrightarrow Cl \text{ (neutral chlorine atom)} + e^-$$

$$OH^- \longrightarrow OH \text{ (neutral hydroxyl radical)} + e^-$$

The resultant neutral atoms of gaseous element combine together to form stable molecules. Thus,

$$Cl + Cl \longrightarrow Cl_2 \uparrow$$

The resultant neutral radical (i.e. group) is not liberated as such at the anode, since it does not exist in the free state, but the neutral radicals combine together to form stable molecules. Thus,

$$4(OH) \longrightarrow 2H_2O + O_2 \uparrow$$

Thus, at the *'primary stage',* electrons are given up by anions at anode. At the *'secondary stage',* these neutral atoms or radicals combine to form stable products.

SO_4^{--}
NO_3^-
OH^-
Cl^-
Br^-
S^{--}
I^-

Activity series of Anions : If two or more types of anions are present, the selective discharge takes place according to the activity series of anions, as per the table given aside.

The anions at the bottom of the series are discharged more easily than those at the top. Thus, I^- and S^{--} ions will be more easily discharged than Cl^- ions. Similarly, OH^- ion is more easily discharged than NO_3^- and SO_4^{--} ions. *"As a rule, if the negative ion does not contain oxygen, that radical is discharged in preference to the one which contain oxygen."*

Besides the position of an anion in the above series, the discharge of anion also depends upon its concentration in the solution.

If the anodes are made up of metals like copper and silver, the atoms of these may lose electrons and form ions which go in the solution. Thus,

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

Thus, the discharge of an anion depends upon :

(i) the position of anion in the anion series,

(ii) the concentration of anion in the solution,

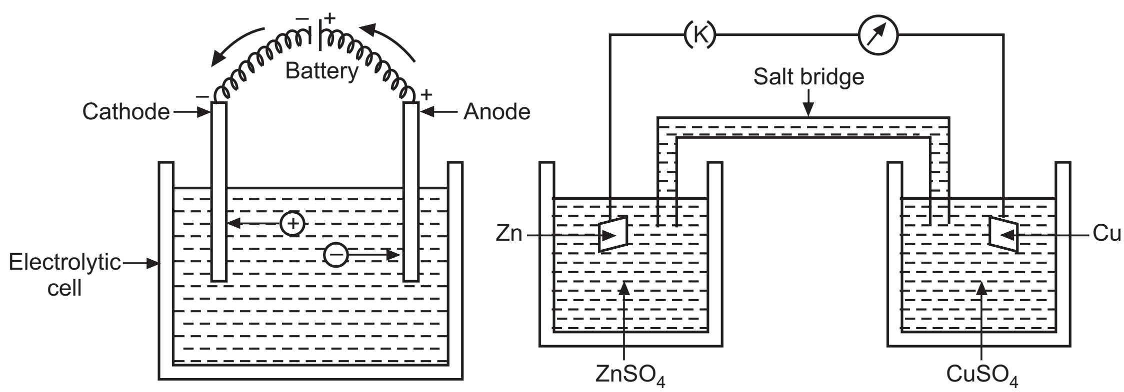
(iii) on the nature of the anode material.

2.9 TYPES OF CELLS

The cells (or vessels) in which the electrolysis can be carried out are of two types : (a) electrolytic cell and (b) electrochemical cell.

(a) Electrolytic cell : A cell in which the non-spontaneous chemical reaction is produced by the passage of electric current is known as *electrolysis.* The production/liberation of H_2, O_2, Cl_2, NaOH and the processes like extraction of metals, electroplating etc. are carried out in electrolytic cells. These cells are mainly used in gold plating, silver plating and also applicable to many engineering and military appliances.

(b) Electrochemical cell (or Galvanic cell) : A cell in which the electricity can be generated by spontaneous redox chemical reactions is known as *'electrochemical cell'* or '*Galvanic cell'* (after Galvani in 1780) or *'Voltaic cell'* (after Volta in 1800). e.g. Daniel cell and dry cell are the combination of two half cells connected internally by salt bridge and externally by metal conductors forming an electrochemical cell.



(a) Electrolytic cell (b) Electrochemical cell

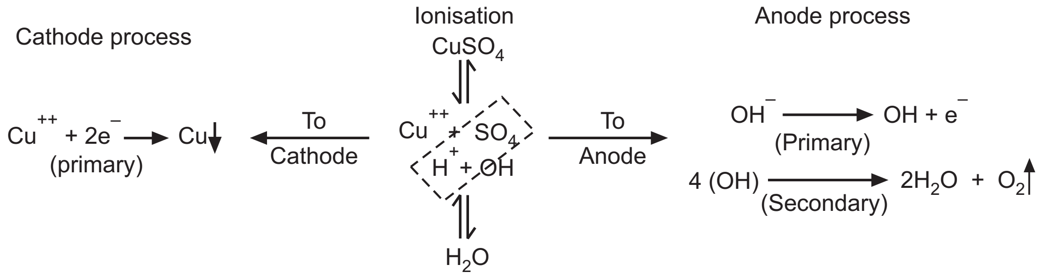
Fig. 2.5

Distinction between Electrolytic cell and Electrochemical cell :

Electrolytic cell	Electrochemical cell
1. It converts electrical energy into chemical energy.	1. It converts chemical energy into electrical energy.
2. It is used to bring about non-spontaneous chemical reaction by electrolysis.	2. It is used to produce electricity from spontaneous chemical reaction.
3. Electrical energy is consumed/used e.g. production of metals, electroplating etc.	3. Electrical energy is produced e.g. lead accumulators, dry cells.
4. These cells are also applicable in many engineering and military appliances.	4. Dry cell and Daniel cell are electrochemical cells. Dry cells are used for torches, calculators, transistors, etc. Daniel cell is used for protection of metals from corrosion.

Examples of Electrolysis :

1. Electrolysis of copper sulphate solution (By using platinum electrodes) : An aqueous solution of $CuSO_4$ contains Cu^{++}, SO_4^{--}, H^+ and OH^- ions. According to the activity series, at cathode, Cu^{++} ions are discharged in preference to H^+ ions and copper is deposited at cathode. At anode, OH^- ions are discharged in preference to SO_4^{--} ions and oxygen gas is liberated at anode. The schematic representation of electrolysis of $CuSO_4$ is as follows :



The net result of electrolysis is :

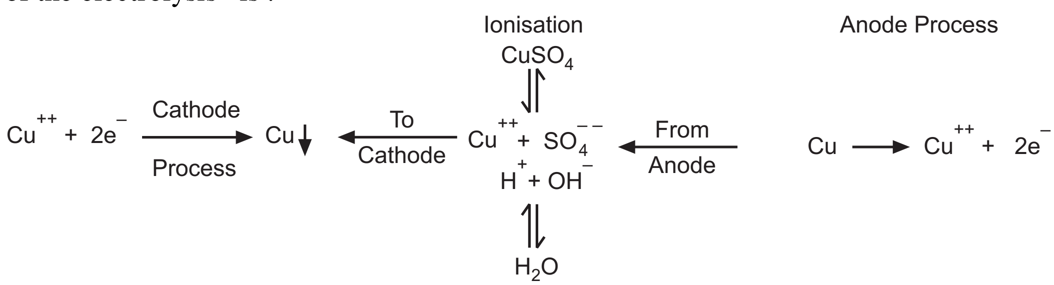
(a) Deposition of copper on the platinum cathode and liberation of oxygen gas at the anode.

(b) As only Cu^{++} ions (blue) are discharged and not the SO_4^{--} ions, the solution is slowly converted from a blue solution of $CuSO_4$ to a colourless solution of H_2SO_4.

Similarly, when a silver nitrate ($AgNO_3$) solution is electrolysed between platinum electrodes, silver is deposited on the platinum cathode, while oxygen gas is evolved at the anode. The solution of HNO_3 accumulates in the cell.

In the above example, the electrodes like platinum or carbon (graphite) are quite stable. The anode is therefore, not dissolved into the solution.

2. Electrolysis of copper sulphate solution (By using copper electrodes) : There are four types of ions, namely Cu^{++}, SO_4^{--}, H^+, OH^- present in the solution. According to the activity series, Cu^{++} ions are discharged at cathode in preference to H^+ ions. At anode, Cu^{++} ions are formed and it appears to dissolve. The schematic representation of the electrolysis is :



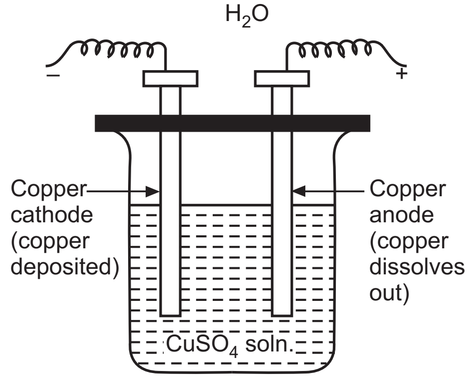


Fig. 2.6 : Electrolysis of copper sulphate solution using copper electrodes

The net result of electrolysis is :

(a) The deposition of Cu on copper cathode, while the copper on anode slowly dissolves in the solution by giving Cu^{++} ions.

(b) As no SO_4^{--} ions are discharged, the strength of $CuSO_4$ solution in the cell remains the same.

3. Electrolysis of sodium chloride (NaCl) solution (By using platinum electrodes) : The solution contains Na^+ and Cl^- ions. Due to slight dissociation of water, very small amount of H^+ ions and OH^- ions are also present. Under the influence of electric current, Na^+ and H^+ ions migrate towards the cathode and Cl^- ions and OH^- ions migrate towards the anode. The discharge potential of Na^+ ions is very high in comparison with H^+ ions (energy required for discharging/liberating the ion is called discharge potential). Hence, at applied voltage, H^+ ions get discharged and H_2 gas is liberated at cathode.

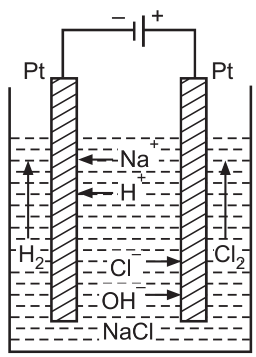


Fig. 2.7 : Electrolysis of NaCl

Similarly, the discharge potential of OH^- ions is high in comparison to Cl^- ions. Hence, at applied voltage, Cl^- ions get discharged and Cl_2 gas is liberated at anode. In short, the schematic representation of electrolysis of aqueous NaCl solution is as follows :

Cathode Process (Pt) | Ionisation | Anode Process (Pt)

Ionisation: $NaCl \rightleftharpoons Na^+ + Cl^-$; $H_2O \rightleftharpoons H^+ + OH^-$

To Cathode ← | → To Anode

Cathode Process (Pt):

$$H^+ + e^- \longrightarrow H \quad \text{(Primary)}$$

$$H + H \longrightarrow H_2 \quad \text{(Secondary)}$$

Anode Process (Pt):

$$Cl^- \longrightarrow Cl + e^-$$

$$Cl + Cl \longrightarrow Cl_2\uparrow$$

$$Na^+ + OH^- \longrightarrow NaOH$$

The net result of electrolysis is :

(a) H_2 gas liberated at cathode and Cl_2 gas is liberated at anode.

(b) The concentration of Na^+ ions and OH^- ions increases in the solution and sodium hydroxide (NaOH) is formed. Due to the strong alkaline solution left in the cell, the pH of the solution increases.

4. Electrolysis of fused sodium chloride (By using carbon electrodes) : Since the salt is in the fused state, there is no solvent. Therefore, there is only one type of positive ion (Na^+) and one type of negative ion (Cl^-). At cathode, Na^+ ions are discharged and at anode, Cl^- ions are discharged. The schematic representation of electrolysis is :

Cathode Process (C) | Ionisation | Anode Process (C)

Ionisation: $NaCl \longrightarrow Na^+ + Cl^-$

At Cathode ← | → To Anode

Cathode Process (C):

$$Na^+ + e^- \longrightarrow Na \quad \text{(Primary)}$$

(Secondary)

Anode Process (C):

$$Cl^- \longrightarrow Cl + e^-$$

$$Cl + Cl \longrightarrow Cl_2\uparrow$$

The net result of electrolysis is the liberation of sodium at cathode and chlorine gas ($Cl_2\uparrow$) at anode.

Table 2.1 : Products of Electrolysis of some Electrolytes

Electrolyte	Electrode	Product obtained at anode	Product obtained at cathode
Aqueous NaCl	Pt or graphite	Cl_2	H_2
Fused NaCl	Pt or graphite	Cl_2	Na
Aqueous NaOH	Pt or graphite	O_2	H_2
Fused NaOH	Pt or graphite	O_2	Na
Aqueous $CuSO_4$	Pt or graphite	O_2	Cu
Fused $CuSO_4$	Copper	Cu^{++}	Cu
Aqueous $AgNO_3$	Pt or graphite	O_2	Ag
Fused $AgNO_3$	Silver	Ag^+	Ag

2.10 FARADAY'S LAWS OF ELECTROLYSIS

The quantitative aspect of experimental electrolysis was summarised by *Faraday* in year 1834 in two statements which are now known as Faraday's Laws of Electrolysis. To understand the full significance of these laws, we must know the definitions of some important terms.

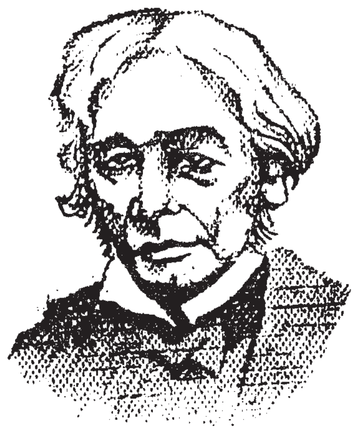


Fig. 2.8 : Michael Faraday (1791 - 1867)

Michael Faraday, a genius of experimentation, started his career as an apprentice to a book-binder. He advanced rapidly by dint of his determination and studious habits to become professor of chemistry at the Royal Institution in 1813. He is famous for his monumental work on electrolysis.

Coulomb : It is the quantity of electricity that passes through a circuit when a current of one ampere strength is passed through the circuit for one second. Coulomb can also be defined as *"the quantity of electricity which when passing through the circuit liberates 0.001118 g of silver or 0.0000104 g of hydrogen."* Thus,

$$\text{Coulomb} = \text{Ampere} \times \text{Second}$$

Hence, coulomb is the unit quantity of electricity.

Ampere : It is the unit of current which when passing through a circuit for one second liberates 0.001118 g of silver or 0.0000104 g of hydrogen.

Faraday : "*It is the quantity of electricity required to liberate or deposit one gram equivalent of a substance from its solution.*"

It is also the unit of quantity of electricity but it is a bigger unit than coulomb.

One Faraday (F) = 96,500 coulombs.

First Law : *"This law states that the weight of a substance liberated or deposited at an electrode during electrolysis is directly proportional to the quantity of electricity passed through an electrolyte."*

If *'W'* g is the weight of a substance liberated or deposited at an electrode during the electrolysis and 'Q' be the quantity of electricity passed through the electrolyte, then,

$W \propto Q$ But $Q = c \times t$

$\therefore$ $W \propto c \times t$ where Q = number of coulombs

c = current in amperes

t = time in seconds.

or $W = z \times c \times t$ where z = constant known as electrochemical equivalent (E.C.E.) of a substance.

In the above relation if c = 1 ampere and t = 1 second then,

$$W = z \times 1 \times 1$$

$$\therefore \quad W = z$$

Hence electrochemical equivalent (E.C.E.) of a substance is defined as *"the weight of a substance liberated or deposited when a current of one ampere flows for one second through its solution."* It may also be defined as *'the weight z (in g.) of a substance liberated or deposited'* by one coulomb known as electrochemical equivalent (E.C.E.) of a substance.

The electrochemical equivalent of silver, hydrogen, oxygen, magnesium and aluminium are 0.001118 g, 0.0000104 g, 0.000026 g, 0.000126 g, and 0.0000935 g respectively.

By actually weighing the quantity of a substance liberated or deposited at an electrode by a particular current and by measuring the time in seconds for which the current flows, the strength of the current in amperes can be calculated. We have,

$$W = zct \quad \therefore \quad c = \frac{W}{z \times t} = \frac{\text{Weight of a substance liberated}}{\text{E.C.E. of a substance} \times \text{time}}$$

In fact knowing any three quantities out of the above four, the remaining fourth can be calculated.

Second Law : This law states that *when the same quantity of electricity is passed through different electrolytes arranged in series, the weights of substances liberated at the respective electrodes are directly proportional to their chemical equivalents (equivalent weights of substances).*

Let the same number of coulombs be passed through two cells connected in series and containing the solution of say (1) Copper sulphate and (2) Silver nitrate respectively. (Refer Fig. 2.9). If the relative amounts of copper and silver deposited on their respective electrodes are 'x' and 'y' grams, then these weights according to the law will be proportional to their respective chemical equivalents (C.E.). Thus,

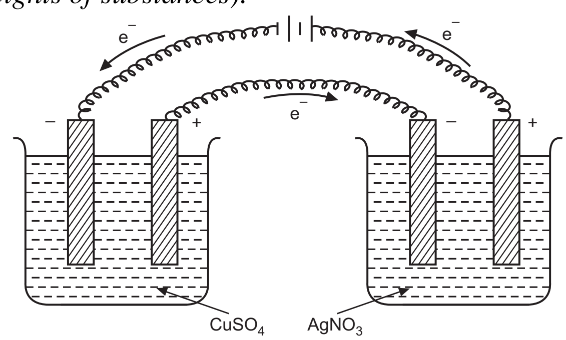


Fig. 2.9 : Electrolysis showing Faraday's second law

1. Wt. of copper deposited (x) $\propto$ chemical equivalent of copper (E_1)
2. Wt. of silver deposited (y) $\propto$ chemical equivalent of silver (E_2).

Dividing equation (1) by equation (2), we get,

$$\frac{\text{Wt. of copper deposited}}{\text{Wt. of silver deposited}} = \frac{x}{y} = \frac{\text{C.E. of copper}}{\text{C.E. of silver}} \frac{(E_1)}{(E_2)}$$

Thus, knowing the weights of any two metals deposited and the chemical equivalent (i.e. equivalent weight) of any one, the equivalent weight of other can be calculated.

Relation between Faraday and Coulomb :

It follows from the second law that the quantity of electricity (one Faraday) which liberates one gram equivalent of copper i.e. 31.75 g. of copper or one gram equivalent of silver i.e. 107.88 g of silver or one gram equivalent of any other element. Since the electrochemical equivalent of silver is 0.001118 g, one coulomb of electricity liberates this quantity of silver.

Hence, to liberate one gram equivalent i.e. 107.88 g of silver, the quantity of electricity would be,

$$\text{For silver} = \frac{107.88}{0.001118} = 96496 \text{ coulombs.}$$

$$\text{For copper} = \frac{31.75}{0.000329} = 96504 \text{ coulombs.}$$

(Electrochemical equivalent of copper is 0.000329 g.)

Faraday experimentally determined the *'average'* quantity of electricity to liberate one gram equivalent of any substance from solution as 96500 coulombs and this quantity is known as one Faraday (F). Hence,

$$\boxed{1 \text{ Faraday} = 96500 \text{ coulombs}}$$

"One Faraday is the quantity of electricity required to liberate or deposit one gram equivalent of a substance from its solution."

2.11 RELATION BETWEEN C.E. AND E.C.E.

The quantity of electricity, 96500 coulombs (or 1 Faraday) required to liberate/deposit 1 gram-equivalent (i.e., eq. wt. in grams) of a substance. One coulomb liberates/deposits the quantity of same substance (in grams) equal to its electrochemical equivalent (e.c.e.). Thus, equivalent weight of a substance is 96500 times the electrochemical equivalent.

$$\therefore \quad \boxed{\text{C.E. (Eq. wt.)} = 96{,}500 \times \text{E.C.E.}}$$

Numerical Examples on Faraday's Laws of Electrolysis :

Example 1 : *0.1978 g of copper were deposited by a current of 0.2 ampere in 50 minutes. What is the electrochemical equivalent of copper ?*

Solution : From first law of Faraday, we have,

$$W = z\,ct$$

$$\therefore \quad z = \frac{W}{ct} = \frac{0.1978}{0.2 \times 50 \times 60} = \mathbf{0.0003296\ g.}$$

Example 2 : *What quantity of electricity is necessary to deposit 216 m gms of silver from its solution ? (At. wt. of Ag = 108)*

Solution : Eq. wt. of Ag $= \frac{\text{At. wt.}}{\text{valency}} = \frac{108}{1} = 108$

$$216 \text{ mg} = 0.216 \text{ g}$$

96,500 coulombs of electricity will deposit 1 gm eq. i.e. 108 g of Ag.

$\because$ 108 g of Ag is deposited by 96,500 coulombs

$\therefore$ 0.216 g of Ag is deposited by

$$= \frac{0.216 \times 96{,}500}{108} = \mathbf{193\ coulombs.}$$

Example 3 : *A solution of a salt of metal was electrolysed for 150 minutes with a current of 0.15 amperes. The weight of metal deposited was 0.783 g. Find the equivalent weight and valency of the metal in the salt.*

[At. wt. of metal = 112].

Solution : We have,

$$Q = c \times t$$

$$= 0.15 \times 150 \times 60 = 1350 \text{ coulombs.}$$

Now, since 1350 coulombs deposit 0.783 g of metal

$$\therefore \quad 96{,}500 \text{ coulombs deposit} = \frac{0.783 \times 96500}{1350} = 55.97 \text{ g of metal}$$

$\therefore$ Eq. wt. of metal = 55.97 g

Now, $\text{Valency} = \dfrac{\text{At. wt. of metal}}{\text{Eq. wt. of metal}} = \dfrac{112}{55.97} = \mathbf{2}$

The valency metal is always in integers and not in fraction.

Example 4 : *A current of 3 amperes passing through silver nitrate solution for 20 minutes deposit 4.0 g of silver. What is the E.C.E. of silver ?*

Solution : By first law of Faraday,

$$W = z\,c\,t$$

$$4 = z \times 3 \times 20 \times 60$$

$$\therefore \quad z = \frac{4}{3 \times 20 \times 60} = \mathbf{0.001111\ g/coulombs}$$

Example 5 : *Calculate the time in seconds in which 0.3 g of copper is liberated from copper sulphate solution, when a current of 0.5 ampere is passed. (Eq. wt. of Cu = 31.6)*

Solution : $\text{E.C.E. of copper} = \dfrac{\text{Eq. wt. of copper}}{96500} = \dfrac{31.6}{96500} = 0.000327\ \text{g/c}$

From first law of Faraday,

$$W = z\,c\,t$$

$$0.3 = 0.000327 \times 0.5 \times t$$

$$\therefore \quad t = \frac{0.3}{0.000327 \times 0.5} = \mathbf{1832\ seconds}$$

Example 6 : *A spoon having an area 20 sq. cm. is to be coated with silver to a thickness of 0.1 mm. If a current of 1.5 amperes is used, calculate the time required for completing the process. (E.C.E. of Ag = 0.001118 g/c, density of Ag = 10.5 g/cc)*

Solution : By first law of Faraday, W = z c t … (a)

Both 'W' and 't' are unknown.

W can be calculated from the relation

mass (i.e., W) = volume × density … (b)

But volume of spoon to be coated = area × thickness … (c)

$= 20\ \text{cm}^2 \times 0.01\ \text{cm}.$

$= 0.2\ \text{cm}^3$

$\therefore$ W = volume × density

$= 0.2 \times 10.5$

$= 2.1$ g.

Putting this value in equation (a), we get,

$$W = z\,c\,t$$

$$2.1 = 0.001118 \times 1.5 \times t$$

$$\therefore \quad t = \frac{2.1}{0.001118 \times 1.5}$$

$$= \mathbf{1252\ seconds.}$$

Example 7 : *Calculate the weight of metallic chromium deposited from a solution of chromium chloride ($CrCl_3$) by a current of 0.2 ampere passing for 100 minutes. (At. wt. of Cr. 52).*

Solution : Given C = 0.2 ampere, t = 100 minutes = 100×60 = 6000 seconds, W = ?

Now, Atomic weight = Eq. wt. × Valency

$$52 = \text{Eq. wt.} \times 3$$

$$\therefore \quad \text{Eq. wt.} = \frac{52}{3} = 17.33$$

$$\text{C.E. (Eq. wt.)} = 96500 \times \text{E.C.E.}$$

$$17.33 = 96500 \times \text{E.C.E.}$$

$$\therefore \quad \text{E.C.E.} = \frac{17.33}{96500} = 0.0017962$$

By first law of Faraday,

$$W = z\,c\,t = 0.0017962 \times 0.2 \times 6000 = \mathbf{2.155\ g.}$$

Example 8 : *What current strength in amperes will be required to liberate 20 g of iodine from potassium iodide solution in one hour ? (E.C.E. of iodine = 0.00131 g)*

Solution : Here, W =20 g; z = 0.00131 g and t = 60 × 60 sec.

By first law of Faraday, $c = \frac{W}{z \times t} = \frac{20}{0.00131 \times 60 \times 60} = \mathbf{4.2\ amperes}$

Example 9 : *A given quantity of electricity is passed through two cells containing copper sulphate and silver nitrate solutions respectively. If 0.99 g of silver and 0.29 g of copper are deposited, find the equivalent weight of silver when that of copper is 31.6.*

Solution :

Given : Wt. of silver deposited = 0.99 g

Wt. of copper deposited = 0.29 g.

Eq. wt. of copper = 31.6 g

Eq. wt. of silver = x (say)

According to Faraday's second law of electrolysis,

$$\frac{\text{Wt. of silver deposited}}{\text{Wt. of copper deposited}} = \frac{\text{Eq. wt. of silver}}{\text{Eq. wt. of copper}}$$

$$\frac{0.99}{0.29} = \frac{x}{31.6}$$

$$\therefore \quad x = \frac{0.99 \times 31.6}{0.29}$$

$$\therefore \quad \text{Eq. wt of silver} = \mathbf{107.8\ g}$$

Example 10 : *Calculate the amount of NaOH that could be produced in the cell when an aqueous solution of sodium chloride is electrolysed with a current of 10 amperes passed for one hour.*

Solution :

Quantity of electricity in coulombs = Amperes × Seconds

$$= 10 \times 60 \times 60 = 36000$$

∴ 96500 coulombs of electricity will form 40 gms of NaOH

∴ 36000 coulombs of electricity will form $= \frac{40 \times 36000}{96500} = \mathbf{14.92\ g.}$

Example 11 : *A current of 5 amperes is passed through a solution of NaCl for 3.25 hrs. Find the weight of NaOH formed.*

Solution : Quantity of electricity passed,

$$Q = c \times t$$

$$= 5 \times 3\frac{1}{4} \times 60 \times 60 = 5 \times \frac{3}{4} \times 60 \times 60$$

$$= \mathbf{58500\ coulombs}$$

Now, $NaCl \equiv NaOH$

$58.5 \text{ gms} \equiv 40 \text{ gms (eq. wt. of NaOH)}$

$\therefore$ 96500 coulombs of electricity will form 40 gms of NaOH

$\therefore$ 58500 coulombs of electricity will form

$$= \frac{40 \times 58500}{96500}$$

$$= \mathbf{24.25 \text{ gms of NaOH}}$$

Example 12 : *A solution of the metal salt was electrolysed for 10 minutes with a current of 1.5 amperes. The weight of metal deposited was 0.685 gm. What is the equivalent weight of the metal ?*

Solution : Given :

$t = 10 \text{ minutes} = 10 \times 60 \text{ seconds.}$

$c = 1.5 \text{ amperes}$

$W = 0.685 \text{ g}$

$\text{C.E.} = ?$

By first law of Faraday,

$$W = z \times c \times t$$

$$\therefore \quad z = \frac{W}{c \times t} = \frac{0.685}{1.5 \times 10 \times 60}$$

$$\text{E.C.E., } z = 0.00076 \text{ g.}$$

Now, $\text{C.E.} = 96{,}500 \times \text{E.C.E.}$

$= 96{,}500 \times 0.00076$

Eq. wt. of metal = **73.34**

Example 13 : *When the same amount of current is passed through the solutions of $CuSO_4$ and $ZnSO_4$ then 0.7 g and 0.716 g of Cu and Zn get deposited on respective electrodes. Calculate equivalent weight of zinc. (Atomic wt. of Cu = 63.5)*

Solution : Given :

Wt. of Cu deposited (x) = 0.7 g

Wt. of Zn deposited (y) = 0.716 g

Equivalent wt. of Cu, $E_1 = \frac{\text{At. wt.}}{\text{Valency}} = \frac{63.5}{2} = 31.75$

Equivalent wt. of Zn, $E_2 = ?$

From second law of Faraday,

$$\frac{\text{Wt. of Cu deposited (x)}}{\text{Wt. of Zn deposited (y)}} = \frac{\text{Eq. wt. of Cu } (E_1)}{\text{Eq. wt. of Zn } (E_2)}$$

$$\frac{0.7}{0.716} = \frac{31.75}{E_2}$$

$$\therefore \quad E_2 \times 0.7 = 0.716 \times 31.75$$

$$\therefore \quad E_2 = \frac{0.716 \times 31.75}{0.7}$$

$$\therefore \quad \text{Eq. wt. of Zn } (E_2) = \mathbf{32.4757 \text{ g.}}$$

Example 14 : *Calculate the weight of copper (Eq. wt. = 31.77) in kilogram, deposited by passing a electric current of 2 amperes for 20 minutes. Also calculate equivalent weight of silver, if same quantity of electric current can deposit 2.6834×10^{-3} kg. of silver from silver nitrate solution.*

Solution : The amount of electric current passed

$$= c \times t$$
$$= \text{(Current strength in amperes)} \times \text{(time in seconds)}$$
$$= 2 \times 20 \times 60$$
$$= 2400 \text{ coulombs.}$$

Now a current of 96500 coulombs can deposit 31.77×10^{-3} kg (equivalent weight) of copper, hence 2400 coulombs can deposit

$\because$ 96500 coulombs deposit 31.77×10^{-3} kg of Cu

$$\therefore \quad 2400 \text{ coulombs deposit} = \frac{31.77 \times 10^{-3} \times 2400}{96500}$$

$$\therefore \quad \text{Weight of Cu deposited} = \mathbf{7.901 \times 10^{-4}\ kg}$$

Similarly according to second law,

$$\frac{\text{Eq. wt. of silver}}{\text{Eq. wt. of copper}} = \frac{\text{Wt. of silver deposited}}{\text{Wt. of copper deposited}}$$

$$\frac{\text{Eq. wt. of silver}}{31.77} = \frac{2.6834 \times 10^{-3}}{7.901 \times 10^{-4}}$$

$$\therefore \quad \text{Eq. wt. of silver} = \frac{2.6834 \times 10^{-3} \times 31.77}{7.901 \times 10^{-4}} = \mathbf{107.89}$$

Thus

(i) wt. of copper deposited = 7.901×10^{-4} kg

(ii) Equivalent wt. of silver = 107.89.

2.12 APPLICATIONS OF ELECTROLYSIS

The important applications of electrolysis are :

1. Electroplating
2. Electro-refining
3. Electrotyping
4. Electrometallurgy

1. Electroplating :

"The process of producing metallic coating of more resistant metals (like silver, gold, nickel, chromium etc.) on the base metal with the help of electric current is called electroplating."

Purposes : Electroplating is done to achieve the following objectives :

(i) Decoration : Electroplating of a superior metal over an inferior metal is done in order to have attractive and beautiful appearance. e.g. ornaments, picture frames and luxury articles are electroplated with silver, gold, nickel and chromium etc. It is also increasing the commercial and decorative value of the article in the market.

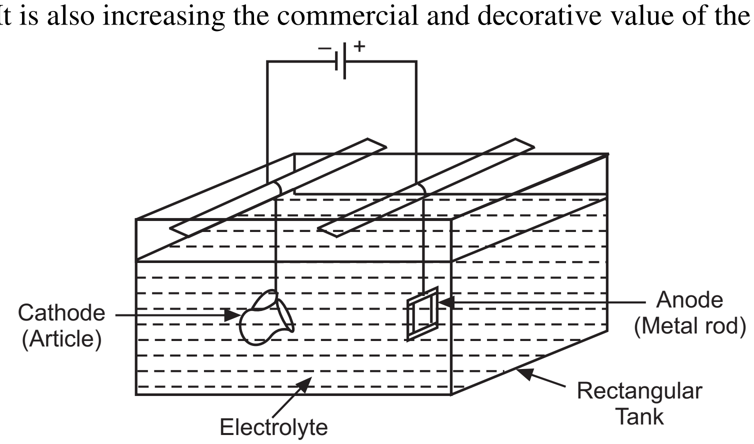


Fig. 2.10 : Electroplating

(ii) Protection : A coating of more resistant metal (or nobler metal) like silver, tin, nickel, chromium etc. is applied on the base metal like iron by electroplating in order to save the latter from rusting, corrosion and atmospheric action.

(iii) Repairs : Sometimes, broken pieces or worn out parts of a machinery are repaired by electro-deposition of metal in between the broken or at the defective part of the metal.

Process : The surface of the article to be electroplated is first of all cleaned thoroughly by hot solution of alkali or soap to remove the grease. Then, it is treated with dil-acid to remove the oxide layer or other impurities stick upto the article. The treatment with dil-acid is called *'pickling'*. Further, it is washed with water and then carefully polished.

The cleaned article is then suspended into the electrolytic cell (i.e. rectangular tank) and made as cathode. The anode is a pure strip or plate of metal whose coating is desired on the article, is also suspended in the cell. The electrolyte consists of solution of the salt of the metal with which the article is to be electroplated. On passing the electric current, the metallic ions from the electrolyte get deposited on the article which is made as cathode. The equivalent amount of anode gets dissolved in the form of metal ions and passes into the electrolyte. A smooth and brighter deposits are obtained (i) at low temperature, (ii) high current density and (iii) high metal ion concentration of the electrolyte.

(iv) Silver plating : Electroplating of silver on iron spoon is carried out in a rectangular tank of steel. Iron spoon which is to be electroplated is cleaned thoroughly by boiling with caustic soda in order to remove the grease and dirt. Further it is washed with water until free from caustic soda and carefully polished. The iron spoon is then made as cathode and anode consists of pure silver metal plate. The anode and cathode both are suspended in the electrolyte in the cell of potassium argentocyanide, $K[Ag(CN)_2]$. On passing the direct electric current at the applied voltage, the iron spoon gets plated with a smooth and brighter deposit of silver. Silver anode gets slowly dissolved in the solution by giving Ag^+ ions. The schematic representation is

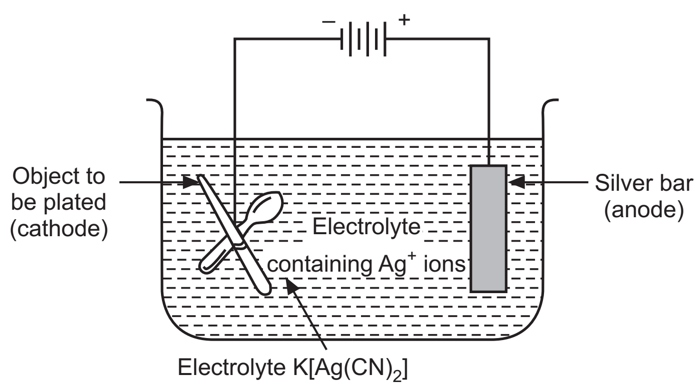
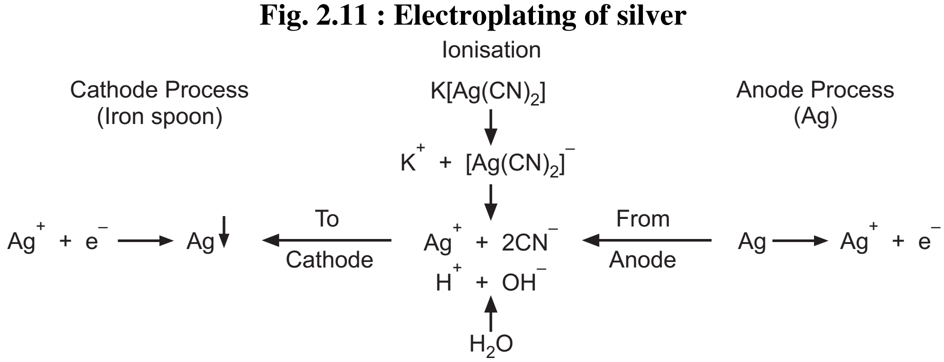


Fig. 2.11 : Electroplating of silver



The net result of electrolysis is :

1. The Ag^+ ions are formed at the anode and also from the electrolyte, which are discharged at the cathode thus the concentration of Ag^+ ions increases in the solution and silver gets deposited on the iron spoon.
2. The more active K^+ ions and H^+ ions remain in the solution, as they require very high voltage for their discharge.

2. Electro-refining :

"The process in which a pure metal can be obtained from the impure metal by the method of electrolysis is known as electro-refining." Impure metal in the form of a thick rod or thick plate is made as anode and a thin sheet of the same metal is made cathode. The electrolyte is the solution of the salt of metal to be refined. By using proper voltage, the anode of impure metal goes in solution in the form of metal ions. The electrolyte also breaks up into positively charged metal ions and negative ions. Positively charged metal ions go to the cathode and are deposited thereafter neutralising their charge. The negatively charged ions go to the anode (impure metal) and take an equivalent amount of pure metal and again change into electrolyte. The process is continued till whole of the pure metal gets transferred to cathode. As a result of electrolysis the anode gets dissolved (finishes) and impurities get settle down below the anode as *'anode mud'*. The cathode is the refined metal. It is washed, dried and put to use.

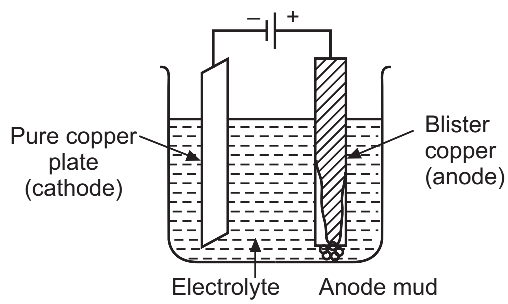


Fig. 2.12 : Electro-refining

A number of metals like Zn, Cu, Sn, Ag and Al etc. are refined by the process of electrolysis. The electrolytic refining of copper is given below.

Electro-refining of Copper : Impure (or Blister) copper obtained by extraction, contains about 3 to 5 % impurities like S, As, Zn, Fe, Ni, Ag, Au and Pt etc. Such impure copper is not fit to be used as an electrical conductor because the conductivity is appreciably lowered by the traces of impurities present in it. Copper with 100 % purity is required for electrical conductivity. Hence, the crude (or blister) copper is refined by the process of electro-refining.

The electro-refining of copper is carried out in large lead-lined tank. Crude or impure copper is cast into large plates which are suspended into the tank at intervals and act as anodes. Cathodes are thin plates of pure copper and each is suspended between two plates of anode. The electrolyte is 15 % $CuSO_4$ solution containing 5-10% free H_2SO_4. A direct current at low voltage is used.

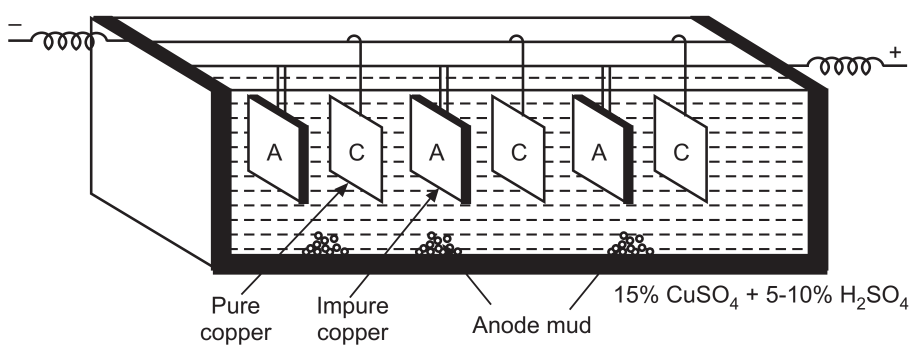
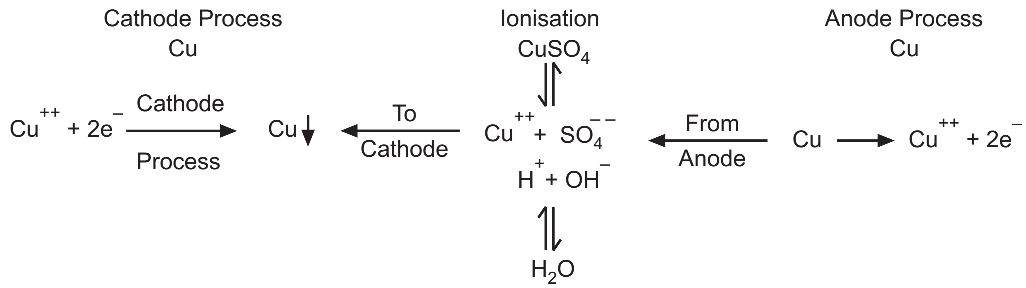


Fig. 2.13 : Electro-refining of copper

When current is turned on, copper from the anodes with traces of more active metals like Zn, Fe, Ni present as impurities go into the solution as metallic ions, whereas less active metals like Ag, Au and Pt are not ionised but crumbles down from the anodes and settle below the anodes as *'anode mud.'* From the anode mud, precious metals like silver, gold and platinum are recovered. These costly metals pay the cost of electro-refining process. At the applied voltage, Cu^{++} ions alone are discharged at the cathode (copper is very low in the activity series of metals) and thus, pure copper is deposited on the cathodes. Electro-refined copper is about 99.99 % pure. The schematic representation of electrolysis is :



3. Electrotyping :

The blocks used for large-scale printing purposes are prepared by the process of electrotyping. The impressions of the words to be printed are taken on the mould of wax. The wax is coated with a layer of graphite in order to make it a good conductor and it is made cathode. This cathode mould is suspended and dipped in the solution of copper sulphate as the electrolyte in an electrolytic cell. The anode consists of a rod of pure copper which is also suspended and dipped into the electrolyte. As a result of electrolysis, the copper gets deposited in the impressions of the mould. After a good deposit is formed in the impressions, the wax is melted. The back of the copper block is coated with lead to make it heavy and strong for printing purposes. e.g. currency note printing, newspaper printing.

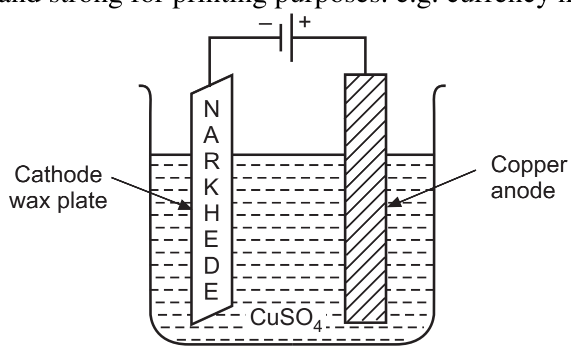


Fig. 2.14 : Electrotyping

4. Electro-metallurgy :

It is the process of obtaining metal from its ore by electrolysis. The metals like sodium, potassium, calcium, magnesium, etc. are prepared by the electrolysis of fused sodium hydroxide while aluminium is obtained by the electrolysis of alumina dissolved in fused cryolite (Na_3AlF_6).

2.13 CONDUCTIVITY OF ELECTROLYTE

The mobility of electrons through the metallic lattic of metals make them good conductors of electricity. Metals offer some resistance to the flow of an electric current. Solutions of electrolytes have a much higher resistance than metallic conductors. So, the electrolytic conduction depends upon the free movement of ions through solution. The factors which affect the electrical conductivity of solutions of electrolytes are

1. the inter-ionic attraction
2. the solvation of ion
3. the viscosity of the solvent.

(i) Ohm's Law : Metallic conductors as well as electrolytes obey *'Ohm's law'* which states that :

The strength of current (I) flowing through a conductor is directly proportional to the potential difference (E) applied across the conductor and inversely proportional to the resistance (R) of a conductor.

Thus, mathematically, the Ohm's law becomes as :

$$I = \frac{E}{R}$$

In relation to electrolytes, the term conductance (C) is used more frequently than the resistance. Conductance implies the case with which the electric current can flow through a conductor. It is therefore, defined as the reciprocal of resistance.

$$\text{Conductance} = \frac{1}{R}$$

Units : It is expressed in units of reciprocal ohm or inverse ohms (ohm^{-1}) or mhos.

Resistance : The resistance R of a conductor is

(i) directly proportional to its length and

(ii) inversely proportional to its area of cross-section.

Hence, $R \propto \frac{l}{a}$

i.e. $R = \rho \frac{l}{a}$ ... (1)

where 'ρ' is a constant depending on the nature of the material of conductor, and is called the *'specific resistance'* or *'resistivity'*. If $l = 1$ cm and a = 1 sq. cm, then ρ = R ohms.

Hence, specific resistance may be defined as,

"The resistance of a uniform column of the material of the conductor having a length of 1 cm and a cross-section of 1 sq. cm."

Units : As we know that,

$$\rho = R \cdot \frac{a}{l} = \frac{\text{ohm (cm}^2)}{\text{cm}} = \text{ohm. cm.} \quad \text{... (2)}$$

(ii) Specific Conductivity (k) : The specific conductance of a conductor is the reciprocal of specific resistance, and is generally denoted by κ (Greek, small kappa). Equation (2) can be written as :

$$R = \frac{1}{\kappa} \cdot \frac{l}{a} \text{ ohms} \qquad \left[\because \rho = \frac{1}{\kappa}\right]$$

$$\kappa = \frac{1}{R} \cdot \frac{l}{a} \text{ ohm}^{-1}\text{. cm}^{-1} \quad \text{... (3)}$$

If l = 1, and a =1 sq. cm. then the equation (3) becomes as

$$\kappa = \frac{1}{R} = \rho$$

or $\kappa = \rho$

Thus, the specific conductance (κ) of a conductor is defined as *'the conductivity offered by a solution of length 1 cm and area of unit cross section or specific conductivity (κ) is the conductance of a one centimeter cube of the substance or solution.'*

Units : The unit of specific conductance is $\text{ohm}^{-1}\ \text{cm}^{-1}$ or mhos/cm.

S.I. System : (It is the unit named as Sir. W. Siemens a eminent electrical engineer.)

In SI system, unit of specific conductivity is S.m^{-1} (where S is Siemens, which is the unit for conductance i.e. ohm^{-1} or mho).

Since, $\kappa = \frac{1}{\rho} = \frac{l}{Ra} = \frac{1}{R} \times \frac{l}{a} = \frac{1}{\text{ohm}} \times \frac{\text{cm}}{\text{cm}^2} = \text{ohm}^{-1}\ \text{cm}^{-1}$

The greater the specific conductance, the more readily does the electrolyte allow the passage of an electric current through it. The specific conductance of an electrolyte depends not only upon its nature, but also upon the concentration of solution.

(iii) Equivalent Conductivity (λ_v) **:** It is defined as the conductivity of a solution containing 1 gm equivalent of the solute/electrolyte, when placed between two sufficiently large electrodes, which are placed 1 cm apart. It is denoted by (lambda), λ_V, where 'V' ml is the volume of solution containing 1 gm equivalent of electrolyte/solute when placed between the electrodes.

$$\therefore \text{ Equivalent conductivity } (\lambda_V) = \left\{\begin{matrix}\text{Volume (in cm}^3)\\ \text{containing 1 gm}\\ \text{equivalent of}\\ \text{solute}\end{matrix}\right\} \times \left\{\begin{matrix}\text{Sp. conductivity}\\ \text{of solution}\\ \text{i.e. kappa}\end{matrix}\right\}$$

or $\lambda_V = V \times k$

Therefore, equivalent conductivity can also be defined as, *the product of specific conductivity and the volume (V ml) of the solution containing 1 gm equivalent of the solute.*

If 'c' is the concentration in gm equivalent per litre, then,

$$\lambda_V = \frac{1000\ k}{c} \qquad \text{... (4)}$$

It is measured in reciprocal ohm or mho.

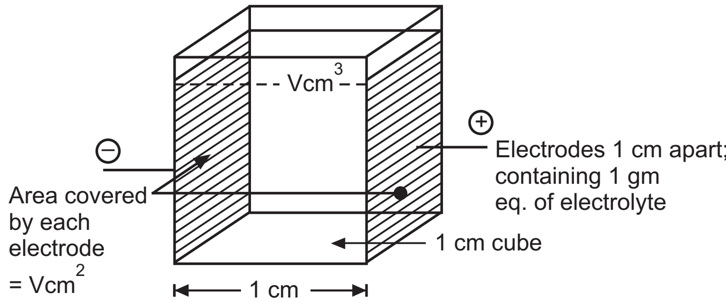


Fig. 2.15 : Relation between specific and equivalent conductivity

(iv) Measurement of conductance : This is normally carried out by the use of Wheatstone bridge. However, the measurement of the conductivity of an electrolyte is complicated, if the direct current is used with usual "Wheatstone bridge apparatus" as the products of electrolysis collect at the electrodes and set up a back potential, which apparently increases the resistance of the electrolyte. This difficulty is overcome by using an alternating current from an induction coil with a frequency of 1000 cycles per second (i.e. the direction of the current is reversed 1000 times, in a second) and detecting the flow of current with a head-phone in place of galvanometer. The arrangement of the apparatus is as shown in Fig. 2.16. Now the conductance of the solution can be directly measured by using conductivity meter and conductivity cell, which are available in the market.

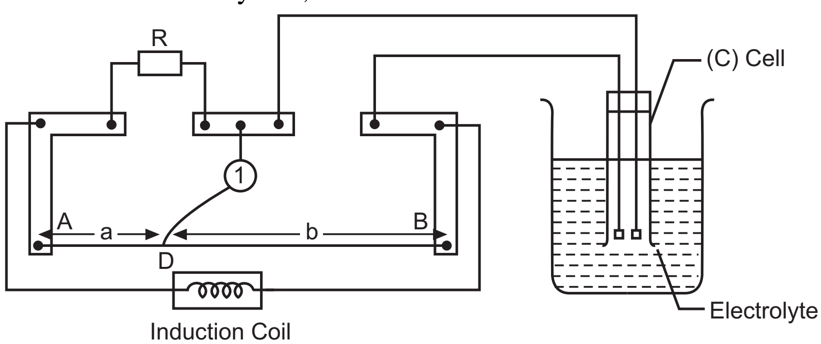


Fig. 2.16 : (Wheatstone bridge) Determination of equivalent conductance

(a) The solution whose conductance is to be measured is taken in the conductivity cell 'C'. The conductivity cell is made up of specially resistant glass and is fitted with two platinum electrodes coated with finely divided platinum, which are fixed rigidly in ebonite cover so that their distance apart is constant. The copper wires of the circuit dip in mercury placed in glass tubes to complete the circuit.

(b) The cell is connected to a resistance box R on one side and to a long thin wire AB stretched along a scale on the other side.

(c) Some known resistance 'R' is taken out of the resistance box. An alternating current of about 1000 – 4000 cycles per second is passed through the solution. The sliding contact 'd' is moved on the wire AB so that no sound is heard in the head phone. This gives the null point, then,

$$\frac{\text{Resistance of cell (X)}}{\text{Resistance (R)}} = \frac{a}{b}$$

$$\therefore \quad \text{Resistance of cell (X)} = R.\frac{a}{b}$$

$$\therefore \quad \text{Conductivity of the solution} = \frac{1}{\text{Resistance of cell (X)}}$$

The reciprocal of the resistance gives the conductance of a cell, where R is the known resistance corresponding to the plugs, which have been removed from the resistance box while 'a' and 'b' are the lengths of wire between movable contact and the ends of the bridge wire.

(v) Determination of Cell Constant : In order to calculate the specific conductance of an electrolyte or the observed resistance (x) of the cell, the dimensions, *'l'* and 'A' of the latter must be known. *Since, the electrodes of an ordinary cell are not exactly 1 cm apart and may not possess the surface area of 1 cm^2, then the reciprocal of the resistance of cell does not give the exact value of specific conductivity, but a value proportional to it.* The cell constant is determined by substituting the value of specific conductance of N/50 KCl solution at 25°C as accurately determined by Kohlrausch (0.002765).

We know that,
$$R = \rho \times \frac{l}{A}$$
$$R = \frac{1}{\kappa} \cdot \frac{l}{A}$$
or
$$\kappa = \frac{1}{R} \cdot \frac{l}{A}$$
$\therefore$
$$\kappa = \frac{1}{R} \cdot x$$
$\therefore$
$$x = \kappa R = \frac{l}{A}$$
or
$$\frac{1}{\text{Obs. conductance}} = \frac{1}{\text{Sp. conductance}} \times \frac{l}{A}$$
or
$$\text{Sp. conductance} = \text{Obs. conductance} \times \frac{l}{A}$$
$$= \text{Obs. conductance} \times x$$
$$\text{Sp. conductance} = \text{Obs. conductance} \times \text{cell constant}$$

As l and 'A' are constant for a given cell, so that the ratio $\frac{l}{A}$ is constant and is known as cell constant.

Therefore, the cell constant (x) may be defined as *the factor which must be multiplied to observe conductance (1/R) to get the specific conductance.*

$$\text{Cell constant} = \frac{\text{Sp. conductance}}{\text{Obs. conductance}}$$
$$= \frac{0.002765}{\text{Obs. conductance}}$$
$$\text{The unit of cell constant} = \text{cm}^{-1}$$

2.14 ELECTRIC CELLS AND BATTERY

Battery is a device that stores chemical energy for later release of electricity. Alternatively, battery is defined as an electrochemical cell or often several electrochemical cells connected in series, that can be used as a source of direct electric current at a constant voltage.

Types of cells : Cells or batteries are of two types :

1. **Primary cells :** "The non-rechargeable cells are called primary cells".

(a) The chemical action taking place in primary cells is **'irreversible'**. Hence, once the terminal voltage goes down then we have to replace the primary cell by a new one.

(b) The best example of primary cell is the dry cell available in the market that are used for radio, walkman, calculators, torch, etc.

(c) The primary cells have limited energy producing capacity.

(d) Examples of primary cells are dry cell, Leclanche cell, alkaline cell, mercury cell etc.

2. **Secondary cells :** "The rechargeable cells are called secondary cells or storage cells".

(a) The chemical action taking place in secondary cell is **'reversible'**. So it is possible to recharge the cell.

(b) In the charging process we have to pass the charging current through the cell in the opposite direction to that of discharging current.

(c) The secondary cells are capable of producing large amount of energy.

(d) Examples of secondary cells are lead-acid storage cell, Nickel-Cadmium (Ni-Cd) cell, silver-cadmium (Ag-Cd) cell etc.

2.15 DRY CELL

Dry cell is a modified form of Leclanche cell. Dry cell is not dry inside, but it is pasty. It consists of :

(i) a zinc vessel, which acts as a negative electrode;

(ii) a graphite rod surrounded by a paste of ground carbon, manganese dioxide and water, placed in a muslin cloth. This acts as a positive electrode and

(iii) a paste of ammonium chloride, zinc chloride and water.

Reactions : (i) At the negative electrode (zinc anode) : Dissolution of zinc electrode to form zinc ions.

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

Ammonia combines with zinc ions to form complex :

$$Zn^{2+} + 4NH_3 \longrightarrow Zn(NH_3)_4^{2+}$$

(ii) At the positive electrode (graphite cathode) : Manganese dioxide reacts with ammonium ions to liberate ammonia :

$$2MnO_2 + 2NH_4^+ + 2e^- \longrightarrow Mn_2O_3 + H_2O + 2NH_3$$

Ammonia is not liberated as a gas, but combines with Zn^{2+} to form $Zn(NH_3)_4^{2+}$ ions at the zinc anode.

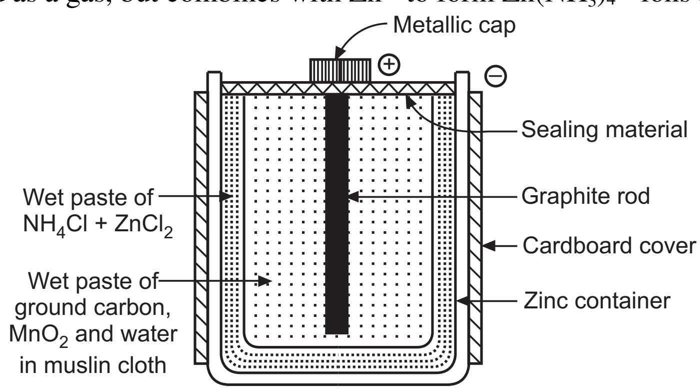


Fig. 2.17 : Dry cell

The cell develops a potential of 1.5 V. Dry cell does not have an indefinite life, since acidic NH_4Cl corrodes the zinc container, even when not in use. With usage, the voltage falls, until eventually the cell is discarded. These cells are, however, compact in size, portable, clean and required little attention.

Uses : Such cells are useful for applications where small amounts of current are required for short period of time, e.g., torches, transistors, tape-recorders, door-bells, gas-engine ignition etc.

Secondary Cells :

Electric current cannot be produced on a large scale by primary cells, because it needs the periodic replacement of exhausted cells by new ones, causing inconvenience as well as additional expenses. However, there are *reversible cells* in which not only the transformation of chemical energy into electrical energy can be carried out, but also the reverse transformation (i.e. electrical energy to chemical energy) can be carried and the spent electrodes can be regenerated by passing electric current through the cell in the reverse direction. Such cells which allow electrical energy to be stored and expended are called *storage cells* or *secondary cells* or *accumulators*. Accumulators or storage cells owe their name "secondary", because of the fact that they can give electrical energy only after they have been charged. The process of storing electrical energy in an accumulator is called charging; while the reverse process of providing electrical energy, in the form of an electric current, is called discharging. Several storage cells are, usually, connected in series to make up a storage battery. They may be of acid (or lead) type and alkaline (nickel-cadmium) type.

2.16 LEAD-ACID STORAGE CELL

A storage cell is one that can operate both as a voltaic cell and as an electric cell. When operating as a voltaic cell, it supplies electrical energy and as a result eventually becomes "run down". It must then be recharged. When being recharged, the cell operates as an electrolytic cell. Thus, storage cell has the great advantage of its ability to work both ways, to receive electrical energy and also to supply it.

Construction :

The common example of a storage cell is the *lead storage cell*. One of its electrodes is made of lead. The other electrode is made of lead dioxide (PbO_2) or rather a paste of PbO_2 is pressed into a grid, made of lead. A number of lead plates (–ve plates) are connected in parallel and a number of lead dioxide plates (+ve plates) are also connected in parallel. The lead plates fit in between the lead dioxide plates. Various plates are separated from the adjacent ones by insulators like strips of wood or rubber or glass fibre. The entire combination is then immersed in approximately 20% dil. H_2SO_4.

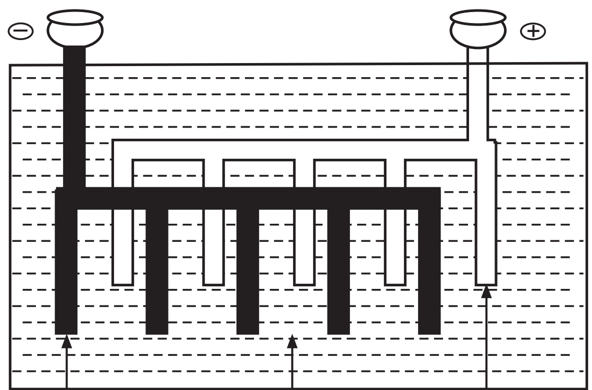


Fig. 2.18 : Lead-acid storage battery

Discharging : When the storage cell is operating as a voltaic cell (i.e. for supplying electrical energy), it is said to be discharging. The lead electrode loses electrons, which flow through the wire. In this reaction, oxidation of lead takes place at the anode.

$$Pb \longrightarrow Pb^{2+} + 2e^- \qquad \text{(At lead anode)}$$

The Pb^{2+} ions then attach to sulphate (SO_4^{2-}) ions.

$$Pb^{2+} + SO_4^{2+} \longrightarrow PbSO_4 \downarrow$$

The electrons released from the anode (lead plate) flow to the dioxide electrode. Here, lead in PbO_2 gains electrons to form Pb^{2+} ions. In other words, lead undergoes reduction at the cathode from oxidation state +4 to +2. The Pb^{2+} ions then combine with SO_4^{2-} ions.

$$PbO_2 + 4H^+ + 2e^- \longrightarrow Pb^{2+} + 2H_2O \qquad \text{(At } PbO_2 \text{ cathode)}$$

$$Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4 \downarrow$$

So, the net reaction in the lead storage cell is :

$$\boxed{Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \longrightarrow 2PbSO_4 \downarrow + 2H_2O + \text{Energy}}$$

It may be noted that lead sulphate is precipitated at both the electrodes. The voltage of each cell is about 2.0 volts at a concentration of 21.4% H_2SO_4 at 25°C. Lead cell commonly used in automobile is a combination of six such cells in series to form a battery with an e.m.f. 12 volts.

Charging : When both anode and cathode become covered with $PbSO_4$, the cell ceases to function as a voltaic cell. To recharge a lead storage cell, the reactions taking place during discharging are *reversed* by passing an external e.m.f. greater than 2 volts from a generator. The +ve pole of the generator is attached to the +ve pole of the cell (or battery) and the following reactions take place :

Reaction at the –ve terminal (Cathode) :

$$PbSO_4 + 2e^- \longrightarrow Pb + SO_4^{2-}$$

Reaction at the +ve terminal (Anode) :

$$PbSO_4 + 2H_2O + 2e^- \longrightarrow PbO_2 + 4H^+ + SO_4^{2-}$$

Hence, the net reaction during charging is :

$$\boxed{2PbSO_4 + 2H_2O + \text{Energy} \longrightarrow Pb + PbO_2 + 4H^+ + 2SO_4^{2-}}$$

During the process of charging, the electrodes of the cell are restored to their original conditions (to Pb and PbO_2 respectively). It may also be noted that during discharging operation, the concentration of acid (H_2SO_4) decreases; while the concentration of acid increases during the charging operation.

The net cell reaction during discharging and charging can be shown as :

$$\boxed{PbO_2 + Pb + 2H_2SO_4 \underset{\text{charging}}{\overset{\text{discharging}}{\rightleftharpoons}} 2PbSO_4 + 2H_2O}$$

Since both these changes are associated with variation in the specific gravity of the acid, the extent of charge or discharge of the cell at any time can be determined by testing the specific gravity of the acid. The cell voltage lies in the range of 1.88 V to 2.15 V as the concentration of H_2SO_4 varies from 5% to 40%.

The complete process of charging and discharging of storage cell is depicted in Fig. 2.19.

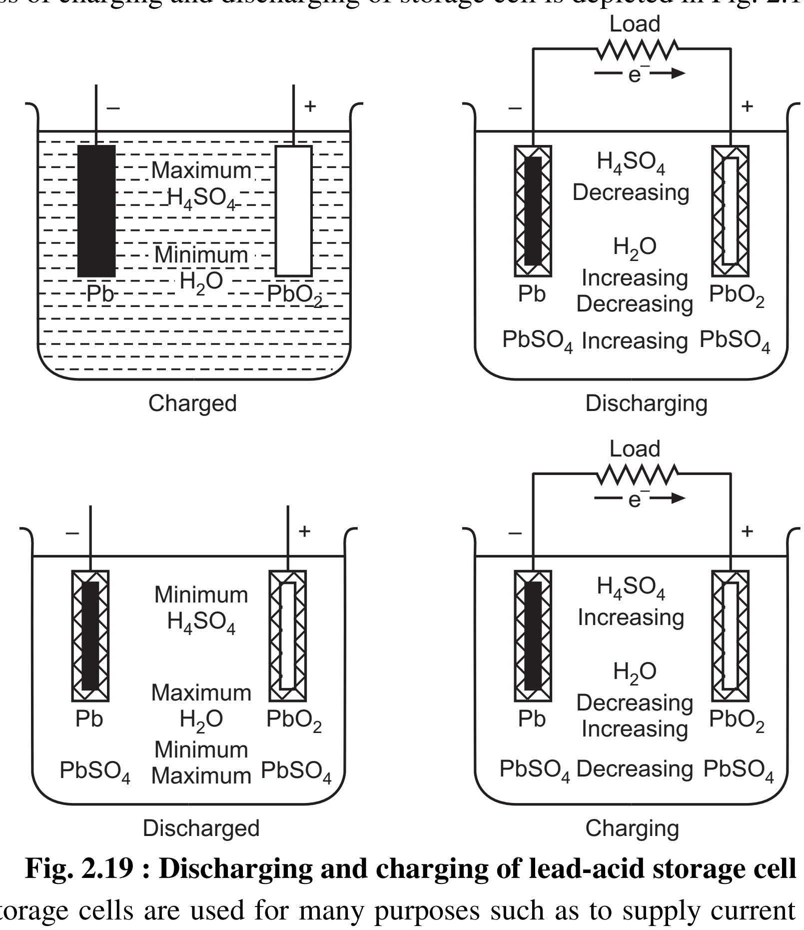


Fig. 2.19 : Discharging and charging of lead-acid storage cell

Uses : Lead acid storage cells are used for many purposes such as to supply current for electric vehicles, gas engine ignition in telephone exchanges, railway trains, mines, laboratories, hospitals, broadcasting stations, automobiles, power stations and distribution works, etc.

EXERCISE

1. (a) Define the terms (i) Atom, (ii) Ion, (iii) Ionisation, (iv) Electrolytic dissociation.
   (b) Distinguish between Atom and Ion.
   (c) Define the following terms : (i) Faraday, (ii) Coulomb.
2. What is ionisation ? State and explain the ionic theory or Arrhenius theory of Electrolytic dissociation.
3. (i) Define degree of ionisation. State and explain the factors on which the degree of ionisation depends.
   (ii) With the help of a figure, explain the mechanism of electrolysis of copper sulphate solution using platinum electrodes. Define e.c.e.
4. Define and explain the following terms :
   (i) Conductor, (ii) Insulator, (iii) Electrolyte, (iv) Non-electrolyte, (v) Electrolysis, (vi) Cathode, (vii) Anode, (viii) Cation, (ix) Anion, (x) Current density.
5. (i) Define electrolysis. Explain the mechanism of electrolysis, by drawing a suitable diagram.
   (ii) State any two points of Arrhenius theory of ionisation.
6. Distinguish between :
   (a) Atom and Ion
   (b) Strong and Weak electrolyte.
   (c) Ionisation and Electrolytic dissociation.
   (d) Electrolyte and Non-electrolyte.
7. Schematically represent the reactions taking place in the electrolysis of
   (a) Copper sulphate solution by using copper electrodes.
   (b) Copper sulphate solution by using platinum electrodes.
   (c) Sodium chloride solution by using platinum electrodes.
   (d) Fused sodium chloride by using carbon electrodes.
8. (a) Define (i) Coulomb, (ii) Ampere and (iii) Faraday.
   (b) State and explain the First Law of Faraday and show how it helps to determine the electro-chemical equivalent of an element ?
9. What are the applications of electroplating ?
10. State and explain the Faraday's second law of electrolysis. How is it used for finding out the equivalent weight of an element ?
11. (a) State and explain the Faraday's laws of electrolysis.
    (b) Establish the relation between chemical equivalent and electrochemical equivalent.
12. Write notes on the following :
    (a) Electroplating.
    (b) Electrorefining of metals.
    (c) Electrotyping.
13. State Faraday's laws of electrolysis. Explain the electrolysis of copper sulphate solution by using platinum electrodes.
14. How is electroplating carried out ? Draw a suitable diagram and give two applications of this process.
15. State whether the process of electrolytic dissociation is reversible. Why ? Give two examples in support.
16. By which law of electrolysis equivalent weight of a metal can be calculated ? State the law and derive it mathematically.
17. (a) Why copper is electrorefined ? Describe the processs of electro-refining of copper.
    (b) Describe the process of electrolytic refining stating suitable example.
18. Give any four assumptions of Arrhenius theory.

19. Describe the process of electroplating or electrorefining with the help of labelled diagram.
20. Schematically represent the reactions taking place in the electrolysis of copper sulphate solution using copper electrodes.
21. You are provided with an iron spoon and you have been asked to electroplate it with silver. Describe the process with labelled diagram.
22. Define the following terms :
    (a) Ohm's law (in reference to electrolytes)
    (b) Specific conductivity
    (c) Equivalent conductivity.
23. How is electrolytic conduction of an electrolyte determined experimentally ?
24. What is a cell constant ? How can it be determined ?
25. Define specific conductance and equivalent conductance of an electrolyte. What is the relationship between the two ?
26. Explain electrorefining of impure copper with the help of a labelled diagram. Write one advantage of this process. Define solubility or specific conductivity.
27. Explain what is electrochemical equivalent for a $CuSO_4$ solution.
28. Define cell constant and state the mathematical relation between cell constant and specific conductance.
29. State Faraday's second law of electrolysis and derive the mathematical relation.

    OR

    Describe the primary reaction at the anode during the electrolysis of an electrolyte.
30. Which of the following substances will conduct electric current ? Give reasons :
    (i) Solid NaCl, Fused NaCl, (ii) Solid $ZnSO_4$, Solution of $ZnSO_4$,
    (iii) Solid $CuSO_4$, Solution of $CuSO_4$, (iv) Benzene alcohol.
31. Explain electrorefining of copper with the help of figure.
32. Define the terms (a) cell, (b) battery. Explain with figure the working of a dry cell.
33. Write a note on lead-acid storage battery.

SHORT ANSWER QUESTIONS

1. Define Coulomb.

   Ans. It is the quantity of electricity that flows through a circuit when current of 1 ampere is passed for 1 second.

   Coulomb = Ampere × Second.
2. What is Faraday ?

   Ans. It is the quantity of electricity required to liberate or deposit one gram equivalent of a substance from its solution.
3. State the relation between Faraday and Coulomb.

   Ans. 1 Faraday = 96,500 coulombs.
4. What is an electrolytic cell ?

   Ans. The cell in which electrical energy is converted into chemical energy.
5. Define electrochemical cell.

   Ans. A cell in which chemical energy is converted into electrical energy. e.g. Daniell cell, Leclanche cell, Lead-acid storage cell.

6. What are primary and secondary cells ?

   Ans. Primary cell : The cell once discharged cannot be recharged again. This is because the reaction in the cell cannot be reversed. e.g. Dry cell, Daniell cell, Leclanche cell.

   Secondary cell : The cell can be recharged again and again. It is also called storage or reversible cell. e.g. Lead-acid storage cell, Ni-Cd cell. These can be used in cars, inverters etc.

7. What is battery ?

   Ans. Battery is a device that stores chemical energy for latter release of electricity.

8. Define reduction potential.

   Ans. The tendency of an electrode to lose electrons, when it is in contact with solution of its own ions.

9. What is oxidation potential ?

   Ans. The tendency of an electrode to gain electrons when it is in contact with its own ions.

10. What is a fuel cell ?

    Ans. A device for converting the energy of a fuel directly into electrical energy.

11. Why do electrochemical cells stops working after some time ?

    Ans. An electrochemical cell produces electrical energy at the cost of redox reaction. When the redox reaction is completed, the cell stops working, since it is incapable of undergoing redox reaction any more.

12. Why does dry cell become dead after a long time, even if it has not been used ?

    Ans. Acidic NH_4Cl slowly corrodes the zinc container of dry cell even when the cell is not in use.

13. What is lead-acid accumulator ?

    Ans. A secondary cell consisting of lead electrodes, the positive one covered with PbO_2 dipping into H_2SO_4 solution. The e.m.f. is about 2 V.

14. When $CuSO_4$ solution is electrolysed using Pt electrodes, the blue colour of the solution gradually fades. Why is this ?

    Ans. The blue colour is due to the presence of Cu^{2+} (aq). During electrolysis these ions are changed into Cu (s). Hence, the blue colour fades.

15. When does an electrolysis of $CuSO_4$ using Cu electrode stops ?

    Ans. When the anode has been worn away (consumed) so much that it no longer dips properly into the electrolyte.

16. What is the purpose of MnO_2 in dry cell ?

    Ans. It is an oxidising agent.

17. What is the voltage generated by the H_2-O_2 fuel cell operating under standard conditions ?

    Ans. 1.23 V.

18. Alkaline dry cells are considered better than Leclanche cell. Why ?

    Ans. Alkaline dry cell lasts longer, because zinc electrode does not corrode easily.

19. State the relation between C.E. and E.C.E.

    Ans. Chemical equivalent (eq. wt.) = 96,500 × Electrochemical equivalent.

    OR $\boxed{\text{C.E.} = 96{,}500 \times \text{E.C.E.}}$

20. Give the applications of dry cells.

    Ans. Dry cells are used in torch, radio, calculator and electronic devices.

21. Give the uses of battery or lead-acid storage cell.

    Ans. (i) An automobile, (ii) In railway signalling, (iii) In telephone systems and (iv) Inverters.

22. What is Magnus Rule ?

    Ans. When solution of salts of different metals electrolysed, there is a certain definite voltage at which one and only one of the metals is deposited on the electrode.

23. State the mathematical relations of first and second laws of Faraday.

Ans. First law : $W = z \times c \times t$

Second law : $\frac{W_1}{W_2} = \frac{E_1}{E_2}$

EXAMPLES

1. A current of 0.25 ampere while flowing for one hour through a solution of copper sulphate deposits 0.2936 g of copper. Find the electrochemical equivalent and chemical equivalent of copper. (**Ans.** 0.003262; 31.49)
2. An electric current is passed through a solution of copper sulphate and a solution of zinc sulphate connected in series. If in a given time 0.70 g of copper is deposited, what would be the weight of zinc that would be deposited at the same time ? (Atomic weight of copper is 63.5 and that of zinc is 65). (**Ans.** 0.7164 g)
3. A current of 1.5 amperes was passed through a solution of a salt of a metal for 15 minutes when 0.783 g of the metal was deposited. Calculate the equivalent weight of the metal. (**Ans.** 55.98 g)
4. What current strength in amperes will be required to liberate 12.7 g of iodine from potassium iodide solution in half an hour ? (Given : E.C.E. of iodine = 0.00131 g) (**Ans.** 5.360 amperes)
5. Calculate the equivalent weight of copper if 8.9 g of it are deposited by passing 1.5 amperes of current for 5 hours through copper sulphate solution. (**Ans.** 31.75 g)
6. The same current is passed through two cells connected in series containing copper sulphate and silver nitrate solution respectively. What weight of silver would be deposited in the second cell if the weight of copper deposited in the first cell is 0.159 g ? (Eq. wt. of silver = 108; Eq. wt. of copper = 31.8) (**Ans.** 0.54 g)
7. 965 coulombs of electricity is passed through a soluton of sodium chloride. Find the weight of sodium hydroxide formed by electrolysis. (**Ans.** 0.4 g)
8. A current of 1.93 amperes is passed through a solution of silver nitrate for 25 minutes. What is the amount of silver deposited on the cathode ? (Given E.C.E. of silver is 0.001118 g). (**Ans.** 3.237 g)
9. A current strength of 5 amperes is passed through silver nitrate solution in an electrolytic cell for 30 minutes. What is the weight of silver deposited at cathode ? (Given E.C.E. of silver is 0.001118 g.) (**Ans.** 10.06 g)
10. Find the weight of copper deposited from copper sulphate solution by a current of 0.25 amperes flowing for one hour on copper electrode. Equivalent weight of copper is 31.75. (**Ans.** 0.2961 g)
11. The same quantity of electricity was passed through two cells, one containing molten sodium chloride and other containing silver nitrate solution. If 2.3 g of sodium are liberated in the process, what weight of silver is deposited in the second cell ? (**Ans.** 10.8 g)
12. A current of 4 amperes is passed through copper sulphate solution for one hour. Calculate the weight of copper deposited at the cathode. (Given : E.C.E. of copper is 0.000326 g) (**Ans.** 4.69 g)
13. Current of 5 amperes flowing for 0.5 hour deposits 3.048 g of a metal at the cathode. Calculate the equivalent weight of the metal. (1 Faraday = 96500 coulombs) (**Ans.** 32.68 g)
14. 10.07 g of silver were deposited when 5 ampere current was passed through $AgNO_3$ solution for half an hour. Calculate the electrochemical equivalent of silver. (**Ans.** 0.001119 g)
15. A solution of the metal salt was electrolysed for 15 minutes with a current of 1.5 amperes. The equivalent weight of the metal is 55.9. Calculate the weight of the metal deposited at the cathode. (**Ans.** 0.7820 g)
16. An electric current is passed through a solution of zinc sulphate and copper sulphate connected in series. If in a given time 0.716 g of zinc is deposited, what would be the weight of copper that would be deposited in the same time ? (At. wt. of Cu = 63.5 and that of Zn = 65). (**Ans.** 0.6994 g)
17. A current of 2.5 amperes is passed into a solution of an electrolyte. The weight of metal deposited after one hour is 3.6 g. Calculate the equivalent weight of metal.

    (One Faraday = 96,500 coulombs). (**Ans.** 38.6 g)

18. A current of 1.5 ampere is passed through two cells arranged in series containing $CuSO_4$ and $AgNO_3$ solution. After 30 minutes, 0.89 g of copper was found to be deposited at the cathode in the first cell. Calculate the weight of silver deposited in the second cell. (Eq. wt. of Ag = 107.9) (**Ans.** 3.016 g)
19. Calculate the time in seconds in which 0.3 g of copper is liberated from copper sulphate solution, when a current of 0.5 ampere is passed (Eq. wt. of Cu = 31.6) (**Ans.** 1199 sec.)
20. When an electric current was passed through a solution of silver nitrate for 45 minutes, 8.0 gms of silver was deposited at the cathode. Calculate the strength of the current. (E.C.E. of Ag. = 0.001118 g.)(**Ans.** 2.65 amp.)
21. When an electric current of 6 amperes was passed through a solution of magnesium nitrate for 7 minutes, 0.3175 g of magnesium was liberated at the cathode. Calculate the E.C.E. of Mg.
22. The same quantity of electricity was passed through two cells connected in series, one containing acidified water and the other containing copper sulphate solution. During electrolysis, 0.27 g of hydrogen and 8.44 g of copper were liberated at the respective electrodes. Calculate the eq. wt. of copper. (Eq. wt. of hydrogen = 1.008) (**Ans.** 31.50 g)
23. When the same amount of current of 3.5 amperes was passed through solutions of copper nitrate and zinc chloride, it deposits 0.698 g of copper and 0.813 g of zinc. Atomic weight of Cu = 63.5. Calculate equivalent weight of zinc. (**Ans.** 36.98 g)
24. If a current of 5 amperes is passed in a solution of $AgNO_3$ for 20 minutes, what is the amount of silver deposited on the cathode ? (Electrochemical equivalent of Ag = 0.001118 gm) (**Ans.** 6.708)
25. Same quantity of current was passed through solutions of copper sulphate and silver nitrate. If the amount of copper liberated in this process is 3.177 g, calculate the weight of silver deposited on cathode in silver nitrate solution.
26. A current of 5 amperes is passed through a solution of NaCl for 3.25 hrs. Find the weight of NaOH formed. (**Ans.** 24.248 g)
27. What current strength in amperes will be required to liberate 12.7 g of iodine from KI solution in 30 minutes ? (Given : e.c.e. of iodine = 0.00131 g/C) (**Ans.** 5.36 amperes)
28. A current of 1.5 amperes was passed through a solution of a metal for 15 minutes when 0.783 g of metal was deposited. Calculate e.c.e. of metal. (**Ans.** 0.00058 g/C)
29. Same quantity of current was passed through $CuSO_4$ and $AgNO_3$ solutions. If 3.207 g of Cu is deposited, calculate weight of silver deposited. (Eq. wt. of Cu = 31.77; Eq. wt. of Ag = 108). (**Ans.** 10.9 g)

❑❑❑

Chapter **3**

METALS AND ALLOYS

3.1 Introduction
3.2 Characteristics of metals
3.3 Metalloids
3.4 Occurrence of metals
3.5 Metallurgy
3.6 Physical properties and applications of metals
3.7 Alloys
3.8 Preparation of alloys
3.9 Purposes of making alloys
3.10 Classification of alloys
3.11 Composition, properties and applications of alloys

3.1 INTRODUCTION

Metals play an important role in the progress of the country. From the very ancient times, man has been using metals for various purposes. Today we find that the metals are being used in such a way that almost every article we use or see around us is either made from a metal or an alloy. Without the use of metals and alloys there would be no railway, aeroplane, motor car, telephone, television, space vehicle or even common articles such as cooking utensils, coins etc. It should be noted that pure metals have a limited use, but they are largely converted into more useful alloys.

Tata was a great Indian industrialist possessing a keen insight. He founded the iron and steel industry in our country and established the giant concern Tata Iron and Steel Company Ltd. He could foresee the role Science would play in the progress of our country and founded the Indian Institute of Science, Bangalore for the advancement of science.

Fig. 3.1 : Jamshedji Nusserwanji Tata (1839 - 1904)

3.2 CHARACTERISTICS OF METALS

Out of the 112 elements known so far about 84 are metals or metalloids and the rest are non-metals. The metals though differing in many properties among themselves, some of the important properties which are common about them determine their utility. The properties which are common among the metals are termed as physical and mechanical properties. For an engineer the knowledge of mechanical properties of the metal is important which includes mainly the hardness, ductility, malleability, toughness, elasticity and tensile strength etc. The physical properties are mainly the melting point, boiling point, electrical conductivity, thermal conductivity, magnetic permeability etc.

The description about the important mechanical properties of the metals is given below :

1. Hardness : Hardness is the ability of the metal to resist wear or abrasion and resist penetration. For example, tungsten metal is found to be the hardest and potassium is found to be the softest among the metals.

2. Ductility : It is the property of the metal by which it can be stretched in length without breaking. Metals like gold, silver, platinum having this property can be easily drawn into wires.

3. Malleability : It is the property by virtue of which a metal can be hammered into shapes without cracking or rolled into thin sheets without tearing or breaking e.g. gold, silver, platinum, aluminium, copper etc. are most malleable.

4. Toughness : The property of a metal to resist repeated shocks or vibrations without breaking is called as toughness. It is a highly desirable property of any metal. e.g. gold and silver are tough metals.

5. Brittleness : It is just the opposite of toughness. It is the property of a material (like glass) which does not permit permanent deformation without breakage. Dropping a brittle material from a certain height on a hard floor causes it to break into pieces. Brittleness is an undesirable property of an engineering material.

6. Tenacity : Tenacity of a metal is measured by the weight which its wire (1 sq. inch cross-section) can support.

7. Tensile strength : The strength of a metal is the ability to carry a load without breaking. A tensile strength of a metal is its ability to resist pull without breaking.

8. Weldability : It is the process of uniting two pieces of metal by means of heat, by bringing their ends together in the molten state.

9. Machinability : It is the property due to which a material can be easily cut by cutting tools to produce a desired shape and surface finish on its surface.

10. Casting : "*The process of pouring molten metal into a mould and allowing it to solidify is known as casting.*"

By this process, intricate parts can be given strength and rigidity, which is not obtained by any other method.

Although all metals can be cast, but iron is much more suited for this process. It is because molten iron possesses good fluidity, small shrinkage on cooling. *"Fluidity is the property due to which a metal is melted by heating and which can flow easily into the mould."*

11. Forging : "*The process of giving pre-determined shape to a piece of metal at sufficiently high temperature when metal is in the plastic state is known as forging.*"

The predetermined shape is given by compressive forces.

12. Extrusion : *"The process by which a piece of metal is reduced in cross-section by forcing it to flow through a die orifice under high pressure is known as extrusion process."*

Generally, extrusion is used to produce cylindrical bars or hollow tubes but shapes of irregular cross-section may be made from the more easily extrudable metals like aluminium.

13. Brazing : *"A method of joining metal surfaces by introducing molten non-ferrous alloy with melting point above 400°C between them, is known as brazing."*

In brazing, a mechanical or chemical cleaning is essential in the joint preparation in addition to the flux (borax or boric acid) used during the process. It is useful in joining dissimilar metals which are difficult to weld.

14. Soldering : *"A method of joining the metal surfaces by introducing a molten non-ferrous alloy with melting point below 400°C between them, is known as soldering".*

The operation of soldering consists of joining two metallic surfaces by causing a metal or alloy to adhere to the surface by a process of diffusion or alloying. e.g. lead and tin alloys having melting range 150 to 370°C are generally used in soldering.

3.3 METALLOIDS

There are some elements which behave like metals under some condition and act like non-metal under different conditions. These elements are called as *metalloids*. The good examples of metalloids are arsenic and antimony.

Arsenic has a metallic appearance and is a conductor of electricity and forms alloys. Just like metals such as copper or mercury, arsenic is precipitated as sulphide As_2S_3 by passing hydrogen sulphide through any arsenic salt solution. On the other hand, like other non-metals, the oxides of arsenic As_2O_3 and As_2O_5 are acidic in nature and form salts. The hydride of arsenic AsH_3 is quite stable just as other non-metals. Hence, arsenic shows some properties of metals and some properties of non-metals also. Therefore, arsenic is a borderline case and is called as *metalloid.*

3.4 OCCURRENCE OF METALS

Metals occur in nature in (i) Native state (or free state), (ii) Combined state.

(i) Native state (free state) : The inactive metals like silver, gold, platinum etc. are found in the free state i.e. in the elementary form in nature. Such metals are placed at the bottom of the activity series.

(ii) Combined state : Most of the metals occur in nature in the form of their compounds due to the action of moisture, air, carbon dioxide and the non-metals present in the earth crust. "*A naturally occurring substance present in earth's crust which contains metal in the native (or free state) or in combined state is known as mineral*". "*A mineral from which the metal can be extracted economically is known as an ore.*" Thus, all ores are minerals, but all minerals are not ores. For example, clay ($Al_2O_3.2SiO_2.2H_2O$) and bauxite ($Al_2O_3.2H_2O$) are two minerals of aluminium, but aluminium can be profitably extracted only from bauxite and not from the clay. Hence, bauxite is an ore of aluminium, while clay is a mineral.

Ores obtained from earth's crust are always associated with impurities like sand, clay, rocks etc. and these unwanted impurities associated with the ores are known as *'gangue'* or *'matrix'*.

Metals occur in the combined state such as their oxides, sulphides, carbonates, sulphides etc. The following are the important ores from which the metals can be extracted :

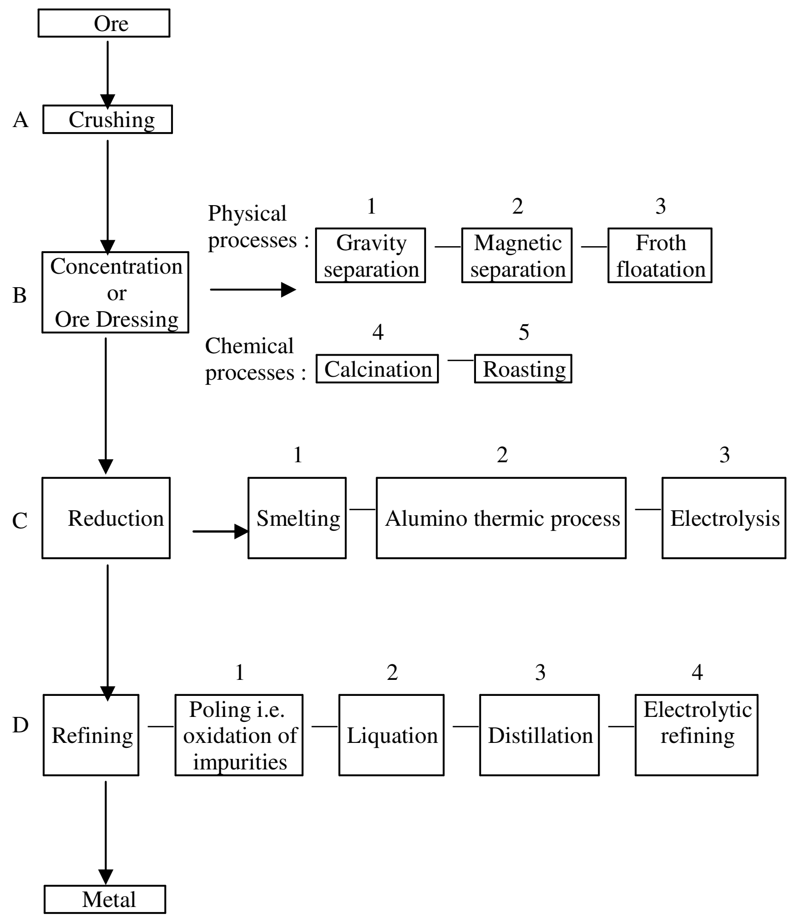
Type of ore	Ore or mineral	Composition	Metal Present
1. Oxides	Haematite	Fe_2O_3	Fe
	Bauxite	$Al_2O_3 \cdot 2H_2O$	Al
	Cuprite	Cu_2O	Cu
	Zincite	ZnO	Zn
	Tinstone	SnO_2	Sn
2. Sulphides	Copper pyrite	$CuFeS_2$	Cu
	Copper glance	Cu_2S	Cu
	Zinc Blende	ZnS	Zn
	Cinnabar	HgS	Hg
	Galena	PbS	Pb
3. Carbonates	Limestone	$CaCO_3$	Ca
	Magnesite	$MgCO_3$	Mg
	Dolomite	$CaCO_3 \cdot MgCO_3$	Mg
	Calamine	$ZnCO_3$	Zn
	Malachite	$CuCO_3 \cdot Cu(OH)_2$	Cu
4. Sulphates	Epsum salt	$MgSO_4 \cdot 7H_2O$	Mg
	Gypsum salt	$CaSO_4 \cdot 2H_2O$	Ca
	Barytes	$BaSO_4$	Ba
	Anglesite	$PbSO_4$	Pb

3.5 METALLURGY

"Metallurgy is a process of extraction of metals from their ores economically and profitably". The extraction of metals cannot be carried out by any other method, because extraction depends upon the nature and properties of metal. Consequently, different types of ores like oxides, sulphides, carbonates, sulphates etc. have to be treated differently for the recovery of pure metals from them. Generally, an ore is subjected to the following operations :

(A) Crushing or processing the ore, (B) Concentration, (C) Reduction and (D) Refining.

Following flow chart shows the different processes used in the extraction of metal from the ore :



Schematic representation of extraction of metal from ore

(A) Crushing : The ore is obtained from mines in the form of big lumps (big stones). These lumps are unsuitable for further treatment. Hence, these are crushed to a suitable size in big jaw crushers. These are then pulverised (i.e., converted into a fine powder) in ball mills or stamping mills.

(B) Concentration : The ore is generally associated with useless earthy or rocky impurities (like clay, sand etc.) called gangue or matrix. "*The process of removal of gangue or matrix from the ore is known as concentration of ore.*" Thus, the percentage of metal in the concentration of ore can be brought about by the following methods depending upon the nature of ore.

(1) Gravity separation : In this process, the finely powdered ore is placed on a sloping platform and washed with a running stream of water. The lighter gangue particles are washed away, while the heavier ore particles sink at the depressions or at the bottom of sloping platform. (Refer Fig. 3.2) Generally, oxide ores like haematite (Fe_2O_3) and tinstone (SnO_2) are concentrated by gravity separation method.

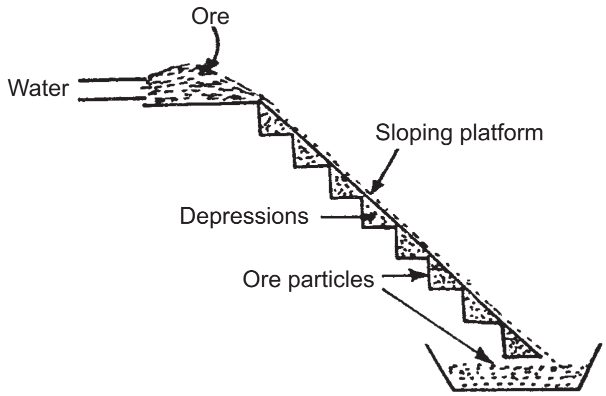


Fig 3.2 : Gravity separation

(2) Electro-magnetic separation : This process is used especially for separating magnetic impurities from non-magnetic ore particles. For example, tinstone (an ore of tin) in which tinstone (SnO_2) is non-magnetic, while the impurities like tungstates of iron and manganese are magnetic. The powdered ore (containing the magnetic impurities) is made to fall through the hopper on a non-magnetic belt of leather or rubber moving over the electromagnetic roller M. The magnetic impurities fall from the belt in a heap near the magnet, due to attraction; while the non-magnetic concentrated ore falls in a separate heap away from the magnet (Refer Fig. 3.3).

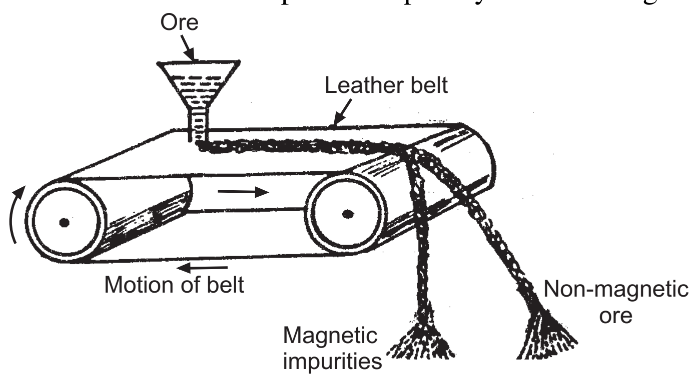


Fig. 3.3 : Electromagnetic separation

(3) Froth floatation process : This process is specially suitable for the concentration of sulphide ores like galena (PbS), nickel sulphide (NiS), zinc blende (ZnS), copper pyrites ($CuFeS_2$) etc. This process is based on the principle of different wetting characteristics of the ore and gangue particles with water and oil. The ore is preferentially wetted by oil and the gangue particles by water.

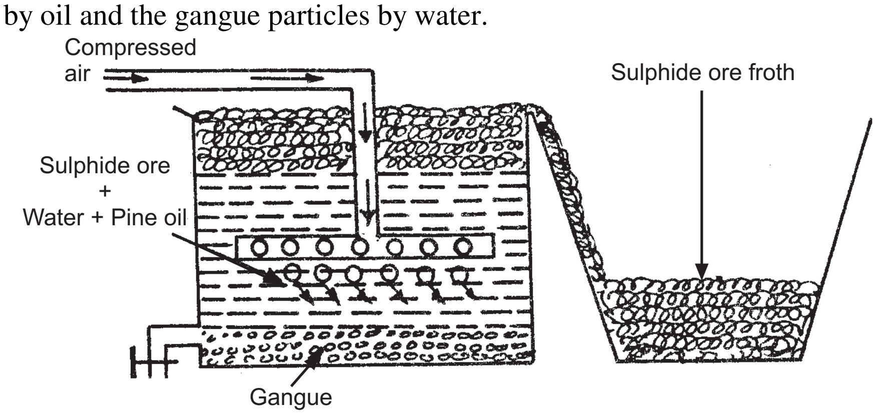


Fig. 3.4 : Froth floatation process

In this process, the powdered sulphide ore is mixed with water and pine oil. The whole mixture is then stirred vigorously by passing compressed air. The oil forms a froth with air bubbles. The sulphide ore particles get attached with the froth and floats on the surface, while the gangue or earthy impurities are wetted by water and sink to the bottom of the tank. The floating froth is then skimmed off into settling basins from where by filter press a concentrated ore is recovered.

(4) Calcination : "*Calcination is the process of heating the ore strongly in the absence of air to a temperature insufficient to melt it*".

Calcination is done in the hearth of a reverberatory furnace when the doors are kept closed. (i.e. in absence of air).

Generally, carbonate and hydroxide ores such as limestone ($CaCO_3$); malachite [$CuCO_3 \cdot Cu(OH)_2$] are concentrated by this method.

The main purposes of calcination are :

1. To convert carbonate and hydroxide ore into oxide.

   $CaCO_3 \longrightarrow CaO + CO_2\uparrow$

   Lime stone

   $CuCO_3 \cdot Cu(OH)_2 \longrightarrow 2\,CuO + CO_2\uparrow + H_2O\uparrow$

   Malachite

   $Fe_2O_3 \cdot 3\,H_2O \longrightarrow Fe_2O_3 + 3\,H_2O$

   Haematite
2. To remove the moisture.
3. To remove the volatile impurities.
4. To make the mass porous, so that it can be easily reduced to the metallic state.

(5) Roasting : "*Roasting is the process of heating the ore strongly in the presence of excess of air to a temperature insufficient to melt it*".

Roasting is done in the hearth of a reverberatory furnace when the doors are kept open for the free supply of air. This process is generally used in case of sulphide ores.

The main purposes of roasting are :

1. To convert sulphide into oxide and sulphate.

   $2\,ZnS + 3\,O_2 \longrightarrow 2\,ZnO + 2\,SO_2\uparrow$

   $ZnS + 2\,O_2 \longrightarrow ZnSO_4$
2. To remove the moisture.
3. To remove the volatile impurities like sulphur, arsenic, antimony and phosphorus in the form of their oxides.
4. To oxidise easily oxidisable substances.

It is difficult to reduce sulphide ore to a metal and hence it should be converted to its oxide before reduction.

Roasting is usually carried out in a special furnace known as a *reverberatory furnace* in which the ore is heated by flames of a fuel. These flames are reverberated, i.e. reflected from the arch-roof of the furnace. On one side of the furnace there is fire place and at the other side is an outlet (flue) for the waste gases. Air is admitted through the doors of the furnace.

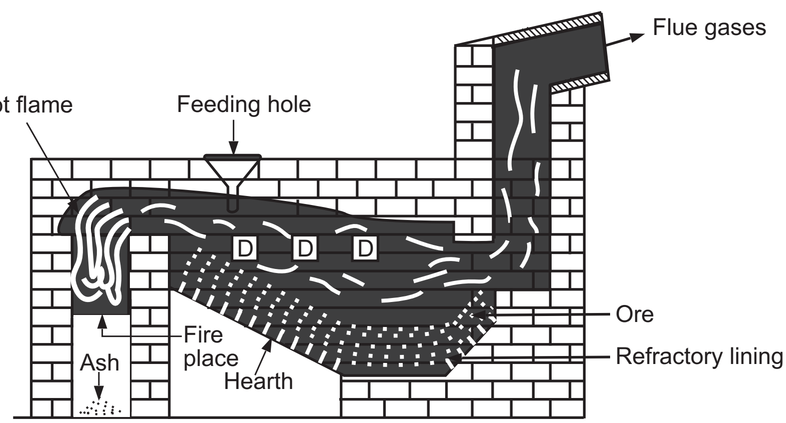


Fig. 3.5 : Reverberatory furnace

Similarly, when galena is roasted, a mixture of lead oxide and lead sulphate is formed.

$$2\,PbS + 3\,O_2 \longrightarrow 2\,PbO + 2\,SO_2\uparrow$$

$$PbS + 2\,O_2 \longrightarrow PbSO_4$$

Distinction between Calcination and Roasting

Calcination	Roasting
1. It is the process of heating the ore strongly in absence of air below its melting point.	1. It is the process of heating the ore strongly in excess of air below its melting point.
2. Generally, this process is used to convert carbonate and hydroxide into their oxides.	2. Generally, this process is used to convert sulphide into oxide and sulphate.
3. The main object of calcination is to remove the moisture and volatile impurities from the ore.	3. The main object of roasting is to remove the moisture and oxidation of ore and the impurities like S, As etc.
4. In calcination, the mass becomes porous, so that it can easily be reduced to metallic state.	4. In roasting, the sulphide ore is chemically changed into a suitable form (oxide or sulphate) and can be reduced to metallic state.

(C) Reduction : This is the main part in the metallurgical operation (except the ores containing metals in native state). A reducing agent is used but it must be powerful and also cheap. Carbon in the form of coke is a satisfactory reducing agent. Other reducing agents like carbon monoxide or aluminium can also be used. Reduction is also carried out by an electric current.

Hence, there are three processes of reduction, namely :

(i) Smelting, (ii) Alumino thermic process and, (iii) Electrolysis.

(i) Smelting : Carbon reduces the oxide of a metal and the process is known as carbon reduction process. It is applicable in the cases of oxides of metals whose atomic weights are higher than that of manganese (55). Thus, zinc oxide, lead oxide, tin oxide, iron oxide etc., are reduced by carbon.

In this process, the calcined oxide ore is mixed with coke and flux (like CaO) and the mixture is strongly heated to high temperature. The reducing agent (coke) converts the ore into molten metal, while the flux removes the gangue in the form of fusible mass (slag). The process is also called *smelting*. (To smelt means to melt). In some cases, the smelting is carried out in the reverberatory furnace at higher temperature while in many cases it is carried out in the blast furnace.

The hot blast of dry air is blown into the furnace just above the hearth through a number of pipes called *twyers.* In the well of the furnace there are two outlets known as *tap holes.* The upper tap hole is used to remove the slag and the lower one is used to remove the molten metal. Haematite ore is reduced by this method.

$$\underset{\text{Haematite}}{Fe_2O_3} + \underset{\text{Coke}}{3\,C} \longrightarrow \underset{\text{Iron}}{2\,Fe} + \underset{\text{Carbon monoxide}}{3\,CO\uparrow}$$

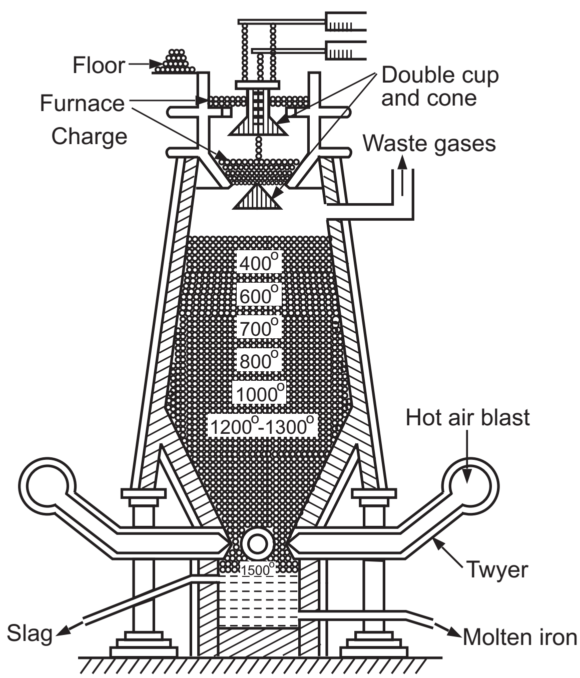


Fig. 3.6 : Reduction in blast furnace

Flux : In the above reduction of haematite, lime-stone is used as a flux. It decomposes at high temperature to give lime. This lime reacts with silica to form slag.

$$\underset{\text{Flux}}{CaO} + \underset{\text{Gangue}}{SiO_2} \longrightarrow \underset{\text{Fusible slag}}{CaSiO_3}$$

The various processes of concentration described above do not remove the gangue completely. To remove the gangue still present in the ore, certain oxides are added to the ore while melting it. Such '*a substance which is used to remove the gangue is called a 'flux'*. The flux combines with the gangue and forms an easily fusible compound which is called *slag*. The choice of a suitable flux depends upon the nature of the gangue. If the gangue is acidic in nature, CaO or MgO is used as a flux, which is basic in nature.

$$\underset{\text{(Acidic) Gangue}}{SiO_2} + \underset{\text{Flux}}{CaO} \longrightarrow \underset{\text{Slag}}{CaSiO_3}$$

If the gangue is basic in nature, acidic flux is used i.e. iron oxide as a gangue is removed by the addition of silica as a flux.

$$\underset{\text{(Basic) Gangue}}{FeO} + \underset{\text{Flux}}{SiO_2} \longrightarrow \underset{\text{Slag}}{FeSiO_3}$$

Hence, the terms gangue and flux in smelting are complementary to each other.

Slag : Even after concentration, the ore contains a considerable proportion of gangue which often contains oxides of very high melting point. These infusible oxides of metals and non-metals are converted into some fusible mass known as slag by the addition of suitable flux.

Thus slag is the fusible chemical compound formed by combination of the added flux and the gangue (impurity) present in the ore. Therefore

$$\text{Gangue} + \text{Flux} \longrightarrow \text{Slag (fusible compound)}$$

$$\underset{\text{Silicious gangue}}{SiO_2} + \underset{\text{Flux}}{CaO} \longrightarrow \underset{\text{Slag}}{CaSiO_3}$$

(2) Aluminothermic process (or Thermite process) : If the oxides of a metal are very stable, aluminium is used as a reducing agent in place of carbon at high temperature. The oxides like Fe_2O_3 and Cr_2O_3 are very stable and can be reduced by aluminium powder at high temperature. A mixture of aluminium powder and metallic oxide (generally in the ratio 1 : 3 parts by wt.) is known as *thermite.* Aluminium at high temperature has a great affinity for oxygen. The reaction is exothermic, hence it liberates large amount of heat. Hence, aluminium can reduce metallic oxide to metal as shown by the following reactions :

(1) $Fe_2O_3 + 2\,Al \longrightarrow Al_2O_3 + 2\,Fe + \text{Heat}$

(2) $Cr_2O_3 + 2\,Al \longrightarrow Al_2O_3 + 2\,Cr + \text{Heat}$

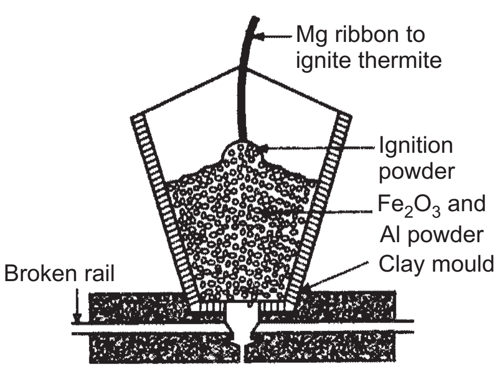


Fig. 3.7 : Thermite welding of a broken rail

[The ends of the broken rail are surrounded with a clay mould. A mixture of iron (III) oxide and aluminium powder (thermite) is ignited by magnesium ribbon in a funnel above. The molten iron produced by the reduction of iron (III) oxide runs into the mould. The molten iron melts the broken ends of the rail and produces a perfect union upon cooling.]

Metals obtained by this method are highly pure. Iron used in thermite welding, chromium and manganese needed for special steels are obtained by this method.

(3) Electrolysis : This method is used in the case of oxide of very active metals like sodium, calcium, magnesium, aluminium, etc. which are not reducible by carbon. Hence, fused halides of such metals are electrolysed, when the metal is liberated at the cathode and halogen (Cl_2, Br_2, I_2, F_2) is liberated at the anode. Metallic sodium, potassium, calcium, magnesium etc, are obtained by this method. These metals cannot be obtained from their aqueous salt solutions by electrolysis as H^+ ion is discharged at cathode in preference to metallic ion. If more voltage is applied then the metal which may be obtained by electrolysis of fused sodium hydroxide or sodium chloride, aluminium by electrolysis of alumina in fused cryolite (Na_3AlF_6).

(D) Refining : After reduction it is necessary to remove the small amounts of other elements that are usually present in that metal (except when the metal is obtained by electrolysis).

The process of purification of metal to get extra-pure metal is known as refining.

There are several ways of refining metal depending upon the nature of the metal to be purified. Some of the refining methods are

(i) Poling (ii) Liquidation (iii) Distillation (iv) Electrolytic refining.

(i) Poling : (i.e. oxidation of impurities) : This method consists of stirring the hot crude molten metal with green logs of wood. The wood gases (hydrocarbons like methane etc.) so produced reduce any metal oxide impurity present to the metallic form. Moreover, during stirring large quantities of air is absorbed by the molten metal and such absorbed air oxidises the easily oxidisable impurities. The oxidised impurities escape either as vapour or form 'scum' over molten metal. The scum so formed is removed by perforated ladle e. g. blister copper is refined by poling. The impurity is oxidised by absorbed air to As_2O_3, which escape away as vapour.

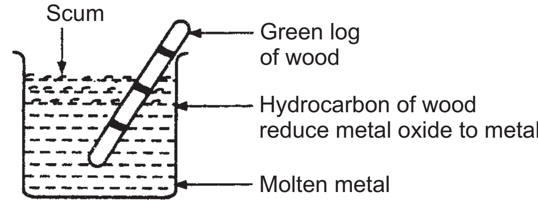


Fig. 3.8 : Poling process

(ii) Liquidation : This method is useful for metals having comparatively low melting points (like Pb, Sn etc.). The crude metal is heated on the slopping hearth of a furnace. The metal in the pure form melts first and flows down the slope leaving the infusible impurities behind called "*dross*".

(iii) Distillation : The volatile metals (such as Hg, Zn, etc.) are purified by this method. When the crude metal is subjected to the distillation, pure metal distils over leaving behind the high boiling point (non-volatile) impurities in the retort.

(iv) Electrolytic refining : "*The process of purification of metal to get extra pure metal with the help of electric current is known as electrolytic refining.*" In this method, the anode consists of thick plates of impure metal and the cathode consists of thin plates of pure metal obtained by the previous operation or by chemical methods. The bath is an aqueous solution of a suitable salt of the metal which is to be refined. When an electric current with a definite voltage is passed through the bath, anode goes on dissolving and only the pure metal is deposited on the cathode which grows in size. Metals which are less electropositive than the one being refined settle below the anode and is known as *anode mud.*

Those metals which are more electropositive than the one being refined remain in solution as ions, as these ions accept electrons only at higher voltage. *Applied voltage is insufficient for these ions to be discharged at the cathode and thus the metal is refined.* This method is applicable to many metals such as copper, lead, nickel, zinc, silver etc.

3.6 PHYSICAL PROPERTIES AND APPLICATIONS OF METALS

1. **IRON (Fe) :**

Properties :

1. Pure iron is soft and has silvery white greyish colour.
2. Its specific gravity is 7.86.
3. Its melting point is 1530°C and boiling point is 2450°C.
4. It is malleable and ductile.
5. It is strongly magnetic in nature.
6. Its thermal conductivity is high.

Applications :

1. It is used for making chains, nails, hooks, pipes, etc.
2. In making heavy machinery, agricultural implements.
3. In building of ships and bridges.
4. In the manufacture of wrought iron and steel.

2. COPPER (Cu) :

Properties :

1. It is reddish brown in colour.
2. It is a heavy metal having specific gravity 8.93.
3. Its m.p. is 1089°C and b.p. is 2350°C.
4. It is soft, malleable and ductile.
5. It is a very good conductor of heat and electricity.
6. It is tough and resistant to corrosion.

Applications :

1. Pure copper is used in making electrical wires and cables.
2. In heating utensils, pans.
3. In making coins, ornaments.
4. In electroplating and electrotyping.
5. In making alloys such as brass, bronze, monel metal, gun metal, bell metal, etc.

3. ALUMINIUM (Al) :

Properties :

1. It is a bluish white metal and reflects light.
2. It is the lightest metal having specific gravity 2.7.
3. Its m.p. is 658°C and b.p. is 1800°C.
4. It is tough, ductile and malleable.
5. It is a very good conductor of heat and electricity.
6. It can be easily cast and welded.

Applications :

1. It is used in making household utensils, frames, etc.
2. Since aluminium is a very good conductor of electricity, it is used in making electric wires and cables.
3. In making surgical instruments.
4. As foil in wrapping cigarettes and confectionary.
5. Aluminium powder is used as a reducing agent and in flashlight bulbs, in thermite welding.
6. For making alloys used in aircraft, automobiles and speed boats.

4. CHROMIUM (Cr) :

Properties :

1. It is a silvery white metal having specific gravity 7.14.
2. It is very hard and brittle metal.
3. Its m.p. is 1900°C and b.p. is 2480°C.
4. It can take high polish and resists atmospheric corrosion.

Applications :

1. It is used in chrome plating.
2. In making alloy steels such as stainless steel, tungsten steel etc.
3. In domestic utensils and surgical instruments.
4. Its alloy 'nichrome' is used in resistance coils.

5. NICKEL (Ni) :

Properties :

1. Nickel is a silvery white or greyish white metal.
2. Its specific gravity is 8.8, hence it is heavy metal.
3. Its m.p. is 1453°C and b.p. is 2730°C.
4. It is highly ductile, malleable and tenacious metal.
5. It does not rust and is extremely resistant to corrosion.
6. It can be forged, welded and magnetised.

Applications :

1. It is used in nickel plating.
2. In making important alloys like Monel metal, Nichrome, German silver etc.
3. For manufacturing chromium-nickel stainless steels.
4. It is used as a catalyst in hydrogenation of oils (ghee).
5. In making spatulas, crucibles and tongs required in laboratory.

6. TIN (Sn) :

Properties :

1. It is a lustrous silvery white metal and does not tarnish on exposure to air.
2. Its specific gravity is 7.3.
3. Its m.p. is 232°C and b.p. is 2275°C.
4. It is malleable and ductile.
5. It is softer than zinc but harder than lead.
6. When a rod of tin is bent, it produces 'crackling noise' (tin cry) due to crystals rubbing against one another.

Applications :

1. In tinning household utensils.
2. It is also used in the manufacture of alloys like solder, babbit metal, gun metal, bronze, type metal, rose metal etc.
3. For tin plating sheets of iron and steel, since it is resistant to corrosion.
4. For making collapsable tubes for tooth pastes, ointments etc.
5. Tin foils are used for wrapping cigarettes and other articles.
6. In the form of tin-amalgam, it is used in the manufacture of mirrors.

7. LEAD (Pb) :

Properties :

1. Lead is a soft, bluish-grey metal which is bright and lustrous when freshly cut.
2. It is also a heavy metal and has a specific gravity of 11.34.
3. Its m.p. is 327°C and b.p. is 1725°C.
4. It is highly malleable and ductile.
5. It can be scratched by finger's nail and cut with knife.
6. It marks paper black.
7. It is a poor conductor of electricity.

Applications :

1. Lead is used in making lead pipes and roofing sheets.
2. Lead sheets are used for making lead chambers in manufacturing sulphuric acid.
3. In the manufacture of storage batteries.
4. In making bullets and lead shots.
5. In making alloys like casting metal, type metal etc.
6. In the manufacture of pigments such as red lead (Pb_3O_4), litharge (PbO), white lead etc.
7. For covering underground telephone cables.

8. ZINC (Zn) :

Properties :

1. It is a bluish-white metal and soon gets tarnished in moist air due to the formation of basic carbonate.
2. Its specific gravity is 7.14.
3. Its m.p. is 419°C and b.p. is 920°C.
4. It is malleable and ductile between 100 – 150°C and brittle at 200°C.
5. It is a good conductor of heat and electricity.

Applications :

1. In galvanising iron sheets to protect from corrosion.
2. In the manufacture of alloys like brass, bronze, German silver etc.
3. In making electric bells.
4. Amalgamated zinc plates and rods are used as electrodes in primary batteries such as Daniell cells, Leclanche cell.
5. Powdered zinc is used as a reducing agent in the manufacture of perfumes, synthetic drugs and dye stuffs.
6. In extraction of metals like silver and lead.
7. In the preparation of paints like zinc oxide (ZnO).

9. COBALT (Co) :

Properties :

1. It is a silvery white metal.
2. It is also a heavy metal having specific gravity of 8.7.
3. Its m.p. is 1478°C and b.p. 3000°C.
4. It is hard and feebly magnetic in nature.

Applications :

1. In cancer treatment.
2. Its alloy 'alnico' in making small powerful permanent magnets for magneto loud speakers, radio and T.V. sets.
3. Its salt is used in colouring glass and pottery etc.

10. TUNGSTEN (W) :

Properties :

1. It is a silvery white metal.
2. Its sp. gr. is 19.3, hence it is one of the heaviest metal.
3. Its m.p. is 3370°C and b.p. is 5700°C. It has the highest melting point than any metal.
4. It is hard, brittle and crystalline in the powdered form.

Applications :

1. It is mainly used for preparing filaments of electric bulbs.
2. It is used as anticathodes in X-ray tubes.
3. In surgical instruments, spark coils, gramophone needles, contact points.
4. In the manufacture of gauzes in centrifugal machines as it resists both acids and alkalies.
5. In high-speed tool steels because they retain hardness even at higher temperatures.

11. SILVER (Ag) :

Properties :

1. It is a silvery white metal with brilliant lustre.
2. Its sp. gr. is 10.5.
3. Its m.p. is 961°C and b.p. is 2199°C.
4. It is hard, very malleable and ductile.
5. It is fairly a good conductor of heat and electricity.

Applications :

1. For coinage, jewellery and decorative purposes.
2. In silver plating metallic articles e.g. tableware.
3. Dentists use silver for filling cavities of tooth in the form of silver amalgam.
4. In preparation of silver salts used in silvering of mirrors, photography and medicine.

Table 3.1 : Physical properties and Applications of Metals

Metal	Colour	Sp. Gra.	M.P. & B.P.	Hardness	Conductivity of heat and electricity	Malleability and Ductility	Any special property	Applications
1. Iron	Greyish	7.86 Heavy metal	M.P. = 1530°C B.P. = 2450°C	Hard	Fair	Malleable and ductile	Magnetic	Heavy machinery, agricultural implements, pipes, ship building, bridge construction, railings, fire gates, articles like chains, nails, hooks etc.
2. Copper	Red	8.93 Heavy metal	M.P. = 1089°C B.P. = 2350°C	Soft	Very good	Highly malleable and ductile	Tough and resistant to corrosion	Alloys, electrical wires and cables, heating utensils, pans etc. In making coins, ornaments. In electroplating and electrotyping etc.
3. Aluminium	Bluish white	2.7 Light metal	M.P. = 658°C B.P. = 1800°C	Not very hard	Good	Malleable and ductile	Tough and high tensile strength, reflector of light.	Electric wires, cables for transmission lines, household utensils, air-craft, making alloys, Al foil for packing cigarettes and chocolates, in thermite etc.
4. Chromium	Silvery white	7.14 Heavy metal	M.P. = 1900°C B.P. = 2480°C	Very hard brittle	Fair	Malleable	Tough can take high polish, highly corrosion resistant.	In chorme plating, making alloy steels (stainless steel, tungsten steel). An alloy of nichrome in resistance coils, domestic utensils and surgical instruments etc.
5. Nickel	Silvery white	8.8 Heavy metal	M.P. = 1453°C B.P. = 2730°C	Fairly soft	Fair	Malleable and highly ductile	Tenacious does not rust can be forged, welded and magnetised.	In nickel plating, as a catalyst in hydrogenation of oils, in alloys, in making spatulas, crucibles and tongs required in laboratory.

6. Tin	Silvery white	7.3 Heavy metal	M.P. = 232°C B.P. = 2275°C	Fairly hard	Moderately good	Malleable and brittle at 200°C	Shows allotropy, on bending produce cracking noise "tin cry"	In tin plating, tinning of utensils, alloys, foils, collapsible tooth pastes and ointments.
7. Lead	Bluish grey	11.34 Heavy metal	M.P. = 327°C B.P. = 1725°C	Soft	--	Malleable and ductile	Marks paper, can cut with knife and scratched by finger nail.	Lead pipes, cable covering, making bullets, shots, lead-accumulators, lead chambers, pigments, alloys etc.
8. Zinc	Bluish white	7.14 Heavy metal	M.P. = 419°C B.P. = 920°C	Hard	Fair	Malleable and ductile between 100-150°C Brittle at 200°C	--	Galvanising, sherardizing, in desilverising lead, alloys, extraction of gold and silver, batteries, reducing agent etc.
9. Cobalt	Silvery white	8.7 Heavy	M.P. = 1478°C B.P. = 3000°C	Hard	Fair	Malleable and ductile	Feebly magnetic	Its alloy 'alnico' is making small permanent magnets for magneto-loud speakers, radio and T.V. sets, cancer treatment, salt used for colouring glass and pottery etc.
10. Tungsten	Silvery white	19.3 Very heavy	M.P. = 3370°C B.P. = 5700°C	Hard	Good	Malleable and more ductile than even gold	Can take high polish and welded. It has lowest vapour pressure and highest M.P.	Filaments of electric lamps, High speed tool steels, as anticathode in X-ray tubes, musical and surgical instruments, spark coils, gramophone needles, contact points etc.
11. Silver	Silvery white	10.5 Heavy	M.P. = 961°C B.P. = 2199°C	Soft	Good	Malleable and ductile	Tough and resistant to corrosion	In coins, jewellery, in electric and electronic equipments for wires. Dentists use silver for filling cavities of tooth as silver amalgam.

3.7 ALLOYS

In nature, it is difficult to get any substance in its pure state. This is true for the metals also. When we extract metals from their natural sources - minerals or ores - they contain some impurities. Hence these metals have to be purified. Various methods are used for purification of metals. But when we get the pure metal it is found that it becomes practically useless for engineering uses. These pure metals have very few useful properties like metallic lustre, good electrical conductivity, high malleability and ductility. The pure metals are very soft, highly chemically reactive. These properties like softness and high malleability reduce their shock and wear resistance. The high chemical reactivity makes the pure metals susceptible for corrosion and therefore they cannot be used for engineering purposes. Iron is used in the form of steel which shows the desired properties such as hardness, toughness, corrosion resistance etc. The steel is nothing but an alloy of iron with carbon, nickel, chromium, manganese etc.

The properties of a given metal can be improved by alloying it with some other metals or non-metals like carbon, phosphorus. When two or more metals are mixed in their molten state, they solidify without separation. On solidification they form a homogeneous substance called an alloy. Thus an alloy is a substance formed by solidification of a metallic solution. An alloy can also be defined as a *"solid solution where the solutes are the alloying elements and the solvent is the element in excess proportion."* In alloys, the chemical properties of constituent elements are retained while physical properties are improved.

An alloy is a homogeneous mixture of two or more metals. In some alloys, non-metals like carbon, boron, phosphorus, sulphur can be mixed with metals. For example, plain carbon steel is an alloy of iron and carbon; phospher bronze contains copper, tin and phosphorus. *Hence an alloy is to be defined as a homogeneous mixture of two or more elements one of which must be a metal.*

When alloy contains mercury as one of the components then it is called *amalgam, e.g. sodium amalgam* (Na - Hg), aluminium amalgam (Al - Hg), zinc amalgam (Zn - Hg) etc.

3.8 PREPARATION OF ALLOYS

An alloy can be prepared by any of the following methods :

(1) Fusion, (2) Electro-deposition, (3) Compression, (4) Reduction.

(1) Fusion method : In this method, the component metal having higher melting point is melted first in a crucible and the other components having lower melting points are added to it in the required quantity. In the manufacture of alloys, the molten metals are at higher temperature and hence react with atmospheric oxygen to form oxide. This oxidation is prevented by covering the molten mass with a fine charcoal powder. To get a uniform alloy, the molten mixture is stirred using graphite rods. The specific gravities of constituents have also to be considered. The heavy metals are generally mixed at the end to avoid its settling due to gravity which gives uneven composition in alloys. The molten mass is then allowed to cool which gives the required alloy.

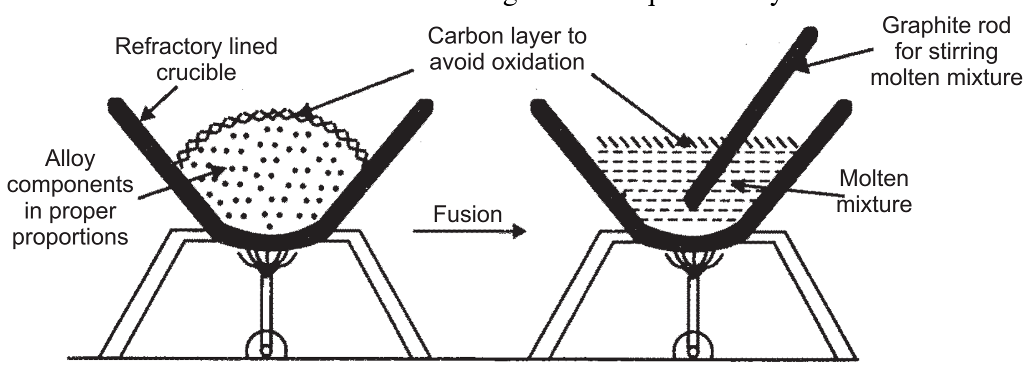


Fig. 3.9 : Fusion method for making alloys

In the manufacture of brass, an alloy of copper and zinc, the copper (melting point 1089°C) is melted first and the required quantity of zinc (melting point 419°C) is added to it which melts immediately. The molten mass is stirred and allowed to cool. To avoid oxidation of copper and zinc, the surface of molten mass is covered with charcoal powder. The mass is allowed to cool slowly to get brass.

Manufacture of bronze, an alloy of copper and tin, is exactly similar to the above process. In this case, requisite quantity of tin (m.p. 232°C) is added to the molten copper (m.p. 1089°C) to get bronze.

(2) Electro-deposition : The alloys can be prepared by simultaneous electro-deposition of the components from electrolyte containing their salt solution. An alloy, brass of copper and zinc can be obtained by this method. The electrolysis of a mixed solution of copper and zinc cyanides dissolved in potassium cyanide is carried out to obtain brass.

(3) Compression : The alloy is made by intimately mixing two or more metal powders and the intimate mixture is compressed under a high pressure in a mould. The moulded article is then heated to a temperature just below the melting point of an alloy. Due to this, the tiny particles of metals are firmly welded to one another. *Solder alloy,* an alloy of lead and tin, is obtained by this method. An alloy known as *Wood's metal* containing lead, tin, bismuth and cadmium is similarly obtained by this method.

(4) Reduction : The alloy is obtained by the reduction of a suitable compound, generally oxide of one component metal in the presence of the other component metal. The component metal oxide is reduced to metal in the presence of other metal. For example, aluminium bronze is prepared by reducing aluminium oxide in the presence of copper in an electric furnace.

3.9 PURPOSES OF MAKING ALLOYS

Metals are used as a basic material in the manufacture of machinery, household articles, ships, railways, aircrafts, bridges, buildings etc. The properties of one metal do not fulfil all the service requirements. The mechanical properties such as tensile strength, malleability, ductility, elastic limit, hardness are to be modified to make the metal suitable for a given purpose. This modification in the properties of the metal can be effected by addition of one or more metals or elements to the original metal to form an alloy. By making alloys the required properties can be developed. The deficiency of one metal can be corrected by the addition of one or more metals and while doing so care is taken to see that the valuable properties of original metal are not lost.

The main purposes of alloying are :

(1) To improve the hardness of metal.

(2) To lower the melting point.

(3) To increase the tensile strength.

(4) To increase corrosion resistance.

(5) To get good casting.

(6) To modify the colour.

(7) To reduce the malleability and ductility.

(8) To modify chemical activity.

The metal which constitutes the major portion of the alloy is known as base metal and others are called as alloying metals or elements.

The general improvements in properties of metals which can be obtained by alloying are as follows :

(1) To improve the hardness of metal : Pure metals are generally soft. But when the metal is alloyed with another metal or non-metal, its hardness is increased. *"An alloy is harder than its component metals."*

For example :

(1) Pure gold and silver are soft. Hence they are hardened by the addition of a small amount of copper while using them in ornaments and coins. The addition of small amount of copper makes them hard enough to resist wear and tear.

(2) Pure iron is very soft and cannot be used as such for making machinery parts. Hence the iron has to be converted to steel by the addition of small quantity (0.05 - 1.5 %) of carbon. Thus, presence of carbon imparts hardness to steel.

(3) Brass (an alloy of Cu and Zn) and bronze (an alloy of Cu and Sn), both are harder than the base metal copper.

(4) Lead is soft metal but its hardness can be improved by the addition of 0.5 % arsenic to it. This alloy is used for making lead shots.

(2) To lower the melting point : When an alloying element is added to a base metal, it acts as an impurity in base metal and the melting point of base metal is lowered. *"In general, the melting point of an alloy is lower than those of its constituent elements."* Thus, alloying makes the metal easily fusible. This property of the metal is used in making useful low melting alloys called *solders.* The solder metal must have lower melting point than the metal to be soldered and should contain the same metal as one of its constituents.

For example :

(1) Wood's metal is an alloy of bismuth, lead, tin, and cadmium. It has the melting point of only 71°C, which is much lower than those of its components Bi, Pb, Sn, and Cd.

(2) Rose metal is an alloy of bismuth, lead and tin having the melting point 100°C. Other alloys which are easily fusible are Newton metal, Solder alloy etc.

(3) To increase the tensile strength : When a metal is alloyed with proper elements (like Ni, Cr, V etc.), the elasticity and tensile strength is adjusted to the requirement i.e. the tensile strength of pure metal is increased by alloying.

For example :

(1) The addition of 1 % carbon increases the tensile strength of pure iron by about ten times.

(2) The addition of 1 % nickel or chromium to mild steel increases its tensile strength tremendously. The tensile strength of steel is further increased by the addition of 0.15 % vanadium and 1 % chromium to it.

(3) Tensile strength of copper can be doubled by adding about 5 % of silicon to it.

(4) To increase corrosion resistance : The metals in pure form (like Fe and Cu) are quite reactive and are easily corroded by surrounding atmospheric gases, moisture, etc., thereby their life is reduced. But if a metal is alloyed, it resists corrosion. In other words, "*alloys are more resistant to corrosion than pure metals"*.

For example :

(1) Pure iron is corroded even in moist air, but its alloy like stainless steel (an alloy of Fe - C - Cr - Ni) does not even get stained i.e. it is totally resistant to corrosion.

(2) Bronze (an alloy of Cu - Sn) is more corrosion resistant than copper.

(3) Zinc is readily attacked by sulphuric acid, but brass (an alloy of Cu - Zn) is not attacked.

(4) The alloys of copper such as Naval brass (Cu - Zn - Sn) and German silver (Cu - Zn - Ni) are non-corrosive.

(5) To get good castings : To get good castings from a metal or alloy, it is essential that the metal must expand on solidification and it should be easily fusible so that sharp impression can be taken easily. Generally, pure molten metals contract on solidification. Hence, in order to get good castings, metals have to be alloyed, because alloys expand on solidification.

For example :

(1) Type metal (an alloy of lead, tin and antimony), which is used for casting types of printing due to its exceptionally good casting properties. Small addition of antimony gives the property of expanding on solidification while tin gives hardness.

(2) Bronze (an alloy of Cu-Sn) and duralumin (an alloy of Al-Cu-Mg-Mn) possess good casting properties.

(3) The casting property of aluminium can be improved by the addition of small amount of copper or magnesium to it.

(4) Gun metal (Cu - 88%, Sn - 10%, Zn - 2%) and phosphor bronze (Cu - 96%, Sn - 3.75%, P – 0.25 %) are the other alloys of copper having good casting properties.

(6) To modify colour : The colour of the metal is its characteristic property, hence we cannot change the colour of a given metal. But the colour of a metal can be modified to a desired one by alloying it with another suitable element. Thus an alloy can be prepared having colour quite different from the colour of the base metal.

For example :

(1) Both aluminium and tin are silvery white in colour, but their alloy, aluminium bronze (Cu-Al-Sn) has a beautiful golden colour.

(2) Brass is an alloy of copper (red) and zinc (silvery white) and is yellow in colour.

(3) Silver is white, but alloy of silver and tin has pink colour, similarly, an alloy of gold and silver is purple.

(7) To reduce malleability and ductility : Pure metals are highly malleable and ductile which results in lowering the toughness. The shape of articles prepared from pure metals get changed even due to small force. To increase resistance of metal to such forces i.e. to make it tough it is necessary to reduce its malleability or ductility which is effected by alloying with some suitable metal.

For example : A small amount of copper is added to gold and silver to reduce their malleability and ductility.

(8) To modify chemical activity : The chemical reactivity of a metal can be changed by alloying it with other metals. This does not affect the products of reaction but changes the rate of reaction.

For example :

(1) Sodium is a highly reactive element, but when it is alloyed with mercury to form an alloy called sodium-amalgam (Na-Hg), it becomes less reactive.

(2) The chemical reactivity of aluminium increases when it is alloyed with mercury to form aluminium-amalgam (Al-Hg).

3.10 CLASSIFICATION OF ALLOYS

Alloys are generally classified into two classes :

(1) Ferrous alloys : The alloys containing iron as one of the main components are known as ferrous alloys. e.g. alloy steels are the most common ferrous alloys.

(2) Non-ferrous alloys : The alloys which do not have iron as one of the main components are known as non-ferrous alloys. e.g. brass, bronze (alloys of copper), duralumin (alloy of aluminium) are some of the common non-ferrous alloys.

3.11 COMPOSITION, PROPERTIES AND APPLICATIONS OF ALLOYS

1. Duralumin : It is an important alloy of aluminium.

Composition : Al = 95%, Cu = 4%, Mg = 0.5%, Mn = 0.5%.

Properties :

1. It is light, tough, highly ductile, easily castable, corrosion resistant and good conductor of heat and electricity.
2. It is as strong as mild steel, though its density is $1/3^{rd}$ that of steel.
3. Its tensile strength can be raised by heat treatment upto 2000 kg/cm^2 without affecting ductility.
4. It can be easily worked and possesses high machinability.

Applications :

1. For making aeroplanes, automobile and locomotive parts from the 'alclad' sheets.
2. In making cables, surgical instruments and fluorescent tube caps.
3. For making rivets, bars, body of vehicles and housing cases etc.

2. Dutch Metal : It is an alloy of copper.

Composition : Cu = 80%, Zn = 20%.

Properties :

1. It is golden in colour.
2. It is suitable for all drawing and forming operations.

Applications :

1. In musical instruments.
2. In cheap jewellery, name plates, tubes etc.
3. In battery caps and flexible hoses, etc.

3. German Silver (or Nickel Silver) : It is also an alloy of copper.

Composition : Cu = 60%, Zn = 20%, Ni = 20%.

Properties :

1. It looks like silver.
2. Extremely malleable and ductile.
3. It has good strength and corrosion resistance to salt and water.

Applications :

In decorative articles, coins, utensils, resistance coils, ornaments, screws, bolts, tablewares and cutlery etc.

4. Gun Metal : It is an alloy of copper (i.e. bronze).

Composition : Cu = 88%, Sn = 10%, Zn = 2%.

Properties :

1. It is hard, tough and stronger to resist the force of explosion.
2. It is resistant to corrosion by water and atmosphere.

Applications :

1. For making gun-barrels and foundry works.
2. In hydraulic and boiler fittings.
3. In heavy load bearings.

5. **Monel Metal :** It is an copper-nickel alloy named after the president of International Nickel Company, Mr. Monel.

Composition : Cu = 30%, Ni = 67%, Fe + Mn = 3%.

Properties :

1. It has a bright attractive appearance, strong, tough and having high tensile strength (5500 kg/cm^2).
2. It has good mechanical properties even at high temperatures. So it can be easily cast, forged, machined, soldered, welded, rolled and can be drawn into wires.
3. It is very much resistant to chemicals and sea-water corrosion.
4. It has low magnetic permeability.

Applications :

1. It is used in turbine blades and automobile engine parts.
2. In parts of machines used for processing food and dyes.
3. In kitchen-sinks, counter tops, hot-water boilers, pump rods, valves and resistance wires, etc.

6. **Wood's Metal :** This is a fusible alloy of lead.

Composition : Bi = 50%, Pb = 25%, Sn = 12.5%, Cd = 12.5%.

Properties : It is an easily fusible alloy. Its melting point is low, 71°C.

Applications :

1. For making safety plugs of pressure cookers, boilers, fire-alarms, automatic water sprinklers.
2. As a soft solder for joining two metallic parts.
3. As casting for dental work.
4. For taking impressions of coins and medals.
5. For die mounting, fillers for tube bending etc.
6. In fuse wires.

7. **Babbit Metal :** It is a tin, antimony, copper alloy.

Composition : Sn = 88%, Sb = 8%, Cu = 4%.

Properties :

1. It is a silvery white soft metal alloy.
2. It does not tarnish easily and can be polished easily.
3. It has low coefficient of friction.
4. It resists wear and corrosion.

Applications :

1. In making engine bearings since it distributes the load uniformly.
2. As a common bearing metal in cast iron boxes.

8. **Alnico :**

Composition : Al = 20%, Ni = 20%, Co = 10%, Steel = 50%.

Properties :

1. It is highly magnetic in properties.
2. It lifts 4450 times of its own weight.

Applications :

1. For making small powerful permanent magnets of magneto loud speakers, radio and T.V. sets.
2. In transformer cores, dynamos and motors, etc.

Table 3.3 : Composition, Properties and Uses of Important Alloys

Alloy	Composition	Properties	Uses
1. Brasses :	Cu = 60 - 90 % Zn = 40 - 10 %	They have low M. P. than Cu and Zn. They possess greater strength, durability and machinability than pure copper. They are good corrosion resistant against water.	In utensils, condenser tubes, sheets and cartridges.
Main brasses are :			
(i) Commercial brass :	Cu = 90 %, Zn = 10 %	Harder and stronger than pure copper. It is golden in colour.	In making rivets, screws and in forging, hardwares, coustoms, jewellery etc.
(ii) Dutch metal :	Cu = 80 %, Zn = 20 %	Golden in colour, it is suitable for all drawing and forming operations.	In musical instruments, cheap, (jewellery, name plates, tubes), battery caps and flexible hoses etc.
(iii) Cartridge brass :	Cu = 70 %, Zn = 30 %	Harder and stronger than copper but softer and ductile in annealed state. It can be cold deformed by drawing, pressing and extrusion, which hardens quickly.	For making condenser tubes, cartridge cases, sheets, household articles etc.
(iv) Muntz metal :	Cu = 60 %, Zn = 40 %	Stronger than 70/30 brass, suitable only for hot work applications.	In marine fittings, condenser tubes, radiators, chains, screws and springs etc.
2. Special Brasses : Contain metals other than Cu and Zn.			
(i) Admiralty brass :	Cu = 71 %, Zn = 28 %, Sn = 1 %	It possesses high abrasion resistance and corrosion resistance to fresh water and sea water.	In propellers and marine works.
(ii) Naval brass	Cu = 62 %, Zn = 37 %, Sn = 1 %	It possesses high abrasion resistance and corrosion resistance to sea water.	In condenser tubes and marine works.
(iii) German silver or Nickel silver	Cu = 60 %, Zn = 20 %, Ni = 20 %	It looks like silver, extremely malleable and ductile. It has good strength and corrosion resistance to salt water.	In decorative articles, coins, utensils, resistance coils, ornaments, screws, bolts, tablewares and cutlery etc.

3. Bronzes :	Cu = 75 - 90 %, Sn = 25 - 10 %	Generally harder, stronger and tough alloys, resistant to corrosion and wear, can be easily casted and machined.	In utensils, statues, coins and bells etc.
Main bronzes are :			
(i) Gun metal	Cu = 88 %, Sn = 10 %, Zn = 2 %	It is hard, tough, strong to resist the force of explosion. It is resistant to corrosion by water and atmosphere.	For making gun-barrels. In hydraulic and boiler fittings, foundry works and heavy load bearings etc.
(ii) Aluminium bronze :	Cu = 90 %, Al = 10 %	It has a beautiful golden yellow colour. It is light, tough and quite strong, readily fusible, gives good castings, resistant to abrasion and corrosion even at high temperatures.	In coins, utensils, jewellery, golden paint and photoframes etc. For all casting operations, bearings and bushes etc.
(iii) Phosphor bronze :	Cu = 96 %, Sn = 3.75 %, P = 0.25 %	It is hard, tough, ductile. It has low coefficient of friction, good casting properties, resistant to sea-water corrosion.	For making bearings, springs, gears, bushes, spindles for valves and pumps, in electric switches, radio aerial wires and suspension wires for moving coil galvanometer etc.
(iv) Nickel bronze :	Cu = 90 %, Ni = 9 %, Fe = 1%	They are hard having very good tensile strength and better corrosion resistance even more than copper.	For rolling purposes, in valves, shafts and semi-hard bearings.
(v) Bell metal	Cu = 80 %, Sn = 20 %	It is hard and resistant to surface wear. It produces sonorous sound.	In making bells and gangs, utensils etc.
4. Monel metal :	Cu = 30 %, Ni = 67 %, Fe, Mn = 3 %	It has a bright attractive appearance, strong, tough, high tensile strength (5500 kg/cm^2) after annealing. It is very much resistant to chemical and sea-water corrosion. It has good mechanical properties even at high temperature.	For making turbine blades and automobile engine parts, kitchen sinks, valves, pumps, resistant wires and transistor capsules etc.
5. Alnico	Al = 20%, Ni = 20%, Co = 10%, Steel = 50%	It is highly magnetic in properties. It lifts 4450 times of its own weight.	For powerful small magnets in loud speakers, radio and T.V. sets.

6. Duralumin	Al = 95%, Cu = 4%, Mg = 0.5%, Mn = 0.5%	1. It is light, tough, highly ductile, easily castable, corrosion resistant and good conductor of heat and electricity.	1. For making aeroplane, automobile and locomotive parts from the 'alclad' sheets.
		2. It is strong as mild steel, though its density is 1/3rd that of steel.	2. In making cables, surgical instruments and fluorescent tube caps.
		3. Its tensile strength can be raised by heat treatment upto 2000 kg/cm^2 without affecting its ductility.	3. For making rivets, bars, body of vehicles and housing cases etc.
		4. It can be easily worked and possesses high machinability.	
7. Magnalium	Al = 90%, Mg = 10%	It is quite strong, tough and lighter even than aluminium. It can be easily worked on the lathe.	For making balance beams, and light instruments.
8. Babbit metal	Sn = 88%, Sb = 8%, Cu = 4%	1. It is silvery white soft metal alloy. 2. It does not tarnish and can be polished easily. 3. It resists wear and corrosion. 4. It has low coefficient of friction.	1. In making engine bearings since it distributes the load uniformly. 2. As a common bearing metal in cast iron boxes.
9. Y-alloy :	Al = 92.5%, Cu = 4%, Ni = 2%, Mg = 1.5%	It is one of the best light alloys. It possesses high strength and hardness at high temperatures.	1. For making aeroplane parts and non-corrodible vessels. 2. For making pistons, cylinder heads, and crank cases of I.C. engines etc.
10. Wood's metal	Bu = 50%, Pb = 25%, Sn = 12.5%, Cd = 12.5%	It is easily fusible alloy. Its melting point is low (71°C).	1. For making safety plugs of pressure cookers, boilers, fire alarms, water sprinklers. 2. In soft solders, taking impressions of coins. 3. As casting for dental work. 4. Fuse wires.

EXERCISE

1. Explain the terms :
   (a) Mineral, (b) Ore, (c) Flux, (d) Slag, (e) Gangue or matrix.
2. Differentiate the following with suitable examples :
   (a) Ore and mineral, (b) Flux and slag
3. State clearly, the nature of ores of each of the following metals : Iron, Copper, Zinc, Aluminium, Lead, Mercury, Calcium, Magnesium.
4. Define metallurgy. Outline the general principles of metallurgy.

5. Define concentration of ore. Name its physical and chemical processes.
6. What are the different methods by which concentration of ore is carried out ? Explain one of them.
7. (a) Which method can be used to concentrate the sulphide ores ? Name and explain it with the help of a figure.
   (b) Give the principle of froth floatation process and explain the process with the help of figure.
   (c) Define : Mineral, concentration. Draw a figure for froth floatation process and write its principle.
   (d) Write principle of electromagnetic separation. Draw a neat labelled diagram of froth floatation process.
8. Define a flux. What flux is added to remove the impurity SiO_2 ? State the chemical reaction and the name of the product formed.
9. Name the processes used for the concentration of :
   (a) Sulphide ores (b) Oxide ores
   (c) Carbonate ores (d) Tin-stone ore containing tungstates of iron and manganese.
10. Name the methods used for the reduction of :
    (a) Oxides of metals whose atomic weights are higher than that of manganese.
    (b) Oxides of metals which are very stable.
    (c) Oxides of active metals which are not reducible by carbon.
    (d) Noble metals like Ag, Au, Pt etc.
11. (i) Explain the terms :
    (a) Calcination (b) Roasting.
    What are their purposes ?
    (ii) With the help of figure, explain the process of calcination or roasting.
    (iii) Explain the stepwise process in roasting and calcination of an ore.
12. Differentiate between :
    (a) Calcination and roasting.
    (b) Concentration and refining.
    (c) Gravity and electromagnetic separation.
13. What is smelting ? Where is it useful ? Explain the terms gangue and flux are complimentary to each other, or why flux is added during smelting ?
14. Write short notes with respect to their principles :
    (a) Froth floatation process, (b) Electromagnetic separation. (c) Gravity separation,
    (d) Alumino-thermic process, (e) Electrolytic refining.
15. Write the physical properties and applications of the following metals :
    (a) (i) Iron, (ii) Copper, (iii) Aluminium (b) (i) Tungsten
    (c) (i) Zinc, (ii) Nickel, (iii) Tin, (iv) Lead (d) (i) Chromium and (ii) Cobalt.
16. Name the metals having :
    (i) Highest melting and boiling point (ii) Lowest melting point
    (iii) Lightest metal (iv) Heaviest metal
    (v) Very good conductivity
    (vi) Lowest vapour pressure and high M.P. hence used in filaments of electric lamps.
17. (i) Define gravity separation process. State and explain the principle upon which the gravity separation process depends.
    (ii) Describe four applications of cobalt in the engineering field. What are its important properties ?
18. Write four physical properties of iron.
19. How the metals play an important role in the progress of the country ?
20. Short answer questions :
    Name the following :
    (a) The process of extracting metal from the ore.
    (b) The impurities present in the ore.
    (c) Naturally occurring substance containing metal in combined state.
    (d) A mineral from which the metal can be extracted economically.
    (e) The process of removal of gangue or impurities from the ore.
    (f) The process of concentration of oxide and hydroxide ores.
    (g) The ore containing magnetic impurities like tungstates of iron and manganese.

(h) The process of heating ore in absence of air below its melting point.
(i) The process of heating ore in excess of air below its melting point.
(j) The combination of flux and impurities (gangue) to form fusible mass.
(k) The substance used during smelting of iron which acts as a fuel as well as reducing agent.
(*l*) The substance used during smelting of iron to remove gangue in the form of slag.
(m) The process of purification of metals to get extra-pure metals.
(n) The metal used as a protective sheathing for underground telephone and telegraph wires.
(o) The metal used as an anticathode in X-ray tubes.
(p) The metal producing brilliant blue colours in porcelain, tiles, enamels and glass.
(q) Name two physical processes for concentration of ore.
(r) Name two processes for refining of metal.

21. What is an alloy ? How alloys are classified ? Give two examples of alloys.
22. What are the purposes of making alloys ?
23. Give one example of an alloy having low melting point. State its three uses.
24. Define an alloy. Redefine it, if an alloy is considered as a solid solution.
25. Mention any four purposes of making alloys with at least one suitable example in each case.
26. Define alloy. Explain with example method for preparation of alloys.
27. Give the chemical composition of Wood's metal or Monel metal.
28. (a) Name two properties which are imparted to gold when alloyed by copper.
    (b) Write the important uses of (i) Babbit metal, (ii) Monel metal, (iii) Wood's metal, (iv) Duralumin.
29. Distinguish between an alloy and an amalgam. Give the suitable examples where the casting property and tensile strength are increased by alloying.
30. Write the composition and applications of : (i) Monel metal, (ii) Wood's metal
31. (a) Give purposes of alloying metals with suitable examples.
    (b) What are non-ferrous alloys ? Mention the principle constituents of Duralumin, Babbit metal and Phosphor Bronze.
32. Give the composition, properties and uses of the following non-ferrous alloys :
    (a) Duralumin, (b) Phosphor bronze, (c) Monel metal, (d) Wood's metal, (e) Babbit metal.
33. What do you understand by non-ferrous alloys ? Give the composition, properties and applications of Duralumin.
34. What is an alloy ? Describe the fusion method for the preparation of alloy.
35. Give the composition, properties and uses of Wood's metal.
36. Give the composition and four uses of Monel metal.
37. Give the composition, properties and uses of Babbit metal.
38. Give the composition, properties and uses of 'Alnico'.
39. Give the composition, properties and uses of (i) Duralumin, (ii) Dutch metal, (iii) German silver.
40. Write the composition, properties and uses of :
    (i) Gun metal, (ii) Babbit metal, (iii) German silver.
41. Give the properties and uses of Monel metal and Duralumin.
42. Give the composition of Wood's metal and Duralumin.
43. Write a method of preparation of alloys with one example.
44. Write any four applications of Duralumin, Wood's metal.
45. Classify the non-ferrous alloys and give one example of each.
46. State and explain the principle of compression method to prepare an alloy.
47. Explain the stepwise procedure for preparation of any alloy.
48. Define ferrous alloy giving suitable example. State the classification of alloys.

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Chapter **4**

NON-METALLIC MATERIALS

[A] PLASTICS

4.1 Plastics
4.2 What are plastics ?
4.3 Polymerisation
4.4 Formation of plastics
4.5 Structure of plastics
4.6 Types of plastics
4.7 Distinction between thermoplastics and thermosetting plastics
4.8 Compounding of plastics
4.9 Properties of plastics
4.10 Applications of plastics

[B] RUBBER

4.11 Rubber
4.12 Types of rubber
4.13 Drawbacks of natural (or raw) rubber
4.14 Vulcanisation of rubber
4.15 Important properties of synthetic rubber
4.16 Applications of rubber

[C] THERMAL INSULATING MATERIALS

4.17 Thermal insulating materials
4.18 Factors affecting the thermal conductivity of insulators
4.19 Characteristics of good insulating materials
4.20 Classification of thermal insulators
4.21 Glass wool
4.22 Thermocole
4.23 Asbestos
4.24 Cork

[A] PLASTICS

4.1 PLASTICS

The word plastics has originally been derived from the Greek word 'Plastikos' which means fit for moulding. Now-a-days, the use of plastics is so common that the current age can be called as 'plastic age'. Plastics have replaced a number of traditionally used materials like metals, ceramics, etc. Recently, plastics have attained a great importance in every walk of our life, due to their certain unique properties. Therefore, plastics are widely used in manufacturing a large variety of articles like bowls, polythene bags, buckets, pipes, wrappers, insulators, fabrics, toys etc. All the modern industries like radio, telephone television, automobile, electrical and electronics etc. are basically dependent on plastics.

4.2 WHAT ARE PLASTICS ?

''Plastics are basically, the synthetic organic materials of high molecular weight, which can be moulded into any desired shape by the application of heat and pressure in the presence of a catalyst.''

The term 'plastics' is different from 'resins'. Resins are the basic binding materials, which form a major part of plastics. Resins being the major component of plastics actually undergoes polymerisation and condensation reactions during their preparation. However, the terms 'plastics' and 'resins' are considered synonymous now-a-days.

4.3 POLYMERISATION

''The process in which a large number of small molecules (monomers) link together to form a large molecule (polymer) under specific conditions of temperature, pressure and catalyst is known as polymerisation.''

The higher polymers are known as plastics. *''A high polymer is one in which the number of repeating units is in excess of about 100.''* This is termed as degree of polymerisation (DP). There may be hundreds, thousands, ten thousands or even more monomer units linked together in a polymer molecule to form a long open chain or cross-linking.

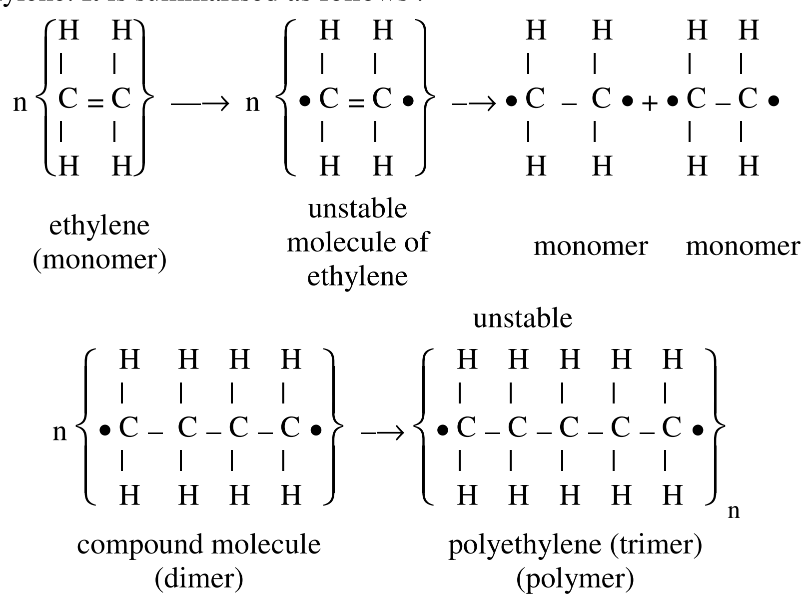
4.4 FORMATION OF PLASTICS

In the formation of plastics, the polymerisation of monomers can take place by two methods : (i) Addition polymerisation, (ii) Condensation polymerisation.

(i) Addition polymerisation : *"It is a process in which the monomers undergo repeated addition, resulting in the formation of long chain polymer without the elimination of simple molecules like H_2O, HCl, NH_3 etc.''*

Examples :

(a) Polymerisation of ethylene to form polythene : Monomers taking part in polymerisation should contain at least one double bond (=). In addition polymerisation, one of the two bonds between the two carbon atoms of ethylene molecule ($CH_2 = CH_2$) is opened up and form an unstable molecule of ethylene ($-CH_2-CH_2-$). Due to opening of the bond, two valence electrons of C-atom are made free. The resulting unstable molecule joins with similar molecule by means of the free valencies. The compound molecule formed by joining the two ethylene molecules, in its turn join with one more molecule of ethylene and the process is continued, ultimately forming a large molecule of polyethylene. It is summarised as follows :



$$n\,(C_2H_4) \xrightarrow[\text{Heat, light, pressure and catalyst}]{\text{Polymerisation}} (C_2H_4)_n$$

ethylene polyethylene or polythene

Similarly, different derivatives of ethylene also undergo addition polymerisation forming different varieties of plastics.

(b) Formation of teflon (PTFE) : In the presence of oxygen, tetra-fluoro ethylene ($CF_2 - CF_2$) undergoes addition polymerisation to give teflon.

$$n\,(C_2F_4) \xrightarrow[O_2]{\text{Addition polymerisation}} (C_2F_4)_n \quad (n = \text{about } 1000)$$

(tetra-fluoro ethylene) (Polytetra-fluoro ethylene)

(c) Formation of polyvinyl chloride (PVC) : It is produced by the addition polymerisation of vinyl chloride ($CH_2 = CH—Cl$) using peroxide (H_2O_2) as a catalyst.

$$n\,(CH_2 = CH - Cl) \xrightarrow[(H_2O_2)]{\text{Polymerisation}} (CH_2 - CH - Cl)_n$$

vinyl chloride Polyvinyl chloride or PVC

(d) Formation of polystyrene (PS) : It is obtained by the addition polymerisation of styrene, an aromatic hydrocarbon ($C_6H_5CH = CH_2$). Polystyrene is a cheap transparent material.

$$n(C_6H_5CH = CH_2) \xrightarrow{\text{Polymerisation}} (C_6H_5CH\,.\,CH_2)_n$$

Styrene Polystyrene

(ii) Condensation polymerisation : *''It is a process in which the monomers of different types are joined together by the condensation forming a large polymer with the elimination of simple molecules like H_2O, HCl, CH_3OH etc.''*

Examples :

(a) Formation of Nylon 6 : 6 : It is obtained by condensation polymerisation of hexamethylene diamine and adipic acid with the elimination of two water molecules.

$$n\,[H_2N - (CH_2)_6 - NH_2] + n\,[HOOC - (CH_2)_4 - COOH]$$

Hexamethylene diamine Adipic acid

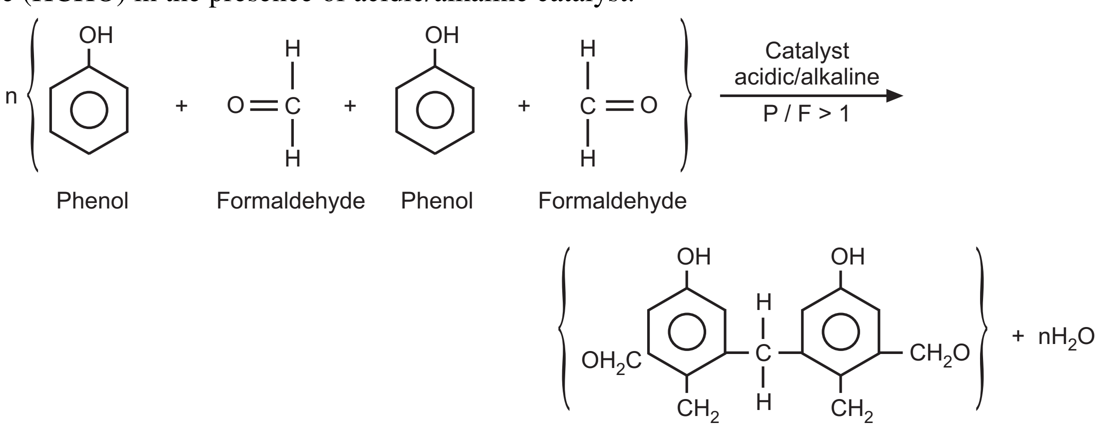
$\downarrow$ Condensation polymerisation

$$[- HN - (CH_2)_6 - NH.CO - (CH_2)_4 - CO -]_n + 2n\,H_2O$$

Nylon 6 : 6

(Poly hexamethylene adipamine)

(b) Formation of Bakelite (or phenol formaldehyde) : It is prepared by condensing phenol (C_6H_5OH) and formaldehyde (HCHO) in the presence of acidic/alkaline catalyst.



Phenol Formaldehyde
or (Bakelite)

Thus, condensation polymerisation is an intermolecular combination, and it takes place through the different functional groups (OH – hydroxyl, NH_2 - amino, COOH - carboxyl etc.) in the monomers having affinity for each other.

4.5 STRUCTURE OF PLASTICS

The monomeric units in a polymer may be present in linear, branched or cross-linked (three-dimensional) structure. If the constituent monomer have two links (–M–) in their structures, then each of these links at each end join chemically with other similar/different monomers. Finally, a linear structure consisting of long chain is formed.

– M – M – M – M – M – M –

Linear polymer

|

Some constituent monomers have three links (–M–) in their structures, the other monomers (or functional groups) can get attached at three different points. So, instead of linear chains, a net-work of chains or cross-linking occurs.

| |

– M – M – M – M – M – where 'M' represents the

| | | constituent monomers.

– M – M – M – M – M –

| |

– M – M – M – M – M –

| | |

– M – M – M – M – M –

| |

cross-linked polymer

4.6 TYPES OF PLASTICS

The plastics are broadly classified into two classes according to their manner of setting and structures as : (i) Thermosoftening, (ii) Thermosetting.

(i) Thermosoftening plastics (or Thermoplastics) : Thermoplastics are formed by addition polymerisation and consist of a long chain linear polymers with little or no cross-linking. The general outline of their structure can be represented as follows :

M – M – M – M – M –

|

M – M – M – M – M where 'M' represents

| the constituent monomers

– M – M – M – M – M

Thermoplastics soften on heating and regain their original properties on cooling. Their hardness is a temporary property subject to change with increase or decrease in temperature. Repeated heating and cooling does not alter the chemical nature of thermoplastics just like our common sealing wax. They soften on heating and remain soft as long as they are hot. They regain their original hardness and rigidity on cooling. 'Thermoplastics are usually soft, weak and less brittle and can be reclaimed from the wastes.' These are soluble in some organic solvents, as their intermolecular bonds are weak.

Examples of thermoplastics : Polyethylene, polypropylene, polystyrene, cellulose nitrate, cellulose acetate, PVC etc.

(ii) Thermosetting plastics : These are formed by condensation polymerisation and consist of three-dimensional network structure joined by strong covalent bonds. The general outline of their structure can be represented as follows :

```
          |
– M – M – M – M – M –
   |      |      |
– M – M – M – M – M –
       |      |
– M – M – M – M – M –
   |      |      |
– M – M – M – M – M –
       |      |
```

where 'M' represents the constituent monomers.

Thermosetting plastics are those which change irreversibly into hard and rigid materials on heating. After cooling, if the set article is again heated, it will not soften again, hence it is irreversible. They are permanent setting plastics like concrete, which once set, cannot be reshaped or reused. During their moulding itself they acquire three-dimensional cross-linked structure with predominantly strong covalent bonds. Hence, these are insoluble in organic solvents. These bonds retain their strength, even on heating. Thermosetting plastics are usually, harder, stronger and more brittle than thermoplastics and they cannot be reclaimed from wastes.

Examples of thermosetting plastics : Bakelite, polyesters, silicone plastics, urea formaldehyde etc.

4.7 DISTINCTION BETWEEN THERMOPLASTICS & THERMOSETTING PLASTICS

	Thermoplastics	**Thermosetting plastics**
1. Formation	1. They are formed by addition polymerisation.	1. They are formed by condensation polymerisation.
2. Structure	2. They consist of linear long-chain polymers with limited cross-links.	2. They consist of three-dimensional network structure joined by strong covalent bonds.
3. Molecular weight	3. They consist of polymers of smaller molecular weight.	3. They consist of polymers of higher molecular weight.
4. Heating effect	4. They are softened on heating and hence can be reshaped and reused.	4. They do not soften on heating, hence cannot be reshaped and reused.
5. Reclaiming	5. They can be reclaimed from wastes.	5. They cannot be reclaimed from wastes.
6. Chemical bonding	6. Their intermolecular bonds are weaker.	6. They are joined by strong covalent bonds.
7. Nature	7. They are softer, weaker and less brittle.	7. They are harder, stronger and more brittle.
8. Solubility	8. They are soluble in suitable organic solvents, as their bonds are weaker.	8. They are insoluble in organic solvents, as their bonds are stronger.

4.8 COMPOUNDING OF PLASTICS

Generally, plastics are compounded with other substances during their manufacturing process, which impart certain definite properties to the finished product. The substances used are resins, fillers, plasticizers, accelerators and pigments etc. The main types of compounding ingredients and their functions are described below :

1. Resins (or binders) : These holds the different constituents together. Thermosetting plastics are usually supplied as linear polymers of comparatively low molecular weights, because at this stage, they are fusible and hence, easily mouldable. The fusible form gets converted into cross-linked infusible form during moulding, in the presence of catalysts.

2. Fillers : Fillers are added to give the plastic better hardness, tensile strength, opacity, finish and workability or to impart special properties to the final finished product of plastics. Fillers also reduce the cost, shrinkage on setting and brittleness of plastics. For example :

(i) Quartz, mica and carborundum are added to provide extra hardness to the plastic.

(ii) The addition of asbestos provides heat and corrosion resistance to the plastic materials.

Fillers may be either of organic or inorganic origin.

Organic origin fillers : These include wood flour, cotton, paper-pulp, graphite, carbon black, powdered rubber, etc.

Inorganic origin fillers : These include asbestos, powdered mica, silicate clays, talc, oxides of zinc and lead, sulphides of barium and cadmium and metals like Fe, Pb, Cu and Al in powdered form.

The percentage of filler varies with the nature of plastic formed and properties required and can be as high as 50% of the total moulding mixture. 'Those fillers which are added to increase the mechanical strength, are called reinforcing fillers.' e.g. addition of carbon black increases the tensile strength of natural rubber to about 40% and also the abrasion resistance.

3. Plasticizers : These are the substances / materials added to increase the plasticity and flexibility of thermosetting plastics. However, they decrease the tensile strength and chemical resistance. Most commonly used plasticizers are : camphor, tributyl phosphate, triphenyl phosphate and triacetin and non-drying vegetable oils, etc.

Camphor : It increases the surface hardness of plastics. Tributyl and Triphenyl phosphates are used for flame-proofing.

Triacetin : It improves the toughness property of plastics.

4. Catalysts or Accelerators : These are used only in case of thermosetting plastics. The function of these catalysts or accelerators is to accelerate the polymerisation of fusible plastic into cross-linked infusible form during moulding operation. In general, catalysts used for compounding are H_2O_2 , benzoyl peroxide, metals such as Pb, Ag, Cu, metallic oxide such as ZnO, ammonia and its salts etc.

5. Colouring matter (or pigments) : The colouring matter used in plastics should be resistant to the action of sunlight. The various coloured pigments are added to the plastics to impart the desired colours to the plastic articles e.g., organic dyestuffs and inorganic pigments are used as colouring materials.

4.9 PROPERTIES OF PLASTICS

In recent years, the use of plastics as an engineering material has been increasing because of their several advantages over other materials and unique properties exhibited by plastics.

1. They are light in weight as their specific gravity varies from 1 to 2.4.
2. They possess low thermal and electrical conductivities.
3. They are highly resistant to corrosion, abrasion and chemicals.
4. They can readily be moulded, drilled, machined.
5. They have low coefficient of thermal expansion.
6. They are not attacked by fungi, insects etc.
7. They are highly resistant to the attack of light, oils, acids and moisture.
8. They have low melting points but high refractive index.
9. Their shades or colours do not fade easily.
10. Plastics have good shock absorption capacity even better than steel.
11. They have very good tensile strength (5500 kg/cm^2)
12. They have low maintenance cost and do not require any protective covering such as that of paints.
13. They possess good optical clarity and smoothness like glass.
14. They can be easily moulded into even intricate and complicated forms and shapes.

4.10 APPLICATIONS OF PLASTICS

These specific properties of plastics are used in practice as follows :

1. Due to their low specific gravity and high tensile strength, the plastics are used in aircrafts, motor cars and structural industries.
2. Plastics can be used when combined with metals for manufacturing steering wheels and plastic covered dash boards.
3. Due to their high tensile strength and resistance to wear and tear, these are used in such parts of machinery which are constantly rubbing over each other like timing gears, self-lubricating bearings, pulleys, etc.
4. Being hard and having shock-absorbing capacity, plastic parts are used in machinery to reduce noise and vibrations in machines.
5. Due to their low cost of fabrication, they can be easily and cheaply moulded with accurate dimensions. Even complicated shapes can be produced easily.
6. Due to their high resistance towards chemicals and corrosive agents, these are used in chemical industries. Here these are used for manufacturing tubes, pipes for underground installations, tanks, absorption towers etc. In many chemical plants, poly-vinyl chloride (PVC) plastic is used in place of stainless steel. This PVC plastics can be processed just like the wood or metal, by sawing, drilling, welding etc. Here the maintenance cost is also quite low.
7. Their lightness, toughness and durability have made them useful in a number of industries e.g. in construction these are used for preparing flush doors, air-vent covers, WC seats, paneling for walls, etc. The super hard boards are useful for table and counter top. Sound insulation boards are also made of plastic paper boards.
8. Being a bad conductor of heat, plastics are used for making handles of hot objects like electric irons, kettles, soldering irons, frying pans, pressure cookers etc.
9. Due to their low electrical conductivity, plastics are used as solid electrical insulators or wire insulators. These are also used in the electronic industry. Radio and television circuits are printed on plastic paper laminated sheets.
10. Being resistant to water, polystyrene reinforced with glass fibres is used in the end sections of the condensers in electricity generating stations.
11. Due to their clear, transparent, translucent, opaque nature and wide range of colours, plastics have a highly decorative value. Thus, these are used as decorative knobs for radio, automobile, and household appliances.
12. Optical clarity combined with strength makes them suitable for making wind screens for automobiles, aircrafts, etc.
13. Miscellaneous uses of plastics are in scientific instruments, optical lenses, goggles, light fitting, various types of wrappers and packings, all sorts of brushes, advertising signs, protective coatings for wooden railings, toys etc.

EXERCISE

1. (a) What are plastics ? Give their importance.
   (b) Define polymerisation.
   (c) Explain the mechanism of polymerisation.
2. How are plastics formed by :
   (a) Addition polymerisation ?
   (b) Condensation polymerisation ?
   Or Explain two types of polymerisation with at least one example for each.

3. How are thermoplastics and thermosetting plastics formed ?
4. Write four substances which are added during compounding of plastics.
5. Distinguish between thermosoftening and thermosetting plastics.
6. Discuss any four engineering uses of plastics depending upon their properties.
7. State the names of most commonly used plasticizers in plastics. What is their effect on plastics ?
8. Write short notes on : (a) Fillers, (b) Plasticizers, (c) Pigments, (d) Accelerators.
9. Write a note on the structure of plastics.
10. Give any two reasons why thermosetting plastics cannot be reshaped and reused ?
11. Bring out the difference between thermosoftening and thermosetting plastics on the basis of their :
    (i) method of preparation, (ii) chemical bonding, (iii) heating effect, (iv) solubility.
12. Name the types of plastics and differentiate between them.
    Or Classify the plastics. Give at least three points of difference between them.
13. Thermosoftening plastics are soluble in organic solvents and can be reused. Why ?
14. P.V.C. plastics are used in chemical industries. Give two reasons.
15. State two purposes of fillers added to plastics.
16. State the purposes of plasticizers and accelerators in compounding of plastics.
17. Name the substances used for compounding of plastics with examples.
18. State four properties of plastics and write the uses based on each of the given properties.
19. What are plastics ? List the industrial applications of plastics.
20. Name the properties of plastics used for auto-wind screens and electrical appliances.
21. Give different properties of plastics which have made them so indispensible in everyday life.
22. (a) Name any one substance used as plasticizers and fillers in plastics.
    (b) State two purposes of fillers added to plastics.
    (c) Define plastics. Write three constituents of plastics with at least one example for each.
23. Thermosoftening plastics are soluble in organic solvents. Explain.
24. Why PVC plastics are used in chemical industries ?
25. Define plastics. Write any three properties of plastics with corresponding uses.
26. Give difference between addition and condensation polymerisation.
27. Write the properties of thermoplastics.
28. Write four constituents of plastics with one function of each.
29. Classify the plastics giving four examples of each plastic.
30. Explain the mechanism of polymerisation.
31. What is the principle of addition polymerisation ? Explain with an example.
32. Distinguish between plastic and rubber.

[B] RUBBER

4.11 RUBBER

Rubber or elastomers are high polymers which sustain or can undergo very large reversible elongations at relatively low stresses. Thus, a rubber-band can be stretched 5 to 10 times its original length and as soon as the stretching force is released, it returns to its original length. In the same way, a block of rubber can be compressed, but it returns to its original shape and dimensions as soon as the load is released. The reversible elastic deformation in elastomer arises from the fact that in the unstressed condition, an elastomer molecule is not a straight chain, but in the form of a coil or spring shaped and consequently it can be stretched like a spring (Refer Fig. 4.1). The chains get reverted back to their original coiled state, as the deforming stress is released. Thus, elasticity to rubber is caused by the lengthening and shortening of these springs of polymeric chains when stretching force is applied and released respectively.

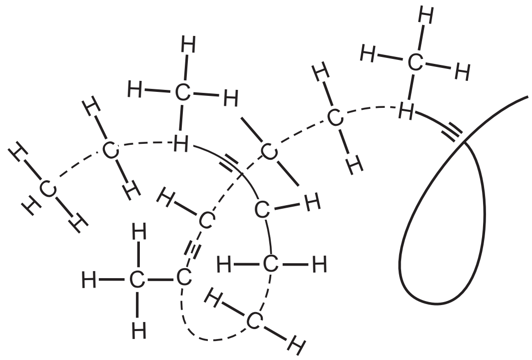


Fig. 4.1 : Coiled elastomer chain of natural rubber (Poly-isoprene)

4.12 TYPES OF RUBBER

1. Natural Rubber : *''Natural rubber is a high molecular weight linear hydrocarbon polymer which exhibits elasticity and other rubber like properties.''* Natural rubber is made from a milky emulsion (white liquid) called 'latex' obtained by cutting narrow strips from the bark of the rubber trees such as Hevea, Gutta-Percha, Balata, Guayule etc. These trees are found in tropical and semi-tropical countries such as Malaysia, Indonesia, Brazil, Ceylon (Sri Lanka) and India. The latex contains about 30 - 40% rubber solids and 55 - 60% water depending upon the age of tree. The solid material is principally isoprene. During the treatment of latex, these isoprene molecules polymerise to form long coiled chain of polyisoprene (Refer Fig. 4.1).

$$n\left[-CH_2-\underset{}{\overset{CH_3}{\overset{|}{C}}}=CH-CH_2-\right] \xrightarrow{\text{Polymerisation}} \left[-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-\right]_n$$

Isoprene — Polyisoprene (rubber)

The unit which is repeated in the rubber is isoprene (C_5H_8) group, so the empirical formula of rubber is $(C_5H_8)_X$, the isoprene unit 'x' may be 5000 in the polymer chain.

Treatment of Latex : The latex is diluted to contain about 30 – 36% of rubber and filtered to remove any dirt present in it. The latex is then coagulated by the addition of coagulants such as 5% solution of acetic acid or 90% formic acid. Potassium or ammonium alum are also used as coagulants. When a weak solution of acetic acid or formic acid is added to the latex, it makes the particles of rubber to come either in strings or clots which rises to the top. This process of separating rubber particles from latex is called coagulation.

After coagulation, the whole mass is left for several hours, then rubber is coagulated to soft white mass known as coagulum. The coagulums are then separated from the liquid by squeezing in the rolls. The sheets of rubber are then washed and dried to give crude rubber, the surfaces of which resemble to crepe paper, hence it is known as crepe or raw rubber.

4.13 DRAWBACKS OF NATURAL (OR RAW) RUBBER

Pure rubber is useless as pure gold. There are number of drawbacks of raw rubber :

1. During summer, the raw rubber becomes soft and sticky, while in cold weather it becomes hard and brittle.
2. It has low tensile strength (200 kg/cm^2).
3. It is too weak to be used in heavy duty operation.
4. On stretching, it undergoes permanent deformation.
5. It has a large water absorbing capacity.
6. It is affected by solvents like gasoline, benzene, carbon tetrachloride (CCl_4), vegetable oils etc.
7. It gets tarnished in air due to oxidation (i.e., it perishes due to oxidation in air). As a result, its durability is considerably decreased.

However, the properties of raw rubber can be improved by vulcanisation.

4.14 VULCANISATION OF RUBBER

To improve the properties of crude or raw rubber, it is compounded with some chemicals like sulphur, hydrogen sulphide, benzoyl chloride etc. Most important of all the processes of compounding (or vulcanising) is the addition of 'sulphur'. The process consists of heating the crude rubber with sulphur to a high temperature. The sulphur combines chemically at the double bonds in the rubber molecule of different rubber springs. Vulcanisation brings about a stiffening of the rubber by a sort of cross-linking and consequently preventing intermolecular movement or sliding of rubber springs. The extent of stiffness or loss of elasticity of vulcanised rubber depends on the amount of sulphur added. For example, a tyre rubber contains 3 – 5% sulphur, but a battery case rubber may contain as much as 30% sulphur.

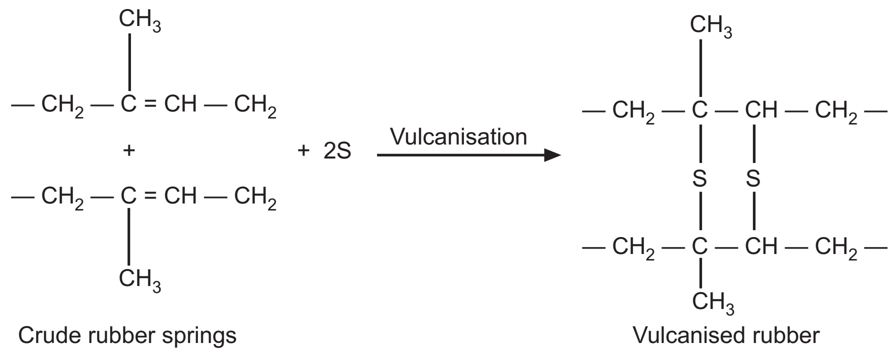


Fig. 4.2 : Vulcanisation of Crude rubber

Vulcanite or ebonite (hard rubber) contains about 52% sulphur. The cross-linking of the isoprene spirals is attained to such an extent that vulcanite has practically no elasticity. Thus vulcanite is tough, has abrasion resistance, can be sawn, drilled and polished. It has extremely good electrical insulation properties.

Synthetic Rubber : ''Synthetic rubber is any vulcanisable artificially prepared rubber like product, which can be stretched to 300% or more of its original length, but returns rapidly to its approximate original shape and dimension when the stretching force is released.'' Strictly speaking, synthetic rubber is not produced in the sense that the synthetic product differs in chemical composition and properties from those of the natural rubber. Therefore, synthetic rubbers are only rubber-like products. Therefore the term 'artificial' rubber is more appropriate than 'synthetic' rubber. The development of automobile industry brought a revolution not only in petroleum industry but also in the rubber industry. Rubber from the plantations could not meet the demand and attempts were made to synthesize natural rubber. As this did not succeed, rubber-like materials were synthesized. At the end of Fourth Five Year plan, the artificial rubber production was increased to about 1,20,000 tonnes per annum.

Distinction between Natural and Synthetic rubber

Natural Rubber	Synthetic Rubber
1. It is an elastic material obtained from a milky emulsion (latex) of rubber trees.	1. It is a rubber-like product obtained by some chemical reaction.
2. It is an polymer of isoprene $(C_5H_8)_x$ molecule.	2. It is a polymer of substances having unsaturated nature.
3. It is non-resistant to oxidation.	3. It is highly resistant to oxidation.
4. It becomes soft and sticky by application of heat.	4. It does not become soft and sticky by application of heat.
5. Its tack property is high.	5. Its tack property is low.
6. It is soluble in organic solvents.	6. It is insoluble in organic solvents.

At present, the following five principal types of synthetic rubbers are in large-scale use :

(1) Buna-S, (2) Buna-N, (3) Butyl Rubber, (4) Neoprene, (5) Thiokol.

4.15 IMPORTANT PROPERTIES OF SYNTHETIC RUBBER

1. Elasticity : *''Elasticity is the property by virtue of which a material undergoes deformation under stress and regains its original shape on removal of the stress."*

Elasticity is thus opposite of plasticity and is measured by measuring plasticity. It is an important property of an elastomer during its processing in factory. If elasticity is high, it requires excessive power and time for processing.

2. Tack : *''Tack is the special characteristic of rubber by virtue of which two or more surfaces can stick or adhere to each other.''* Tack can be increased by making the surface fresh by treating it with some solvent. It is an important property because composite rubber articles like tyres are manufactured by using this property. Synthetic rubbers generally lack this property.

3. Rebound : *"It is the measure of resilience i.e. ability to absorb energy and return without permanent deformation of a synthetic rubber.''* Rebound is determined by determining the height to which a rubber ball will bounce when dropped. In practice, the test for measuring this property is carried out by allowing a weighed pendulum device to travel through a measured arc and to strike a block of the rubber. This property is utilized in mountings and shock absorbers.

4. Hardness : *''Hardness is the ability of the rubber to withstand wear and abrasion and resist the penetration.''* It is measured by an instrument Durometer. A metallic point worked by means of spring is pressed against the surface of stock rubber by means of a spring. The strain produced on the spring denotes the hardness of the rubber. The values of hardness are directly read on the scale of the instrument. The use of rubber as shock absorbers, gaskets etc. are based on this property.

5. Stress-strain properties (Tensile strength) : A dumb-bell shaped piece of synthetic rubber is cut with a die. On narrow portion, make two marks one inch apart as shown in Fig. 4.3 It is then placed in the machine and stretched until it breaks. The load at which it breaks is its 'tensile strength'. This property is used when rubber is used for V-belts and conveyor belts.

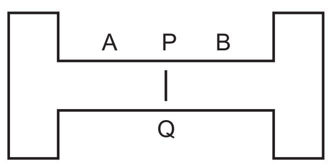


Fig. 4.3 : Dumb-bell shaped piece of synthetic rubber

6. Abrasion Resistance : Abrasion is a process of wearing of surface by friction. *''The property of resisting wearing away of a surface by friction is known as abrasion resistance.''* Abrasion resistance is measured by machines in which an abrasive material is rubbed against the surface of the rubber. The loss in volume is measured directly. The loss in volume in a definite period denotes the loss on abrasion. The greater the loss, less is the abrasion resistance. This property is utilized in rubber linings.

4.16 APPLICATIONS OF RUBBER

Rubber has many valuable properties that make possible its use in home and in industry. It contributes much to man's comfort, health and pleasure. In addition to good tensile strength, rubber possesses desired properties like elasticity, flexibility, electrical and abrasion resistance, chemical resistance, low conductivity and low permeability to gases and liquids. The above properties of rubber make it useful in the manufacture of following types of materials.

1. Due to elasticity, strength and toughness, it is used for making rubber-bands, tubes of bicyles, automobiles and aeroplanes, golf balls, surgical goods and mechanical rubber goods.
2. Due to its excellent abrasion resistance (i.e. resistance to wearing away of surface by friction) it is used for making bicycle, automobile and aeroplane tyres, for shoe heels and soles, conveyor belts (used for conveying grains, coal, rocks, sand, ores etc., as these products are compact, non-slipping, clean and shock absorbing). V-belts (used for transmission of power), shock absorbers, mounting of heavy machineries and automobile parts. Mountings of equipments are rubber sections sandwitched between two metal plates. These reduce machine vibrations, prolong life and also improve the quiteness of the equipments.

3. Due to remarkable resistance to electricity, hard rubber (or ebonite) is largely used in electrical industry as an insulating coating for wires and cables used for electrical power transmission. It is also used in switchboard panels, plugs, sockets, telephone receivers, battery cases and electrician gloves due to its high abrasion resistance and good electrical insulation properties.
4. Due to its chemical resistance, it is used for making rubber-lined metal tanks and vessels used in chemical industry, where corrosive chemicals are to be processed. Due to its chemical resistance to petrol, mineral oil and some solvents, rubber hose pipes are used for their transmission. Rubber hoses are also used for water transmission, for gardening, fire-fighting etc.
5. Due to their good shock absorbing, sound and thermal insulating properties, sponge rubber is used in shock absorbing cords, and bands for helmets and goggles, toys and sport's goods.
6. Due to its resistance to penetration of air and water foam, rubber is used in air-pillows, cushions, mattresses and undercarpet paddings and in rain coats.
7. Due to its hardness, rubber gaskets are used for sealing various types of equipments such as refrigerator cabinet doors, cookers, autoclaves etc.

EXERCISE

1. What is rubber ? What is the difference between natural and synthetic rubber ?
2. Give the examples of synthetic rubber.
3. (a) What is natural rubber ? Describe the processing of natural rubber.
   (b) What is natural rubber ? How is it obtained from natural source ?
4. Specify the properties of rubber, when used in each of the following applications :
   (i) Tyres, (ii) Shock absorbers, (iii) Mounting, (iv) Lining.
5. Explain the following properties of rubber :
   (i) Elasticity, (ii) Tacking, (iii) Rebound, (iv) Abrasion resistance.
6. Define abrasion resistance. Write two uses of rubber depending upon it.
7. Explain the elasticity, tack and abrasion resistance of synthetic rubber.
8. What are the drawbacks of natural rubber ? Name the process which increases stiffness of rubber.
9. Describe vulcanisation of rubber. OR Give four types of synthetic rubber.
10. Write any four uses of rubber based on its different properties.
    Or Explain four properties of rubber and their related applications.
11. Explain the applications of rubber with related properties.
12. State the drawbacks of natural rubber or explain why is it necessary to vulcanise the natural rubber.
13. (a) Explain tacking and elasticity of rubber.
    (b) Write the uses of rubber of tackiness and elasticity.
14. (a) What is abrasion resistance of rubber ?
    (b) What is tacking property of rubber ?
15. Describe the process of vulcanisation of rubber. Why is it necessary to vulcanise natural rubber ?
16. Explain vulcanisation of rubber. Give four types of synthetic rubbers.
17. What is vulcanisation ? Define abrasion resistance and tack. Write any four applications of rubber related to one of the above properties.
18. Define and explain natural rubber and vulcanisation.
19. Define vulcanisation of rubber. Explain the process with chemical equation.
20. Mention four properties and related applications of rubber. Write two points of difference between natural and synthetic rubber.
21. Which organic compound is present in rubber ?
22. Describe the important properties of synthetic rubber.
23. Distinguish between natural and synthetic rubber.

[C] THERMAL INSULATING MATERIALS

4.17 THERMAL INSULATING MATERIALS

"The materials which are used to prevent the flow of heat are known as thermal insulators."

The use of thermal insulators is very important in various industrial and engineering operations where the flow of heat is to be prevented. For example, in cold storage refrigerators, boilers, ovens, steam carrying pipes, brine pipe lines etc. all need thermal insulators.

The good thermal insulators have extremely low thermal conductivity. The most commonly used thermal insulators are glass wool, thermocole, asbestos and cork.

4.18 FACTORS AFFECTING THE THERMAL CONDUCTIVITY OF INSULATORS

1. Moisture : The thermal conductivity of the material is increased by the presence of moisture in the pores, because of the fact that air in the pores is replaced by highly conducting water vapours. Hence the surface of the thermal insulator should be water-proof. Moreover, the pores on the surface should be as close as possible, so that moisture cannot enter them. The insulating material should not react with water.

2. Pores : Common insulating materials are generally the mixture of fibrous or cellular granular materials. The entrapped air or gases in pores have low thermal conductivity and so may act as thermal insulators by preventing the flow of heat to a great extent; but the transfer of heat by convection increases as the pore volume increases. Because in large enclosed space greater convection currents are formed. Consequently, the thermal conductivity of a material can be decreased and hence, the insulating power can be increased by modifying the pore structure of the material to be used as thermal insulator. Therefore, a large number of fine pores are preferred than the few large ones.

4.19 CHARACTERISTICS OF GOOD INSULATING MATERIALS

A good insulator has the following important characteristics :

1. It should be cheap.
2. It should be fire-proof.
3. It should possess extremely low thermal conductivity.
4. Its density should be low.
5. It should be water-proof and hence resist absorption of moisture.
6. It should be chemically inert to water, surrounding atmosphere and high temperature.
7. It should be odourless during use.
8. It should be capable of bearing the load applied on it during working.
9. It should be physically and mechanically stable at the working temperatures.
10. It should withstand the effects of shock and vibrations.

4.20 CLASSIFICATION OF THERMAL INSULATORS

Thermal insulators are of two types :

1. Organic thermal insulators : These are suitable for low temperature work, upto 150°C. These are naturally occurring materials such as wool, cotton, silk, paper, charcoal, powder saw dust, coke powder, rubber etc. which generally have low density and possess very large number of small air pockets.

2. Inorganic thermal insulators : These are suitable for temperatures higher than 150°C. These include asbestos paper, asbestos fibre (felted), glass fibre, glass wool, mineral slag fibres, calcium silicate, porous silica, refractory insulating bricks, etc. The most commonly used thermal insulators are : (1) Glass wool and (2) Thermocole.

4.21 GLASS WOOL

Glass wool is a fibrous wool like material which is made up of intermingled fine filaments of glass, like ordinary wool.

Preparation : Glass filaments are obtained by forcing molten mass of alkali-free glass through sieve holes having the average diameter of 0.0005 cm. continuously. The filaments of glass so obtained are thrown over a rapidly revolving drum to get the material in wool-like form.

Properties :

1. Its density is low.
2. Its thermal conductivity is low (about 0.034 kcal/m^2/^oC/hr).
3. Its electrical conductivity is also low.
4. It is fire-proof and non-combustible.
5. Its average diameter of fibre is 0.0005 cm.
6. It is resistant to chemicals and does not absorb moisture.
7. Its tensile strength is about eight times more than steel.

Uses :

1. It is widely used as a thermal insulating material in domestic and industrial appliances such as motors, ovens, refrigerators, walls and roofs of houses, because it is soft, heat-proof, fire-proof, flexible and even insect-proof.
2. Being resistant to chemicals, glass wool is used as a filtering material for corrosive liquids like acids and acidic solutions in industry.
3. It is also used in air-filters as dust filtering material.
4. It is used for sound and electrical insulation.
5. It is used in the manufacturing of fibre glass by reinforcing it with plastic resins.

4.22 THERMOCOLE

"Thermocole is a foamed plastic obtained by blowing air through molten polystyrene or polyurethanes." It is a spongy, porous (having 3 to 6 million fine air cells or pores per litre) foam like in structure. Due to large number of air cells, it possesses an outstanding insulating property.

1. Its density is low (22 kg/m^3).
2. It is spongy, porous and has a foam-like structure.
3. It is quite strong, though extremely light.
4. It is quite shock-proof.
5. It is chemically inert and resists ageing.
6. Its thermal conductivity is low (0.27 kcal/m^2/^oC/hr).
7. Its electrical conductivity is also low.
8. It can be used upto 55^oC.

Uses :

1. Being light and shock-proof, thermocole is used as an ideal packing material for delicate electrical and electronic equipments.
2. Due to outstanding thermal insulating properties, it is mainly used as a heat insulator in refrigeration and air conditioning.
3. It is used for decorative purposes.
4. It is used for protecting screens in radars.

4.23 ASBESTOS

It is a suitable insulator for heat insulation of boiler and for full head lining a board ship.

Asbestos sheets are used for roof-covering. Asbestos sheets are durable, fire-resistant, weather-resistant and light in weight. They do not require paintings. Their cost of maintenance is negligible. Asbestos is also used for damp-proofing for walls and floor in the form of asbestos felt. It is also a good sound insulator. It is used as a filler for natural and synthetic insulating resins.

4.24 CORK

It is the name given to light bark of an oak tree. The bark is cleaned, ground, sized and baked into moulds. During baking, its natural resin comes out and acts as a binding material. It is then converted into thin sheets by pressing. These sheets are light, porous and resist water and act as an insulating material against heat and electricity.

Uses :

1. Cork is used as a lining material for cold storages, refrigerators, bottle stoppers and packing gaskets.
2. It is used in floats of fishing nets.
3. Floor-tiles, walls and ceilings are made sound-proof with cork board.
4. In shoe industry cork sheet used as a cold filler and cushioning.
5. In water-proof coatings, linoleums etc.
6. In making base for telephones, bulletin-boards and sporting equipment grips etc.

EXERCISE

1. What are thermal insulators ? Describe the properties of thermal insulators.
2. What are the characteristics of ideal insulating material ?

   OR

   Explain four characteristics or properties of a good thermal insulating material.
3. What are thermal insulators ? Give the properties and uses of any one thermal insulator.
4. (a) Write the method of preparation of glass wool.

   (b) What is glass wool ? How is it prepared ? Give its uses.
5. Give two uses of glass wool based on its two different properties.
6. (a) What is thermocole ? Write two uses of thermocole based on its two different properties.

   (b) What is thermocole ? Explain three properties of insulating material and its relative uses of thermocole or cork.

   (c) What is glass wool ? Give its two engineering uses.
7. Explain the role of pores in thermal insulator like thermocole.
8. "A large number of fine pores is preferable to having few large ones in thermal insulators." Explain.
9. Give the properties and uses of the following :

   (i) Glass wool, (ii) Thermocole, (iii) Asbestos.
10. Give the required properties of an insulating material for making it useful in moving vehicles, refrigeration and packing delicate articles.
11. Give two properties and two uses of glass wool and thermocole.
12. Give two uses of thermocole based on its two different properties.

13. How thermocole is prepared ?
14. Why thermocole is used as a packing material for delicate equipments ?
15. Write any two applications of asbestos.
16. Define thermal insulating material. Explain three properties and related applications of thermocole.
17. State two properties and uses of (i) cork, (ii) asbestos.
18. State four properties and related applications of glass wool.
19. What is glass wool ? Give its four characteristics and two uses.
20. Write four uses of cork.

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Chapter 5

ENVIRONMENTAL EFFECTS

5.1 Introduction
5.2 Causes of pollution
5.3 Air pollution
5.4 Types of air pollutants
5.5 Control of air pollution
5.6 Air pollution due to internal combustion engine
5.7 Depletion of ozone
5.8 Green house effect
5.9 Water pollution
5.10 Causes of water pollution
5.11 Sewage
5.12 Biochemical Oxygen Demand (BOD)
5.13 Chemical Oxygen Demand (COD)
5.14 Comparison between COD and BOD
5.15 Methods of preventing water pollution
5.16 Preventive environmental management activities

5.1 INTRODUCTION

In this modern living with the advancement of science and industrial development, we are facing a very serious and dangerous problem of pollution in almost every aspect of our daily life. There are three basic needs (1) air, (2) water and (3) food for human life. If air, water or food is not clean and gets contaminated with hygenically objectionable matters, health of human beings gets affected. Some of our habits, such as cigarette smoking, may cause lung cancer.

From the chemical industries, the effluents are generally discharged into rivers, lakes and finally reach the sea. If such polluted water from river or lake is used for human consumption, it gives rise to health hazards as industrial effluents contain toxic matters. The fish in the polluted water (such as lakes, rivers and sea) die. Certain dangerous heavy metals like Hg, Pb, Cr, As etc. get accumulated in the body of the fish and this fish if consumed by human beings get diseases due to these toxic metals.

The gases generated in the chemical industries such as CO, CO_2, SO_2, NO_2, H_2S, Cl_2, etc. are very dangerous. For example, the accident caused in Calico chemicals, Bombay in 1985, due to leakage of Cl_2 gas has killed one person and hospitalized several people. Bhopal tragedy, due to leakage of methyl iso-cyanate from Union Carbide Company in 1984 killed thousands of people. People from Chembur, Bombay are troubled by the emission of NO_2 gas from nitric acid plant of Rashtriya Chemicals and Fertilizers Ltd, Bombay. Yellowing of Tajmahal by SO_2 fumes is also an example of pollution.

Due to tremendous growth in chemical industries, the effluents coming out create horrible problems for the human life. Recently, the sugar industries are facing a very serious problem of effluent treatment from (a) distillary and (b) paper mills.

Our environment is a complex and dynamic system in which various non-stop, self-generating cycles are going on, in which all forms of life are interdependent and interconnected. For example, plants consume carbon dioxide and provide oxygen to man and other animals by the process of photosynthesis. Plants and micro-organisms provide pure water in lakes and rivers. Biological processes that have being going in the soils for thousands of years provide coal, petroleum, food etc. In other words, the nature has already provided the necessities for human life. However, man in his struggle strives more and more to attain comfort, wealth and power and has been constantly ignoring nature's cycle. In the process of achieving these, man has been constantly changing the basic characteristics of the environment by (i) reducing some of its essential components like oxygen and (ii) adding on some undesirable components like CO, CO_2, SO_2, SO_3, NO_2, Cl_2 etc.

These adverse types of changes caused by misdeeds of man are called *'environmental pollution." Thus, "pollution may be defined as the presence of undesirable substances / foreign matters (like organic, inorganic, biological or radiological or heat etc.) into the environment thereby adversely altering the nature's quality of the environment and causing damage to human/plants/animal life."* The term environment includes the air, water, land, biota (i.e. buildings, oceans, open space parts, vehicles and noise, etc.). "*A substance whose presence causes pollution, is known as a pollutant.''* Heat is not a substance, but still it is considered to be a pollutant. This is because, even small changes in overall temperature conditions of our earth may have disastrous effects on the quality of life.

"A pollution may also be defined as an unwanted / undesirable foreign matter added to the environment."

5.2 CAUSES OF POLLUTION

The main causes of pollution of the environment are as follows :

(i) The uncontrolled growth in number, i.e. tremendous increase in population all over the world.

(ii) The rapid industrialization.

(iii) The rapid urbanisation.

(iv) The exploitation of nature by cutting trees etc. Besides this, the natural phenomena like (a) radioactivity, (b) volcanic erruptions, (c) strong winds, (d) forest-fires, minerals and (e) sands, dusts etc., also cause pollution.

(v) Excessive use of insecticides, pesticides and other chemicals.

Pollution can be classified into three heads : (1) Air pollution, (2) Water pollution, (3) Soil or land pollution.

Atmospheric Pollution : Around 16 km from the surface of the earth, the action of the Sun's rays convert the oxygen to ozone. Ozone is a molecule with three atoms of oxygen (O_3). The proportion of ozone increases from this height until, at about 23 km where the ozone blanket is the thickest. This blanket of ozone is extremely important since it absorbs the harmful ultraviolet radiation from the sun.

At present, many activities of man are responsible for changing the composition of the atmosphere. Urbanization, industrialization, modern agricultural practices and war techniques are adding a variety of substances to the air. These substances bring about degradation of the air that we breathe. All such materials are called pollutants.

The pollutants are of different types. They may be solids, liquids or gases. Generally, they are the outputs of technology. Pollutants may be of natural origin such as the pollen grains, spores or even microbes. In short, a pollutant is defined as any solid, liquid or gaseous substance present in such a large concentration, that it tends to be injurious to the environment and hazardous to life.

The act of releasing pollutant is called as pollution. Basically, there are three types of pollutions : (i) air pollution, (ii) water pollution and (iii) soil pollution.

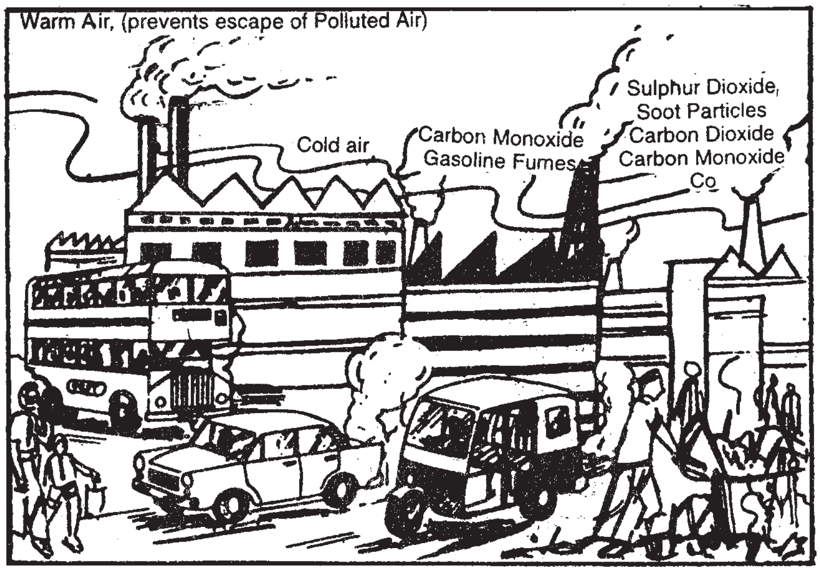

Fig. 5.1 : Air pollution

5.3 AIR POLLUTION

Air pollution is a serious problem in industrialised, congested cities. Heavy traffic in such areas, further contributes to pollution. Pollutants include gases, smoke, fumes, dust, particulate matter and odour. Once in the air, all these pollutants get dispersed over a greater distance. They go on circulating alongwith the air. Some of these pollutants react with the moisture from the air and make them more hazardous. Air pollution is regarded as the most dangerous, as we cannot control the air that we breathe.

Following are some of the common pollutants occurring in the air.

5.4 TYPES OF AIR POLLUTANTS

On the basis of the physical state, there are four major groups of air pollutants :

(A) Gases, (B) Particulates, (C) Deforestation, (D) Radioactive gases.

(A) Gases : Gases are freely miscible with air, without settling down. The concentrations of gaseous pollutants are often expressed as 'parts per million' (ppm) by volume (i.e. number of molecules of pollutant per 1000,000 or 10^6 molecules of the constituent of air. The values for concentration of pollutants are important only with reference to the nature of the pollutant. Some pollutants are so present that even 0.001 ppm value is quite significant. The role of important air-pollutants like SO_2, SO_3, CO, CO_2, NO_2 etc. is given in Table 5.1.

Table 5.1 : Sources and Effects of Gaseous Pollutants

Pollutant	Major Sources	Principal Effects
1. Sulphur dioxide (SO_2)	Thermal power plants, petroleum industry, sulphuric acid plants, oil refinery, sulphide ore roasting plants.	SO_2 is the main air pollutant which causes heart, respiratory diseases (e.g. asthma, bronchitis), throat troubles, eye irritation, plant damage, besides corrosion of metals.
2. Sulphur trioxide (SO_3)	Formed by oxidation of SO_2 in presence of sunlight. Both SO_2 and SO_3 are converted into H_2SO_3 and H_2SO_4 in presence of water-vapour in air. Droplets of these acids remain suspended in air.	Even 1 ppm of SO_3 in air causes severe breathing and irritation in respiratory tract. SO_3 is destructive to vegetation. Acidic atmosphere has harmful effects on materials like clothes, paper, leather, buildings. It corrodes iron and steel. It is very destructive to lungs, tissues and can cause even heart failure.

… Contd.

3. Carbon monoxide (CO)	Released by partial combustion of fuel in automobiles, industries and oil refineries, cigarette, bidi, smoke and domestic heat appliances. About 290 million tonnes of CO is estimated to be discharged in the atmosphere, annually.	It is colourless, odourless, but very toxic in nature. It causes headache, visual difficulty, paralysis and even death. The presence of CO reduces the oxygen carrying capacity of blood due to the formation of carboxy-haemoglobin. This ultimately causes headache and lassitude to tobacco smokers, CO also affects cardiovascular system.
4. Carbon dioxide (CO_2)	Combustion processes, respiration of plants and animals, by deforestation. Air contains about 9325 ppm of CO_2. Increase in CO_2 by 10–15% causes to raise world-wide atmosphere temperature by 0.5°C.	CO_2 is non-poisonous, non-corrosive but too much in the atmosphere causes pollution, respiratory disorders and suffocation. Used as an index of pollution from combustion operations.
5. Nitrogen oxides (NO, NO_2)	Combustion of fuels (coal, diesel, petroleum), manufacturing acid, explosives and acid-picking plants. Estimated that 18 million tonnes of nitrogen oxides are added in atmosphere every year by continuous increase in number of vehicles, power plant industries, pollution due to oxide of nitrogen increasing day by day.	High concentration of NO_2, causes respiratory illness among children; irritation of eyes, lung congestion. NO_2 leads to formation of 'petrochemical smog' (in sunlight oxides of nitrogen and hydrocarbons form smog from combustion of petroleum products. This (i) limits the visibility of roads, (ii) causes eye-irritation, (iii) difficulty in breathing. This results in lung asthma, bronchitis in person living around it. Presence of NO_2 (1 ppm < concentration) adversely affects plant growth (especially tomato plants growth is reduced by 30%).

(B) Particulates : These include dust, smoke, smog, asbestos-dust, lead-dust etc.

1. Dust : Main sources of dust are house cleaning dust, power houses, mines and quarries, vehicles traffic, furnace ashes, natural winds, forest fires, pottery and ceramic factory stacks, combustion operations and several other activities of man raise dust in the atmosphere.

Effects : Atmospheric dust causes allergic and respiratory diseases in man, 'silicosis' if dust contains silica. Moreover, dust causes corrosion and soiling.

2. Smoke : It is composed of tiny particles of carbon, ash, oil etc. Smoke is formed by incomplete combustion of fuel. The major sources of smoke formation are rail roads, locomotives, diesel engines, automobile petrol engines, furnaces, hearths, etc.

Effects : Loss of calorific value through incomplete combustion. The possibility of cancer due to smoke spoiling of clothing, rags, exterior-finish of buildings.

3. Smog : It is the combination of smoke and fog (a natural phenomenon in which minute liquid particles remain suspended in air).

Effects : Smog has some effects similar to smoke, but somewhat prolonged one.

4. Asbestos dust : Its main sources are mining, processing and manufacture of asbestos gaskets and ropes used in automobiles, buildings, flooring and insulating materials.

Effects : In addition to the effects of dust, it causes 'asbestosis' disease.

5. Lead dust : The main sources are lead mining and smelting works, lead batteries, lead paints and manufacture of lead-base alloys, automobile exhausts (TEL is added to gasoline so as to increase its octane rating).

Effects : It causes lead poisoning as lead-dust settles down on plants and food-stuffs meant for human and animal consumption.

(C) Deforestation : Green leaves of plants absorb CO_2 for the manufacture of their food by photosynthesis and give out O_2 in the process, thereby purifying the atmospheric air. Plants also control H_2S, HNO_3 and Cl_2. Thus, plants help in controlling the air pollution. Excessive deforestation (cutting of trees) causes indirectly air pollution.

(D) Radioactive Gases : The radioactive elements, which occur in rocks and soils are derivatives of uranium (^{238}U), thorium (^{232}Th) and actinium (^{231}Ac) series. They evolve radioactive gases, which mainly consist of radon (Rn) and thoron. These gases are harmful to human health.

5.5 CONTROL OF AIR POLLUTION

''To control the air pollution the best way is to reduce or prevent the formation of pollution at the source itself.'' The damages caused by air pollution are generally, much higher than the cost of preventing such damages. Some of our industrial processes may be suitably modified so as to minimise the extent of pollution. The various air pollution control methods are :

1. Dust : To eliminate dust, 'extraction ventilation' is frequently applied. In this, the air stream carrying suspended dust particles is first maintained at a sufficient velocity to keep the dust particles in suspension. Thereafter, the rate is reduced suddenly to the extent, so that the dust particles settled down in a stilling chamber. Other methods used for removing dust are bag filters, centrifugal separators, washers, cyclone dust separators, etc.

2. Smoke : May be reduced by installing ''cottrell-electrostatic precipitators''. Smoke is a colloidal solution of negatively charged carbon particles in air. Before passing the smoke to chimney, it is sent through a chamber provided with a knob maintained to a very high potential of +30,000 volts or more. Under the influence of a strong electric field, the smoke particles get robbed of their negative charges, thereby, the smoke particles precipitate out and settle at the bottom of the chamber itself and only hot dust-free gases go out of the chimney.

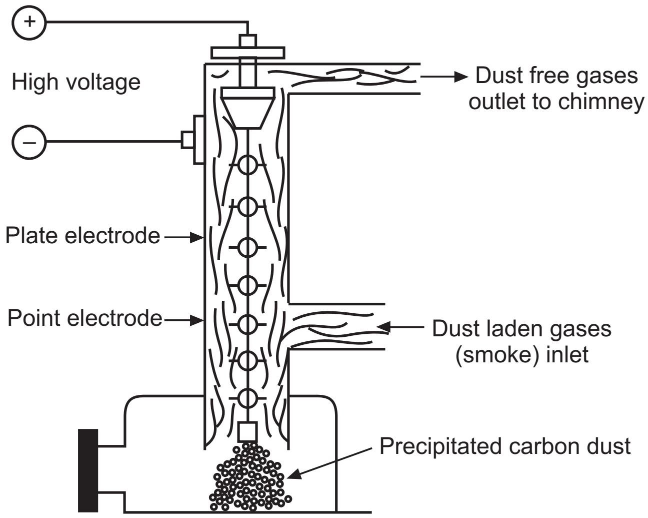

Fig. 5.2 : Cottrell smoke precipitator

Smoke can also be reduced during combustion of fuel by (i) correct method of firing, (ii) admitting correct quantity of air. Even a little supply of air often results in the evolution of smoke, (iii) maintaining high temperatures, because at low temperature the combustion is incomplete and smoky, (iv) feeding the fuel continuously, instead of intermittently. Automatic mechanical strokers used to regulate the draught and temperature within the combustion chamber are now-a-days used for this purpose.

3. The emissions from automobiles and vehicles may be reduced by cleaning the exhaust after combustion by the use of a catalyst.

4. The use of tall chimneys, reduces the concentration of air pollutants near the ground level. The gases discharged through stacks get diluted and are dispersed into the atmosphere. The stacks thus act to provide low concentration pollutants.

5. Sulphur dioxide (SO_2) pollution can be controlled, either by removing sulphur after combustion or by desulphurisation of fuel. SO_2 and acid fumes can be removed by passing the stack/fuel gases through a bed of alkaline Al_2O_3 or activated substances. Reduction of SO_2 in fuel gases can alternatively be done as follows :

(a) Lime water wash : The gases containing SO_2 are passed through lime-water, when SO_2 is removed from flue-gases in the form of calcium sulphite.

$$Ca(OH)_2 + SO_2 \longrightarrow CaSO_3 + H_2O$$

(b) By liquid ammonia : From fertilizer factory, SO_2 containing gases are passed through ammonia solution, when ammonium sulphite is obtained as a by-product.

(c) Cairox method : The oxidation of SO_2 takes place, when SO_2 is mixed with alkaline $KMnO_4$ solution through spray.

$$2KMnO_4 + 3SO_2 + 4KOH \longrightarrow 3K_2SO_4 + 2MnO_2 + 2H_2O$$

6. SO_2 and H_2S evolved in refineries in air, can be reduced by adopting 'Claus process' which yields elementary sulphur as a by-product.

7. Acids/chemical fumes : These can be removed by passing the gases/vapours through a tower filled with coke and by passing the counter-current of water in the reverse direction. By this method, we can recover simultaneously, the volatile products having commercial value.

8. The use of wood and coal as a fuel should be gradually reduced and modern energy resources such as electricity, nuclear power, tidal power, geothermal power and solar energy should be used for domestic as well as industrial purposes.

9. Zoning : The main reason of air-pollution is the lack of proper planning during rapid industrialization. To avoid air-pollution problems 'industrial zoning' should be done. It is desirable to have suitable 'buffer zone' between houses and industrial units in order to facilitate 'dilution of air pollutants' to a degree of harmless even to children by the time the pollutants from industries reach the ground level.

10. Growing more trees : Plants use CO_2 for their preparation of food by photosynthesis and release O_2 to the air. Consequently, they help to reduce the excess of CO_2 and the amounts of H_2S and HNO_3. Moreover, the air passing through vegetation areas, slows down considerably and helps in the deposition of suspended particulate materials (like coal dust, fine silt etc.) on the leaves, which are either washed down by rain or by periodic shedding of leaves. Thus, plants on the whole help in controlling air-pollution. When the trees and vegetations are removed by unnecessary cutting, there will be no control on the amount of CO_2, dust-particles and to remove some extent of ozone, H_2S, HNO_3 etc. from the air. The air then becomes more and more rich in these harmful pollutants.

5.6 AIR POLLUTION DUE TO INTERNAL COMBUSTION ENGINE

One of the major man-made air pollutant is the internal combustion engine used for running motor cars, buses, planes, trucks, scooter, auto-rickshaws etc. When fuels like kerosene, diesel, petrol is burnt, it releases lot of smoke into the atmosphere. These fuels are the mixtures of various hydrocarbons. Out of these, octanes (C_8H_{18}) constitute a major component of gasoline. When a mixture of gasoline vapour and air burns in I.C. engine of an auto-vehicle, the following reaction takes place :

$$\underset{\text{(Octane)}}{2C_8H_{18}} + \underset{\text{(Oxygen)}}{25O_2} \longrightarrow \underset{\text{(Carbon dioxide)}}{16CO_2} + \underset{\text{Water}}{18H_2O} + \text{Heat}$$

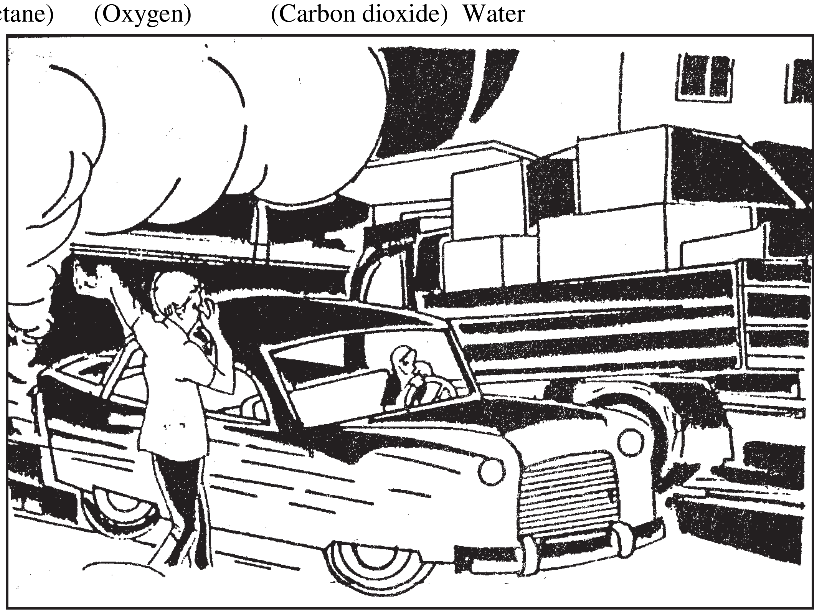

Fig. 5.3 : Air pollution from internal combustion engines

Besides the pollutants, CO_2, CO, unburnt C, SO_2, CH_4, acids, alcohols, NO_2 etc. enter the atmosphere. Hydrocarbons produce a number of petrochemical oxidants and petrochemical smog due to the photo-chemical reaction with O_2 and oxides of nitrogen which act as physiological poisons for human life. Following are the methods used for reducing air pollution due to I.C. engine :

(a) **By using engine with better design :** The extent of unburnt fuel, carbon, CO, hydrocarbons, etc. in the exhaust is cut to a great extent.

(b) **By using suitable catalyst :** The complete oxidation of fuel takes place and pollution is controlled to a large extent.

(c) **By supplying more air for combustion :** The lesser toxic exhaust gases will enter the atmosphere.

(d) **By improving the quality of gasoline :** Gasoline mixed with Tetra-Ethyl-Lead (TEL), known as leaded gasoline, emits less smoke and hence it causes less pollution.

5.7 DEPLETION OF OZONE

Ozone is produced in the upper layer of the atmosphere, about 20 km above the earth's surface, from oxygen gas by the absorption of ultraviolet light.

$$3O_2 \underset{\text{light}}{\overset{\text{u.v.}}{\rightleftharpoons}} 2O_3$$

Thus, air in the upper layer is very rich in ozone. Ozone, an allotrope of oxygen is an important chemical species present in the stratosphere and its concentration at an altitude of about 30 km is nearly 10 ppm. Ozone is quite destructive to fabrics, rubber goods, crops etc., but it checks the entry of u.v. radiations from sunlight. This upper layer of the atmosphere enveloped by ozone is commonly known as "ozone layer or protective layer" or "ozone umbrella". Thus, it acts as a protective shield for life on earth. It strongly absorbs u.v. radiations from the sun in the region 220 to 330 nm and thereby protects the life on earth from severe radiation damage.

If ozone layer in the atmosphere is depleted then the harmful u.v. radiations from the sun would reach the earth's surface and would damage the plants, causes diseases like skin cancer in animals and human and ultimately causes the gradual destruction of life on the earth.

Ozone is formed in the stratosphere by photochemical reactions

$$O_2 + h\nu \rightarrow O + O$$

$$O + O_2 + M \text{ (third body, such as } N_2 \text{ or } O_2) \rightarrow O_3 + M$$

The third body absorbs the excess energy liberated by the above reactions and ozone molecules are thus stabilised. Formation of ozone in atmosphere is a continuous process.

Causes of Ozone Depletion :

The following are the causes of ozone depletion :

(i) The chlorine which is released in the atmosphere due to volcanic activity and due to the reaction with nitric oxide, atomic oxygen, reactive hydroxyl radical causes the ozone destruction.

$$O_3 + NO \rightarrow NO_2 + O_2$$

$$O_3 + O \rightarrow O_2 + O_2$$

$$O_3 + HO \rightarrow HO_2 + HOO^-$$

$$HOO^- + O \rightarrow HO^- + O_2$$

NO is present in the atmosphere due to photochemical and chemical reactions, supersonic jets, nuclear explosions, etc. Chlorine comes from ClFCs, (chloro-fluoro-carbons) and volcanoes, and OH comes from biomass burning and from natural water systems.

(ii) Chloro-fluoro-carbons (ClFCs) are used in refrigerators, air-conditioners, propellants in aerosol sprays and in plastic foams like 'thermocole' causes destruction of ozone in the stratosphere. ClFC molecules escape into the atmosphere and decompose to give chlorine in ozone layer. Each chlorine atom so liberated attacks many of the ozone molecules. i.e., one atom of chlorine can react with 10^5 molecules of ozone converting into oxygen.

$$Cl + O_3 \rightarrow ClO + O_2$$

$$ClO + O \rightarrow Cl + O_2$$

The chlorine atom regenerates and forms a chain process which conserves Cl atoms.

All developed countries produce ClFCs in large quantity and ozone layer is getting thinner and thinner day by day. All these ClFCs must be replaced by suitable materials, otherwise the depletion of ozone layer will go on increasing and will be dangerous to living beings due to damaging effects of increased u.v. radiations.

Effects of Ozone Depletion :

Thinner and weaker ozone layer will allow more and more u.v. radiation to enter causing skin cancer, swelling of skin, sunburns, burning sensation, skin aging, leukemia, breast cancer, cataracts of eyes, haemorrhage, lung cancer, dizziness, premature aging, DNA breakage.

5.8 GREEN HOUSE EFFECT

The green house effect is also called as "atmospheric effect" or "carbon dioxide problem". The heat received from sunlight heats up the earth and some of it is radiated back into space after absorption but certain gases present in the lower atmosphere act like a glass in a green house allow radiations in the range 300 to 2500 nm, while filtering u.v. rays in the range < 300 nm. It however, does not allow the earth to reradiate heat into space. Thus, a green house is that body which allows the short wavelength incoming solar radiation to come in, but does not allow the long wave outgoing terrestrial infrared radiation to escape. A part of the heat so trapped in these atmospheric gases is re-emitted to the earth's surface. The net result is the heating of earth's surface by this phenomenon called the green house effect'. The four major green house gases, which cause adverse effects are carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), chloro-fluoro-carbons (ClFCs). The other gases like ozone and SO_2 also cause some global warming.

Effects of Green House Gases :

The green house gases are responsible for keeping our plant warm and sustaining life on earth. If the green house gases are either too low or very high, life cannot exist since the temperature on earth would reach sub-zero levels or may trap too much heat. The natural source of CO_2 is the biological degradation of vegetable matter. Since the concentration of the green house gases are continuously increasing due to industrialization, deforestation, burning of fossil fuels, automobile exhausts and other anthropogenic activities there is an increasing "global warming". Hence, precautions have to be taken to prevent adverse effects.

Consequences of Green House Effect :

1. The temperature effect of CO_2 and water vapour combine together to have a long range impact on the global climate. With the increased level of CO_2, the temperature on the earth's surface rises, causing more evaporation of surface water, leading to further increase of temperature. It is expected that this combined effect will bring 2-3°C rise due to doubling of CO_2 concentration around 2080 A.D.
2. Such a rise in atmospheric temperature from 2-3°C will result in melting ice-caps in polar regions. This will result in rise of sea-level by 50-100 cm causing submerging of many icelands and continents of low lying regions.
3. Due to increased concentration of CO_2 and due to much warmer tropical oceans, climate may change totally leading to more cyclones and early snow melting in mountains will cause more floods during monsoon.
4. Global warming will adversely affect the world food production and biological productivity will also decrease.
5. Due to increase of population, forest destruction have a serious effect on the levels of atmospheric CO_2.
6. If CO_2 level continues to increase, it would accumulate and may inhibit the cooling effect of aerosols and particulates of atmosphere may rise again.
7. At higher altitudes in the atmosphere, CO_2 undergoes photochemical reactions producing CO, which is drastically dangerous.

   $$CO_2 + h\upsilon \rightarrow CO + O$$

8. In hot tropical environment, an increase of CO_2 content will adversely affect photosynthetic activities and growth of plants.

5.9 WATER POLLUTION

Water is found in the environment as river-water, lake-water, pond-water, sea-water and as water vapour in the atmosphere. Water is needed directly by man for domestic use such as drinking, cooking, bathing, washing in animal husbandry, agriculture, transport and for industries etc. However, the quality required in each case is different. Water which is suitable for drinking purpose may not be suitable for industrial use and vice-versa.

The word ''polluted water is defined as water that does not meet over the minimum standards for any function and purposes for which it would be suitable in its natural state.'' The concept of water pollution may be defined as ''any change in the physical, chemical and biological properties of water, as well as contamination with foreign substance, which results in the decrease in the utility of water or causes diseases."

5.10 CAUSES OF WATER POLLUTION

The principal causes or sources of water pollution are :

1. Industrial Wastes : Water gets polluted by industrial effluents containing acids, alkalies, soaps, detergents, pesticides, insecticides, fungicides and metals like Cu, Zn, Pb, Hg, etc. which are released from chemical industries. Moreover, pollution also causes by wastes coming from industries like sugar, textile, paper, leather, tannaries, breweries, oil refineries, distilleries, slaughter-houses and pharmaceuticals etc.

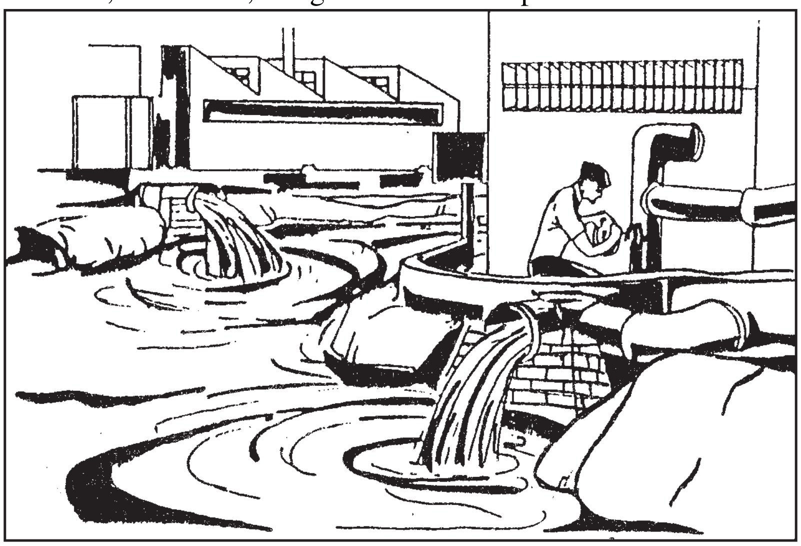

Fig. 5.4 : Water pollution from industrial waste

Industrial wastes (effluents) containing toxic substances damage the biological activity and kill useful organisms.

2. Domestic sewage : It includes human and household waste waters, municipal waste etc. directly drains into canals and rivers causing the pollution of river water. These sewage contains human excreta, urine, kitchen wastes, street wastes and organic substances that provide nutrition for bacteria and fungi.

When sewage is discharged into a stream of water directly into receivers and lakes, the organic nutrients in the sewage help bacteria etc. to grow very fast. As a result of the enhanced activity, the air dissolved in water becomes poorer and poorer in oxygen. This may happen to such an extent that aquatic life like that of fish cannot survive. Organic sewage does not kill fish directly. It is the lack of dissolved oxygen that kills the fish.

3. Suspended particles : The surface water may contain a high concentration of suspended solid (organic as well as inorganic) bacteria, algae etc. This makes water unfit for domestic as well as industrial purposes.

Algae which grows in water and synthetic detergents which are discharged into water, together create conditions for a serious pollution of water. Larger the use of synthetic detergents, greater is the danger of water pollution. Therefore, it is best to use a combination of washing soda and soap for washing clothes and use smaller quantities of synthetic detergents.

4. The pollution of oceans is also becoming very serious these days especially due to oil-spillage. About one million tonnes of oil is spilled into the ocean each year from shipping and drilling operations. This leads to various types of problems such as threat to amenities of sea-shore resort and beach life. The greatest threat is to sea-birds. Oil interferes with their flight and swimming.

Moreover, oil from oil mills and washing of automobiles pollute our rivers.

5. Clays, ores, fine particles of soil through which water flows are added to water and cause water pollution.

6. Drain from land and fields : Residual insecticides, pesticides and fungicides are washed down into lakes, streams, rivers etc. and pollute them.

7. Water from fertilizer plants containing nitrates, phosphates, ammonia etc. are released in water and they cause water pollution.

8. Atomic explosion and processing of radioactive materials near the sources of water cause water pollution.

Out of the causes mentioned above, the biggest contribution of water pollution is industrial wastes and next comes sewage (i.e. street washing, kitchen wastes, urine, human excreta etc).

5.11 SEWAGE

"Sewage is defined as the liquid flowing in ditch". This liquid waste includes human and household waste waters, industrial waste, street washings. Besides, this sewage contain traces of organic and inorganic matters in dissolved, suspension and colloidal states.

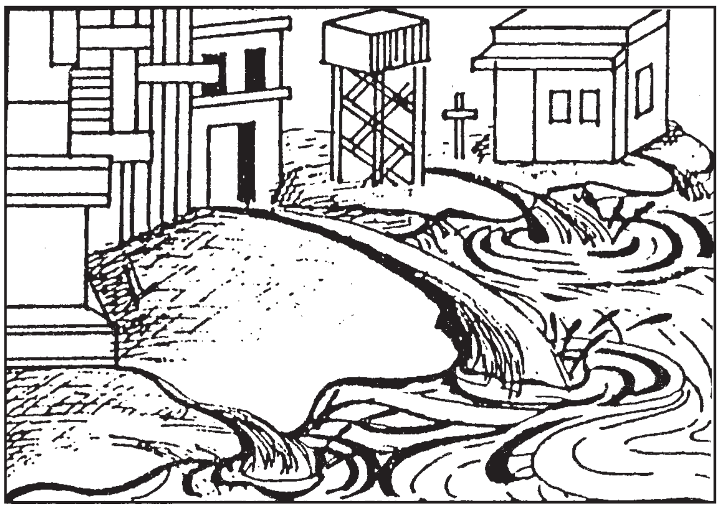

Fig. 5.5 : Water pollution from sewage

Fresh domestic sewage is usually greyish in colour, has rather sweet smell but darkens rapidly with time due to its decomposition, but when 'stale' it has an offensive odour, due to the evolution of H_2S, $(NH_4)_2S$, PH_3 (phosphine), etc.

(a) Characteristic of Sewage

1. Physical characteristics : (a) Fresh sewage is odourless and has an earthy or grey colour. In 3 - 4 hours, it becomes 'stale' when all the oxygen present in it has been exhausted. It then starts emitting offensive odour and the colour becomes dark. (b) Sewage is normally turbid and turbidity goes on increasing as sewage becomes stronger. (c) The normal temperature of sewage is higher than that of the municipal water supply, because of heat added during the utilisation of water.

2. Chemical characteristics : Chemical composition indicates the state of sewage decomposition, its strength and type of treatment needed. Fresh sewage is alkaline and possesses good bacterial action. 'Stale' sewage being acidic, is difficult to be treated. The different chemical characteristics are total solids (such as suspended, dissolved, colloidal and settleable) and gases like H_2S, NH_3, CH_4, CO_2 in addition to oxygen present in sewage.

3. Biological characteristics : These are due to the presence of bacteria and other living micro-organisms (algae, fungi etc.) in sewage. The former are much more active.

Bacteria are present in vast numbers (5 - 50 billion per litre) in sewage. Most of the bacterias are harmless to man and are largely engaged in converting complex organic compounds of sewage into simpler and stable organic compounds. This purifies sewage. Some bacteria are harmful as they can produce diseases such as cholera, dysentry, typhoid, etc. and are called pathogenic bacteria, which are really dangerous to public health.

The harmless bacterias are of two types :

(i) 'Aerobic bacteria' exist in the presence of light only. These are taking dissolved oxygen from sewage or free oxygen from air.

(ii) 'Anaerobic bacteria' exist in dark and develop in the absence of free oxygen. They extract oxygen from oxygen containing radicals of organic compounds and minerals such as nitrites, nitrates and sulphates. These bacteria are of great importance in the process of decomposition of sewage.

(b) Sewage Treatment : It is the process of removing or changing the harmful compounds into harmless compounds so as to make the sewage less offensive and dangerous. The main objects of sewage treatment are :

(i) To render sewage inoffensive so that it causes no odour or nuisance.

(ii) To reduce or eliminate danger to the public health by possible contamination of water supplies (like rivers, canals etc.).

(iii) To prevent the destruction of fish and other aquatic life in river, canals etc. into which sewage discharge is generally made.

Sewage treatment is generally carried out using the artificial treatment method. The basic purposes of this method are :

(a) To reduce the solid contents of the sewage.

(b) To remove all nuisance causing elements.

(c) To change the character of sewage, so that it can safely be discharged into the natural water course such as river or applied on land.

The artificial sewage treatment process, called 'sewage' involves the following steps.

1. Preliminary process : This involves in passing the sewage through bar screens (to remove large suspended and floating matter) and mesh screens (to remove coarse solids, gravels, silt, etc.)

2. Sedimentation process : This removes greater proportion of the suspended organic and inorganic solids from the liquid sewage. For this purpose, continuous flow type sedimentation tanks are employed. Coagulants 'sometimes' added for rapid and complete removal of suspended matter just prior to sedimentation. The coagulants used are alum, $FeSO_4$, etc. These produce large gelatinous flocs which entraps finely divided organic matter (colloidal material) and settles quickly.

$$Al_2(SO_4)_3 + 6H_2O \rightarrow \underset{\text{(floc)}}{2Al(OH)_3\downarrow} + 3H_2SO_4 \text{ (at pH > 5)}$$

3. Biological treatment process : It is essentially aeration or 'aerobic biochemical oxidation'. In this process, sewage water is filtered through specially designed sprinkling filters, so that aerobic conditions are maintained all the times. During this 'aerobic oxidation' process, the carbon of the organic matter is converted into CO_2; the nitrogen into NH_3 and finally into nitrites and nitrates. The dissolved gases present in the sewage water then form salts such as NH_4NO_2 , NH_4NO_3, $Ca(NO_3)_2$ etc.

Thus,

$$\underset{\text{(Urea)}}{NH_2.CO.NH_2} \xrightarrow[\text{oxidation}]{\text{aerobic}} CO_2 + 2NH_3$$

$$NH_3 \xrightarrow{\text{Oxidation}} HNO_2, HNO_3 \text{ etc.}$$

$$\text{Base} + HNO_2, HNO_3 \rightarrow NH_4NO_2, NH_4NO_3, Ca(NO_3)_2 \text{ etc.}$$

Schematic representation of sewage treatment :

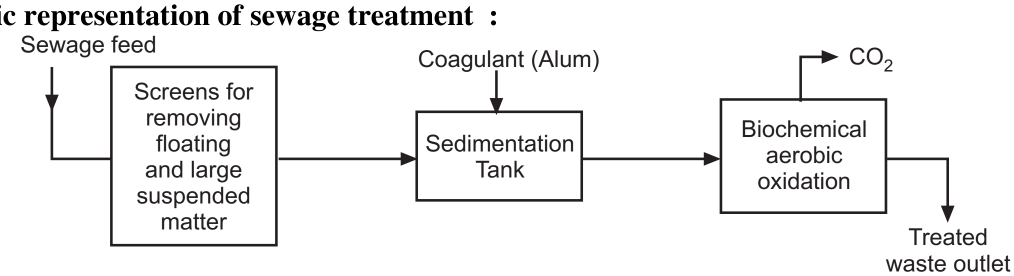

Fig. 5.6 : Flow-sheet diagram for sewage treatment

Trickling filters : These are mostly used for aerobic biochemical oxidation process. They are either rectangular or circular in shape about 2 m deep. They are filled either with coarse, crushed rock or large anthracite coal or broken bricks or graded clinkers. The under-drain is provided in the bottom of bed to collect effluent. Sewage is delivered to the filters by means of a rotating distributor.

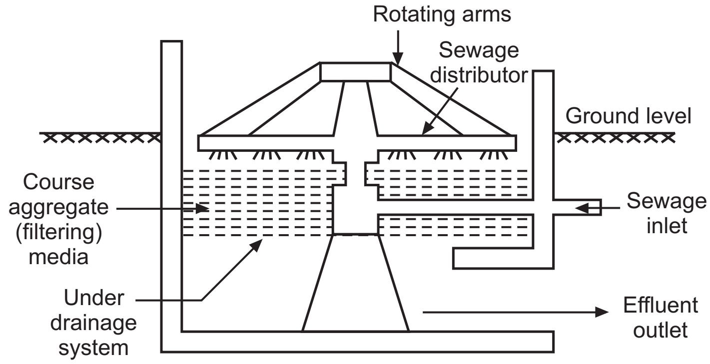

Fig. 5.7 : Trickling filter

Working : The sewage is allowed to trickle over the filtering medium by means of rotating arm distributor. As the trickled sewage starts percolating downwards through the filtering media, micro-organisms present in sewage, grow on the surface of aggregates, using organic material of the sewage as food. Aerobic conditions always prevail and purified sewage is removed from the bottom. The normal trickling filters remove 90% BOD.

5.12 BIO-CHEMICAL OXYGEN DEMAND (BOD)

BOD of a sewage is defined as "the amount of free oxygen required in water for bacteria which consume organic matter (i.e. in the biochemical oxidation of the organic matter) under aerobic conditions at 20°C and for a period of 5 days".

The unit of BOD is mg/litre or ppm. At 20°C, a BOD has an average sewage of 50 mg/litre.

Determination of BOD : This test is based on determination of dissolved oxygen prior to the following 5 days period at 20°C. A known volume of sewage sample is diluted with a known volume of saline solution (water containing nutrients for bacterial growth), whose dissolved oxygen content is pre-determined. The whole solution is incubated in a closed bottle at 20°C for a period of 5 days. After this unused oxygen is determined. The difference between the original oxygen content in saline solution and unused oxygen of solution after 5 days gives BOD.

Importance of BOD : BOD test is most important in sewage treatment as it indicates the amount of decomposable organic matter in sewage. Larger the concentration of decomposable organic matter, greater is the BOD and consequently, more the strength or nuisance potential. This test has a special significance in pollution control as it enables us to determine the degree of pollution at any time in the sewage stream.

5.13 CHEMICAL OXYGEN DEMAND (COD)

"It is an amount of oxygen required for the chemical oxidation of organic matter in sewage". In other words, it is a measure of oxidisable impurities present in the sewage.

Any organic material such as hydrocarbon when brought in contact with oxygen, is oxidised to get CO_2 and H_2O. Because of the presence of carboneous material, the end product is certainly CO_2. If this organic material contains hydrogen, nitrogen, sulphur etc. in addition to carbon, then the chemical oxidation leads to formation of CO_2, H_2O, NO_2, SO_2 etc. To get this oxidation, the oxygen is required and hence demanded by organic material. The possibility of meeting such demand is through dissolved oxygen in the water (effluent) once the organic material is in liquid form along with effluent water. Thus, the dissolved oxygen gets depleted (reduced) and hence survival of bio-organism in such water is difficult and sometimes impossible. Hence, we find the fish dead and floating on the surface in the river and well if polluted water enters in their body. It is therefore, essential to check the C.O.D. of effluent water before letting it out from industry.

Determination of COD : The chemical oxygen demand (COD) is a measure of the oxygen equivalent of that portion of organic matter in a sample that is susceptible to oxidation by strong chemical oxidant. This is an important and quickly measured parameter for stream and industrial waste studies and control of waste treatment plants. Most types of organic matter are completely oxidised by a boiling mixture of chromic and sulphuric acid to produce CO_2 and H_2O. A measured quantity of the sample is refluxed with a known amount of $K_2Cr_2O_7$ and H_2SO_4 and the excess of dichromate remaining unreacted is titrated with ferrous ammonium sulphate $[FeSO_4(NH_4)_2SO_4 \cdot 6H_2O]$. The $K_2Cr_2O_7$ consumed is proportional to the amount of oxidisable organic matter measured as oxygen equivalent.

5.14 COMPARISON BETWEEN COD AND BOD

1. COD is a measure of oxidisable impurities present in sewage, whereas BOD measures the oxygen consumed by living organisms while assimilating organic matter present in the water.
2. BOD indicates the amount of decomposable organic matter in sewage, while COD is a measure of both the biologically oxidisable and biologically inert organic matter such as cellulose. Due to this, COD values are higher than BOD values.
3. The main advantage of COD is that its determination takes about 3 hours, compared to more than 5 days for the BOD determination. Thus, COD determination is very quick.
4. In case where BOD test fails, COD exceeds. For example, when municipal or industrial waste contains toxic organic compounds to biological life, it produces erroneous BOD results.
5. The ratio of COD/BOD shows the types of sewage treatment required for a particular waste water sample. When the ratio is 0.6, the waste is rich in putreascible matter, hence biological treatment is best for it and if the ratio is 0.3, chemical treatment is required.

5.15 METHODS OF PREVENTING WATER POLLUTION

The water pollution can be prevented and controlled by the following methods :

1. Stabilisation of the ecosystem : Ecosystem stabilisation is the most scientific way to control water pollution. The principle involved in this technique includes reduction of the waste at source, harvesting and removal of biomass, trapping of nutrients, fish management and aeration.

2. Reutilisation and recycling of the waste : In developed countries, the waste water consisting of industrial effluents, domestic sewage, thermal and radioactive pollutants, sullage of municipal and other pollutants receive some sort of treatment, before it gets mixed into the water sources (like rivers, lakes, ponds etc.). For example, urban sewage, sullage etc. may be recycled and reused to generate cheaper fuel, gas and electricity.

In India, the National Environmental Engineering Research Institute (NEERI), Nagpur has developed the technology for management of radioactive wastes and chemical waste of atomic power plants, reuse of waste water to provide cheap piped gas and generate electricity by recycling of urban water.

Oxidation method (or stabilisation of ponds) : Domestic or industrial wastes are stored in large, in well defined shallow ponds and kept in it for few days. Because of the presence of sufficient sunlight and organic nutrients in waste, a healthy bloom of algae flourish along with large number of bacteria. In this natural process, the bacteria speedily digest the organic waste and render it harmless. These effluents then can be reused for irrigation of the land without any danger of pollution. No foul smell is emitted if the process is properly operated. By this method, capital cost can be slashed down by as much as 80% and the running cost upto 90%.

NEERI has also recommended other low cost methods :

(i) As 'oxidation ditches' for extended mechanical aeration.

(ii) 'Aerated lagoons' can be used for less populated middle size towns, because they require much smaller surface areas than oxidation ponds. Their cost is also much lower than those of conventional method of treatment viz. trickling filter or activated sludge treatment.

Waste-water Reclamation : Reclamation or reuse of sewage effluents can be achieved for industrial purposes. On treatment of sewage yields, irrigation water that contains all the essential nutrients such as nitrogen, phosphorus and potassium to make it a good fertilizer. The treated sewage also finds its use for air-conditioning and other purposes.

Removal of pollutants : Techniques like adsorption, electrodialysis, ion-exchange and reverse osmosis etc. can be used for removal of biological, chemical and radioactive water pollutants.

Using solar powers : Very recently, scientists of America have claimed the usage of solar power for purifying the polluted waste water cheaply. Experiments concluded that a combination of sun light and a catalyst such as titanium dioxide can dissociate chemical toxicants of water. Such photolytic reactions can kill pesticides (like DDT), maladrous bacteria and destroy explosive solvents, dioxines and cyanides.

Use of chemicals : Effective filtration and chlorination or ozonisation of waste water provides safe water to drink and for domestic uses.

Use of Bioreactors : Organic dirty sewage and factory waste, if pumped into the bioreactors would remove about 95% of impurities. Even corrosive acids and alkalies, industrial effluents can also be circulated through bioreactors. Use of bioreactors should be encouraged as they neither produce odourous smell nor toxic byproducts during the reactions.

5.16 BIOMEDICAL WASTE

Biomedical waste is hazardous and infectious waste from hospitals and pathological laboratories. It contains discarded human blood, blood products, plasma, serum and body fluids. Body fluids are the fluids which are generated or removed during surgery, autopsy, emergency care or embalming and includes cerebrospinal fluid, synoviyal fluid, pleural fluid, pericardinal fluid etc. These may include items such as sponges, surgical gloves and masks, drapes, aprons, dressings, disposable sheets and towels, undepads, plastic tubings and dialysis unit wastes.

Biomedical waste list :

1. Human anatomical waste (human tissues and organs).
2. Animal waste.
3. Blood and body fluids.
4. Microbiological waste.
5. Discarded medicines.
6. Discarded glassware.
7. Disposables.
8. Waste sharp such as needles, syringes, blades etc.
9. Liquid waste.
10. Slaughter house waste.
11. Biotechnical waste.
12. Incineration waste (ash from incineration of any biomedical waste).

Effects of Biomedical Wastes :

If biomedical waste is not treated or disposed carefully then

1. It may spread diseases like cholera.
2. The wastes from hospital may cause disease like TB.
3. It causes pollution.
4. It may cause hazardous problem in the society.

Control Measures :

Biomedical waste can be hazardous to health and environment if not disposed off properly. Lakhs of people are reported as victims of infection every year.

Following are the control measures :

1. Use of incinerator.
2. Use of safety boxes.
3. It should be disposed carefully.
4. Autoclaving or steam sterilisation.
5. By awareness, education and training of the individual.

5.17 E-WASTE

Electronic Waste (E-Waste) or Waste Electrical and Electronic Equipment (WEEE) is a waste part of computer, electronic devices, mobile phones, electrical appliances and other items that have been discarded by their original users. There is no generally accepted definition of electronic waste. In most cases, electronic waste consists of expensive and more or less durable products used for data processing telecommunication or entertainment in private household and business. Disposal of electronic equipment are a considerable category or secondary resource due to their significant suitability for direct reuse e.g. computer parts discharge during upgrades can be used again on recycling.

First electronic waste recycling system was implemented in Switzerland in 1911. Over the years all other electric and electronic devices gradually added to the system. Legislation followed in 1998 and since January, 2005 it has been possible to return all the electronic waste to the sale points and other collection points free of charge. Bangalore in India has electronic waste processing unit. Every country has recycle at least 4 kg of E-waste per capita.

List of E-waste Materials :

1. Small household appliances (toasters, vacuum cleaners etc.)
2. Large household appliances (ovens, refrigerators etc.)
3. Office and communications (PCs, printers, phones, faxes etc.)
4. Entertainment electronics (TVs, portable CD players etc.)
5. E-tools (drilling machines, electrical lawnmovers etc.)
6. Lighting equipment (mainly fluorescent tubes).
7. Sports and leisure equipment (electronic toys, training machines etc.)
8. Automatic issuing systems (ticket issuing machines).
9. Medical appliances and instruments.

Effects of E-waste :

Rapidly change of technology, such as use of computers, mobile phones, TVs created E-waste problem for both manufacturers and users. The computers are not designed for recycling. With the advancement of new technology, improved models come to the market generating more E-waste. In short, ill effects of E-waste can be summarised as follows :

1. E-waste contains some toxic materials like Pb, Hg, Cd etc. Processing of the waste effecting environment badly.
2. E-waste in water decreases the fertility of land.
3. E-waste is a problem because there are many difficulties in recycling of E-waste. The E-waste which cannot be recycled end up in land fills. 70% of heavy metals found in landfills come from the E-waste. They contaminate the ground water.
4. E-waste leads to hazards emission.

Control measures :

To minimise environmental pollution due to E-waste following measures should be considered.

1. Landfill of E-waste should be banned legally. This created an E-waste processing industry in Europe.
2. The manufacturers of electronic equipment should be forced for recycling of useless equipments. European Union, South Korea, Japan and Taiwan have already demanded the sellers and manufacturers of electronics be responsible for recycling at least 75% of them.
3. The research fellows should develop eco-friendly technology for manufacturing electronic equipments.

5.18 PREVENTIVE ENVIRONMENTAL MANAGEMENT (PEM) ACTIVITIES

To control pollution and degradation of environment, following activities should be exercised by government, non-government and social bodies.

1. Regulating the exploitation of natural resources.
2. Aware and educate the public about health and environmental issues.
3. Advice industries on ways to minimize solid and hazardous waste.
4. Monitor the quality of public water supplies.
5. Controlling over population.
6. Monitor emissions from industrial sources.
7. Inspect waste management and treatment facilities and give positive suggestions.
8. Underground the all drainage systems and storage sewage tanks.
9. Frequent inspections of public pools, water parks and natural swimming areas should be done.
10. Ensure safe transport of hazardous waste.
11. Balancing ecosystem.
12. Introducing education and training at schools, colleges and universities.

EXERCISE

1. Define pollution. What are the causes of pollution ?
2. State the types of pollutants. What are the major sources of gaseous pollutants ? State their principal effects.
3. Discuss the role of particulates in air pollution.
4. List the various sources of air pollution and discuss their effects.
5. Discuss the effects of various water pollutants.
6. Carbon monoxide is a colourless and odourless gas, even then it is a pollutant. Why ?
7. (a) What is air pollution ? Explain by giving examples.
   (b) What are the major sources of air pollution ?
8. (a) Write a detail note on radioactive pollution.
   (b) Define pollutant. What is the role of plants or forestation in controlling air pollution ?
9. (a) What is water pollution ? List its major sources. How can it be minimised ?
   (b) Sewage disposal in rivers, canals etc. is the major source of pollution. Explain.
10. (a) Heat is not a substance but still it is considered as a pollutant. Comment on it.
    (b) Carbon monoxide is a colourless and odourless gas and even then it is a pollutant. Why ?
11. (a) How does internal combustion engine causes air pollution ? How it can be reduced ?
    (b) Suggest the methods to minimise water pollution in big cities.
12. How does the pollution due to SO_2 is controlled ?
13. State the four factors for reducing air pollution due to I.C. engine.
14. Explain four sources causing water pollution.
15. Define pollutant -
    Explain the role of plants or forestration in controlling air pollution.
16. Define pollution and pollutant. Name the types of pollution.
17. Define pollutant. Name and explain any three particulates responsible for air pollution.
18. Explain role and effect of CO or NO_2 gases as air pollutants. How the effect of smoke from industries can be eliminated ?
19. Define water pollution. Mention and explain any three different sources of water pollution.
20. Define and explain pollution and deforestation.
21. Write the causes of air pollution due to vehicles.
22. Define pollutant. Explain the role of plants in controlling air pollution.
23. Explain any four types of impurities present in water and how they can cause water pollution ?
24. State two disadvantages of deforestation.
25. What are the sources of water pollution ? Discuss the effects of various water pollutions.
26. What is green house effect ? What are its consequences ?
27. What is depletion of ozone layer ? What are its effects on human beings ?
28. Define BOD and COD. State the comparison between BOD and COD.

SHORT ANSWER QUESTIONS

1. What is a pollutant ?
   Ans. An unwanted/undesirable foreign matter added to environment.
2. What is meant by pollution ?
   Ans. Addition of undesirable substances/matters into the environment, thereby adversely altering the natural quality of the environment and causing damage to the life.
3. Name four important causes of pollution.
   Ans. (i) Tremendous increase in population, (ii) rapid industrialization, (iii) rapid urbanization, (iv) cutting of trees.

4. How do plants control pollution ?

   Ans. By their photosynthesis activity, plants consume CO_2 and release O_2 in the atmosphere. Moreover, plants and micro-organisms purify water in lakes and rivers.

5. Name three toxic metals that can pollute the environment.

   Ans. Arsenic, lead and mercury.

6. Mention one advantage of ozone in the atmosphere.

   Ans. Ozone at an elevation of about 30 km absorbs the most harmful UV radiations coming from the sun.

7. Give one disadvantage of ozone in the atmosphere.

   Ans. Even 0.3 ppm of ozone near the earth's surface promotes the photochemical reaction responsible for the formation of **'smog'**.

8. What is air pollution ?

   Ans. The exclusive discharge of undesirable foreign substances into the atmosphere, thereby adversely affecting the quality of air.

9. What are the disadvantages of presence of sulphur oxides in air ?

   Ans. It causes respiratory, cardiac, eye-irritation, throat disease to man. Also damages agriculture and causes corrosion of metals.

10. Mention the disadvantage of presence of hydrogen sulphide in the atmosphere.

    Ans. It causes corrosion of metals and blacken lead paints.

11. What is smog ?

    Ans. It is a mixture of smoke and fog.

12. How is photochemical smog formed ?

    Ans. In sunlight oxides of nitrogen and hydrocarbons form photochemical smog.

13. What is acid rain ?

    Ans. Acidic oxides (present in atmosphere) dissolve in moisture of atmosphere to form corresponding acids which then fall slowly on earth as acid-rain.

14. Name three gases in atmosphere which cause acid-rain.

    Ans. SO_2, NO_2, HCl gas etc.

15. Mention three harmful effects of smog.

    Ans. (i) Causes eye irritation, (ii) limits the visibility of roads, (iii) causes difficulty in breathing.

16. Mention four harmful effects of acid-rains.

    Ans. (i) Decreases pH of rain water, (ii) causes damage to fresh water life, (iii) accelerates the corrosion of metals, (iv) causes damage to buildings like Taj Mahal.

17. What causes depletion of ozone layer ?

    Ans. Excessive use of chemicals called aerosol spray propellants (e.g. fluorocarbons and chlorofluorocarbons).

18. What are the harmful effects, if ozone layer in the atmosphere is depleted ?

    Ans. Harmful UV radiations from sun would reach the earth and cause (i) damage of plants, (ii) diseases like skin cancer in men and animals, (iii) ultimately the gradual destruction of life on the earth.

19. What is Green House effect ?

    Ans. CO_2 in the atmosphere heats the latter by trapping the infrared rays from the sun.

20. At what rate the temperature of earth's atmosphere is increasing due to green house effect ?

    Ans. About 0.05°C per year.

21. What are aerosols ?

    Ans. Chemicals released in the atmosphere with force in the forms of mist or vapour.

22. What are the harmful effects of presence of carbon monoxide in the atmosphere ?

    Ans. It reduces the oxygen-carrying capacity of blood, thereby causing symptoms like laziness, exhaustion, head-ache, vision problems and cardiac diseases.

23. What is ozone hole ?

Ans. A part of atmosphere from where ozone concentration has been depleted.

24. What is the main source of lead in the atmosphere ?

Ans. Tetra-Ethyl-Lead (TEL) is added to automobile gasoline to raise octane rating.

25. What is the effect of deforestation ?

Ans. Causes increased air pollution, since green plants use CO_2 during photosynthesis and release O_2. By cutting trees, concentration of CO_2 increases and that of O_2 decreases.

26. What are particulates ? Name particulates that cause air pollution.

Ans. Small solid particles and liquid droplets in the atmosphere are called particulates.

Examples : Dust, smoke, smog, asbestos dust, lead dust etc.

27. Name any two diseases caused by the presence of particulate pollutants in the atmosphere.

Ans. (i) Respiratory diseases, (ii) lung cancer.

28. How much air does a man normally inhale in a day ?

Ans. About 16 kg.

29. Mention two ways to reduce air pollution caused by automobiles.

Ans. (i) By using engines with better design, (ii) By using suitable catalyst.

30. Name the most dangerous pollutant emitted in air during incomplete combustion of fuel.

Ans. Carbon monoxide (CO).

31. What is water pollution ?

Ans. Any alteration in the physical, chemical and biological properties of water as well as contamination with any foreign substance which would contribute to a health hazard or otherwise decrease the utility of water.

32. Name two important sources of water pollution.

Ans. (i) Domestic sewage, (ii) Industrial waste waters.

33. What is sewage ?

Ans. The liquid waste, which includes human and household wastes, industrial wastes, ground waste, street washings and storm waters.

34. What is BOD ?

Ans. The amount of free oxygen in mg required for the biological oxidation of the organic matter present in 1 litre of sewage.

35. Give one importance of BOD.

Ans. It enables us to determine the degree of pollution at any time in the sewage.

36. What is COD ?

Ans. A measure of oxidisable impurities present in the sewage.

37. What is the main harmful effect of oxides of nitrogen in the atmosphere ?

Ans. Formation of photochemical smog.

38. What is E-waste ?

Ans. Electronic waste (E-waste) or Waste Electrical and Electronic Equipment (WEEE) is a waste part of computer, electronic devices, mobile phones, electrical appliances and other items that have been discarded by their original users.

39. Give two examples of E-waste.

Ans. (i) Large household appliances (ovens, refrigerators etc.)

(ii) Entertainment electronics (TV, portable CD polymers etc.)

40. What are biomedical wastes ?

Ans. Biomedical waste is hazardous waste from hospital and pathological laboratories. It includes discarded human blood, body fluids, surgical gloves and masks, dressing material, tubing etc.

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April 2018

Time : 3 Hours **Marks : 80**

1. Choose the correct answer from the four alternatives :

(i) ${}_{11}Na^{23}$ and ${}_{12}Na^{24}$ are ……

(a) Iostopes (b) Isobars (c) Isodiapheres (d) Isotones

(ii) What is the purpose of MnO_2 in Dry cell ?

(a) as an oxidising agent (b) as a reducing agent

(c) as an antioxidising agent (d) none of these

(iii) Slag is formed by the reaction between ……

(a) impurities and coke (b) impurities and ore

(c) impurities and flux (d) flux and coke

(iv) The process of vulcanisation of rubber makes it ……

(a) hard (b) soft (c) less elastic (d) none of these

(v) Most abundant water pollutant is ……

(a) Detergents (b) Pesticides (c) Industrial wastes (d) Ammonia

(vi) The principal ore of Aluminium is ……

(a) Bauxite (b) Corrundum (c) Cryolite (d) Feldspar

(vii) In Gun-metal which metal have highest percentage ?

(a) Cu (b) Sn (c) Pb (d) Zn

(viii) BOD is a measure of ……

(a) Organic pollution in water (b) Oxides of S, P, N in air

(c) Inorganic pollutant in water (d) Particulate matter in water

Answers : (i) – (d), (ii) – (c), (iii) – (c), (iv) – (a), (v) – (c), (vi) – (a), (vii) – (a), (viii) – (a).

2. (a) Define electrovalent and covalent bond with suitable examples and distinguish between them.

Ans. Electrovalent bond : Same as chapter-1.

Covalent bond : Same as chapter-1.

Distinguish between them : Same as chapter-4.

(b) Write electronic configuration according to Aufbau principle of the following atoms :

(i) Cu (ii) Cr (iii) Cl (iv) Ca

Ans. (b)

(i) Cu : $1s^2, 2s^6, 2p^6, 3s^2, 3p^6, 3d^5, 4s^1$ (ii) Cr : $1s^2, 2s^6, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^1$

(iii) Cl : $1s^2, 2s^2, 2p^6, 3s^2, 3p^5$ (iv) Ca : $1s^2, 2s^2, 2p^6, 3s^1$

3. Write short notes on :

(a) Faraday's law of electrolysis **(b) Global warming and their effects**

(c) Biomedical waste **(d) BOD.**

Ans. (a) Faraday's law of Electrolysis : Same as chapter-2.

(b) Global warming and their effects : Global warming is the phenomenon of increasing average air temperature near the surface of earth over the past one to two centuries.

Effects :

- Increased sea level.
- Changes in water supply.
- Rising temperature.
- Damage to habitats.

(c) Biomedical waste : Biomedical waste is any kind of waste containing infectious (or potentially infectious) materials. It may also include waste associated with the generation of biomedical waste that visually appears to be of medical or laboratory origin (e.g., packaging, unused bandages, infusion kits, etc.), as well as research laboratory waste containing biomolecules or organisms that are restricted from environmental release.

(d) BOD : Same as chapter-4.

4. (a) What are alloys ? Describe briefly the method employed for the manufacture of alloys.

Ans. Alloys : Same as chapter-3.

Methods :

Preparation of alloys : There are four commonly employed methods for the manufacture of alloys : the fusion method, the electro-deposition method, the reduction method and powder metallurgy.

The fusion method : This method uses alloying elements in a fixed proportion and fuses them together in a refractory melting pot or in a brick-lined crucible. The component metal with a higher melting point is melted first and then the other component with a lower melting point is added to the melt. Both metal components are mixed well and allowed to melt further. The molten mass is covered by powdered carbon to avoid oxidation of the molten alloy components because they are very reactive to the surrounding atmospheric oxygen. The resulting molten mass is allowed to cool at room temperature.

The electro-deposition method : This method involves simultaneous deposition of different component metals from the electrolytic solution containing their salts solution mixture by passing direct electricity.

The reduction method : Metal may exist in the form of compounds. Reduction is a chemical process in which a compound of one component can be separated from another component, to get a pure metal. This method is performed in an electric furnace.

Powder metallurgy : Powder metallurgy may be defined as the art of producing fine metal powders and then making articles from individual metal powders or alloyed metal powders.

(b) What is air pollution ? Discuss their sources. How do they afect man and environment ?

Ans. Air pollution : Same as chapter-5.

1. **Mobile sources :** Mobile sources such as cars, buses, planes, trucks and trains.
2. **Stationary sources :** Power plants, oil refineries, industrial facilities and factories.
3. **Area sources :** Such as agricultural areas, cities and wood burning.

Effects :

- Human effects e.g. diseases
- Environmental effects : Same as chapter-5.

5. (a) Write composition and uses of the following alloys :
(i) Brass, (ii) German silver, (iii) Gun metal.

Ans. (i) Brass : Copper, Zinc.
(ii) German silver : Cupper, Zinc, Nickel.
(iii) Gun metal : Cupper, Tin, Zinc.

(b) Bring out the differences between thermoplastics and thermosetting plastics. Discuss engineering applications of plastic.

Ans. Differences between thermoplastics and thermosetting plastics. Same as chapter-4.
Plastics are used in a growing range of applications in the construction industry. They have great versatility and combine excellent strength to weight ratio, durability, cost effectiveness, low maintenance and corrosion resistance which make plastics an economically attractive choice throughout the construction sector.

6. (a) Discuss briefly the process of vulcanisation of rubber. Differentiate between natural rubber and synthetic rubber.

Ans. "Vulcanization of rubber" : Same as chapter-4.

Differentiate between natural rubber and synthetic rubber. Same as chapter-4.

(b) 0.1948 gm of copper is deposited by a current of 0.2 ampere in 50 minutes. What is the electrochemical equivalent of copper ?

Ans. M = 0.1948; I = 0.2 ampere, t = 50 min = 50×60 = 3000 seconds, A = ? = electrochemical equivalent

Since $M = Z\,It \quad \therefore\ 0.1948 = Z \times 0.2 \times 3000 \quad \therefore\ Z = \frac{0.1948}{0.2 \times 3000} = 0$

7. (a) Define Aufbau principle. Also write Hund's rule and applications.

Ans. Same as chapter-1.

(b) Discuss electrochemical series. What are its important applications and properties ?

Ans. Same as chapter-2.

Applications of electrochemical series :

- Reactivity of metals.
- Electropositive character of metals.
- Displacement reactions.
- Reducing power of metals.
- Oxidising nature of nonmetals.
- Thermal stability of metallic oxides.
- Increasing order of deposition.
- Increasing order of discharge.

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